The solid resevoir of Hg ions was prepared by powdering a mixture of 6 parts Amberlite XE305 (Rohm & Haas Co.) and 4 parts of $Hg(SCN)_2$.

Transport Experiments. The polyphasic dynamic reactor used has been previously described.[8] The appropriate solvent (MeOH or $CHCl_3$) was introduced with a flow rate of 0.017 mL/s in all experiments. Crown ether **1** was dissolved at 1×10^{-3}M whereas crown ethers **2** and **3** were used as 2×10^{-3}M solutions. Typically 3 g of the reservoir $Hg(SCN)_2$ source was used and 2 g of the trapping resin **4** was employed. A discussion of transport facilitation and its relationship to experimental parameters may be found in ref 13.

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Addition of Arylchlorocarbenes to α,β-Unsaturated Esters. Absolute Rates, Substituent Effects, and Variable Reactivities[†]

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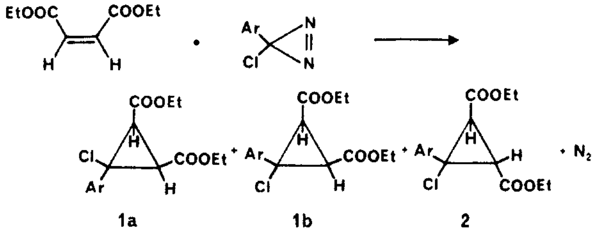
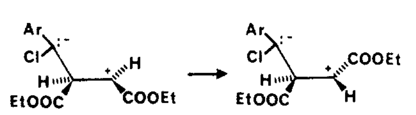
Abstract: Addition of arylchlorocarbenes to α,β-unsaturated esters occurs with remarkable facility, even though these carbenes are characterized as electrophilic. Reactions with diethyl maleate, which exhibits isomerization to diethyl fumarate and produces cyclopropanes formally derived from both olefin geometries, are most simply interpreted as concerted additions with isomerization of diethyl maleate resulting from a chemical species generated during decomposition of the reactant diazirine. Absolute rate constants for quenching of a series of para-substituted arylchlorocarbenes with electron-rich and electron-poor alkenes have been obtained. Consistent with concerted addition, diethyl fumarate is more reactive toward cyclopropanation by arylchlorocarbenes than diethyl maleate by factors of more than 20. Absolute rate constants for other alkenes, including *n*-butyl vinyl ether, 1-hexene, and 1-pentene together with the α,β-unsaturated esters ethyl acrylate, ethyl crotonate, and diethyl ethylidenemalonate are also reported. Relative reactivities for comparatively electron-rich alkenes are less than those for some electron-poor α,β-unsaturated esters. Increasing solvent polarity has only a moderate influence on the reaction rates of phenylchlorocarbene additions to electron-rich and electron-poor alkenes, and activation parameters do not distinguish between these electronically disparate olefins. Both classifications of alkenes undergo cycloadditions that are dominated by entropy. Hammett correlations have been obtained for reactions of para-substituted arylchlorocarbenes with each alkene substrate, and the resultant positive ρ-values are dependent on the nature of the olefin substituent. Frontier orbital analysis establishes the necessity of including the nucleophilic term in estimating the stabilization energy of the transition state when electron-poor olefins add to reactive carbenes.

We recently reported that arylchlorocarbenes, generated photochemically or thermally from their corresponding diazirines, underwent addition to diethyl maleate (DEM) resulting in the formation of cyclopropane products having both the cis and trans ester geometries (eq 1).[2] With diethyl fumarate (DEF) only one cyclopropane product was produced, and its structure retained the trans geometry of the carbethoxy groups. Isomerization of diethyl maleate to diethyl fumarate accompanied cyclopropane production. These and related observations led Doyle, Liu, and co-workers to propose that arylchlorocarbenes reversibly form a carbene–alkene dipolar adduct (**3**) whose lifetime is sufficiently long that bond rotation can occur (eq 2).[2b] Results reported from other laboratories concerning rearrangements that accompany reactions of carbenes with alkenes,[3-5] especially the isomerization of *trans*-cyclooctene to *cis*-cyclooctene during addition of dibromocarbene,[5] fortified this explanation. However, we are cautioned in this interpretation by the relative ease for conversion of maleate esters to the thermodynamically more stable fumarate



(1)

1a **1b** **2**



(2)

3a **3b**

[†] Dedicated to Professor Maitland Jones Jr. on the occasion of his 50th birthday.

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Table I. Product Distribution from the Thermal Decomposition of 3-Chloro-3-phenyldiazirine in the Presence of Diethyl Maleate as a Function of Reaction Time[a]

		rel yield,[c] %					
time, min	DEM/DEF[b]	**1a**	**1b**	**2**	**1**/**2**	**1a**/**1b**	DEF/**2**
0	360						
15	114	59	23	18	4.6	2.6	0.74
30	131	58	23	19	4.3	2.5	0.31
45	175	59	24	17	4.9	2.6	0.21
60	197	60	23	17	5.0	2.5	0.14
120	214	60	24	16	5.3	2.6	0.14
180	189	60	24	16	5.2	2.6	0.11

[a] Reactions performed in refluxing carbon tetrachloride. Yield **1** + **2** equals 14%, with the azine derived from 3-chloro-3-phenyldiazirine constituting the remainder of the product. Initial [DEM]/[phenylchlorodiazirine] was 3.0 with [phenylchlorodiazirine] = 1.5 M. [b] Ratio ±10 from duplicate runs. [c] Relative yield ±0.5%.

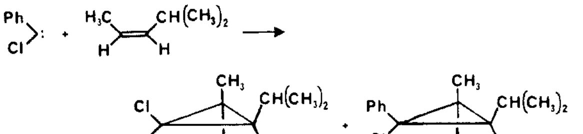
isomers. This rearrangement has been shown to occur under thermal,[6] free-radical,[7] both acid- and base-catalyzed conditions,[8,9] and, more recently, with tight ion pairs that included those derived from phenylbromodiazirine but not phenylchlorodiazirine.[10] Furthermore, more recent work on the CBr_2/*trans*-cyclooctene system has revealed that isomerization was not caused by the carbene.[5b]

Arylchlorocarbenes belong to the classification of carbenes identified as electrophilic.[11] Accordingly, selectivity for addition to alkenes is proposed to be greatest when the olefin possesses electron-donating substituents. Yet, as we have reported,[2] α,β-unsaturated esters react readily with phenylchlorocarbene to produce cyclopropane products in high yields, and their relative reactivities do not appear to be greatly different from alkenes possessing electron-donating substituents. The present investigation was undertaken to examine the authenticity of the apparent carbene-induced rearrangements of maleate esters and to define the reaction characteristics of carbene addition to electron-poor alkenes exemplified by α,β-unsaturated esters.

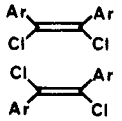
Results

Product Analyses. Thermal decomposition of 3-chloro-3-phenyldiazirine was performed in the presence of 3.0 molar equiv of diethyl maleate (DEM/DEF >300) in refluxing carbon tetrachloride, and product formation was followed as a function of time. We reasoned that if **2** was formed from DEF generated during the course of the reaction then, as the concentration of DEF increased with time, the ratio **1**/**2** should decrease. Alternatively, if both **1** and **2** were produced from the same reaction intermediate, the **1**/**2** ratio should remain constant as the reaction progresses to completion even though the DEM/DEF ratio is decreasing. As is evident in the data presented in Table I, neither situation is consistent with our observations. The **1**/**2** ratio increases slightly after reaching a minimum at 30 min, when approximately half of the diazirine is decomposed. The concentration of DEF increases initially but then decreases with time to a limiting value that is twice that of its initial concentration. Even at the maximum DEF concentration observed at 15 min, the concentration of DEF is more than 30 times less than the initial concentration of the reactant diazirine and only ~30% higher than that of the total amount of **2** formed in this reaction. If **2** is formed by addition of phenylchlorocarbene to DEF in direct competition with addition to DEM, the relative reactivity of DEF could be no less than 20 assuming that the DEM/DEF ratio remained constant at 100 throughout the reaction. As will be described in the following subsection, laser flash photolysis (LFP) studies reveal that the relative reactivity of phenylchlorocarbene toward DEF/DEM is 21.6 in toluene at 25 °C.

Diethyl maleate in refluxing carbon tetrachloride was not converted to diethyl fumarate during a 25-fold greater time period than that employed for diazirine decomposition, and photolytic isomerization was not observed. In addition, no isomerization of DEM was observed in the presence of 3-chloro-3-phenyldiazirine at reaction temperatures (<60 °C) that precluded diazirine decomposition. Control experiments established that neither isomerization nor decomposition of either DEM or **1** occurred during product analysis. As a further control experiment on the stereospecificity of alkene addition reactions by phenylchlorocarbene, photolysis of 3-chloro-3-phenyldiazirine in the presence of *cis*- or *trans*-4-methyl-2-pentene gave only the two cyclopropane isomers that had retained the original olefin geometry (eq 3), and isomerization of the cis to the trans alkene did not accompany photolysis.


(3)

As is common in thermolytic or photolytic decomposition of diazirines,[12] the carbene dimer (**4**) and/or symmetric azine (**5**)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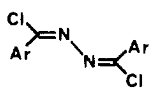
5

were the principal byproducts identified for these transformations. Their yields were dependent on the molar ratio of olefin to diazirine. Increasing the relative concentration of olefin resulted in enhanced cyclopropane yield with a corresponding decrease in the yield of carbene dimer and/or azine so that, even with diethyl maleate, cyclopropane yields were as high as 60% when [DEM]/[diazirine] > 50. Other byproducts, formed in low yield, included benzal chloride, which was presumably formed by chloride abstraction from the reactant diazirine. Photolysis or thermolysis of 3-chloro-3-phenyldiazirine alone in carbon tetrachloride yielded, in addition to **4** and **5**, hexachloroethane, 1,2-diphenyl-1,1,2,2-tetrachloroethane, and pentachloroethylbenzene which apparently result from chlorine atom abstraction reactions of phenylchlorocarbene (eq 4).

$$PhCCl + CCl_4 \rightarrow [Ph^{\bullet}CCl_2 + {}^{\bullet}CCl_3] \rightarrow Cl_3CCCl_3 + PhCCl_2CCl_2Ph + PhCCl_2CCl_3 \quad (4)$$

Similar results were obtained at higher and lower dilutions of 3-chloro-3-phenyldiazirine in carbon tetrachloride. The reactions described by the data in Table I were performed with [diazirine] = 1.5 M. At [diazirine] = 0.95 M with reactant [DEM]/[diazirine] = 3.1, **1**/**2** was 2.4–3.2 and [DEM]/[DEF] reached a limiting value of 60. At [diazirine] = 0.10 M under the same conditions, **1**/**2** = 1.4 and [DEM]/[DEF] = 92 at the completion of the decomposition. Obviously isomerization is a function of the diazirine concentration, although no linear relationship is evident. However, thermal or photochemical decomposition of 3-chloro-3-phenyldiazirine in the presence of the 10-fold molar excess of DEM to which had been added an equivalent molar amount of cumene only resulted in the production of **1a** and **1b** (ratio = 2.6 from thermolysis and 5.1 from photolysis). Neither **2** nor DEF was formed under these conditions, suggesting that the isomerization of DEM to DEF is a free-radical process and is effectively inhibited by cumene.

Like diethyl maleate, dimethyl citraconate is prone to undergo geometrical isomerization, but comparative studies have shown

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Table II. Product Distribution from Photolytic Decomposition of 3-Aryl-3-chlorodiazirines in the Presence of Diethyl Maleate[a]

		rel yield,[b] %				
aryl group	temp, °C	1	2	4	5	1/2
p-$CH_3OC_6H_4$	15	52	11	14	23	4.7
	−196	49	0	20	31	
p-$CH_3C_6H_4$	15	46	15	16	23	3.1
	−196	55	0	17	28	
C_6H_5	15	50	15	16	19	3.3
	−196	52	0	13	35	
p-ClC_6H_4	15	48	16	17	19	3.0
	−196	53	0	18	29	
p-$CF_3C_6H_4$	15	52	14	15	19	3.7
	−196	51	0	16	27	

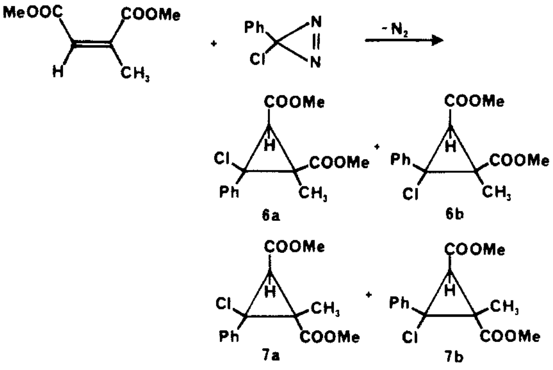
[a] Reactions performed in toluene with [DEM]/[diazirine] = 10 and [diazirine] = 0.10 M. [b] Absolute yields were between 80 and 90% based on reactant diazirine.

Table III. Product Distribution from the Photolytic Decomposition of 3-Chloro-3-phenyldiazirine in the Presence of Diethyl Maleate as a Function of Temperature[a]

	rel yield, %			
temp, °C	**1a**	**1b**	**2**	**1/2**
20	56	23	21	3.7
−50	59	30	11	8.1
−75	60	32	8	12
−196	62	38	0	

[a] Reactions performed in toluene. Initial concentrations of diazirine and DEM were 0.1 and 1.0 M, respectively.

that its rearrangement is not as facile as that of DEM.[13] The same is true in its reactions with phenylchlorocarbene. Thermal decomposition of 3-chloro-3-phenyldiazirine in the presence of 3.0 molar equiv of isomerically pure dimethyl citraconate in refluxing carbon tetrachloride yielded four cyclopropane isomers, two each possessing the cis and trans geometries of the carbomethoxy groups (eq 5), with those having the cis geometry dominant (**6**/**7** = 18). Isomerization of dimethyl citraconate to dimethyl mesoconate was negligible (<0.1%).



(5)

Similar results were obtained from the photolytic decomposition of a series of para-substituted 3-aryl-3-chlorodiazirines in the presence of a 10-fold molar excess of DEM (DEM/DEF = 350). Both **1** and **2** were formed from reactions performed at 15 °C with little apparent and no systematic variation in the **1**/**2** product ratio (Table II). However, neither DEF nor **2** were observed in reactions carried out at −196 °C, and as shown by the data in Table III, the formation of **2** is temperature dependent.

Absolute Rate Constants and Substituent Effects. The composite results suggest that **2** is not formed by collapse of a carbene–DEM dipolar adduct after bond rotation (**3b**) but, rather, directly from DEM on condition that the relative reactivity of DEF for carbene addition is more than 20 times greater than that of DEM and that DEM is converted to DEF by some chemical species generated prior to or during decomposition of the diazirine. To evaluate the latter mechanistic possibility, absolute rate constants for the reactions of a series of para-substituted arylchlorocarbenes with DEM and DEF have been determined, and these results are reported in Table IV. As is evident from this data, the relative reactivity of DEF is more than 20 times that of DEM, which may seem surprising in view of extensive studies which have previously established that carbene additions to 2-butene favor the *cis*-alkene over the *trans*-alkene,[14] but ordinarily by less than a factor of 2.

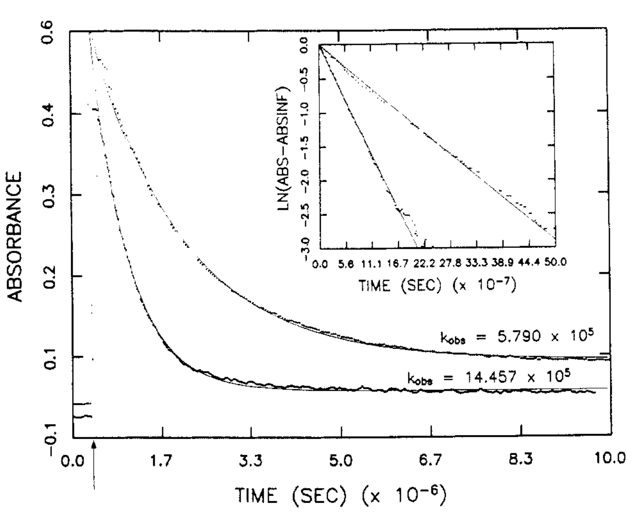


Figure 1. Typical examples of kinetic data for decay of PhCCl, monitored at 318 nm, at low and medium concentrations of quencher (DEF, in this case). The faster trace has been displaced by −0.02 absorbance units to avoid overlap. The arrow marks the point where the laser was fired.

Laser flash photolysis (LFP) of the p-MeO-, p-Me-, p-Cl-, and unsubstituted 3-chloro-3-phenyldiazirines produced the well-known transient absorption spectra of the corresponding carbenes.[15] All of the LFP studies were performed with 351-nm pulses of a XeF excimer laser, and all carbene kinetics were monitored at 318 nm with the exception of the p-methoxy derivative which was monitored at 340 nm. The attribution of the transient spectra to the postulated carbenes was secured by comparison to the spectra obtained by Turro, Moss, and co-workers using matrix isolation spectroscopy and by the fact that the relative rates of reaction for these carbenes with a series of simple quenchers agreed with the same ratios obtained by product analyses (vide infra).

Carbenes generated from the 3-chloro-3-phenyldiazirines by LFP decay slowly ($\tau_{1/2} > 50$ μs) in the absence of quenchers. The decay is not described by a simple first-order rate law under these conditions. However, the addition of olefinic quenchers accelerates the carbene decay kinetics and produces a time course that can be described by a single-exponential rate process (eq 6), where

$$k_{\mathrm{obsd}} = k_0 + k_Q[Q] \qquad (6)$$

k_{obsd} is the observed pseudo-first-order decay rate constant, k_0 is the sum of all first-order and pseudo-first-order rate constants for all carbene-consuming processes that do not involve the quencher, and k_Q is the second-order rate constant for the reaction of a phenylchlorocarbene with olefinic quencher Q. The k_Q values are obtained from the slope of a plot of k_{obsd} versus [Q] (e.g., Figures 1 and 2), and correlation coefficients r obtained from these plots always exceeded 0.96. Individual values of k_{obsd} at a specific concentration of Q were obtained by a simple pseudo-first-order kinetic analysis utilizing the equation $\ln(A_t - A_\infty/A_0 - A_\infty) = -k_{\mathrm{obsd}}t$, where A is the absorbance at time = 0, t, and ∞. The correlation coefficients generally exceeded $r = 0.99$. In this manner, the absolute rate constants for the reactions of para-

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Table IV. Absolute Rate Constants for the Reactions between Para-Substituted Arylchlorocarbenes and Representative Alkenes[a]

alkene	k, M^{-1} s^{-1} p-ClC_6H_4CCl	 C_6H_5CCl	 p-$CH_3C_6H_4CCl$	 p-$CH_3OC_6H_4CCl$
2,3-dimethyl-2-butene[b] (TME)		1.31×10^8		
butyl vinyl ether (BVE)	4.97×10^6	4.71×10^6	9.92×10^5	1.65×10^5
diethyl fumarate (DEF)	3.84×10^6	3.32×10^6	2.55×10^6	1.52×10^6
diethyl ethylidenemalonate (DEE)	3.09×10^6	2.78×10^6	2.43×10^6	4.60×10^6
ethyl acrylate (ETA)	2.66×10^6	2.24×10^6	1.29×10^6	6.07×10^5
1-pentene (PEN)	1.54×10^6	1.18×10^6	4.23×10^5	2.58×10^5
1-hexene (HEX)	1.44×10^6	1.10×10^6[c]	4.11×10^5	1.36×10^5
ethyl crotonate (ETC)	1.57×10^6	1.14×10^6	5.08×10^5	2.92×10^5
diethyl maleate (DEM)	1.63×10^5	1.54×10^5	9.58×10^4	7.80×10^4

[a] Reactions were performed by laser flash photolysis at 25 °C in toluene. Rate constants were reproducible to less than ±5%. Correlation coefficients for individual determinations were generally >0.99. [b] Lit.[17] 1.4×10^8 M^{-1} s^{-1} in toluene. [c] Lit.[17] 2.2×10^6 M^{-1} s^{-1} in isooctane.

Table V. Relative Reactivities for Addition of Chlorophenylcarbene to Alkenes. Comparison of Competition Studies with Absolute Rate Data

olefin 1	 2	k_1/k_2 from product ratio[a]	 from rate constants[b]
BVE	DEF	1.57	1.42
BVE	ETA	2.35	2.29
BVE	ETC	4.19	4.13
BVE	HEX	4.84	4.28
DEF	ETC	3.12	2.91
DEF	HEX	3.01	3.23
ETA	ETC	(1.31)[c]	1.81
ETA	HEX	2.14	1.87
ETC	HEX	1.18	1.04

[a] Competitive studies were performed at 25 °C in a Rayonet reactor using light from 350-nm lamps to photolyze the diazirine. Reproducibility was ±10%. [b] Data taken from Table IV. [c] Value is too low due to polymerization of ETA during the reaction. Cross-checks using ETA/HEX, BVE/ETA, BVE/HEX, BVE/ETC, and ETC/HEX pairs give ratios of 1.78 and 1.80 for the ETA/ETC combination.

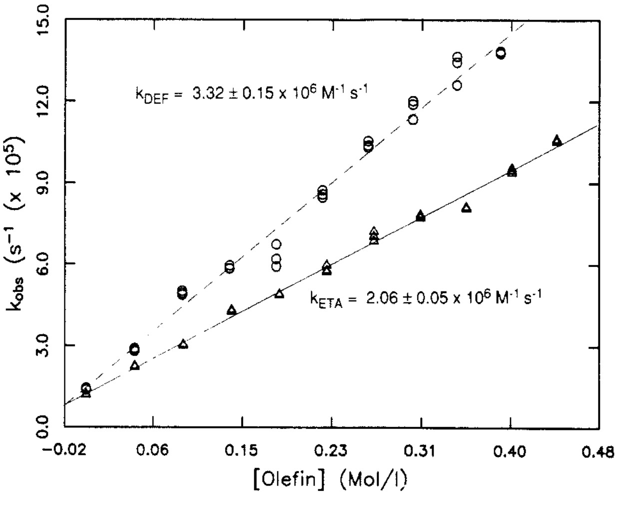

Figure 2. First-order dependence on alkene concentration of the observed (pseudo-) first-order rate constant for quenching of phenylchlorocarbene by (○) DEF, $k = 3.32 \times 10^6$ M^{-1} s^{-1}, and (△) ETA, $k = 2.06 \times 10^6$ M^{-1} s^{-1}. Reactions were performed in toluene.

Table VI. Solvent Dependence of the Reactions of Phenylchlorocarbene with Representative Olefins

alkene	solvent	temp, °C	k,[a] M^{-1} s^{-1}
2,3-dimethyl-2-butene (TME)	isooctane[b]	23	2.8×10^8
	toluene[c]	25	1.31×10^8
	acetonitrile[b]	27	1.1×10^8
1-hexene (HEX)	isooctane[b]	23	2.2×10^6
	toluene	21	1.10×10^6
	ethyl acetate	23	0.83×10^6
diethyl fumarate (DEF)	heptane	23	9.21×10^6
	toluene	28	3.32×10^6
	ethyl acetate	23	3.00×10^6
ethyl acrylate (ETA)	isooctane[d]	RT	5.01×10^6
	toluene	22	2.06×10^6
	ethyl acetate	22	1.58×10^6
	acetonitrile[d]	RT	1.3×10^6
fumaronitrile (FCN)	ethyl acetate	22	3.26×10^6
maleic anhydride (MAH)	ethyl acetate	23	9.38×10^6

[a] Values ±5%, correlation coefficient ≥0.97. [b] Data from ref 18. [c] Lit.[18] 1.4×10^6 M^{-1} s^{-1}. [d] See Table IX, footnote *u*.

Table VII. Activation Parameters for Carbene Reactions. Quenching of Phenylchlorocarbene by Olefins

quencher	solvent	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	temp range,[a] °C
DEF	heptane	1.2	7.6	0.64	−25.4	70
DEF	toluene	1.6	7.6	0.85	−25.8	45
ETA	toluene	1.8	7.7	1.33	−25.1	60
PEN	toluene	1.9	7.5	1.33	−26.3	40
HEX[b]	isooctane	1.1 ± 0.5	7.4	0.51	−27	115

[a] Temperature range always had ambient (23–27 °C) as the highest temperature. The four- or five-point Arrhenius plots showed good linearity over the reported temperature ranges. [b] Data taken from ref 18.

substituted arylchlorocarbenes with representative alkenes were obtained (Table IV).

Relative rate studies with photolytically generated phenylchlorocarbene in the presence of selected alkene combinations were performed as a cross-check on relative reactivities obtained from ratios of absolute rate constants, and these results are reported in Table V. Except for the combination of ETA and ETC, in which polymerization of ETA lowered the ratio obtained by product analysis, the agreement between the relative rate constants obtained by LFP and those from product ratios is excellent.

The solvent dependence of the absolute rate constants for quenching of phenylchlorocarbene with selected olefins has also been investigated (Table VI). In all cases, the rate constants exhibit a modest decrease with increasing polarity of the solvent. Acetone has recently been shown to trap [p-(trifluoromethyl)phenyl]chlorocarbene, (p-chlorophenyl)chlorocarbene,[16a] and (p-nitrophenyl)chlorocarbene[16b] as ylide intermediates. However, neither acetone nor ethyl acetate quenches the phenylchlorocarbene signal. The only transients observed upon LFP of the diazirines employed in this investigation with any of the solvents utilized were those due to the arylchlorocarbenes. Table VI also reports the rate constants for phenylchlorocarbene quenching by maleic anhydride and fumaronitrile in ethyl acetate; although the rate constant for the reaction of phenylchlorocarbene with fumaronitrile is almost identical with that for quenching by DEF, the rate constant for reaction of phenylchlorocarbene with maleic anhydride is almost 2 orders of magnitude greater than that for reaction with diethyl maleate (see Table IV).

Activation parameters for the reactions of phenylchlorocarbene with selected olefins have been measureed (Table VII). The

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(16) (a) Unpublished research at Ohio State University. (b) Liu, M. T. H.; Soundararajan, N.; Anand, S. M.; Ibata, T. *Tetrahedron Lett.* **1987**, *28*, 1011.

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Table VIII. Competitive Trapping Ratios Obtained with Phenylchlorocarbene and Selected Pairs of Olefins as a Function of Temperature

alkene 1/alkene 2	temp, °C	product ratio
BVE/DEF	70	1.32
	25	1.57
	−70	1.47
DEF/HEX	70	3.35
	25	3.01
	−70	3.29

temperature range employed always included room temperature as the highest temperature data point. The results obtained for 1-pentene are in qualitative agreement with those determined by Moss and co-workers for 1-hexene.[18] The fact that carbene–olefin reactions in alkane solvents are typically twice as fast as those in toluene (Table VI) is manifested in the slightly lower E_a (and hence $\Delta H^{\ddagger}$) obtained in heptane or isooctane relative to toluene.

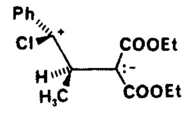
Finally, competitive product ratios from reactions of phenylchlorocarbene with selected pairs of olefinic quenchers were also measured as a function of temperature (Table VIII). As can be seen from these data, the product ratios and, by inference, rate ratios are insensitive to temperature over the 140 °C range employed.

Discussion

The comprehensive investigations by Moss and co-workers on carbene selectivities in addition reactions with alkenes[19] have prompted common use of the term "carbene philicity" to describe differential reactivities of carbenes in cyclopropanation reactions.[20] Electrophilic carbenes are described as being more reactive toward electron-rich alkenes such as tetramethylethylene, whereas nucleophilic carbenes react at faster rates with electron-poor alkenes such as ethyl acrylate.[21] Phenylchlorocarbene is identified with the class of electrophilic carbenes.[19] However, a superficial analysis of the data in Tables IV–VI reveals that the four carbenes examined in this study are all ambiphilic. These carbenes react more rapidly with olefins substituted with *either* electron-donating or electron-withdrawing groups than with 1-pentene or 1-hexene. Several mechanistic explanations for this observation will now be considered.

Dipolar (σ) Adducts. The ambiphilicities of the carbenes examined in this study may result from a change in mechanism with a change in olefin substituents. In this scenario, the addition of the arylchlorocarbene to electron-rich olefins is a concerted electrophilic process, but these carbenes behave as nucleophiles toward electron-deficient alkenes to produce dipolar adducts such as **3a** and **3b**. This hypothesis would seem to have the virtue of explaining the formation of the *trans*-cyclopropane isomer **2** produced in the reactions of arylchlorocarbenes with DEM (Tables I–III), and if formation of the dipolar adduct is reversible, isomerization of DEM to DEF under the reaction conditions is also explained. However, the LFP data demonstrate that the absolute reactivities of the arylchlorocarbenes are 19–27 times greater toward DEF than DEM. This means that the *trans*-cyclopropane products (**2**) observed from reactions betwen arylchlorocarbenes and DEM probably arise from DEF produced during decomposition of the corresponding diazirines, and thus, a dipolar intermediate is not required to explain the formation of **2**.

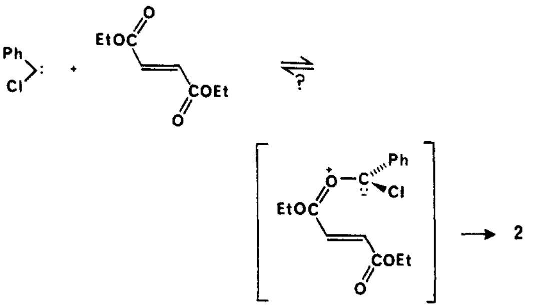
The LFP data ultimately lead us to reject dipolar adducts as the basis of the observed ambiphilicity. First, arylchlorocarbenes react slightly less rapidly with diethyl ethylidenemalonate (DEE) than with DEF, despite the fact that a hypothetical dipolar adduct **8** would be more stable than the one formed from DEF. Second, the rate constant for reaction of phenylchlorocarbene shows little of the dependence on solvent polarity (Table VI) that would have been expected for a reaction producing a zwitterionic species. Third, it is difficult to accept that concerted cycloaddition of phenylchlorocarbene to 1-pentene and 1-hexene and the nucleophilic addition of this same carbene to ethyl acrylate and DEF would have essentially identical activation parameters (Table VII). Thus, formation of a dipolar intermediate cannot explain the observed ambiphilicity.



8

Olefin Isomerization. Several mechanisms can explain the isomerization of DEM to DEF. In thermal or photochemical decomposition reactions, ionization of 3-chloro-3-phenyldiazirine near its decomposition temperature could have effected this rearrangement, by analogy with the corresponding 3-bromodiazirine which is active at room temperature.[10] Intermediates that are formed through chloride ion transfer from phenylchlorodiazirine, which normally results in the formation of benzal chloride, might have produced isomerization, and so also could free-radical intermediates produced by chlorine atom abstraction by arylchlorocarbenes from carbon tetrachloride (eq 4). In none of these cases can the cause be proven, but there is no requirement that isomerization occurs concurrently with carbene addition.

Ylide Intermediates. The ambiphilicity of phenylchlorocarbene has been attributed to the initial formation of an ylide due to association of the carbene at one of the ester oxygens[2a] followed by rearrangement to give product (e.g., eq 7) However, data that we have obtained render this explanation unlikely. First of all, this viewpoint requires the unlikely coincidence that concerted cyclopropanation of 1-hexene or 1-pentene and ylide formation–rearrangement with DEF have identical activation parameters. Even more seriously, LFP of diazirines in ethyl acetate, ethyl formate, diethyl oxalate, or γ-butyrolactone provides no evidence for ylide intermediates; arylchlorocarbenes are the only detectable intermediates, and the carbenes decay very slowly in these solvents—about as slowly as they decay in toluene or heptane. Furthermore, the absolute rate constants for reactions of DEF in nonpolar and polar solvents are nearly the same, which is inconsistent with a polar intermediate such as **9**.



9 (7)

One can attribute our failure to detect an ester–carbene ylide either to its having a very poor chromophore or a very short lifetime. However, the rationalizations do not explain the long carbene lifetimes in ester solvents. Recourse could be found in the hypothesis that an ylide formed with ethyl acetate is very long-lived and formed reversibly (i.e., the invisible ylide serves as a carbene reservoir), but this viewpoint predicts that the rate constant for carbene addition to alkenes should vary considerably from toluene to ethyl acetate as solvents, which is not observed. Furthermore, reactions of selected arylchlorocarbenes with acetone do form readily detectable ylides which can be trapped by dipolar addition to DEF.[16] Such species were not found when arylchlorocarbenes were generated in the presence of ethyl acetate. Finally, kinetic results have previously established that phenylchlorocarbene does not react reversibly with DEM to form a ylide which subsequently transfers the associated carbene intermole-

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[21] Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1979**, 4721.

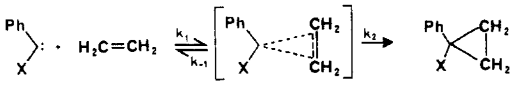
cularly to DEM to form **1** and **2** (eq 1).[2b]

Ylide Transition Structures. Although ylide intermediates do not explain the ambiphilicity of arylchlorocarbenes, the involvement of ylides as transition structures or even as nonstationary points on the potential surface connecting carbene plus, for example, DEF to the cyclopropane product should be considered as an alternative explanation. In this view, a carbethoxy or cyano substituent of an electron-deficient alkene directs the carbene to the double bond without ever forming an ylide intermediate. Although the nearly identical activation parameters determined for DEF, ethyl acrylate, 1-pentene, and 1-hexene, particularly their entropies of activation, mitigate against such an explanation, ylide transition structures cannot be ruled out per se.

The perfluoroalkyl-substituted ethylene $CF_3(CF_2)_2CH{=}CH_2$ (**10**) whose strongly electron-withdrawing substituent is incapable of ylide formation appeared to be an ideal candidate for evaluation of the ylide mechanism. Our LFP studies revealed that **10** did not quench phenylchlorocarbene ($k \leq 2 \times 10^4$ M^{-1} s^{-1}). This observation strongly supports an ylide explanation of ambiphilicity. However, the frontier molecular orbital interpretation advocated by Moss and Houk[22] also predicts (vide infra) that **10** will be very unreactive toward carbene addition. The two interpretations make the same predictions, and consequently, the lack of reactivity for **10** does not reveal a mechanistic preference.

We note that the ylide transition structure mechanism is kinetically indistinguishable from an "undirected" concerted addition. Thus, the directing effect of carbethoxy or cyano substituents, while possible, is not a testable proposition.

Reversibly Formed Carbene–Olefin Complexes. Turro, Moss, and co-workers measured the activation parameters for reactions of phenylhalocarbenes with simple olefins.[18,23] The very small and, in some cases, negative values of $\Delta H^{\ddagger}$ led them to consider reversibly formed carbene–olefin complexes (**11** in eq 8). Their more recent investigations of volumes of activation are kinetically consistent with the intermediacy of a reversibly formed complex.[24] The recently observed changes in the Z/E ratios of β-clorostyrenes formed by 1,2 hydrogen migration in benzylchlorocarbenes as a function of olefin and olefin concentration in the thermolysis and photolysis of 3-benzyl-3-chlorodiazirines have also been interpreted in terms of a carbene–olefin complex.[25] This model implies that the carbene and alkene form a complex at relatively long distances and are rather "loose" or weakly bound so that dissociation (k_{-1}) can compete with product formation (k_2).



(8)

11

In order to have a negative activation energy, both the complex and the barrier between complex and cyclopropane must be *lower* in enthalpy than carbene + olefin. Thus, this mechanism requires that the complex be a true intermediate with a finite but short lifetime. Calculations of (k_{-1}/k_2) from kinetic measurements that are consistent with a weakly bound complex between highly reactive carbenes and olefins have been reported, but only recently has the nature of these complexes been described as, perhaps, an encounter pair in a solvent cage.[18] The data require that the complex be bound by at least 2 kcal/mol, the value of the negative enthalpy of activation.

A reasonable conceptional model for the carbene–olefin complex may be an exciplex. Exciplexes are formed (eq 9) by reaction of electronically excited states (X*) with electron donors or acceptors (Y). Exciplexes can be detected directly by their fluorescence, which is distinct from that of X or Y.[26] The zwitterionic nature of exciplexes is well established. Their fluorescence spectral onsets,[27] fluorescence quantum yields,[28] lifetimes,[29] and the products that they form are strongly affected by increasing solvent polarity as well as by the redox properties of X and Y. Time-resolved fluorescence studies have demonstrated that exciplexes can revert to X* and Y.[30] Of particular significance is the fact that the quantum yield of products derived from exciplexes actually increases as the temperature is decreased.[31]

$$X \xrightarrow{h\nu} X^* \underset{}{\overset{Y}{\rightleftharpoons}} [X^+Y^-] \text{ or} [X^-Y^+] \rightarrow \text{product} \qquad (9)$$

It would seem reasonable to relate the putative carbene–olefin complexes **11** to the exciplex, where the ground-state carbene is substituted for X*, the excited partner in the exciplex. This would imply substantial or complete charge transfer in **11** and that the polarity in **11** would depend on the types of substituents on the olefin. One major problem with the exciplex analogy is the meager dependence of carbene kinetics on solvent polarity. However, because k_1 (eq 8) is likely (and generally assumed) to be diffusion controlled, and both k_{-1} and k_2 will respond to solvent polarity changes in the same qualitative manner, it is difficult if not impossible to predict the magnitude of the solvent effect on the observed carbene rate constants.

There is a further difficulty with the notion of a carbene–olefin complex intermediate. If all the cyclopropanations discussed in this work proceed by the same mechanism (and there is no evidence that any do not), then the weakly bound exciplex-like carbene–olefin complex appears along the paths for all these reactions, in spite of significant variations in the nature and placement of substituents surrounding the double bond. Exciplex formation is strongly affected by substituent variations in the exciplex-forming partners. Thus, we must conclude that while our data are formally consistent with the idea of the reversibly formed complex, there is no evidence that compels us to invoke its existence, and it is difficult to imagine that such a subtly bound species could retain its essential character across the wide range of carbenes and substrates that have now been examined.

Concerted Cycloaddition of Arylchlorocarbenes to Electron-Rich and Electron-Deficient Olefins. The simplest explanation for the data that we have amassed regarding the reactions of arylchlorocarbenes with alkenes is concerted cycloaddition. However, while this is the most economical interpretation, it does not immediately reveal the origin of the apparent ambiphilicity.

Moss, Turro, and co-workers discovered that the activation enthalpies of reactions of phenylhalocarbenes with electron-rich alkenes are near to zero and that activation entropies are large and negative. Our data with electron-deficient alkenes are very similar. These cyclopropanation reactions are entropy-controlled—a viewpoint anticipated much earlier by Skell and Cholod.[32] However, the reactivity can still be explained (vide infra) in terms of enthalpic concepts based on frontier molecular orbital interactions.[22]

Simple explanations based upon decreasing electrophilic reactivities of arylchlorocarbenes toward increasingly electron-poor alkenes are difficult to justify with current kinetic data for additions to α,β-unsaturated esters. For example, we should have expected that substitution of a methyl group onto the β-position

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[32] Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131.

of the unsaturated ester would increase the rate for carbene quenching. Instead, β-methyl substitution (ethyl crotonate versus ethyl acrylate) decreases the reactivity of the carbon–carbon double bond by a factor of ~2. Furthermore, diethyl ethylidenemalonate is significantly more reactive than ethyl crotonate, and both of them are less reactive than DEF (see Table IX). In contrast, both 1-hexene and 1-pentene exhibit reactivities toward arylchlorocarbenes that are generally less than those for either ethyl acrylate or ethyl crotonate but greater than those for quenching by DEM.

Qualitatively, relative reactivities for arylchlorocarbene additions to unsaturated esters and nitriles follow the same order that is found in Diels–Alder reactions,[33] 1,3 dipolar cycloadditions,[34] and in diylophilic reactions of singlet or triplet trimethylenemethanes.[35] Except for DEM, olefins with single electron-withdrawing substituents are less reactive than those with two electron-withdrawing substituents, and maleic anhydride (MAH) has the greatest reactivity in the series that we have measured. If, as appears reasonable based on the 61-fold difference in rate constants for phenylchlorocarbene addition to DEM and MAH (Tables IV, VI, and IX), DEM is not planar and therefore not fully conjugated, its low reactivity is due to a combination of electronic and steric influences. On the other hand, the rate enhancement caused by increasing substitution of unsaturated polar substituents onto the carbon–carbon double bond signifies charge development in the transition state, but only to the extent that solvent stabilization plays no important role.

Hammett plots of the data in Table V show that arylchlorocarbenes react as electrophiles with each of the listed alkenes. Correlations are observed with σ^+, and the calculated ρ-values are positive: BVE (+2.9), DEF (+0.45), DEE (+0.28),[36] ETA (+0.75), PEN (+1.3), HEX (+1.3), ETC (+1.2), and DEM (+0.35). Close examination of these results allows identification of three substrate categories: (1) highly responsive alkenes (BVE, PEN, HEX, and ETC) whose ρ-values are greater than +1.0, (2) weakly responsive alkenes (DEF, DEE, and DEM) whose ρ-values are less than +0.5, and (3) a moderately responsive alkene (ETA) whose ρ-value lies betwen those in the first two categories. Highly responsive alkenes possess an electron-donating alkyl or alkoxy substituent, whereas weakly responsive alkenes have two electron-withdrawing carbalkoxy substituents. Relative reactivities of these alkenes toward each of the reactant carbenes are variable.

These observations are not surprising when one recalls that these reactions are dominated by entropy. Predictions of the influence of electron-withdrawing or electron-donating groups on $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ and, ultimately, the reaction rate constant are difficult at best. Perhaps it is more surprising that any trends in carbene philicities are observed with a given set of olefins, considering that the free energy barrier has little or no enthalpic component.

Calculations performed by Houk provide an answer to this dilemma.[37] Calculations for dihalocarbenes and both isobutylene (DME) and tetramethylethylene (TME) are qualitatively similar. In each case, ΔH and $-T\Delta S$ continuously decrease as the reaction progresses. However, the tetramethylethylene ΔH surface decreases more steeply than does the corresponding surface for isobutylene. This results in an earlier and smaller free energy barrier for the TEM reaction and causes the apparent philicity. One suspects that the phenylchlorocarbene surface behaves similarly. If steep enthalpic descents are realized with ethylenes substituted with electron-donor (e.g., butyl vinyl ether) or electron-withdrawing groups (e.g., DEF), then increased reactivity relative to 1-pentene will result and ambiphilicity will be observed.

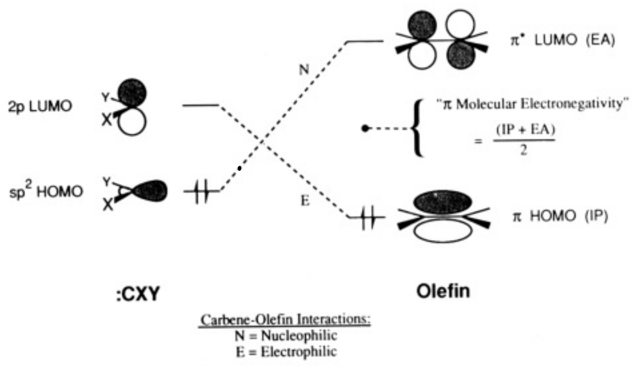

Figure 3. Schematic illustration of frontier molecular orbital interactions, showing the definitions of "π molecular electronegativity" and the electrophilic and nucleophilic interaction terms.

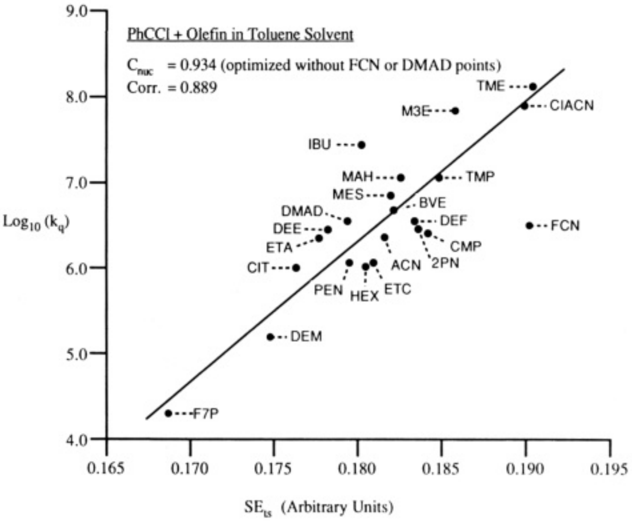

Figure 4. Plot of $\log_{10}(k_{\text{Ole}})$ vs SE_{ts} (definition in text). See Table IX for a complete key to the olefin names. In optimizing the values of C_{nuc}, FCN and DMAD were left out in order to avoid biasing the result with outliers. The slope is 161 ± 20, which implies a very rough value of 15 kcal/mol (electrophilic) and 14 kcal/mol (nucleophilic) for the average resonance integral in the full expression for the SE_{ts}. Comparison with the commonly cited value of 43 kcal/mol for the resonance integral in ethylene suggests that the average frontier orbital overalp in the transition state for PhCCl attack on olefins is $^1/_3$ as large as the p–p π overlap in a double bond.

Frontier Molecular Orbital (FMO) Analysis. We have applied a simplified version of the Houk–Moss–Schoeller[22,38,39] FMO analysis in an attempt to rationalize the observed rates of PhCCl reaction with the new, wider range of olefins. Moss has devised a scale of carbene "philicities" based on experimental relative reactivities of carbenes at room temperature. With Houk and others he has rationalized these data using simple HOMO–LUMO arguments and some assumptions about the nature of carbene–olefin reaction transition states (TSs). For example, the usual FMO expressions can be used to give the stabilization energy of the transition state (SE_{ts}):

$$\text{SE}_{\text{ts}} = \left[\frac{\langle \text{LU}_{\text{CXY}}|\text{H}|\text{HO}_{\text{Ole}}\rangle^2}{E_{\text{LU}_{\text{CXY}}} - E_{\text{HO}_{\text{Ole}}}}\right] + \left[\frac{\langle \text{LU}_{\text{Ole}}|\text{H}|\text{HO}_{\text{CXY}}\rangle^2}{E_{\text{LU}_{\text{Ole}}} - E_{\text{HO}_{\text{CXY}}}}\right]$$

where LU = LUMO, HO = HOMO, CXY = carbene, Ole = olefin, and E_{XX} is the orbital energy of orbital XX (see Figure 3). If one assumes that these TSs are early and (less reasonably) that the "electrophilic" (first term) and "nucleophilic" (second term) resonance integrals (∝ overlap) in the numerators are unchanged for all olefins (see below),[40] then the whole range of

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Table IX. Rates, IP, EA, and SE_{ts} Data:[a] Quenching of Phenylchlorocarbene by Olefins

olefin	k_q ± 2SD[b]	log k_q	T[c]	solvent[d]	IP, eV	EA, eV	Elec[e]	Nuc[f]	SE_{ts}[a]	log $(k_q)_T$[g]
TME[h]	1.31 ± 0.10 × 10^8	8.12	25	T	8.27[i]	−2.27[i]	0.1115	0.0842	0.191	8.12
TME[j]	1.4 × 10^8	8.15	25	T						
TME[j]	2.8 × 10^8	8.45	23	I						
TME[j]	1.1 × 10^8	8.04	27	A						
M3E[j]	1.3 × 10^8	8.11	RT	I	8.68[i]	−2.24[i]	0.1066	0.0845	0.186	7.81
ClACN[k]	2.1 × 10^8	8.32	RT	P	10.58[l]	+0.34[k]	0.0887	0.1080	0.190	7.87
ClACN[k]	5.3 × 10^7	7.72	RT	A						
IBU[j]	5.49 × 10^7	7.74	RT	I	9.24[i]	−2.19[i]	0.1006	0.0848	0.180	7.44
TMP	1.14 ± 0.07 × 10^7	7.06	22	T	8.98[m]	−1.9[n]	0.1033	0.0870	0.185	7.06
MAH	9.38 ± 0.56 × 10^6	6.97	22–3	E	12.0[o]	+0.57[p]	0.0787	0.1107	0.183	7.06
MAH	14.4 ± 0.23 × 10^6	7.16	23	E						
MES	7.23 ± 0.62 × 10^6	6.86	21	T	10.2[q]	−0.8[q]	0.0917	0.0962	0.182	6.86
2PN[j]	5.5 × 10^6	6.74	RT	I	9.04[m]	−2.0[n]	0.1027	0.0862	0.184	6.44
BVE	4.71 ± 0.33 × 10^6	6.67	23	T	9.14[r]	−2.06[s]	0.1016	0.0858	0.182	6.67
DMAD	3.58 ± 0.16 × 10^6	6.55	25–6	T	11.5[t]	0.0[q]	0.0820	0.1042	0.179	6.55
DEF	3.32 ± 0.15 × 10^6	6.52	28	T	10.7[t]	−0.2[q]	0.0877	0.1020	0.184	6.55
DEF	3.79 ± 0.11 × 10^6	6.58	23	T						
DEF	9.21 ± 0.73 × 10^6	6.96	23	H						
DEF	11.86 ± 1.17 × 10^6	7.07	27–8	H						
DEF	3.00 ± 0.28 × 10^6	6.48	23	E						
FCN	3.26 ± 0.31 × 10^6	6.51	21–2	E	11.15[l]	+0.78[l]	0.0844	0.1134	0.190	6.50
FCN	3.05 ± 0.47 × 10^6	6.48	23	E						
DEE	2.78 ± 0.17 × 10^6	6.44	23	T	10.9[q]	−0.6[q]	0.0862	0.0980	0.178	6.44
CMP	2.56 ± 0.14 × 10^6	6.41	23	T	8.98[m]	−2.0[n]	0.1033	0.0862	0.184	6.41
ACN[u]	5.4 × 10^6	6.73	RT	I	10.92[l]	−0.21[v]	0.0861	0.1019	0.182	6.39
ACN[k]	7.0 × 10^6	6.85	RT	P						
ACN[k]	1.8 × 10^6	6.26	RT	A						
ETA	2.06 ± 0.05 × 10^6	6.31	22	T	10.72[t]	−0.8[w]	0.0876	0.0962	0.178	6.35
ETA	2.43 ± 0.07 × 10^6	6.39	23	T						
ETA	1.58 ± 0.08 × 10^6	6.20	22	E						
ETA[u]	5.1 × 10^6	6.71	RT	I						
ETA[u]	1.3 × 10^6	6.11	RT	A						
PEN	1.18 ± 0.05 × 10^6	6.07	22	T	9.52[x]	−1.88[n]	0.0978	0.0871	0.180	6.07
HEX	1.10 ± 0.05 × 10^6	6.04	21	T	9.48[x]	−1.80[n]	0.0982	0.0877	0.181	6.04
HEX	8.31 ± 0.36 × 10^6	5.92	23	E						
HEX[j]	2.2 × 10^6	6.34	23	I						
HEX[u]	9.4 × 10^5	5.97	RT	A						
ETC	1.14 ± 0.05 × 10^6	6.06	22	T	10.11[t]	−1.0[q]	0.0925	0.0943	0.181	6.06
CIT	1.01 ± 0.10 × 10^6	6.00	21	T	10.1[q]	−1.6[q]	0.0926	0.0893	0.176	6.00
DEM	1.53 ± 0.18 × 10^5	5.18	23	T	10.47[t]	−1.4[q]	0.0895	0.0909	0.175	5.18
DEM	1.54 ± 0.19 × 10^5	5.19	26–7	T						
F7P[y]	<2.0 × 10^4	<4.30	RT	T	11.4[z]	−1.3[z]	0.0826	0.0917	0.169	<4.30

[a] IP = ionization potential; EA = electron affinity; SE_{ts} = stabilization energy of the transition state, as estimated by the FMO method outlined in the text. We use HO_{CXY} = 9.6 eV and LU_{CXY} = −0.7 eV. These estimates are based on the calculated values found for several other carbenes by Moss et al. and reported in: Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Lawrynowicz, G.; Włostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341, and references therein. Key to compound abbreviations: TME = 2,3-dimethyl-2-butene; M3E = 2-methyl-2-butene; ClACN = α-chloroacrylonitrile; IBU = 2-methylpropene; TMP = *trans*-4-methyl-2-pentene; MAH = maleic anhydride; MES = diethyl mesoconate; 2PN = 2-pentene; BVE = *n*-butyl vinyl ether; DMAD = dimethyl acetylenedicarboxylate; FCN = fumaronitrile; DEF = diethyl fumarate; DEE = diethyl ethylidene malonate; CMP = *cis*-4-methyl-2-pentene; ACN = acrylonitrile; ETA = ethyl acrylate; PEN = 1-pentene; HEX = 1-hexene; ETC = ethyl crotonate; CIT = diethyl citraconate; DEM = diethyl maleate; F7P = 3,3,4,4,5,5,5-heptafluoropent-1-ene. [b] Bimolecular rate constants, in units of L/mol·s. [c] Temperatures in °C. [d] Solvents: T = toluene; I = isooctane; A = acetonitrile; P = pentane; E = ethyl acetate; H = heptane. [e] Elec = "electrophilic" interaction: $(LU_{CXY} - HO_{Ole})^{-1}$. [f] Nuc = "nucleophilic" interaction: $(LU_{Ole} - HO_{CXY})^{-1}$. We obtain a C_{nuc} value (see text) of 0.934, which yields the fairly poor correlation coefficient of 0.889, even when DMAD and FCN, whose EA values are likely to be off, are excluded from the calculation. [g] Rates corrected to values expected in toluene, where these are not available. See text and footnote *k* for discussion of the corrections. [h] This work. [i] IP and EA values from: Jordan, K. D.; Burrow, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 6882. [j] Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjial, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587. [k] Moss, R. A.; Fan, H.; Hadel, L. M.; Shen, S.; Włostowska, J.; Włostowski, M.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1987**, *28*, 4779. The absolute rates of reaction of ClACN and ACN with PhCCl in toluene were estimated from our measured ETA rate and the known relative reactivities of ClACN, ACN, and ETA in hydrocarbon solvents. The EA value for ClACN was estimated by adding the difference between the ab initio LUMO energies for ClACN and ACN to the known EA of ACN (−0.21 eV). [l] Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937. This EA value for FCN is probably too large, leading to an overestimation of SE_{ts}. [m] Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213. The IP for TMP was assumed to be the same as for CMP based on similar equalities in the but-2-enes and the pent-2-enes. [n] EAs estimated from the data in: Kadifachi, S. *Chem. Phys. Lett.* **1984**, *108*, 233 (which were scaled to Jordan's EA scale, ref *i*). Giordan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6544. [o] Almemark, M.; Bäckvall, J. E.; Moberg, C.; Åkermark, B.; Åsbrink, L.; Roos, B. *Tetrahedron* **1974**, *30*, 2503. [p] Samuilov, Ya. D.; Uryadov, U. G.; Uryadova, L. F.; Konovalov, A. I.; *Zh. Org. Khim.* **1985**, *21*, 1249. [q] "Wild" guesses projected from known trends and available values. [r] Friege, H.; Klessinger, M. *J. Chem. Res., Synop.* **1977**, 208. [s] This is the EA for ethyl vinyl ether. Choi, Y.; Jordan, K. D., personal communication. We are very grateful to Professor K. D. Jordan for obtaining this result and communicating it prior to publication. [t] Sustmann, R.; Trill, H. *Tetrahedron Lett.* **1972**, 4271. [u] Moss, R. A.; Lawrynowicz, W.; Hadel, L. M.; Hacker, N. P.; Turro, N. J.; Gould, I. R.; Cha, Y. *Tetrahedron Lett.* **1986**, *27*, 4125. These "ETA" rates were actually obtained with *methyl* acrylate. [v] Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341. For a more recent review of EA values, see: Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557. [w] This EA value, which is actually for *methyl* acrylate, is taken from: Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58. It is quoted as coming from earlier estimates by Houk and co-workers (*J. Am. Chem. Soc.* **1973**, *95*, 7287) but the sign was reversed in translation. Because this seems a reasonable guess at the EA of ETA, we use this value nonetheless. [x] Masclet, P.; Grojeau, D.; Mouvier, G.; Dubois, J. *J. Electron. Spectrosc. Relat. Phenom.* **1973**, *2*, 225. [y] Note that this rate represents an upper bound. We were unable to measure any rate changes up to solutions of 50% F7P in toluene. [z] IP (measured) and EA (calculated) values are scaled from those for 3,3,3-trifluoropropene: Grant, J. L.; Hale, P. D.; Stair, P. C. *J. Electron. Spectrosc. Relat. Phenom.* **1986**, *40*, 271.

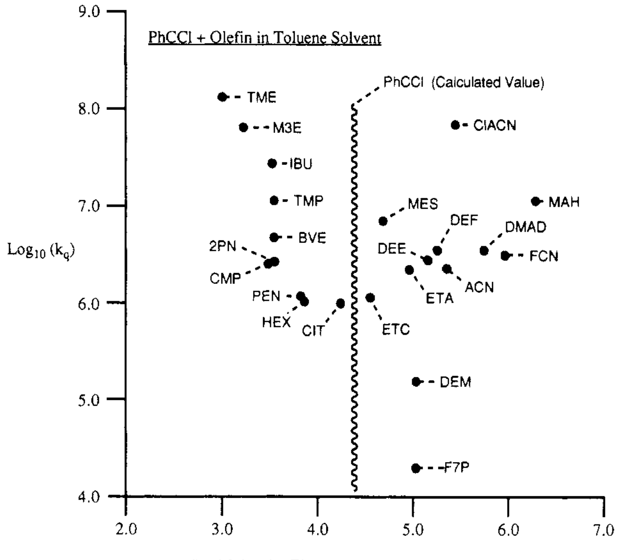

Figure 5. Plot of $\log_{10}(k_{\mathrm{Ole}})$ vs π molecular electronegativity. See Table IX for a complete key to the olefin names. The zig-zag line in the middle marks the location of the carbene's "molecular electronegativity" as calculated from our estimated carbene IP and EA values.

carbene reactivity can be plotted against a weighted sum of the denominator terms above:

$$\frac{1}{E_{\mathrm{LU_{CXY}}} - E_{\mathrm{HO_{Ole}}}} + \frac{C_{\mathrm{nuc}}}{E_{\mathrm{LU_{Ole}}} - E_{\mathrm{HO_{CXY}}}}$$

where the E's used are the vertical ionization potentials (IP) and electron affinity (EA) values for their respective fragments and C_{nuc} is the average ratio between electrophilic and nucleophilic resonance integrals. The results of such an analysis are shown in Table IX and Figure 4.

As discussed by Rondan, Houk, and Moss,[22] transition structures (i.e., maxima on the ab initio potential energy surfaces) for carbene–olefin reactions occur later as carbenes become more nucleophilic. While the $\langle \mathrm{HO_{Ole}} | \mathrm{LU_{CXY}} \rangle$ overlaps (and therefore the electrophilic resonance integrals) calculated for various transition structures are fairly insensitive to such variations in philicity, the $\langle \mathrm{HO_{CXY}} | \mathrm{LU_{Ole}} \rangle$ terms increase strongly with increasing carbene nucleophilicity. An ideal FMO treatment would include such variations in overlap as well as orbital energy differences. However, since carbene–olefin reactions are entropy dominated (see below), we believe that the true average transition structures (i.e., free energy maxima) are considerably more alike than are the potential energy maxima.[41] Given the large number of estimates and approximations already in the data, we prefer to employ the simplest picture available—that of geometrically similar transition states for all the cyclopropanation reactions of one carbene (PhCCl) with all olefins.

Relatively recent work shows that carbene–olefin reactions are entropy controlled, at least around ambient temperatures and above. Typical activation parameters are on the order of $\Delta H^{*} \simeq -3$ to 3 kcal/mol and $\Delta S^{*} \simeq$ 20–25 eu.[18] We must therefore be skeptical of a rationalization of reactivity that depends on enthalpic terms like $\mathrm{SE_{ts}}$. We have now looked at a reasonable range of olefins reacting with PhCCl and covering a rate range of 3 orders of magnitude. We find only a gross overall correlation of rates with $\mathrm{SE_{ts}}$ as defined above. Unfortunately, E_{HO} and E_{LU} for the carbene must be estimated from calculations, whereas we use mostly experimental data for the olefin numbers (see below, however). Many of the EA and some of the IP data have simply been estimated on the basis of "reasonable" interpolations between known species (see Table IX). Although these approximations were made before the data were plotted in order to avoid bias, the plots (Figures 4 and 5) are based on some very weak numbers, in spite of the availability of quite a few good rate constants.

The reproducibility of the rate constants reported here is typically ±10%. Where we and others[18] have measured rate constants in the same solvents, we find agreement to within this range as well. Because there is some systematic variation in rates with solvent, we have estimated the toluene rates from those measured in other solvents using one of two approaches: (1) To broaden the range of electron-poor olefins, we have incorporated data for ACN (acrylonitrile) and ClACN (α-chloroacrylonitrile) based on their known rates relative to ETA.[42] (2) We have observed that $k_{\mathrm{toluene}} \simeq {}^{1}/_{2}k_{\mathrm{isooctane}}$ for both TME and HEX. *Relative* rates for the methylated ethylenes, as measured by product distributions, are fairly insensitive to solvent. Therefore, $k_{\mathrm{toluene}} = {}^{1}/_{2}k_{\mathrm{isooctane}}$ is assumed to hold for these simple alkenes. Where data in toluene and in ethyl acetate were obtained, a rate ratio of roughly $k_{\mathrm{EtOAc}} \simeq {}^{5}/_{4}k_{\mathrm{toluene}}$ is observed. These differences fall amost within typical error bounds and would represent very small corrections on the ln k scale, so we use the ethyl acetate data uncorrected.

A reasonably self-consistent set of olefin vertical *electron affinity* (EA) values is essential if an any understanding of carbene nucleophilic behavior is to be extracted from the FMO analysis. Sadly, few experimental values are available, especially for the electron-poor olefins which are the focus of this work. Most available data have been obtained by electron transmission spectroscopy. Several of the EA values were estimated by "reasonable" extrapolations from the few known values and trends. Maleic anhydride (MAH) and fumaronitrile (FCN) have bound negative ion states, placing their *vertical* EAs out of experimental reach. Since there is no simple correction to convert adiabatic to vertical EAs, we have chosen to use the adiabatic values, recognizing that they may result in overestimation of the nucleophilic term in $\mathrm{SE_{ts}}$ for MAH and FCN.

Experimental *ionization potentials* (IPs) are available for nearly all of the olefins listed in Table IX. With the large number of reference species available, an IP could be fairly confidently estimated for DEE, the one substrate for which no experimental IP values are found.

At the simple level to which we are restricted by the available data, $\mathrm{SE_{ts}}$ gives only a rough reflection of the relative reactivities of olefins with PhCCl and completely fails in the cases of IBU and FCN. However, the substrate set under consideration here includes mono-, di-, tri-, and tetrasubstituted olefins and is analyzed in terms of IP and EA data collected from a variety of sources. Schoeller[38] has pointed out that consideration of olefin π-orbital coefficients can substantially improve the performance of such treatments, as might some means of including steric effects. Perhaps the inherent self-consistency in a purely theoretical analysis would show that this simple FMO picture can accurately describe carbene–olefin reactivity trends. In any case, one observation is clear: inclusion of the nucleophilic term in the estimation of $\mathrm{SE_{ts}}$ is necessary when the substrate set includes electron-poor olefins. Plotting log k_{obsd} versus the electrophilic term along for our expanded data set gives uninterpretable scatter.

Perhaps a more informative way of relating rates to the orbital interactions discussed above is to plot log k_{Ole} against the "π molecular electronegativity" for each olefin. This approach avoids the need for an estimate of the carbene's FMO energies. We define π molecular electronegativity of an olefin to be (IP + EA)/2, the average of its π- and π*-orbital energies as approximated by the IP and EA values. If the IP–EA energy difference were constant for all olefins, a U-shaped plot would be expected.

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(40) This really is a gross approximation as shown by the detailed analysis presented in ref 22. Rondan et al. analyzed a range of carbenes attacking ethylene and found substantial differences between the geometries and overlap integrals of the calculated transition states for attack by electrophilic and nucleophilic carbenes. However, in this analysis, we are examining a series of mono-, di-, tri- and tetrasubstituted olefins reacting with a single carbene, and without explicitly calculating transition states for each reaction, it is difficult to guess a priori how the overlaps (and hence resonance integrals) will change with varying olefin substitution.

(41) See, however, the discussion of this topic: Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.

(42) Moss, R. A.; Fan, H.; Hadel, L. M.; Shen, S.; Włostowska, J.; Włostowski, M.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1987**, *28*, 4779.

The data of Table IX (Figure 5) show roughly this behavior, with rate increases at the ends where the electrophilic or nucleophilic interactions become strong. The minimum at the center coincides remarkably well with the carbene's molecular electronegativity calculated from its estimate HO and LU energies (Table IX). The DEM and F7P points lie far below the curve, which we attribute to steric blockage by the *cis*-dicarboxylate groups in DEM and to the wide IP–EA gap in F7P. There is still considerable scatter in the plot, especially toward the nucleophilic end. However, it is clear from this picture that phenylchlorocarbene can be induced to react rapidly as a nucleophile in the presence of sufficiently electron-poor olefins. Similar conclusions have been reached by Moss and co-workers.[42]

Experimental Section

General Methods. ^{1}H NMR spectra were obtained on a Varian VXR-300 spectrometer; chemical shifts are reported in δ units with tetramethylsilane as the internal standard. Infrared spectra were recorded on an IBM IR/32 FT spectrometer, and mass spectra were obtained with the Hewlett-Packard 5995C GC/MS system operated at 70 eV. Analytical gas chromatographic analyses were performed on a Hewlett-Packard 5890A capillary GC using either or both SP-2330 or methylsilicone columns or on a Perkin-Elmer 8500 capillary GC using a 5% DB-1701 column. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. 3-Aryl-3-chlorodiazirines were prepared from their corresponding benzamidine hydrochlorides by Graham's procedure.[43] Diethyl maleate having a DEM/DEF ratio >300 was obtained commercially and further purified by distillation before use. Methyl citraconate was prepared from the corresponding acid by treatment with diazomethane. 1-Hexene was purified by simple distillation. *n*-Butyl vinyl ether was distilled from sodium/benzophenone. Diethyl ethylidenemalonate was dried over basic alumina. Other esters were distilled from anhydrous potassium carbonate and dried over phosphorus pentoxide. Alkenes were packaged for use under nitrogen over 4-Å molecular sieves.

Product Analyses. Thermal Decomposition. 3-Chloro-3-phenyldiazirine (0.1–1.0 mmol) in variable amounts of dry carbon tetrachloride containing DEM was heated to reflux under nitrogen and maintained at that temperature for 3 h. GC analysis on an SP-2330 capillary column provided the DEM/DEF ratio. After reaction was complete, the solvent was removed under reduced pressure, and the residue was subjected to ^{1}H NMR and then GC and GC/MS analyses. Product ratios obtained by these different methods corresponded to within 2%. An internal standard, dibenzyl ether, was employed to obtain product yields. **1a**: ^{1}H NMR ($CDCl_3$) δ 7.50–7.30 (m, Ph), 4.29 (q, J = 7.1 Hz, 2 CH_2), 2.63 (s, 2 H), 1.34 (t, J = 7.1 Hz, 2 CH_3); MS, *m/e* 261 (1.4, M – Cl), 224 (10), 222 (11), 159 (21), 151 (33), 149 (83), 131 (28), 115 (100), 105 (34), 103 (27), 89 (25), 77 (29). **1b**: ^{1}H NMR ($CDCl_3$) δ 7.50–7.30 (m, Ph), 4.07 (q, J = 7.2 Hz, 2 CH_2), 2.95 (s, 2 H), 1.15 (t, J = 7.2 Hz, 2 CH_3); MS, *m/e* 261 (4.4, M – Cl), 224 (20), 222 (22), 159 (22), 151 (35), 149 (90), 131 (29), 115 (100), 105 (36), 103 (28), 89 (22), 77 (36). **2**: ^{1}H NMR ($CDCl_3$) δ 7.50–7.30 (m, Ph), 4.31 (q, J = 7.1 Hz, CH_2), 3.96 (q, J = 7.1 Hz, CH_2), 3.18 (d, J = 7.1 Hz, 1 H), 3.12 (d, J = 7.0 Hz, 1 H), 1.36 (t, J = 7.1 Hz, CH_3), 1.04 (t, J = 7.1 Hz, 3 H); MS, *m/e* 251 (14), 224 (30), 222 (28), 178 (22), 160 (27), 159 (26), 151 (40), 149 (100), 131 (27), 115 (84), 105 (30), 103 (24), 89 (18), 77 (25). Anal. Calcd for $C_{15}H_{17}ClO_4$: C, 60.71; H, 5.77; Cl, 11.92. Found: C, 60.47; H, 5.77; Cl, 12.13.

Reactions with dimethyl citraconate were performed under the same conditions. **6a**: ^{1}H NMR ($CDCl_3$) δ 7.60–7.25 (m, Ph), 3.65 (s, OCH_3), 3.50 (s, OCH_3), 2.54 (s, 1 H), 1.88 (s, CH_3); MS, *m/e* 282 (2, M), 250 (19), 222 (36), 187 (24), 165 (39), 163 (100), 159 (55), 157 (35), 155 (98), 129 (40), 128 (80), 127 (58), 115 (24), 105 (43), 77 (33). **6b**: ^{1}H NMR ($CDCl_3$) δ 7.60–7.25 (m, Ph), 3.83 (s, OCH_3), 3.82 (s, OCH_3), 2.43 (s, 1 H), 1.20 (s, CH_3); MS, *m/e* 250 (18), 222 (37), 165 (43), 163 (100), 159 (64), 157 (31), 155 (88), 129 (36), 128 (80), 127 (52), 115 (16), 105 (33), and 77 (32). **7a**: ^{1}H NMR ($CDCl_3$) δ 7.42–7.25 (m, Ph), 3.86 (s, OCH_3), 3.72 (s, OCH_3), 3.29 (s, 1 H), 1.53 (s, CH_3); MS, *m/e* 250 (16), 222 (33), 165 (38), 163 (100), 159 (49), 157 (32), 155 (98), 129 (45), 128 (85), 127 (55), 115 (22), 105 (39), 77 (35). **7b**: ^{1}H NMR ($CDCl_3$) δ 7.42–7.25 (m, Ph), 3.82 (s, OCH_3), 3.37 (s, OCH_3), 3.36 (s, 1 H), 1.87 (s, CH_3); MS, *m/e* 282 (1, M), 250 (16), 222 (31), 165 (37), 163 (100), 159 (49), 157 (22), 155 (90), 129 (38), 128 (81), 127 (49), 115 (18), 105 (30), 77 (30). Anal. Calcd for $C_{14}H_{15}ClO_4$: C, 59.47; H, 5.35. Found: C, 59.33; H, 5.33.

Product Analyses. Photolytic Decomposition. A solution of arylchlorodiazirine (0.10 mmol) and freshly distilled DEM (1.0 mmol) in 1.00 mL of dry toluene was sealed in a Pyrex tube under nitrogen. Photolysis was performed in a thermostated bath maintained at 15 °C for 3 h and, in a separate experiment, at liquid nitrogen temperature for 6 h using a battery of 350-nm bulbs in a Rayonet photoreactor. Analysis of products was performed by GC at room temperature, and peak identities were established by retention time and GC/MS comparisons with authentic samples. Except for resonances of aromatic protons, the ^{1}H NMR signals for each of the cyclopropane isomers were the same (±0.03 δ) as those reported in the previous section for **1a**, **1b**, and **2**, and mass spectral fragmentations for each member of the isomeric set were approximately identical.

Photolysis of 3-Chloro-3-phenyldiazirine in the Presence of *cis*-4-Methyl-2-pentene. A solution of phenylchlorodiazirine (31 mg, 0.002 mM) in freshly distilled *cis*-4-methyl-2-pentene (2 mL) was sealed in a Pyrex tube under nitrogen. Photolysis was performed in a water bath maintained at 20 °C for 3 h using a battery of 350-nm bulbs in a Rayonet photoreactor. The excess solvent was evaporated under reduced pressure. The cyclopropane was isolated by preparative TLC using a 0.5-mm silica gel precoated plate: yield 28 mg, 67%. GC/MS analysis of this purified cyclopropane showed the presence of two adducts (syn and anti) in the ratio of 70:30. Attempted separation of the syn and anti forms using preparative GC (Carbowax or SE-30 column) was not successful. Both the isomers showed identical mass spectral fragmentations: anal. calcd (high-resolution MS) for $C_{13}H_{17}Cl$ 208.723, found 208.721.

The above experiment was repeated under identical conditions using *trans*-4-methyl-2-pentene yielding a mixture of two adducts (syn and anti) in the ratio of 47:53 (62% yield). The two adducts were shown to be different from the cis adducts obtained in the previous experiment by GC analysis: anal. calcd (high-resolution MS) for $C_{13}H_{17}Cl$ 208.723, found 208.718.

Kinetic Determinations. Solutions of the diazirines were prepared in spectral-grade toluene solvent, and the concentration of diazirine was adjusted to have an absorbance of 0.1 at 350 nm in each case. The solutions were placed in 1-cm^2 Suprasil quartz cells and deoxygenated by bubbling with high-purity nitrogen. The samples were irradiated with the pulses of a Lumonics TE-861-4 excimer laser using a $Xe/F_2/He$ gas mixture (350 nm, 80 mJ, 10 ns) which impinged on the sample at a right angle to the 1000-W xenon arc lamp monitoring beam. The monitoring beam was focused on the slit of an Oriel monochrometer with ~1 mm front and rear slits. Signals were obtained with an IP 28 photomultiplier tube detector and were digitized by a Tektronix 7912 A/D converter. The experiment was controlled by an Apple IIe microcomputer which was also used for storage, processing, and hard copies of the data. Kinetic studies were performed using 6–11 separate static samples in each case. Typically three independent measurements of k_{obsd} were obtained for each olefin concentration.

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(43) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.