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Laser Flash Photolysis Study of Phenylcarbene and Pentafluorophenylcarbene

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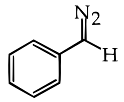
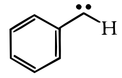
Laser flash photolysis (LFP) (XeCl, 308 nm, 17 ns) of phenyldiazomethane and pentafluorophenyldiazomethane releases phenylcarbene (PC) and pentafluorophenylcarbene (PFPC), respectively. In acetonitrile solvent the carbenes react rapidly to form nitrile ylides which have convenient absorption maxima for optical detection ($\lambda_{\max} = 350$ nm). Phenylcarbene and pentafluorophenylcarbene each react with acetonitrile with an absolute rate constant of 2.4×10^6 M^{-1} s^{-1} in $CF_2ClCFCl_2$ (Freon-113) at ambient temperature. The lifetimes of spin-equilibrated PC and PFPC are 190 and 500 ns in Freon-113, respectively, and the lifetime of each carbene is deduced to be 22 ns in neat acetonitrile. LFP of phenyl and pentafluorophenyldiazomethane in the presence of pyridine leads to the expected pyridine ylide. The observed absolute rate constants of reaction of spin equilibrated PC and PFPC with pyridine are 1.9×10^7 and 5.1×10^7 M^{-1} s^{-1}, respectively, in Freon-113 at ambient temperature. From this data, one can deduce singlet−triplet splittings (ΔG_{ST}, 298 K) of 2.3 and 3.1 kcal/mol for PC and PFPC, respectively, which is the difference in energy between the triplet minimum and the point of intersection of the singlet and triplet carbene plus pyridine surfaces. LFP of phenyldiazomethane and pentafluorophenyldiazomethane in acetonitrile containing carbene scavengers (e.g., alcohols, alkenes, and silanes) gives reduced yields of nitrile ylides. Analysis of the yield of ylide as a function of quencher by the Stern−Volmer method gives $k_Q\tau$ values of carbene quenching. Low-temperature (77 K) photolysis of pentafluorophenyldiazomethane generates the persistent EPR spectrum of triplet pentafluorophenylcarbene which is the ground state of this carbene. However, photolysis of pentafluorophenyldiazomethane at ambient temperature generates stable reaction products derived from capture of singlet pentafluorophenylcarbene. Thus the properties of pentafluorophenylcarbene are remarkably similar to those of phenylcarbene. Each carbene has a triplet ground state but reacts in solution at ambient temperature through a low-lying excited singlet state. The lack of a fluorine substituent effect on the behavior of phenylcarbene is compared to that in singlet phenylnitrene.

I. Introduction

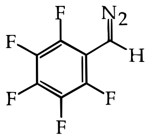
In the past decade, numerous studies of the dynamics of arylcarbenes have been reported.[1] Laser flash photolysis (LFP) studies of diphenylcarbene,[2] fluorenylidene,[3] and 1- and 2-naphthylcarbene,[4,5] and halophenylcarbenes[6] have been described. The absorption spectra of these transient species and their absolute rate constants of reaction were tabulated. Strangely enough, the parent arylcarbene, phenylcarbene (PC), was not studied by LFP techniques until very recently,[7] a fact which provided partial motivation for this study. A stronger impetus driving this work was the finding of very dramatic effects of fluorine substitution on the properties of phenylnitrene.[8] Whereas PC is easily intercepted by a variety of trapping agents to give good yields of products,[9] the generation of phenylnitrene invariably leads to polymeric tar, or interception of its ring-expanded ketenimine isomer.[10,11] The absolute kinetics of PC and pentafluorophenylcarbene (PFPC) were determined in this study in an attempt to discover fluorine effects in the carbenic system and to place the fluorine effect on arylnitrene chemistry into clearer focus. In addition to time-resolved studies, the matrix EPR spectrum of PFPC has been obtained, and the stable products of its chemical reactions at ambient temperature identified in cyclohexane and in methanol. The data indicates that, in contrast to phenylnitrene, the effect of fluorine substitution on the chemistry and dynamics of PC is negligible.[8,11]



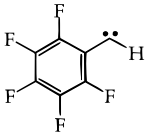
PDM



PC



PFPDM

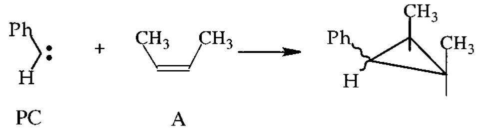


PFPC

II. Results

Chemical Analysis of Reaction Mixtures. PC has been well studied by the many classical tools of carbene chemistry.[9] Photolysis of phenyldiazomethane (PDM) and other precursors at cryogenic temperatures generates PC as a persistent species in rigid media. This has allowed its study by UV−Vis,[12] fluorescence,[13] IR,[12] and EPR[14] spectroscopies. There is no question that the triplet is the lowest energy state of phenylcarbene.

PDM and other precursors have been photolyzed in several solvents, and the stable mixture of products formed have been analyzed.[9] Generation of PC in the presence of alkenes (**A**) produces the expected cyclopropane with almost perfect stereospecificity.[9,15]



PC A

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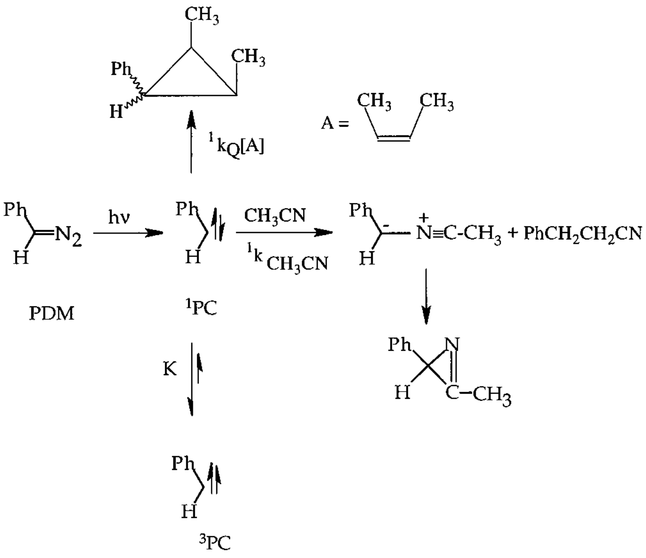
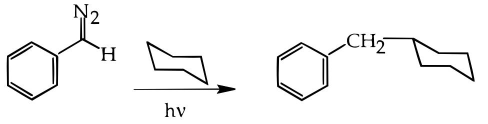
SCHEME 1

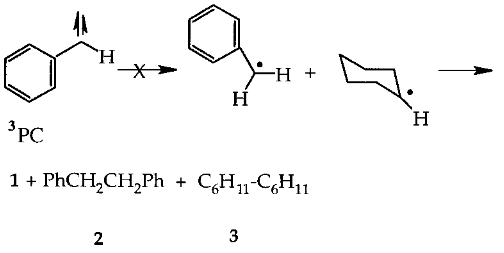


This result does not change upon dilution of the alkene with less reactive cosolvents.[9b] This result and the work of Baer and Gutsche[16] indicate that spin equilibration of PC is rapid in solution relative to the rate of its bimolecular reactions. Typically, interception of the higher energy, more reactive singlet state predominates (Scheme 1), as shown by Moss and Tomioka who have chemically intercepted ^{3}PC, but at −196°, where the equilibrium greatly favors the ground triplet state.[9b,17]

We have obtained results consistent with expectations, and with Scheme 1, upon photolysis of PDM in cyclohexane. The product isolated is formed rather cleanly and is that of singlet carbene CH insertion (**1**). Only trace amounts of diphenylethane **2** or bicyclohexyl **3** were detected, which indicated that there is very little chemistry of triplet phenylcarbene in this solvent at ambient temperature.

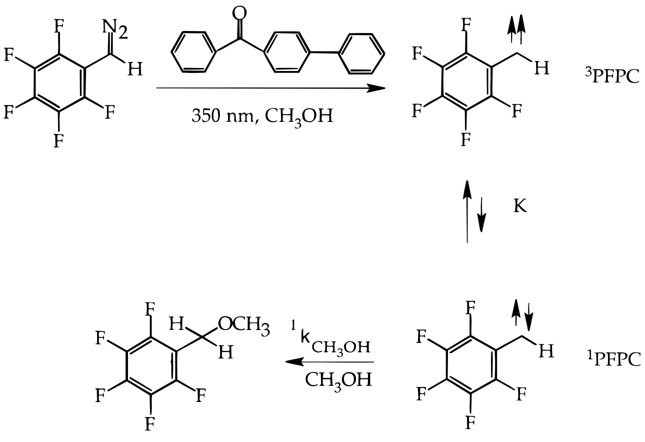


PDM **1**

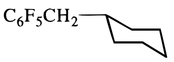


The isotope effect (C_6H_{12} vs C_6D_{12}) to singlet insertion CH in cyclohexane is approximately 2. This was determined by photolyzing PDM in a 1:1 (v:v) mixture of cyclohexane and cyclohexane-d_{12} followed by GC-MS of the product mixture. Adducts **1** and **1**-d_{12} were easily separated and their relative intensities measured to determine the isotope effect. The isotope effect of **2** realized with PC is very similar to that obtained with 1-naphthylcarbene[4] and is characteristic of singlet carbenes.[1,9c] Substantially larger isotope effects are observed in the reaction of triplet carbenes (e.g., diphenylcarbene) with C−H bonds.[2c]

SCHEME 2



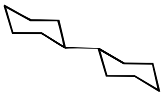
Photolysis of PFPDM in cyclohexane cleanly produces adduct **4** (>98% of the volatile reaction products) at ambient temperature.



4

$C_6F_5CH_2CH_2C_6F_5$

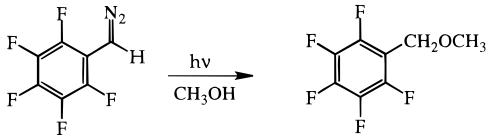
5



3

Significantly neither radical dimer **5** nor **3** was formed in this reaction. Apparently, only the singlet state of pentafluorophenylcarbene (^{1}PFPC) reacts with cyclohexane at ambient temperature.

Photolysis of PFPDM in methanol cleanly yields the product of OH insertion, a reaction that is characteristic of singlet carbenes.[2]



PFPDM **6**

No products other than **6** were formed in methanol in more than trace quantities. Photolysis of PFPDM in the presence of a triplet sensitizer, under conditions where all of the light is absorbed by the triplet sensitizer, again leads cleanly to the formation of **6**. This demonstrates that the low-lying singlet state of PFPC is easily accessed from the ground triplet state (Scheme 2).

The triplet nature of the ground state of pentafluorophenylcarbene (^{3}PFPC) was confirmed by low-temperature spectroscopy. A solution of PFPDM in perfluorohexane was cooled to −196° and irradiated with 350 nm light. Photolysis generated a new set of EPR absorption bands characteristic of a ground state triplet carbene. The zero-field parameters $|D/hc| = 0.521$ cm^{-1} and $|E/hc| = 0.0259$ cm^{-1} are very similar to those of PC which have $|D/hc| = 0.515$ cm^{-1} and $|E/hc| = 0.0251$ cm^{-1}.[14] The photogenerated resonance absorption bands disappear upon thawing the matrix. It is clear that the triplet is either the ground state of PFPC or is within a few cal/mol of the ground state.

The product studies and low-temperature EPR studies reveal that, although PFPC has a triplet ground state, the singlet state is readily accessible. The singlet state of PFPC must be much more reactive than the triplet state as its chemistry predominates at ambient temperature. The chemistry of PC and PFPC follows the same pattern. Thus it seems safe to assume that, as per

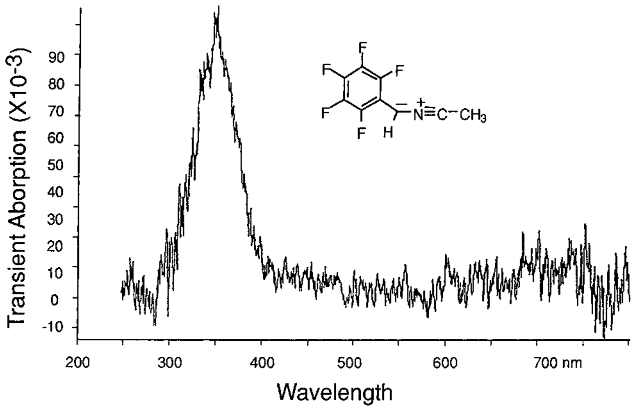
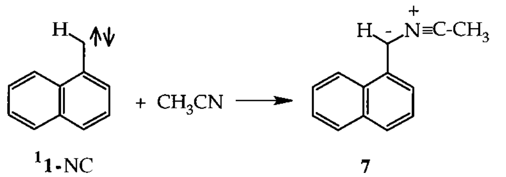


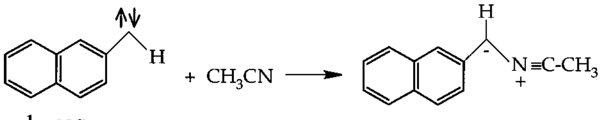
Figure 1. The transient absorption spectrum of ylide **10** produced by LFP of PFPDM in acetonitrile.

PC, diphenylcarbene, fluorenylidene, and 1-naphthylcarbene,[1-5,9] singlet and triplet pentafluorophenylcarbene are in rapid equilibrium in solvents of relatively low reactivity at ambient temperature.

Laser Flash Photolysis Studies of PC and PFPC. 1-Naphthylcarbene (NC) was among the first aryl carbenes to be studied by the LFP technique.[4] It is difficult to detect the ground triplet state (^{3}NC) directly by optical methods because its UV absorption maximum falls underneath that of 1-naphthyldiazomethane. Thus we were not surprised when LFP of PDM and PFPDM in pentane did not lead to significant transient absorption between 300 and 700 nm. 1-Naphthylcarbene (and later 2-naphthylcarbene[5]) were most easily studied by capture with acetonitrile solvent to form ylides **7** and **8** which were easily monitored because of a favorable absorption maximum ($\lambda \geq$ 386 nm), intense molar absorptivity, and very long lifetime (τ > 100 μs) relative to the carbene.

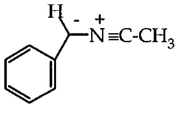


^{1}**1**-NC **7**

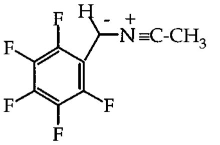


^{1}**2**-NC **8**

Thus we were not surprised when LFP of PDM and PFPDM in various nitrile solvents gave intense transient absorption spectra attributed to **9** and **10**, respectively (see Figure 1 and Table 1).



9



10

It was possible to resolve the growth of ylide **9** in Freon-113 ($CF_2ClCFCl_2$) containing dilute acetonitrile. The growth of **9** was a simple exponential process (Figure 2), which could be fit to yield observed rate constant k_{obs} (eq 1) for spin-equilibrated PC. Equation 1 is predicted by Scheme 1,

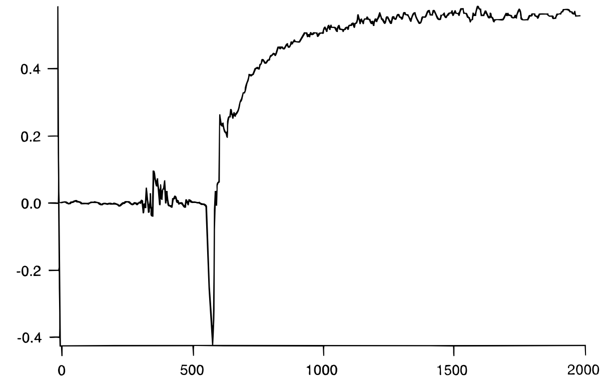


Figure 2. The formation of ylide **9** following LFP of PDM in Freon-113 containing 1.12 M acetonitrile-d_6.

TABLE 1: Absorption Maxima of Arylcarbene Ylides

ylid former	PC (nm)	PFPC (nm)
C_5H_5N	474	486
CH_3CN	345	351
CD_3CN	340	351
^tBuCN	345	356
PhCN	343	392
C_6F_5CN		343

$$k_{obs} = 1/\tau + k_{CH_3CN}[CH_3CN] \qquad (1)$$

where k_{CH_3CN} is the rate constant of the spin-equilibrated mixture of singlet and triplet carbene in Freon-113 with acetonitrile, and τ is the lifetime of spin-equilibrated carbene in this solvent in the absence of acetonitrile. As expected, a plot of k_{obs} vs [CH_3CN] is linear (Figure 3). Similar results were obtained with pentafluorophenylcarbene. The results are collected in Table 2.

It was also possible to trap PC and PFPC with pyridine upon LFP of the appropriate precursor (see Table 1 and Figure 4). The formation of these ylides was resolved as a function of pyridine concentration, and rate constants of reaction were deduced as per acetonitrile (Table 2). According to Scheme 1, ground state triplets ^{3}PC and ^{3}PFPC serve as reservoirs for the more reactive singlet states.[9] If Scheme 1 is correct then the rate constants of the spin-equilibrated carbenes with pyridine are related to those of the singlet carbenes by eq 2.

$$^1k_{pyr}K = k_{pyr} \qquad (2)$$

If we assume that $^1k_{pyr} = 1 \times 10^9$ M^{-1} s^{-1}, a common value for singlet carbenes,[18] we deduce that

$$K_{PC} = 0.019 \quad \text{and} \quad \Delta G^{298}{}_{ST}(PC) = 2.3 \text{ kcal/mol}$$

$$K_{PFPC} = 0.005 \quad \text{and} \quad \Delta G^{298}{}_{ST}(PFPC) = 3.1 \text{ kcal/mol}$$

The singlet-triplet gaps of PC and PFPC have not been determined by experiment. However, recently high-level calculations on PC have been reported which predict $\Delta E_{ST} = 4$ kcal/mol.[19] Thus, our data, when interpreted within the context of Scheme 1, gives a somewhat smaller singlet−triplet splitting than the theoretical estimate. As the calculations are for gas phase species, one is tempted to attribute this discrepancy to a solvent effect although other interpretations are possible (*vide infra*). The magnitude of k_{pyr} varies somewhat in pentane, cyclohexane-d_{12}, Freon-113, and acetonitrile, which indicates that the role of solvent on K and $^1k_{pyr}$ is small but not zero. As

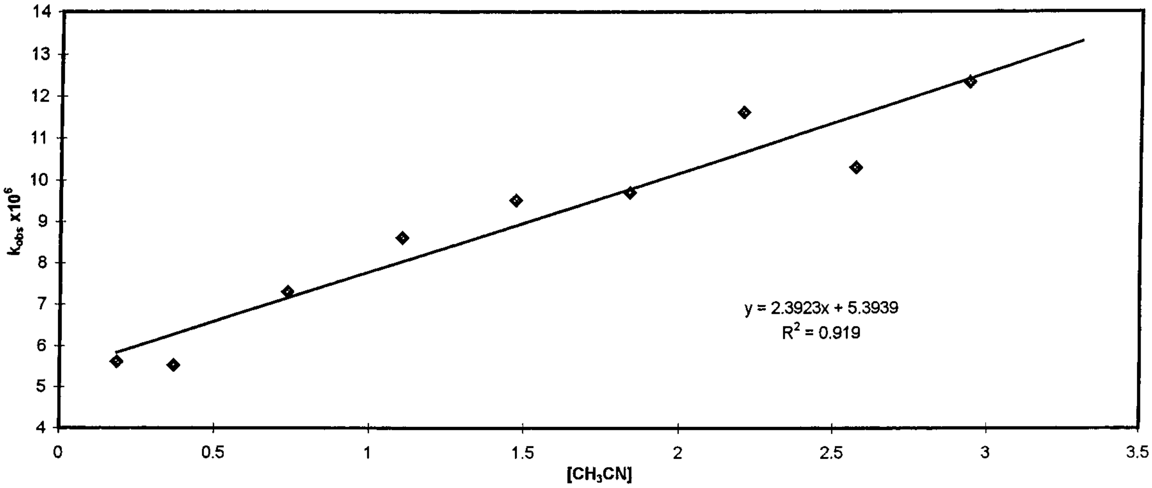


Figure 3. A plot of k_{obs} vs [acetonitrile]; see text.

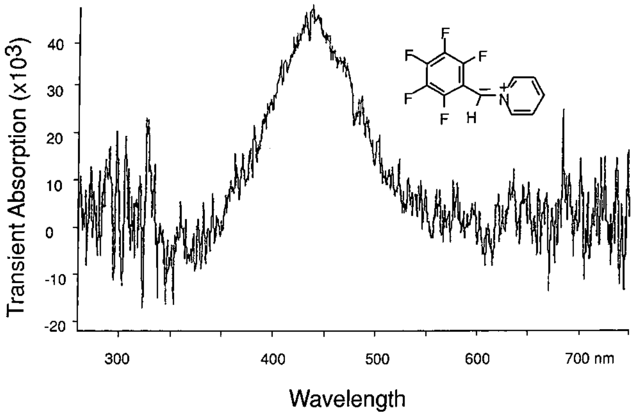


Figure 4. The transient absorption spectrum of the ylide formed upon reaction of pentafluorophenylcarbene with pyridine. The spectrum was obtained by LFP of PFPDM in 1:1 pentane:pyridine (v:v).

TABLE 2. Lifetimes of Spin-Equilibrated PC and PFPC in Various Solvents

carbene	solvent	quencher	k^{obs}_Q ($\times 10^6$ M^{-1} s^{-1})	τ (ns)
PC	$CF_2ClCFCl_2$	CD_3CN	2.1	260
		CH_3CN	2.4	190
		pyridine[a]	19	205
PC	C_6H_{12}	pyridine[a]	9.3	74
PC	C_5H_{12}	pyridine[a]	8.5	85
PFPC	$CF_2ClCFCl_2$	pyridine[a]	5.1	500
		CH_3CN	2.4	214
		CD_3CN	2.8	236

[a] Reference 7.

is typical, the rate constants of the bimolecular reactions of singlet carbenes are slower in the more polar solvent.[6]

The molarity of neat acetonitrile is 19.2 M. If we assume that k_{CH_3CN} is the same in Freon-113 and in acetonitrile, we can calculate the pseudo-first-order rate of formation of ylides **9** and **10** as $k_{CH_3CN}[CH_3CN] = {}^1/_\tau$ and deduce lifetimes of spin-equilibrated PC and PFPC in neat acetonitrile as 22 ns in each case.

On the basis of this analysis, it seems reasonable that the lifetime of PC and PFPC in neat acetonitrile is limited solely by reaction of the singlet carbene with solvent. However, ylide formation is not the only possible mode of reaction of PC and PFPC with acetonitrile, because CH insertion is possible as well. However, the isotope effects (Table 2) are much smaller than those observed (2) for other singlet carbenes[1,4] in cyclohexane and probably are unity within experimental error, which indicates that CH insertion is a rather minor reaction of PC in acetonitrile and even less important for PFPC where an inverse isotope effect is actually observed. The latter is likely a result of experimental error.

One can shorten the lifetime of the carbene and reduce the yields (ϕ_y) of ylides **9** and **10** by adding a competitive quencher (Q) to neat acetonitrile (Scheme 1). A Stern-Volmer analysis of this mechanistic scenario predicts eq 3 and 4 where τ is the

$$\frac{\phi_y^o}{\phi_y} = 1 + \frac{k_Q[Q]}{k_{CH_3CN}[CH_3CN]} \tag{3}$$

$$\frac{\phi_y^o}{\phi_y} = 1 + k_Q[Q]\tau \tag{4}$$

carbene lifetime in neat acetonitrile, ϕ_y^o is the yield of ylide in neat acetonitrile when [Q] = 0, and Q is a typical carbene quencher, such as an alkene (Q = **A**, Scheme 1) or an alcohol, and k_Q is the absolute rate constant of spin-equilibrated carbene with Q.

Plots of ϕ_y^o/ϕ_y vs [Q] are predicted and are found to be linear. A typical plot is given in Figure 5, values of $k_Q\tau$ are collected in Table 3.

A plot of ϕ_y^o/ϕ_y vs [CF_3CH_2OH] shows two linear regions with distinctly different slopes (Figure 6). This type of behavior has been previously observed in the reaction of carbenes and alcohols.[6,20] The data obtained at low concentrations of alcohol is attributed to reaction of the carbene with monomeric alcohol. The data at concentrations of alcohol >0.2 M is attributed to the reaction of carbene with dimeric or oligomeric alcohol. Water as quencher yields a linear plot at all concentrations employed. The data seems more consistent with water as an oligomeric rather than as a monomeric species.

III. Discussion

Mechanism of the Reaction of ^{1}PC and ^{1}PFPC with Alcohols. Singlet carbenes can, in general, react with the OH group of alcohols by one of three mechanisms. The reaction can proceed by (a) proton transfer to give an ion pair which subsequently collapses to product,[21] by (b) formation of an oxonium ion type ylide, or by (c) concerted C−H insertion.

TABLE 3: Stern−Volmer $k_Q\tau^a$ Values of PC and PFPC with Various Carbene Traps in CD_3CN at Ambient Temperature

	PC			PFPC		
	<0.20 M		>0.20 M	<0.20 M		>0.20 M
$(CH_3)_2CHOH$	2.68		1.30	1.05		0.15
CH_3CH_2OH	7.80		4.39	1.99		0.13
CH_3OH	11.91		5.71	3.58		8.32
CH_3OD	4.31		2.65	1.29		0.57
H_2O		3.09			1.45	
D_2O		2.41			0.46	
CF_3CH_2OH	27.68		14.78	4.04		0.80
triethylsilane		4.71			3.44	
trans-1,2-dichloroethylene		22.22			11.55	
cyclohexene		7.99			4.30	
benzene		1.05			0.98	
toluene		1.02			1.06	
mesitylene		6.00			1.25	

[a] $\tau(PC,CD_3CN) = 26$ ns; $\tau(PFPC,CD_3CN) = 20$ ns.

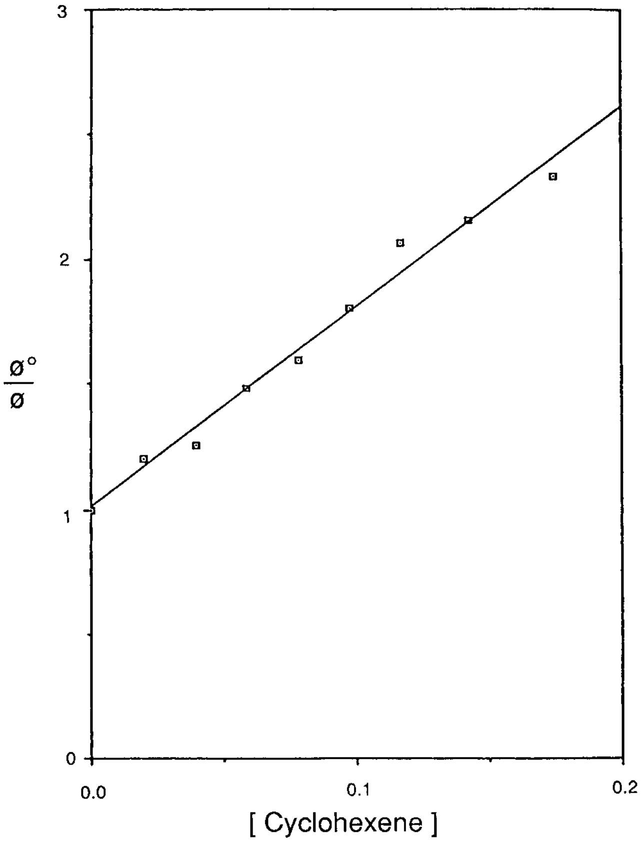
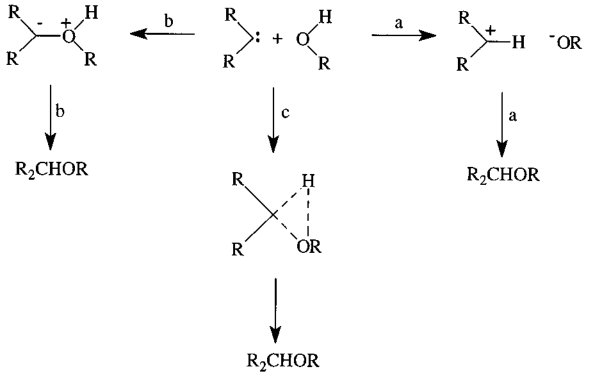


Figure 5. A plot of ϕ_y^0/ϕ_y vs [cyclohexene], obtained by LFP of PDM in neat acetonitrile containing cyclohexene; see text.

The exact choice of mechanism will depend, of course, on the nature of the carbene and the alcohol.[22]



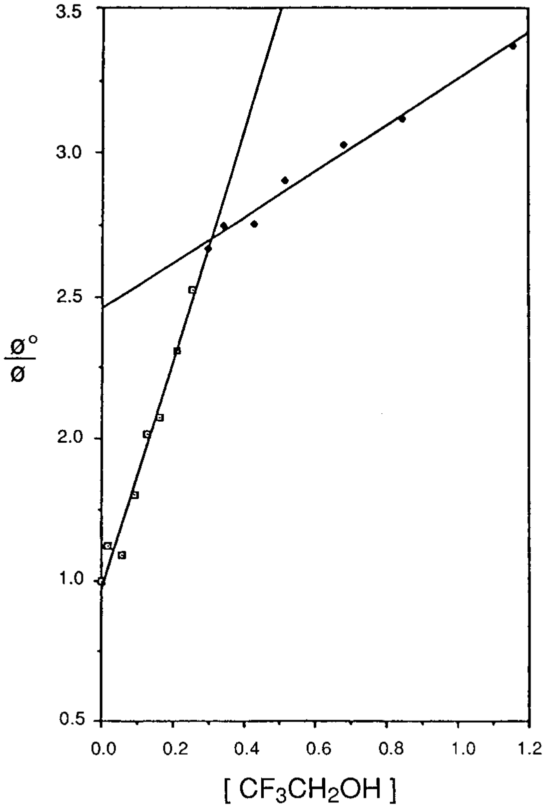
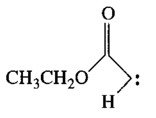


Figure 6. A plot of ϕ_y^0/ϕ_y vs $[CF_3CH_2OH]$ obtained by LFP of PDM in neat acetonitrile containing CF_2CH_2OH; see text.

Pathway a has been demonstrated for diphenylcarbene and methanol.[21,22] Laser flash photolysis data with carboethoxycarbene **11**[23] and tetrachlorocyclopentadienylidene **12**[24] has been interpreted in favor of pathway b.



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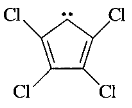

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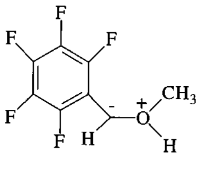
The data of Table 3 indicates that the reactivity of both PC and PFPC with alcohols increases with the acidity of the alcohol. This immediately excludes oxonium ylide mechanism b for both carbenes. This result was surprising for PFPC as oxonium ylide **13** appears to have a favorable structure.

The existence of isotope effects in the reaction of PC and PFPC with the OH bond is further evidence against the oxonium ion mechanism.



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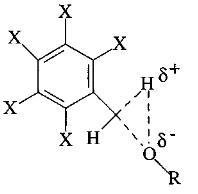
Thus the data supports either proton transfer to form ions which are not detected (pathway a) or a highly polarized, concerted insertion reaction.



X = H, F

The other data of Table 3 is unremarkable. PC and PFPC react rapidly with alkenes, aromatics, and a silane. As τ of PC and PFPC in neat acetonitrile-d_3 (assuming that k_{CH_3CN} is solvent independent) can be deduced, the $k_Q\tau$ values of Table 3 can be converted to absolute rate constants (τ(PC) = 26 ns, τ(PFPC) = 20 ns).

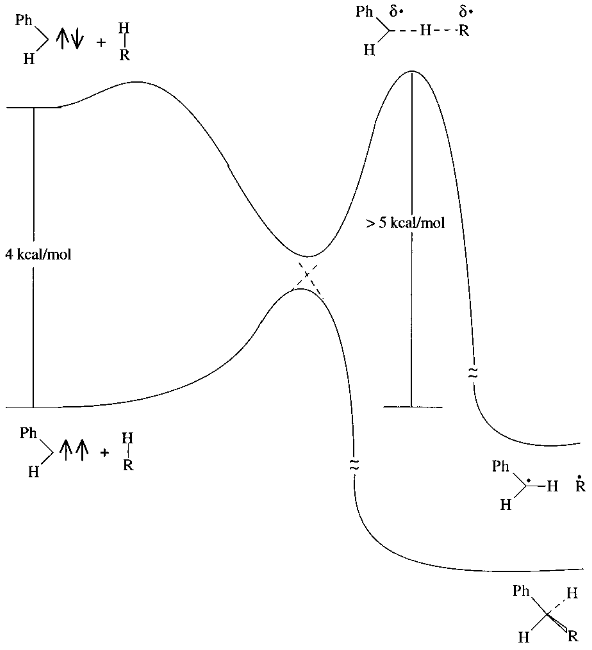
Singlet and Triplet Surface Crossings. Considerable literature suggests that ^{3}PC serves as a reservoir for the more reactive ^{1}PC.[9] ^{3}PC reacts with alkanes, alkenes, aromatics, and alcohols[9] to give products consistent with the trapping of ^{1}PC. This is classically interpreted[9] with the aid of Scheme 1, which predicts that $k_Q = {}^1k_QK$. If we assume that ^1k_Q is 1×10^9 M^{-1} s^{-1} with typical traps, then values of K and ΔG_{ST} can be deduced. This analysis predicts that ΔG_{ST} for PC (and presumably PFPC) is smaller than the value predicted by theory.[19]

This situation has been encountered before, and an interpretation has been put forward by Griller, Nazran, and Scaiano (GNS). In this mechanism there is a surface crossing below the isolated carbene minimum of the singlet surface.[25]

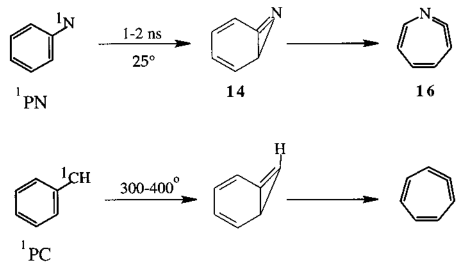
It is easy to demonstrate that the thermodynamics of a GNS type of mechanism are in place for the reaction of PC with hydrocarbons (Scheme 3). Theory and experiment indicate that the insertion of singlet carbenes into simple C−H bonds surmounts little or no barrier.[26] This is clearly the case with phenylchlorocarbene.[26]

The barrier for the reaction of ^{3}PC with hydrocarbons to form radical pairs is not known and cannot be determined at ordinary temperatures as this reaction is slower than the singlet pathway. However, hydrogen atom abstraction reactions of triplet diphenylcarbene are known[2c] and traverse barriers greater than 5 kcal/mol. Thus the activation energy for the reaction of ^{3}PC with R−H exceeds the sum of ΔH_{ST} (4 kcal/mol) and $\Delta H^{\ddagger}$ (of the singlet insertion reaction) predicated by theory. As the reaction of ^{1}PC with RH is highly exothermic and surmounts little or no barrier,[26] the triplet hydrogen atom abstraction surface must cross the surface of the singlet insertion pathway. If there is any coupling of these surfaces, the triplet will cross over to the singlet surface at a point that must be below the singlet carbene minimum. Perhaps the relative reactivity of ^{3}PC with alkanes, alkenes, and aromatics (to give singlet products) merely reflects the strength with which the singlet and triplet surfaces can couple in a particular bimolecular process. The same arguments can be applied to the reaction of arylcarbenes with pyridine. Thus, the singlet−triplet splittings deduced earlier actually reflect the energy separation from the triplet minimum to the point of intersection of the singlet and triplet carbene plus pyridine surfaces.

SCHEME 3

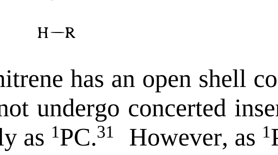


Comparison of Phenylcarbene and Phenylnitrene. Singlet phenylnitrene (^{1}PN) undergoes ring expansion so rapidly (~0.1−1.0 ns) in solution at ambient temperature that it is nearly impossible to trap this species with external reagents.[11,27]

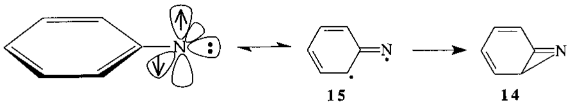


The corresponding reaction of PC is known only in the gas phase, and it requires several hundred degrees.[28] Recent calculations of Borden and Karney indicate that ketenimine formation must be a stepwise process involving an azirine intermediate (**14**).[29]

Insertion reactions of ^{1}PC are rapid because it has a closed shell configuration which allows the empty p orbital to complex with and react quickly with pairs of electrons.[30]

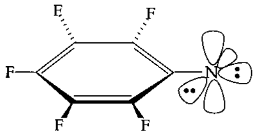


Singlet phenylnitrene has an open shell configuration which means that it cannot undergo concerted insertion and addition reactions as rapidly as ^{1}PC.[31] However, as ^{1}PN can be thought of as an iminyl biradical[31] (**15**), it is easy to see how it can readily cyclize to form azirine **14**.[29]



As the corresponding open shell structure of ^{1}PC is substantially higher in energy than the lower energy closed shell singlet[19] configuration, cyclization of ^{1}PC is much slower than that of ^{1}PN.

It is clear that fluorine substitution retards the rate of rearrangement of pentafluorophenylnitrene.[8] We have argued that the fluorine substituent makes the p$-\pi^2$ configuration of the nitrene less accessible because of differential stabilization of the p$-\sigma^2$ configuration, in part by π backbonding of fluorine, and by delocalization of the filled, in plane, orbital through the σ system onto the electronegative fluorine atom.[32]



Perhaps this effect brings a closed shell singlet configuration below that of the open shell configuration and consequently reduces the rate of rearrangement.[32] This view has received some support by calculations of Cramer.[33] However, unpublished calculations of Borden and Karney suggest another interpretation.[34]

The abundant intermolecular chemistry of ^{1}PFPN is due to its much lower rate of rearrangement than that of singlet phenylnitrene. As singlet PC is closed shell and does not ring expand in solution,[28] fluorine substitution, which will stabilize closed shell configurations, has only a negligible effect on the properties of the aryl carbene.

IV. Conclusions

The absolute kinetics of phenylcarbene (PC) and pentafluorophenylcarbene (PFPC) were determined by laser flash photolysis methods. The absolute rate constant of both spin equilibrated PC and PFPC with acetonitrile is 2.4×10^6 M^{-1} s^{-1} in $CF_2ClCFCl_2$ (Freon-113) at ambient temperature. In this solvent, the rate constants of PC and PFPC with pyridine are 1.9×10^7 and 5.1×10^7 M^{-1} s^{-1} at ambient temperatures. From this data, one can deduce singlet$-$triplet splittings (ΔG_{ST}, 298 K) of 2.3 and 3.1 kcal/mol of PC and PFPC, respectively. These values are smaller than those predicated by theory,[19] which indicates that there is a Griller$-$Nazran$-$Scaiano[25] type of surface crossing mechanism. Absolute rate constants of PC and PFPC with various quenchers are reported.

V. Experimental Section

General. Melting points were taken with an electrothermal capillary melting point apparatus and are reported uncorrected. ^{1}H NMR spectra were recorded with a Bruker AM-200 (200 MHz) or Varian AM-250 (250 MHz) instrument. ^{13}C NMR and ^{19}F NMR spectra were recorded in units of ppm relative to tetramethylsilane (0 ppm). Infrared spectra were recorded on a Perkin-Elmer model 1710 infrared fourier transform spectrometer and are given in cm^{-1}. UV$-$vis spectra were taken using a Perkin-Elmer Lambda 3B UV$-$Vis spectrophotometer and recorded on the Perkin-Elmer 3700 data station or a Hewlett Packard 8452A diode array spectrophotometer interfaced with an IBM portable personal computer. Gas chromatograph$-$fourier transform infrared$-$mass spectra were taken on a Hewlett-Packard 5890 gas chromatograph with infrared and mass detection. Gas chromatography was performed on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector using a 30 m × 0.254 mm column (DB-1). Preparatory gas chromatography was performed on a Varian Aerograph Series 1400 with a thermal conductivity detector using 5% SE-30 GC, and W-HP 80/100 and 5% OV-17, and W-HP 80/100 columns.

Tetrahydrofuran, benzene, hexafluorobenzene, and toluene were purified by distillation from sodium benzophenone. Acetonitrile and methylene chloride were purified by shaking over 4 Å molecular sieves and distilling from calcium hydride. Methanol and ethanol were distilled from sodium metal. Pyridine was distilled from barium oxide and stored over potassium hydroxide pellets. Triethylamine and diethylamine were purified by distillation over barium oxide and stored over potassium carbonate. Olefinic quenchers were purified by distillation and stored over 4 Å sieves. All solvent distillations were performed under a dry nitrogen atmosphere. Deuterated and other solvents were purchased from Aldrich and used as received.

ESR Measurements. ESR measurements were made with a Varian E-112 X-band ESR spectrometer. Carbene spectra were obtained at 10 mW of microwave power. All samples were prepared in 4 mm Suprasil quartz sample tubes. Samples of 15 mmol of diazo precursor were sealed under vacuum after three freeze$-$thaw cycles to remove traces of oxygen and photolyzed for 3$-$5 min using 300 or 350 nm lamps. Samples were stored in liquid nitrogen between measurements.

Laser Flash Photolysis Studies[35]. The laser flash photolysis apparatus for transient absorption and kinetic studies consists of a Lumonics TE-861-4 excimer laser (351 or 249 nm) or a Lambda Physik LPX-100 excimer laser (308 nm). Stock solutions of the photolabile carbene precursors were prepared in the solvents of interest. Hexafluorobenzene, acetonitrile, acetonitrile-d_3, and pentane were commonly used as solvents. Pyridine and various nitrile solvents were used as ylide-forming carbene traps. The concentration of each solution of carbene precursor was adjusted to an optical density of 0.6$-$1.0 at either 351, 308, or 249 nm, depending upon which laser pulse was employed.

Solutions of samples to be studied by laser flash photolysis were contained in quartz cells for excitation at either 308 or 249 nm. The cells were fitted with rubber septa, and the samples were degassed by bubbling with dry, oxygen free nitrogen for three minutes. The sample cells were then irradiated at ambient temperature with excimer laser pulses that impinged on the sample at a right angle to a Xe arc lamp monitoring beam. The monitoring beam was focused on a monochromatomater that was selected for the wavelength of interest. Signals were obtained with a photomultiplier tube and converted to a digitized signal by a Tektronix 7912 transient digitizer. These signals were analyzed by a Macintosh computer.

Transient absorption spectra were obtained using EG and G Princeton Allied Research Model 1460 optical multichannel analyzer (OMA). In a typical optical multichannel analyzer experiment, a cell containing a solution of carbene precursor and/or any additional reagent (usually ylide trap) was placed in the path of the laser pulse and xenon arc beam and four background (no laser pulse) and three active laser pulse signals in an alternating manner were collected with the OMA. The average spectrum was recorded, and the most favorable transient absorption obtained from this spectrum was used as a monitoring wavelength in the subsequent kinetic studies.

In the area of time resolved kinetic studies, two types of measurements were conducted. These were direct measurement of a rate constant and Stern$-$Volmer quenching. In a typical direct measurement, an aliquot of fixed volume of a stock solution of the carbene precursor was syringed into a given number of laser cells. The required ylide-forming reagent was then added in successively larger increments to each cell. Each cell was capped with a septum, degassed, and pulsed with laser radiation, and the data so produced was recorded.

In a typical Stern−Volmer quenching experiment, the samples were prepared in a number of cells by adding a fixed amount of stock solution and a constant volume of ylide-forming reagent. To these solutions was added a known amount of the quencher of interest in successively larger increments to each cell. The quencher concentration in each sample was calculated on the basis of the amount present in the total volume of the solution. The capped, degassed cell was pulsed with laser irradiation, and the data so produced recorded.

Synthesis. The synthesis of phenyldiazomethane has been described previously.[7,9]

2,3,4,5,6-Pentafluorobenzaldehyde Tosylhydrazone.[36] p-Toluenesulfonhydrazide (9.30 g, 0.050 mol) was added to a solution of 9.90 g (0.050 mole) of 2,3,4,5,6-pentafluorobenzaldehyde in 90 mL of absolute ethanol. The suspension was stirred under nitrogen for 48 h at room temperature. The solution was then cooled in an ice bath. The white crystalline solid was filtered and washed with cold absolute ethanol. The filtrate was further concentrated to 90 mL by pumping off the solvent under vacuum. The concentrated solution was cooled in ice bath, and then the crystalline solid was filtered and washed with cold ethanol. The mother liquid and the washing solution were combined to give a third crystallization. The total yield of the colorless crystal was 15.80 g (87%). The melting point of the crystal was 162−163 °C.

^{1}H NMR (DMSO-d_6): δ 2.35 (s, 3H, CH_3); 7.39 (d, 8 Hz, 2H, ArH), 7.56 (d, J = 8 Hz, 2H, ArH); 7.81 (s, 1H, N=CH), 11.96 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): 20.9 (s), 109.1 (dt, J = 4 and 13 Hz), 127.16 (s), 129.66 (s), 134.32 (q, J = 3 Hz), 135.76 (s), 139.0−142.8 (m), 143.78 (s), 142.4−146.4 (m), ^{19}F NMR (DMSO-d_6): 139.84 (dd, J = 7 and 22 Hz, 2F, 2ArF), δ −150.5 (t, J = 22 Hz, 1F, ArF), δ −159.94 (m, 2F, 2ArF).

Sodium Salt of 2,3,4,5,6-Pentafluorobenzaldehyde Tosylhydrazone. To an ice-cooled solution of 2.00 g (5.50 mmol) of 2,3,4,5,6-pentafluorobenz-aldehyde tosylhydrazone in 60 mL freshly distilled ether was added 0.132 g (5.50 mmol) of NaH (60% in mineral oil) upon stirring. The solution was then stirred at room temperature for 24 h under N_2. The large solid suspension formed was filtered and washed with dry ether. The solid was finally dried under high vacuum at room temperature. The yield of the dry colorless sodium salt was 1.68 g (79%)

(2,3,4,5,6-Pentafluorophenyl)diazomethane. In a two-necked round bottom flask was placed a magnetic stirrer. One of the necks of the round bottom flask was connected to a modified side arm addition flask containing 0.50 g (1.30 mmol) sodium salt of 2,3,4,5,6-pentafluorobenzaldehyde tosylhydrazone while a short distillation path was connected to the second. A receiving flask attached to the distillation path was cooled in dry ice−isopropyl alcohol bath. After the round bottom flask was heated under vacuum (ca. 0.05 mmHg) in a 100 °C oil bath in the dark, the salt was slowly added in small portions upon stirring and by tapping the addition flask in 2 min intervals. The orange-colored gas produced upon decomposition of the sodium salt was collected as an orange solid in the receiving flask. The flasks were finally flashed with nitrogen, and the product was warmed to room temperature to give 0.22 g (82%) of an orange-colored oil. ^{1}H NMR ($CDCl_3$): δ 4.90 (s, 1H, HC−N_2). ^{19}F NMR ($CDCl_3$): δ −147.92 (dd, J = 7 and 22 Hz, 2F, 2ArF), −163.3 (t, J = 22 Hz, 1F, ArF), −164.0 (m, 2F, 2ArF).

Product Analyses. Product studies were performed as follows: Solutions of photolabile carbene precursors (0.015M) were placed in 4 mm pyrex tubing which had been thoroughly washed with ammonium hydroxide and dried prior to use. Solvents used in these studies were purchased from Aldrich Chemical Company (99+%), and were used without further purification. Deuterated solvents were 99.5% atom percent purity. The samples were sealed under vacuum after three freeze pump−thaw cycles and photolyzed for 30−120 min using four Rayonet RPR-3500 lamps (3500A) in a home-built photochemical reactor. After photolysis was complete, the sealed tube was opened and 0.10 mL acrylonitrile was added to remove residual diazo precursor. The samples were allowed to stand in the dark for 2 h prior to analysis to allow for complete reaction with acrylonitrile.

Analysis of product mixtures by gas chromatography was accomplished using a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detector and a 30 m × 0.254 nm column (DB-1). Typical chromatography times were 60−120 min/injection over a temperature range of 70−225 °C. Products of the photolysis mixture were isolated in their pure state from some of the reaction mixtures by using either a Varian Series 1400 preparatory gas chromatograph or by preparatory thin layer chromatograph. In both product isolation methods the reaction mixtures were concentrated by pumping off most of the solvent prior to chromatography.

Product assignments were made on the basis of mass spectra data obtained with a Hewlett Packard 5890 GC/IR/MS and supported by NMR spectroscopy.

Photolysis of (Pentafluorophenyl)diazomethane. Pentafluorophenyldiazomethane was photolyzed in various solvents (15 mM) with a standard Rayonet photoreaction apparatus equipped with 350 nm source bulbs. All photolysis reactions were done at room temperature. After photolysis the solvents were pumped off under vacuum and the major products were isolated by preparative TLC or preparative GC. In these studies the photolysis were done in the following solvents. *(a) Cyclohexane.* Only one product was formed and isolated by preparative TLC, and this product was analyzed by GC-MS, and ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectroscopies. ^{1}NMR ($CDCl_3$): δ 0.83−1.7 (m, 11H, C_6H_{11}), 2.57 (dt, J = 1 and 7 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 26.47 (s), 26.78 (s), 30.32 (s), 32.32 (s), 39.47 (s), 113.7 (m), 135.3−138.0 (m), 139.5−142.5 (m), 143.24−147.12 (m). ^{19}F NMR ($CDCl_3$): δ −144.1 (dd, J = 7 and 22 Hz, 2F, 2ArF), −159.56 (t, J = 22 Hz, 1F, ArF), −164.5 (m, 2F, 2ArF). MS: *m/e* 264 (M^+), 181 (loss of C_6H_{11}).

(b) Methanol. Only one product was formed and isolated by preparative-GC, and this product was analyzed by GC-MS and ^{1}NMR, ^{13}C NMR, and ^{19}F NMR spectroscopies. ^{1}NMR ($CDCl_3$): δ 3.39 (s, 3H, CH_3), 4.55 (t, J = 1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 58.41 (s), 61.11 (s), 111.2 (m), 135.2−139.7 (m), 143.3−147.8 (m). ^{19}F NMR ($CDCl_3$): δ −143.6 (dd, J = 7 and 22 Hz, 2F, 2ArF), −154.85 (t, J = 22 Hz, 1F, ArF), −163.0 (m, 2F, 2ArF). MS: *m/e* 212 (M^+), 181 (loss of OCH_3).

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