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Generation, Reactions, Direct Observation, and Kinetics of Decafluorodiphenylcarbene

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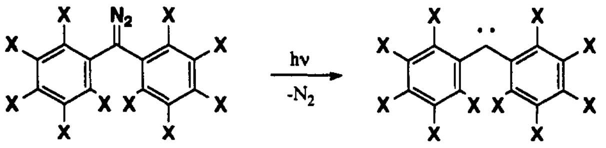
Bis(pentafluorophenyl)diazomethane (**1a**) was prepared, and reactivities of perfluorodiphenylcarbene (**2a**) generated by photolysis of **1a** were investigated not only in terms of product analysis but also by using matrix isolation spectroscopy as well as laser flash photolysis techniques. Product distributions observed in the reactions of **2a** in benzene, cyclohexane, and *trans*-1,2-dichloroethylene suggested that **2a** reacted with those substrates with moderate reactivities toward carbene mostly in its singlet state presumably owing to the increased electrophilicity induced by fluorine substituents while the reaction with the alkane C–H bonds in concerted fashion was retarded partly due to steric effect in the singlet state which thus decayed to the triplet states that underwent predominantly H atom abstraction forming tetraarylethane. Photolysis of **1a** in Ar matrix at 10 K produced **2a** which was observed by IR and UV and shown to react with doped O_2 to produce ultimately perfluorobenzoate by way of the carbonyl oxide and dioxirane, both intermediates being characterized by IR and UV/vis spectroscopy. Laser flash photolysis of **1a** in acetonitrile solution produced a transient absorption (λ = 320 nm) due to bis(pentafluorophenyl)methyl radical (**14a**) obviously produced by H atom abstraction of the triplet **2a**, which was trapped by oxygen to generate the carbonyl oxide (**11a**) showing its absorption maximum at 400 nm (τ = 5 ms) and also by 1,4-cyclohexadiene to form the methyl radical (**14a**) with the rate constant of 1.1×10^7 M^{-1} s^{-1}. The lifetime of the triplet **2a** was estimated to be ~1 μs.

Polyfluorinated molecules often display unique reactivity and solubility properties relative to their nonfluorinated analogues and have been the object of considerable interests for many years.[1] This is also true in the field of carbene chemistry.[2,3] For instance, CF_2 reacts with bicyclo[2.1.0]pentane by two-bond cleavage to give 1,1-difluoro-1,5-hexadiene while other simpler carbenes undergo simple insertion.[3] Given the expected unusual reactivities, it is somewhat surprising that relatively few perfluorinated carbenes have been investigated.[2] In this regard, we have prepared and photolyzed decafluorodiphenyldiazomethane (**1a**) and compared the reactivities of decafluorodiphenylcarbene (**2a**) with those of nonfluorinated diphenylcarbene (**2b**) not only in terms of product analysis studies but also by spectroscopic means.



1

2

a; X=F, **b**; X=H

Results and Discussion

The precursory diazomethane **1a** was prepared starting from pentafluorochlorobenzene as outlined in Scheme I as rather stable yellow crystals (mp 55–57 °C), which can be purified by column chromatography on alumina at −10 °C. All attempts to prepare **1** using other more conventional procedures,[4] e.g., hydrazonation followed by oxidation or diazo transfer, were unsuccessful.

Product Analysis Studies. Irradiation ($\lambda > 300$ nm) of **1a** in methanol resulted in the formation of bis(pentafluorophenyl)methyl methyl ether (**3a**) in essentially quantitative yield, while similar irradiation in cyclohexane gave rise to the formation of tetra(perfluorophenyl)ethane (**4a**, 90%) along with a small amount of bis(pentafluorophenyl)methane (**5a**, 6%). These behaviors observed for **2a** are essentially similar to that observed for "parent" diphenylcarbene **2b** and can be understood as indicating that the carbene generated in methanol is trapped almost exclusively in its singlet state by the solvent O–H bond, which is known to be an efficient trapping reagent for the singlet carbene, while in cyclohexane, the singlet diarylcarbenes are reluctant to undergo insertion into the C–H bonds of alkane and therefore decay to the triplet states

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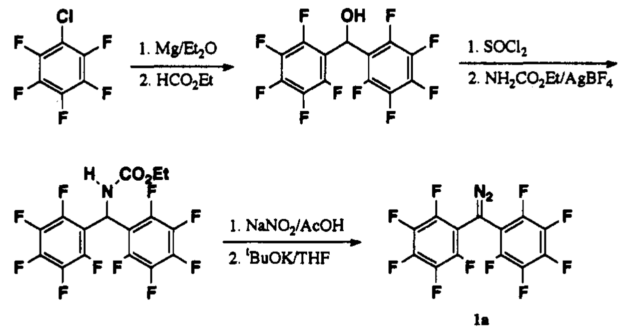
(1) (a) Chambers, R. P. *Fluorine in Organic Chemistry*; John Wiley and Sons, Inc.: New York, 1973. (b) Banks, R. E. *Fluorocarbons and Their Derivatives*; Oldbourne Book Co. Ltd.: London, England, 1964. (c) Smart, B. E. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons, Ltd.: Chichester, 1983; Part 2, Chapter 14, pp 603–655. (d) Riess, J. G.; Le Blanc, M. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 621.

(2) For some representative perfluorinated carbenes, see: (a) Pentakis(trifluoromethyl)cyclopentadienylidene: Janulis, E. P., Jr.; Arduengo, A. J., III. *J. Am. Chem. Soc.* 1983, *105*, 3563 and 5929. Janulis, E. P., Jr.; Wilson, S. R.; Arduengo, A. J., III. *Tetrahedron Lett.* 1984, *25*, 405. (b) Perfluoroacetylmethylene: Murai, H.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* 1981, *103*, 6422. Laganis, E. D.; Janki, D. S.; Curphey, T. J.; Lemal, D. M. *J. Am. Chem. Soc.* 1983, *105*, 7457. Mahaffy, P. G.; Visser, D.; Torres, M.; Bourdelande, J. L.; Strausz, O. P. *J. Org. Chem.* 1987, *52*, 2680. (c) Bis(trifluoromethyl)carbene: Gale, D. M.; Middleton, W. J.; Krespan, C. G. *J. Am. Chem. Soc.* 1965, *87*, 657; 1966, *88*, 3617. Gale, D. M. *J. Org. Chem.* 1968, *33*, 2536. Sander, W. W. *J. Org. Chem.* 1989, *54*, 333. (d) CF_2: Dehmlow, von E. *Mothoden der Organischen Chemie* (*Houben-Weyl*); Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E19, pp 1467–1480.

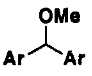
0022-3263/93/1958-7128$04.00/0

Scheme I



which can undergo hydrogen atom abstraction leading to the observed products 4 and 5.[5]

Significant changes in the reaction patterns were observed, however, when the carbenes were generated in substrates having moderate reactivities toward diarylcarbenes. Thus, photolysis of 1a in cyclohexene afforded 3-[bis(pentafluorophenyl)methyl]cyclohexene (6a, 44%) along with 4a (16%) and 5a (18%), while similar irradiation of nonfluorinated diazomethane 1b produced tetraphenylethane 4a (65%) almost exclusively. Furthermore, photolysis of 1a in benzene gave norcaradiene 7a (79%) along with 4a (8%), while 2b generated in benzene produced triphenylmethane 8b (24%) as a solvent adduct along with 4b (3%) and 5b (6%). Among those products, the norcaradiene 7 must be obviously formed from the singlet carbene, whereas the formation of C–H insertion products (6 and 8) can be explicable in terms of either of the multiplicities.[5] However, judging from the amount of products (i.e., 4 and 5) obviously produced from the triplet side via hydrogen atom abstraction, one may interpret these trends in product distributions as indicating that the perfluorinated carbene (2a) tends to react in its singlet state owing to the enhanced electrophilicity caused by fluorine substituents on the aromatic rings compared to the nonfluorinated one (2b).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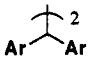
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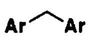
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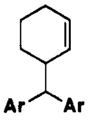
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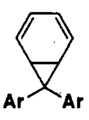
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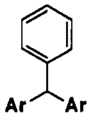
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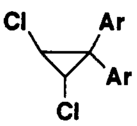
In order to obtain more quantitative insight into the proportion of singlet and triplet carbene undergoing the reaction, the carbenes were generated in *trans*-1,2-dichloroethylene which is known to yield cyclopropanes from stereospecific addition of singlet carbenes, but a rearranged product from addition of triplet carbenes and therefore is conveniently employed as a substrate allowing inferences to be made concerning the proportion.[6] Irradiation of 1a in the dichloroethylene produced two carbene–ethylene adducts which were easily assigned as the dichlorocyclopropane (9a, 33%) and the dichloropropene (10a, 5%) mainly based on ^{1}H NMR spectrum, the ratio of 9a to 10a being 6.70. This ratio is considerably higher than that reported[6d] for 2b (0.25) and even higher than that for fluorenylidene (1.51)[6e] which is usually considered to be much more electrophilic than the diphenylcarbene system. Accepting that the rearrangement product comes entirely from triplet carbene and the cyclopropane principally from the singlet carbene, the results again support the idea advanced above based upon the product distributions in benzene and cyclohexene. In other words, the fluorinated carbene 2a can be regarded as a synthetically useful intermediate to introduce perfluorinated aryl function into the appropriate substrates bearing a carbene-reactive center since it has less opportunity to be "wasted" by abstracting hydrogen from substrates.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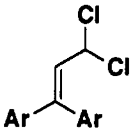
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a; Ar=C$_6$F$_5$, b; Ar=C$_6$H$_5$

Steady-State Irradiation in Matrix. Irradiation ($\lambda > 350$ nm) of Ar matrix-isolated 1a (IR 2082 s, 1524 s, 1503 s, 1248 w, 1099 w, 1052 m, 994 m, 989 m, 880 w, 794 w, 740 w, and 709 w cm^{-1}; UV λ_{max} 420 w, 302 s, and 275 s nm) resulted in a rapid decrease in the bands attributable to the starting material and the concurrent appearance of new bands (IR 1506 s, 1484 s, 1475 s, 1050 s, 992 m, 983 m, and 660 w cm^{-1}; UV λ_{max} 300 nm) (Figure 1). These new absorptions were all assigned to the diphenylcarbene (2a) since the strong sharp absorption band characteristic of the diazo group disappeared, while all other major absorption bands due to C–F bonds changed very little during this transformation. This assignment was further supported by trapping experiments. The irradiation of the diazo compound 1a in an argon matrix containing 0.5% O_2 gave essentially the same spectrum as that observed in the photolysis within the Ar matrix (Figure 2). Warming the matrix containing 2a and O_2 from 10 to 35 K in the dark caused a decrease in the band ascribable to 2a and a simultaneous increase in the absorptions at 1529 s, 1514 s, 1500 s, 1449 m, 1365 m, 1070 s, 998 s, 802 m, 766 m, and 720 w cm^{-1} (Figure 2a). The matrix took on a distinct yellow hue upon warming. In the UV–vis spectra, the disappearance of the carbene absorption and the formation of an intense, broad band with a maximum at 400 nm was observed.

This product (A) was remarkably photolabile and completely disappeared upon irradiation with visible light ($\lambda > 480$ nm) to form an intermediate (B) with absorption bands at 1521 m, 1517 m, 1337 s, 1190 s, 1112 m, 1048 w, 1034 m, 1003 m, 779 w, 700 w, and 550 w cm^{-1} (Figure 2b). Simultaneously, the color in the matrix was bleached: no new UV–vis maximum corresponding to the secondary product was observed in the region between 400 and 300 nm. Subsequent irradiation ($\lambda > 350$ nm) rapidly converted the secondary product into the final product (C) showing the IR absorptions at 1802 m, 1788 m, 1528 s, 1522 s, 1331 w, 1190 m, 1181 m, 1078 m, 1009 m, 905 w, 877 w, and 718 w cm^{-1} (Figure 2c). These observations which are essentially similar to that reported for diphenylcarbene, can be reasonably understood as indicating

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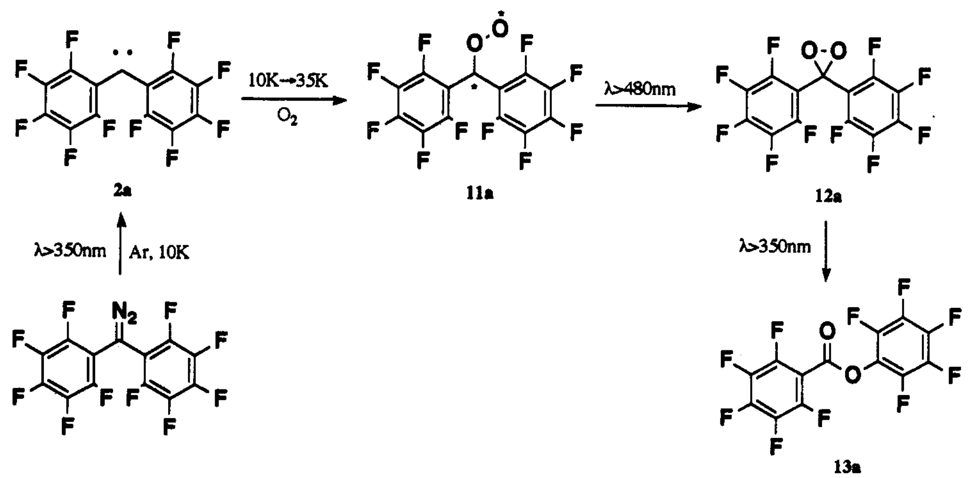
(3) Shiue, G.-H.; Misslitz, U.; Ding, X.-T.; Jones, M., Jr.; de Meijere, A. *Tetrahedron Lett.* **1985**, *26*, 5399.

(4) For a review, see: Regitz, M.; Mass, G. *Diazo Compounds. Properties and Synthesis*; Academic Press: New York, 1986.

(5) For a general aspect of the reactions of diarylcarbenes, see: (a) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973; Vol. 1, pp 73–95. (b) Wentrup, C. In ref 2d, pp 824–1021.

(6) (a) Lambert, J. B.; Kobayashi, K.; Mueller, P. H. *Tetrahedron Lett.* **1978**, 4253. (b) Jones, M., Jr.; Tortorelli, V. J.; Gaspar, P. P.; Lambert, J. B. *Tetrahedron Lett.* **1978**, 4257. (c) Lambert, B. J.; Mueller, P. H.; Gaspar, P. P. *J. Am. Chem. Soc.* **1980**, *102*, 6616. (d) Gaspar, P. P.; Whitsel, B. L.; Jones, M., Jr.; Lambert, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 6108. (e) Gaspar, P. P.; Lin, C.-T.; Wistsel Dunbar, B. L.; Mack, D. P.; Balasubramanian, P. *J. Am. Chem. Soc.* **1984**, *106*, 2128.

Scheme II



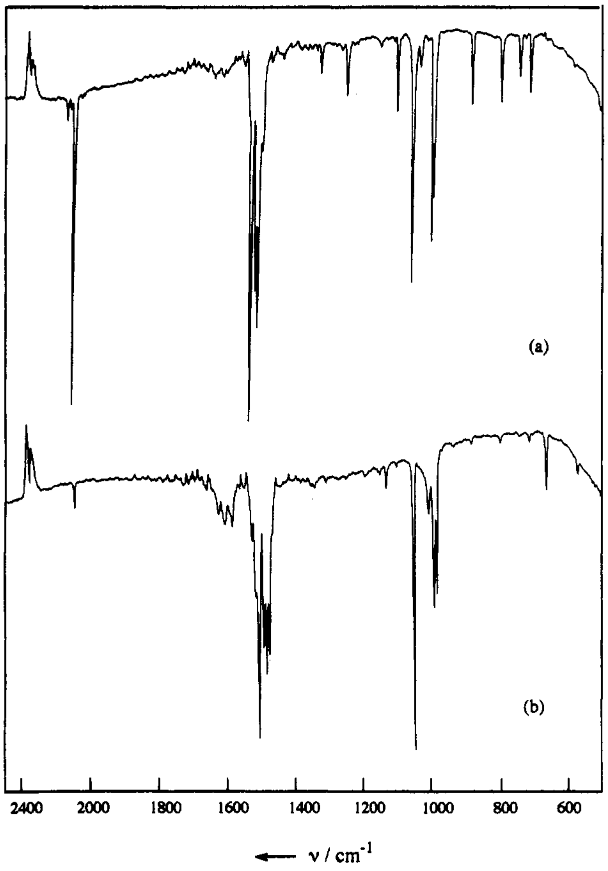


Figure 1. (a) IR spectrum of **1a** matrix-isolated in Ar at 10 K. (b) IR spectrum obtained by irradiation of **1a** in Ar at 10 K.

that the carbene **2a** presumably in the triplet ground state is trapped by O_2 to generate the carbonyl oxide (A = **11a**) showing ν(OO) at 980 cm^{-1} and λ_{max} at 400 nm which then undergoes photoisomerization to form the ester (C = **13a**) by way of the dioxirane (B = **12a**) as these transformations are now well-documented (Scheme II).[7] Actually, the ester **13a** was identified by direct comparison with the authentic sample prepared independently.

Laser Flash Photolysis in Fluid Solution. Flash photolysis of **1a** (4.0×10^{-4} M) in a degassed acetonitrile solution at room temperature with the output of a YAG laser (266 nm, pulse width 5 ns) produced a transient species showing the maximum at 320 nm which appeared with an apparent growth rate of $\sim 10^6\ s^{-1}$ (Figure 3). The oscillogram trace of the transient species at 320 nm shown in the inset of Figure 3 indicated that the decay was second order ($2k/\epsilon l = (4.3 \pm 2.8) \times 10^4\ s^{-1}$, $r = 0.970$). The absorption maximum was apparently different from that observed in the matrix at low temperature for **2a**. Moreover, the observed second-order decay kinetics was not expected for **2a** since product analysis of the spent solution showed no carbenic dimer of **2a** was formed. The product analysis data indicating the formation of **4a** as major product probably as a result of the dimerization of bis(pentafluorophenyl)methyl radical **14a** then suggest that the transient species must be this radical. Support is lent to this assignment by the generation of the radical from a different precursor. Thus, laser flash photolysis of bis(pentafluorophenyl)methyl chloride in acetonitrile resulted in the formation of a transient species showing the absorption at 318 nm which also exhibits second-order decay kinetics with $2k/\epsilon l = 3.0 \times 10^4\ s^{-1}$ ($r = 0.962$). It is well-documented that flash photolysis of diarylmethyl chlorides produces diarylmethyl radicals as well as diarylmethyl cations.[8] However, the cations usually exhibit their absorptions at a longer wavelength region, usually at 500–600 nm, and decay in first order. Moreover, product analysis of the spent solution from the chloride flash photolysis showed the presence of **4a** as major product. Thus, the transient species at 320 nm was unambiguously assigned as the radical, which must be produced from the carbene **2a** by abstraction of hydrogen from the solvent. The transient absorption bands ascribable to **2a** were not observed. Indications based on the reported data[9] for fluorenylidene and diphenylcarbene suggest that the carbenes are usually blue shifted (by $\sim$30 nm) with respect to the corresponding radicals. If the same rule of thumb is applied to **2a**, its absorption maxima would be expected in the 290–300 nm region, which overlaps that for the diazo precursor. It would therefore be in a region of very difficult detection where the samples are usually not sufficiently transparent for adequate monitoring. However, intervention of **2a** was shown by the trapping experiment using oxygen. Thus, when the flash photolysis of **1a** was carried out in aerated cyclohexane solution, a broad absorption

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(7) See for review: Sander, W. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344.

(8) Bartl, J.; Steeken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918 and references cited therein.

(9) See for a pertinent review on the detection and kinetics of arylcarbenes using flash photolysis techniques: Platz, M. S., Ed. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990.

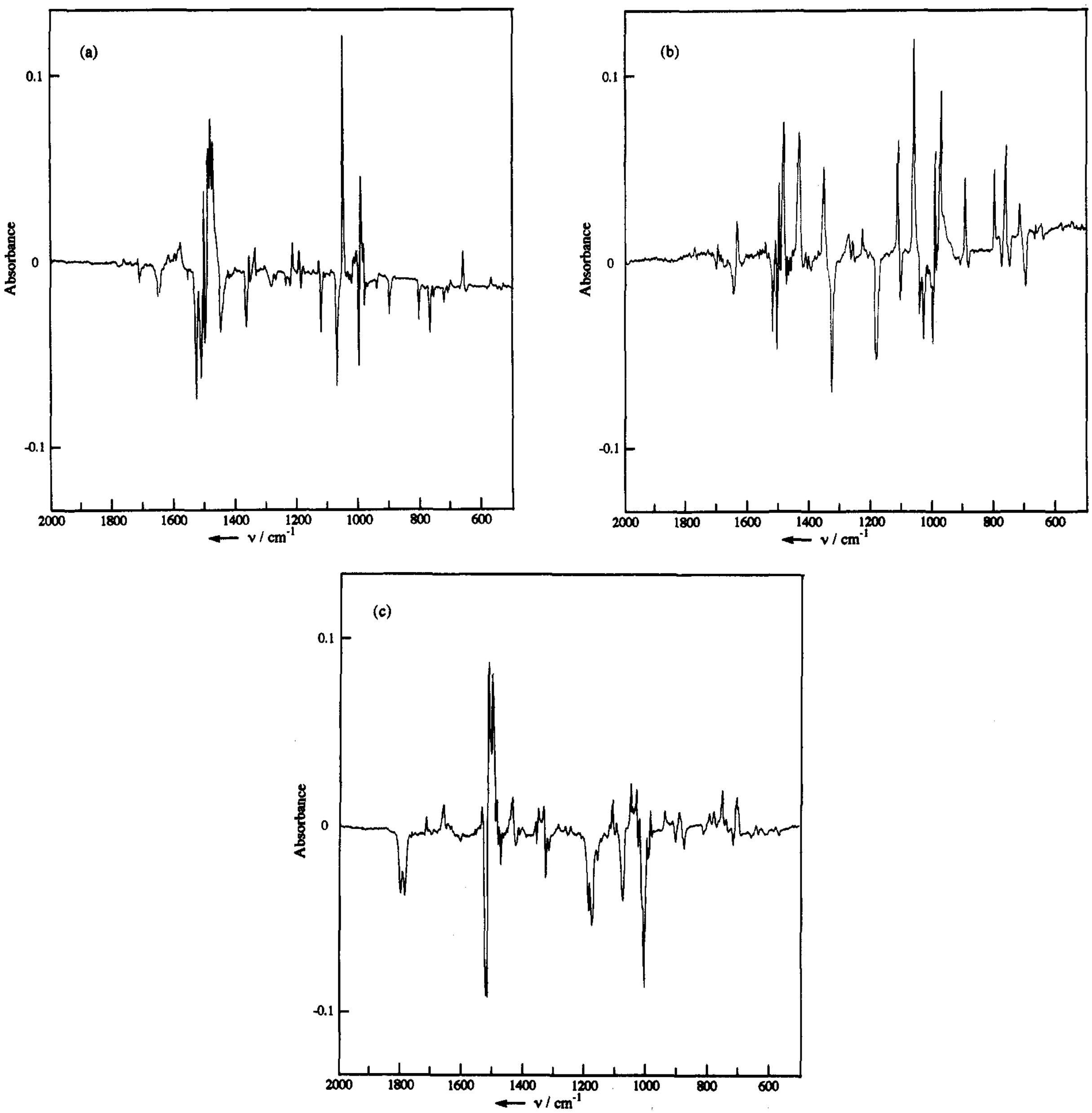
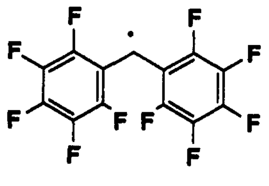
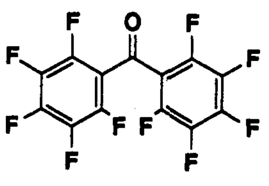


Figure 2. (a) IR difference spectrum obtained by substracting IR spectra of 10 K Ar matrix **2a** and 0.5% O_2 before and after warming to 35 K. Positive peaks are assigned to **2a** and negative peaks to **11a**. (b) IR difference spectrum obtained by substracting IR spectra containing **11a** before and after irradiation at $\lambda > 480$ nm. Negative peaks are assigned to **12a**. (c) IR difference spectrum obtained by substracting IR spectra containing **12a** before and after irradiation at $\lambda > 350$ nm. Negative peaks are assigned to **13a**.

with a maximum at 400 nm appeared at the complete expense of the transient absorption due to the radical **14a**.



14a



15a

Analysis of the spent solution showed the presence of a large amount (about 80%) of the ketone **15a**. It is now well-documented that arylcarbenes with the triplet ground state are readily trapped by O_2 to give the corresponding aryl ketone oxides.[9,10] The broad absorption observed here is in complete agreement with that observed for the oxide **11a** in matrix. Thus, the observations can be interpreted as indicating that the triplet **2a** is trapped by O_2 to generate the oxide before it undergoes hydrogen atom abstraction. The decay of the carbonyl oxide was found to be first order ($k = 1.8 \times 10^2$ s^{-1}), and the lifetime is estimated to be 5.6 ms.

Since we were unable to observe the carbene directly, we have used the probe technique using 1,4-cyclohexadiene in order to know the reactivity.[9] Thus, when a solution of **1a** in a degassed acetonitrile solution containing the diene was excited, the growth rate for the radical formation (monitored at 320 nm) increased with the increase in the diene concentration. The excellent hydrogen donor properties of 1,4-cyclohexadiene have been recognized in its reaction with triplet benzophenone.[11] The apparent built-

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(10) (a) Casal, H. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623. (b) Casal, H. L.; Tanner, M.; Westink, N. H.; Scaiano, J. C. *Ibid.* **1985**, *107*, 4616. (c) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *Ibid.* **1986**, *108*, 3928. (d) Fujiwara, Y.; Tanimoto, Y.; Itoh, M.; Hirai, K.; Tomioka, H. *Ibid.* **1987**, *109*, 1942. (e) Scaiano, J. S.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989**, *54*, 1612.

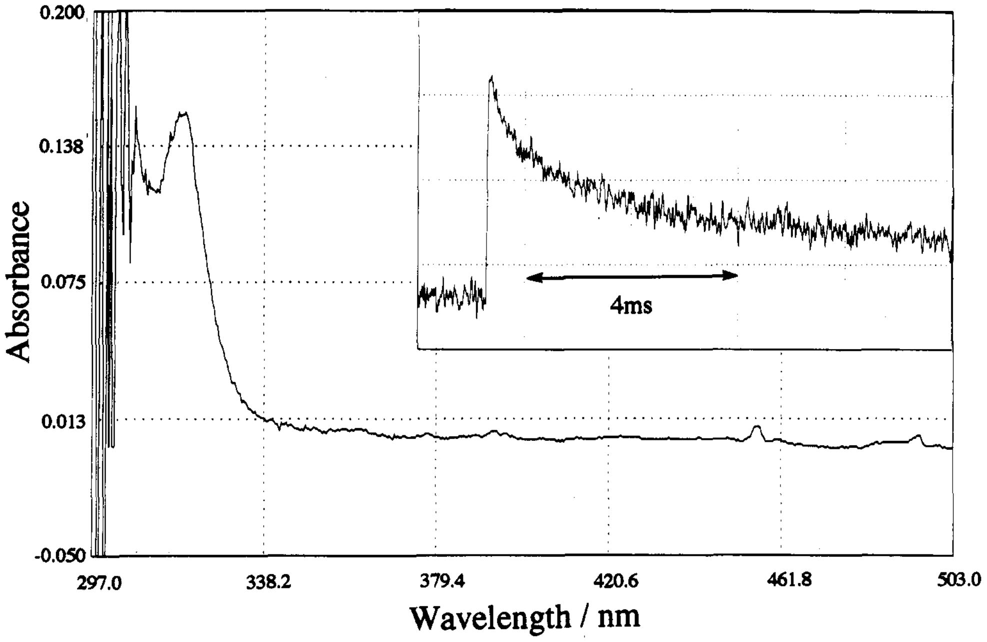

Figure 3. Absorption spectrum of the transient products formed during the irradiation of **1a** in degassed acetonitrile, recorded after 10 μs. Inset shows oscillogram trace monitored at 320 nm.

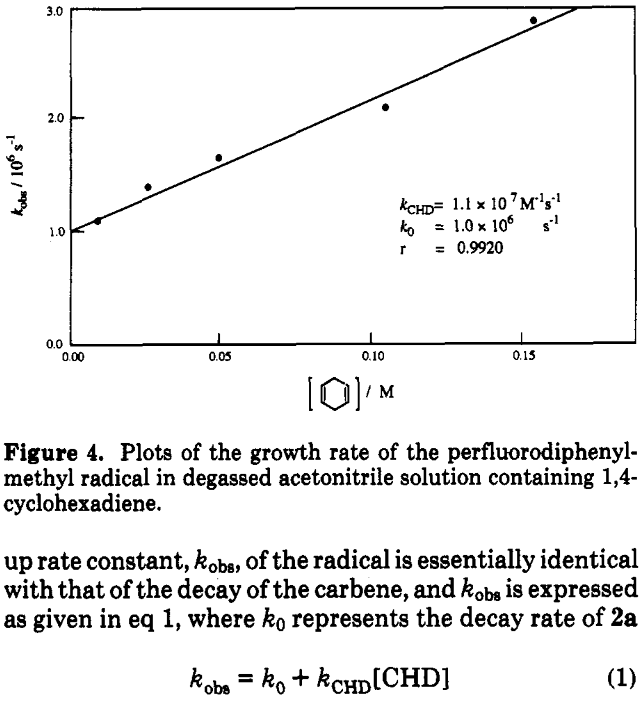

Figure 4. Plots of the growth rate of the perfluorodiphenylmethyl radical in degassed acetonitrile solution containing 1,4-cyclohexadiene.

up rate constant, k_{obs}, of the radical is essentially identical with that of the decay of the carbene, and k_{obs} is expressed as given in eq 1, where k_0 represents the decay rate of **2a**

$$k_{obs} = k_0 + k_{CHD}[CHD] \quad (1)$$

in the absence of the diene and k_{CHD} is a quenching rate constant of **2a** by the diene. A plot of the observed pseudo-first-order rate constant of the formation of the radical against [CHD] in the range of 0.01–0.16 M is linear (Figure 4). The slope of this plot yields the absolute rate constant for reaction of **2a** with the diene, $k_{CHD} = 1.1 \times 10^7\ M^{-1}\ s^{-1}$, and the intercept yields k_0 = 1 μs.

Concluding Remarks. It is conceivable that displacement of all hydrogen atoms on diphenylcarbene with fluorines must result in the enhanced electrophilicity as well as increased steric crowdedness of the carbenic center in the light of the Hammett σ value ($\sigma_m = 0.34$, $\sigma_p = 0.06$) as well as van der Waals radii (1.35) of fluorine substituent. Thus, the carbene **2a** reacts with those substrates having moderate reactivities toward carbene, e.g., benzene and dichloroethylene, mostly in the singlet state owing to the increased electrophilicity. However, the electrophilicity of the singlet **2a** is not so increased as to react with σ electrons of the alkane C–H bonds. Moreover, the singlet carbene C–H insertion process is considered to be sensitive to steric factors if one assumes the trianglar transition state for this process. Thus, the carbene **2a** is forced to undergo intersystem crossing to the triplet which abstracts hydrogen from the solvent with a linear transition state. In this light, it is intriguing to compare the reactivities of **2a** with that of perchlorodiphenylcarbene (**2c**) which shows essentially no reactivity toward benzene and is reluctant to abstract hydrogen from cyclohexane but dimerizes to the carbenic dimer in benzene.[12] The lifetimes of the triplet states also reflect these electronic as well as steric situations. Thus, the triplet state of **2a** has a lifetime almost similar to that of diphenylcarbene (τ = 1.5 μs in cyclohexane), while the chlorinated carbene **2c** has a lifetime of some 4 orders of magnitude greater than **2b**. Taking into account electronic ($\sigma_m = 0.34$, $\sigma_p = 0.23$) as well as steric effects (van der Waals radii of 1.80) of the chlorine substituent, it is rather surprising to note that a rather small change in steric factor exerts tremendous effect on the reactivity of triplet diphenylcarbene.

Experimental Section

General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer, and the mass spectra were recorded on a Shimazu QP-1000 mass spectrometer (70 eV). ^1H and ^{13}C NMR spectra were determined with JEOL JNM-EX 270 spectrometer. UV/vis spectra were determined with a Hitachi 220-S spectrometer. Thin-layer chromatography was done on a Merck Kieselgel 60 PF_{254}. Column chromatography was carried out on a Fuji Davison silica gel BW-127ZH or ICN alumina (neutral). HPLC and GPC were undertaken with a JASCO 800 chromatograph equipped with a UVIDEC-100II UV/vis detector using a Fine pack C18-T5 column (4.6 × 25 cm) and Shodex GPC H-2001 (20 mm × 50 cm) column, respectively, and GLC was

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(11) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

(12) Tomioka, H.; Hirai, K.; Nakayama, T. *J. Am. Chem. Soc.* **1993**, *115*, 1285.

Table I. Kinetic Parameters for Perhalogenated Diphenylcarbenes and Their Oxides

				Ar_2CO_2	
Ar in Ar_2C	λ_{max}/nm	$\tau(t_{1/2})/\mu s$	$k_{CHD}/M^{-1}\,s^{-1}$	λ_{max}/nm	$\tau\ (t_{1/2})$
C_6H_5	315	1.5[a]	$(1.0 \pm 0.1) \times 10^7$[b]	410	(4 ms)[c]
C_6F_5	300	1	$(1.1 \pm 0.1) \times 10^7$	400	5.6 ms
C_6Cl_5[d]	525 w, 493 w, 356 s	$((2.8 \pm 0.2) \times 10^4)$	$(6.2 \pm 0.1) \times 10^3$	390	(510 ± 9 ms)

[a] Hadel, L. M.; Maloney, V. M.; Platz, M. S.; McGimpsey, W. G.; Scaiano, J. C. *J. Phys. Chem.* **1986**, *90*, 2488. [b] Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283. [c] Reference 10e. [d] Reference 12.

carried out with a Yanagimoto G-80 gas chromatograph using a OV-17 on Diazolid L (5.0 mm × 50 cm).

Preparation of Bis(pentafluorophenyl)diazomethane (1a).[13] A solution of decafluorobenzhydrol[14,15] (4.0 g, 11 mmol) and $SOCl_2$ (8.0 mL, 11 mmol) in anhydrous pyridine (10 mL) was refluxed for 2 h. After evaporation of the solvent and washing of the residue taken in Et_2O with 0.2 N HCl followed by the evaporation of the ether, the brownish residue was chromatographed on silica gel eluted with *n*-hexane to give bis(pentafluorophenyl)chloromethane as a yellowish liquid: 3.5 g (83.3%); ^1H NMR (CCl_4) δ 6.58 (s, 1H); MS *m/e* (rel intensity) 382 (M^+, 1.0), 347 (100), 328 (20.0).

A mixture of 2.7 g (13.8 mmol) of $AgBF_4$, 15 g (0.17 mol) of ethyl carbamate, and 60 mL of dioxane was heated until solution was effected. To this the chloride (3.5 g, 9.2 mmol) in dioxane (20 mL) was added at once, and the mixture was heated at 80 °C for 2 h. The cooled mixture was extracted with CCl_4 (20 mL) and H_2O (30 mL). After filtering, the organic layer was washed well with H_2O and then dried (Na_2SO_4). After evaporation of the solvent, the resulting brown liquid was distilled under reduced pressure (80 °C/1.0 Torr) using Kugelrohr to remove excess ethyl carbamate. The residue taken in a minimum amount of CH_2Cl_2 was chromatographed on silica gel eluted first with *n*-hexane to remove the unreacted chloride and then with CH_2Cl_2–*n*-hexane (1:1) to obtain 930 mg (23%) of ethyl *N*-[bis(pentafluorophenyl)methyl]carbamate as white crystals: mp 60–64 °C; ^1H NMR (CCl_4) δ 6.82 (1H, d, J = 10.3 Hz), 6.03 (1H, d, J = 10.6 Hz), 4.16 (2H, q, J = 6.9 Hz), 1.26 (3H, t, J = 6.9 Hz).

To a vigorously stirred mixture of the carbamate (930 mg, 2.1 mmol) in AcOH (2.7 mL) and Ac_2O (12 mL) at 0 °C was added every 20 min for 5 h a 160-mg portion of $NaNO_2$ (total 3.2 g, 46.2 mmol). The mixture was stirred overnight at 0 °C, poured onto ice–water (60 mL), and extracted with Et_2O. The ethereal layer was washed with H_2O, 5% Na_2CO_3, and H_2O and dried (Na_2SO_4). Evaporation of the solvent afforded crude ethyl *N*-nitroso-*N*-[bis(pentafluorophenyl)methyl]carbamate as a yellow oil (965 mg).

To a solution of potassium *tert*-butoxide (700 mg, 5.9 mmol) in 10 mL of anhydrous THF (over benzophenone ketyl) which had been deaerated by repeated cycles of evacuation (10 Torr) and purged with argon and then heated at 60 °C was added at once under an atmosphere of argon a solution of the nitrosocarbamate (950 mg, 1.97 mmol) in THF (10 mL). The mixture was stirred at this temperature for 1 min and poured onto ice–water and extracted with Et_2O. The ethereal layer was washed with H_2O, dried, and evaporated to leave a reddish viscous oil which was chromatographed on neutral alumina (deactivated by adding 6% H_2O) at −10 °C eluted with *n*-hexane. The diazomethane **1a** was eluted as an initial fraction and obtained as yellow crystals in 11.2% (98 mg) yield: mp 55–57 °C dec; IR (KBr) 2090, 1160 cm^{-1}. ^1H NMR spectra showed no peak.

Pentafluorophenyl pentafluorobenzoate (13a) was prepared by the treatment of pentafluorobenzoic acid[16] with thionyl chloride to prepare the benzoyl chloride, which was treated with pentafluorophenol[17] and anhydrous pyridine. The desired benzoate was purified by TLC to give a yellowish oil: ^{19}F NMR (CCl_4) δ 164.0 (2F, t, J = 3.4 Hz), 162.0 (2F, t, J = 3.4 Hz), 158.5 (1F, t, J = 3.4 Hz), 154.8 (2F, d, J = 3.4 Hz), 147.5 (1F, t, J = 3.4 Hz), 138.0 (2F, d, J = 3.4 Hz); MS *m/e* (rel intensity) 378 (M^+, 0.2), 359 (0.7), 195 (100), 167 (35.0), 117 (30.0).

Irradiation for Product Identification. In a typical run, a solution of the diazo compounds (20 mg) in solvents was placed in a Pyrex tube and degassed by subjecting the sample to a minimum of three freeze–degas–thaw cycles at pressure near 10^{-5} Torr before irradiation. Irradiation was carried out with a high-pressure, 300-W mercury lamp at room temperature until all the diazo compound was destroyed. The mixture was then concentrated on a rotary evaporator below 10 °C. Individual components were isolated by preparative TLC and/or gel permeation chromatography and identified by NMR and MS.

Bis(pentafluorophenyl)methyl methyl ether (3a) was isolated in the photolysis of **1a** in MeOH as a yellowish oil: ^1H NMR (CCl_4) δ 6.02 (1H, s), 3.37 (3H, s); MS *m/e* (rel intensity) 378 (M^+, 15), 347 (100), 278 (18).

7,7-Bis(pentafluorophenyl)norcaradiene (7a) was obtained in the photolysis of **1a** in benzene as a white oil: ^1H NMR (CCl_4) δ 6.24–6.22 (2H, m), 5.88–5.83 (2H, m), 2.93–2.90 (2H, m); MS *m/e* (rel intensity) 424 (M^+, 14) 347 (20), 78 (100).

Tetra(pentafluorophenyl)ethane (4a) was isolated in the photolysis of **1a** in cyclohexane as a white solid: mp 200–205 °C; ^1H NMR (CCl_4) δ 6.05 (s, 2H); MS *m/e* (rel intensity) 348 (15), 347 (100), 278 (19).

3-Bis(pentafluorophenyl)methylcyclohexene (6a) was isolated in the irradiation of **1a** in cyclohexene as an oil: ^1H NMR (CCl_3) δ 5.87–5.78 (1H, m), 5.39 (1H, bd, J = 10.2 Hz), 4.46 (1H, d, J = 12.2 Hz), 3.36 (1H, bs), 2.04 (2H, bs), 1.80–1.21 (4H, m); MS *m/e* (rel intensity) 425 (M^+ + 1, 0.5), 424 (M^+, 3), 347 (4), 81 (100).

3,3-Bis(pentafluorophenyl)-*trans*-1,2-dichlorocyclopropane (9a) and 1,1-bis(pentafluorophenyl)-3,3-dichloropropene (10a) were isolated in the photolysis of **1a** in *trans*-1,2-dichloroethene as oils. **9a**: ^1H NMR ($CDCl_3$) δ 4.05 (2H, s); MS *m/e* 444 (M^+ + 2, 1), 443 (M^+ + 1, 3), 442 (M^+, 3), 407 (100). **10a**: ^1H NMR ($CDCl_3$) δ 6.60 (1H, d, J = 9.90 Hz), 6.30 (1H, d, J = 9.90 Hz); MS *m/e* (rel intensity) 442 (M^+) 407 (100), 215 (50).

Irradiation for Analytical Purposes. The irradiations for the quantitative product analysis outlined in the text were carried out in a Pyrex tube of 5.0-mL capacity at below 10 °C. In order to avoid ambiguity of the yields due to the oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze–degas–thaw cycles at pressure near 10^{-5} Torr before irradiation. Product identifications were established by GC–MS comparisons with authentic sample, and product yields were conveniently determined by GC and/or NMR using an internal standard.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by standard techniques[18] using an Iwatani Cryo Mini closed cycle helium cryostat. For IR experiments, a CsI window was attached to the copper holder at the bottom of the cold head. Two opposing parts of a vacuum shroud were fitted with KBr windows for spectroscopic viewing, and the remaining parts were fitted with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For the UV experiments, a sapphire cold window and quartz outer window were used. The temperature of the matrix was controlled by an Iwatani TCU-1 temperature controller.

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(13) The procedure was essentially the same as that reported by Zimmerman for the preparation of 2,2′,4,4′,6,6′-hexachlorodiphenyldiazomethane: Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149.

(14) Borbour, A.; Baxton, M.; Coe, P.; Stephens, R.; Tatlow, *J. Chem. Soc. (London)* **1961**, 808.

(15) Knunyants, I. L., Yakobson, G. G., Eds. *Syntheses of Fluoroorganic Compounds*; Springer-Verlag: Berlin, 1985; p 145.

(16) Reference 15, p 152.

(17) Reference 15, p 170.

(18) (a) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597. (b) Tomioka, H.; Ichikawa, N.; Komatsu, K. *Ibid.* **1992**, *114*, 8045.

Argon (Seitetsu Chemicals, 99.999%), oxygen (Seitetsu Chemicals, 99.9995%), and very volatile organic compounds were mixed in a gas handling system by standard manometric techniques.

Irradiations were carried out using a Wacom 500-W xenon high-pressure arc lamp or Ushio 500-W mercury high-pressure arc lamp. For broad-band irradiation, Toshiba cut-off filters were used (50% transmittance at the wavelengths specified).

Laser Flash Photolysis. All flash measurements were made on a Unisoku TSP-601 flash spectrometer. The excitation source for the laser flash photolyses was a Quanta-Ray GCR-11 Nd:YAG laser which produced 4–5-ns fwhm pulses of up to 30 mJ at 266 nm. The beam shape and size was controlled by a focal length cylindrical lens.

A Hamamatsu 150-W xenon short arc lamp (L2195) was used as the probe source, and the monitoring beam guided using an optical fiber scope was arranged in a perpendicular orientation to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q MOS linear image sensor (512 photodiodes used). Timing among the laser excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu Model DS-8631 digital synchroscope which was interfaced to a NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided hard copy graphics capabilities. Each trace was also displayed on a NEC CRT N5913U monitor.

A sample was placed in a long-necked Pyrex tube which had a side arm connected to a quartz fluorescence cuvette and degassed a minimum of four freeze–degas–thaw cycles at pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was sealed, and the solution was transferred to the quartz cuvette which was placed in a sample chamber of the flash spectrometer. Concentration of sample was adjusted so that the sample absorbed a significant portion of the laser light. For kinetic measurements a suitable concentration range of trapping reagents were added, and the rate constant for the decay of the transient was determined by a computer least-squares fit.

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Supplementary Material Available: ^{1}H NMR and mass spectral data for compounds **3a**, **4a**, **6a**, **7a**, **9a**, and **10a** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.