for the analogous reaction with stannane.[8]

Finally, we are confident that the kinetic data reported in this work will find wide and general use in mechanistic and synthetic applications.

Experimental Section

Materials. Tris(trimethylsilyl)silane and 6-bromohex-1-ene (1) were obtained commercially (Fluka) and used as received. The $(Me_3Si)_3SiD$ was synthesized by reduction of the corresponding chloride with $LiAlD_4$.[27] 6-Bromohept-1-ene (2) and 6-bromo-6-methylhept-1-ene (3) were prepared by reacting 6-oxohept-1-ene with $LiAlH_4$ and MeMgBr, respectively, and consecutive reaction with 1,2-bis(diphenylphosphino)ethane tetrabromide.[28] 6-Oxohept-1-ene was obtained from ethyl acetoacetate and 4-bromobut-1-ene. Allyl *o*-bromophenyl ether (4) was made from allyl bromide and *o*-bromophenol in the usual way.[29] All compounds in this work were at least 97% pure. The purity was checked by GC and/or NMR.

General Procedure. *n*-Octane or *n*-tetradecane containing a small amount of *n*-decane as an internal GC standard was used as solvent. Tris(trimethylsilyl)silane was added at concentrations between 0.5 and 2.2 M, and the bromides were added at a concentration of ca. 0.1 M. Samples of these reaction mixtures were degassed and sealed with rubber septa under argon in Pyrex ampules and were then thermolyzed or photolyzed. Reactions were initiated thermally at temperatures of 333, 363, and 393 K and photolytically at 288 and 303 K. The consumption of the bromides was varied from 5% up to 98%. Reaction times varied from 5 s to 2 min. The products of the reactions of 6-bromohex-1-ene (1), 6-bromo-6-methylhept-1-ene (3), and allyl *o*-bromophenyl ether (4) were analyzed by GC using a 25 m × 0.25 mm SE-54-DE column (Macherey und Nagel) with temperature programming from 40 to 300 °C using a Carlo Erba GC 6000 Vega Series 2 chromatograph. In the case of 6-bromohept-1-ene (2), we used a 25 m × 0.25 mm CW20M-DF column (Macherey und Nagel) with temperature programming from 40 to 200 °C. The hydrocarbon products of interest were identified by comparison of their retention times with authentic material.

Acknowledgment. Financial support from the Swiss National Science Foundation and from the Progetto Finalizzato Chimica Fine II (CNR-Rome) is gratefully acknowledged. We thank a reviewer for some constructive suggestions.

Supplementary Material Available: Schemes III–VI and Tables VII–XI giving reactions of interest, kinetic expressions, and detailed product ratios (12 pages). Ordering information is given on any current masthead page.

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Mechanistic Analysis of the Reactions of (Pentafluorophenyl)nitrene in Alkanes

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Photolysis of pentafluorophenyl azide in *n*-butane, cyclopentane, or 2,3-dimethylbutane releases singlet (pentafluorophenyl)nitrene, which can insert into a CH bond, ring expand to a ketenimine, or undergo intersystem crossing (ISC) to the triplet state of the nitrene. In alkanes at 25 °C ring expansion is the major process, CH insertion is only modest, and ISC is unimportant. At temperatures below −78 °C, ISC is the dominant process. Differential activation parameters are derived and compared with those of phenyl azide

Introduction

Polyfluorinated arylnitrenes are unique amongst aromatic nitrenes in that they react with alkanes to give products of formal C–H insertion in fair to good yields.[1] The reaction was discovered by Banks and Sparkes, who studied the pyrolysis of various polyfluorinated aryl azides in alkanes.[2] The photochemical initiation of this reaction was reported much later by this laboratory.[3] The insertion of a nitrene into an unactivated CH bond is of great importance in photoaffinity labeling, a commonly used technique in biochemistry.[4] To further understand the fluorine effect we have studied the photochemistry of pentafluorophenyl azide 1 in alkanes as a function of temperature.

Table I. Absolute Yield of Products Formed upon Incomplete[a] Photolysis of 1

	n-butane			2,3-dimethylbutane	
T (°C)	4	5	*T* (°C)	6	5
25	7.3	0	25	16	0
25[b]	3.2	9.3	0	26	0
0	7.6	0	−25	23	8.2
−10	3.4	12	−50	20	20
−30	4.0	38	−78	7.8	40
−50	2.4	37			
−78	0	80			

[a] Typically, 10–15% of azide 1 was consumed during the photolysis. The absolute yields of products quoted are based on the percent conversion of the azide. [b] Triplet-sensitized photolysis using 4-methoxyacetophenone; a 2.3% yield of $C_6F_5NH_2$ was formed under these conditions; this product was not observed upon direct photolysis of 1.

Photochemistry of Pentafluorophenyl Azide in Alkanes. Photolysis of 1 at 25 °C in *n*-butane and 2,3-dimethylbutane produces the regiochemically pure prod-

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[1] For a review of the photochemistry of phenylazide, see: Smith, P. A. S. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: New York, 1984; p 95.

[2] (a) Banks, R. E.; Sparkes, G. R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2964. (b) Banks, R. E.; Prakash, A. *J. Chem. Soc.* **1974**, 1365. (c) Banks, R. E.; Medany, I. M. *J. Fluorine Chem.* **1980**, *16*, 325.

[3] Young, M. J. T.; Platz, M. S. *Tetrahedron Lett.* **1989**, *30*, 2199.

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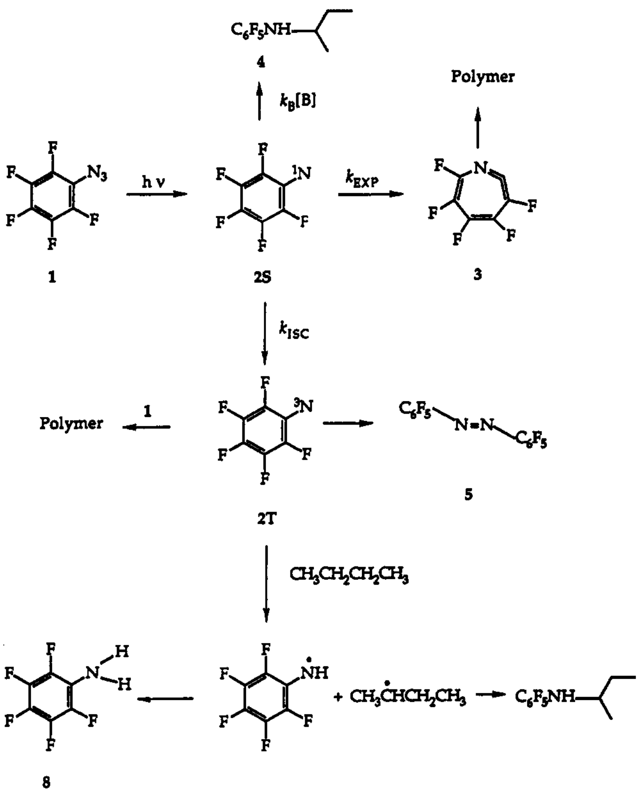
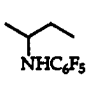
Scheme I



ucts of secondary and tertiary C–H insertion (4 and 6), respectively, along with large amounts of polymeric tar.[5]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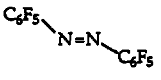
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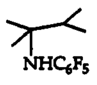
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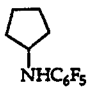
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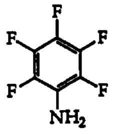
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No other volatile products such as pentafluoroaniline (8) or decafluoroazobenzene (5) are observed at this temperature upon photolysis of azide 1. These products (5 and 8) are characteristic of reactions of triplet (pentafluorophenyl)nitrene 2T and are formed, along with polymeric tar, upon triplet-sensitized photolysis of 1 with p-methoxyacetophenone in n-butane. Thus, direct photolysis of 1 in alkanes at 25 °C gives no evidence of triplet nitrene chemistry. The low yield of C–H insertion product 4 observed upon triplet-sensitized photolysis of 1 can be explained by triplet nitrene hydrogen atom abstraction and radical pair recombination, as shown in Scheme I. Upon lowering the temperature from 25 to 0 °C, photolysis of 1 leads to a modest increase in the yield of adduct. Further cooling results in a steady decrease in the yield of adduct and to an increase in the yield of decafluoroazobenzene 5, a triplet nitrene derived product (Table I). The results mirror those observed previously in cyclopentane,[3] although in cyclopentane some pentafluoroaniline is formed at temperatures below ambient. The yield of insertion adduct 6 formed in 2,3-dimethylbutane is larger than the yield of insertion product realized in n-butane and cyclopentane (with a corresponding reduction in yield of 5 and 8) because of the preference of 2S for insertion into tertiary C–H bonds.

Table II. Differential Arrhenius Parameters to Singlet Nitrene CH Insertion and Intersystem Crossing[a]

alkane	$A_{\text{insertion}}/A_{\text{ISC}}$	ΔE_a (insertion – ISC) (kcal/mol)	r^e
n-butane[b]	$10^{2.9}$	4.28	0.940
2,3-dimethylbutane[b]	$10^{4.7}$	4.85	0.999
cyclopentane[b,c]	$10^{4.75}$	5.09	0.995
cyclopentane[c,d]	$10^{4.9}$	5.27	0.972

[a] The data are derived from plots of the logarithmic ratio of the absolute yield of CH insertion product to decafluoroazobenzene versus 1/T (K). [b] Three data points. [c] Data of reference 3. [d] Four data points; the data are derived from plots of the logarithmic ratio of the absolute yield of CH insertion product to decafluoroazobenzene and pentafluoroaniline versus 1/T (K). [e] Correlation coefficient.

The results are consistent with Scheme I, which assumes that at these temperatures ring expansion, solvent C–H bond insertion, and intersystem crossing (ISC) of the nitrene are *irreversible*.[6] Scheme I is also consistent with the known photochemistry of phenyl azide.[7,8] The effect of the five fluorine substituents is seen to produce a more favorable ratio of rate constants k_B/k_{EXP} with regard to solvent insertion. With both phenyl azide and its pentafluorinated derivative, $k_{ISC} \ll k_{EXP}$ and $k_{ISC} \ll k_B[B]$ (where B = n-butane, cyclopentane, or 2,3-dimethylbutane) at 25 °C. Upon lowering the temperature, ISC gains in importance relative to expansion and insertion. By –78 °C, ISC of singlet C_6F_5N in n-butane has become the dominant reaction. In contrast, ISC does not even become a detectible process in the photochemistry of unsubstituted phenyl azide until –100 °C.

Differential activation parameters to singlet nitrene insertion into a CH bond of an alkane and intersystem crossing to the lower energy triplet state can be obtained from plots of ln [(4 or 6 or 7) ÷ (5 + 8)] versus 1/T. The results of these plots are not very precise because there are only three temperatures per alkane at which both singlet and triplet (pentafluorophenyl)nitrene-derived products are formed in measurable yields. However, the fact that similar results (Table II) are obtained with three separate alkanes lends some credence to the analysis. It is clear that the Arrhenius preexponential factor of C–H insertion is 10^{3-5} times larger than that of intersystem crossing and that the activation energy to CH insertion is 4–5 kcal/mol larger than that of ISC.

Differential Arrhenius Parameters of Singlet Nitrene Processes. Singlet to triplet carbene ISC is a process with little or no temperature dependence;[9] thus, we think it is reasonable that the reaction, 2S → 2T, also has zero activation energy. This assumption immediately pegs the activation energy of CH bond insertion of nitrene 2S as 4–5 kcal/mol. The absolute reactivity of nitrene 2S to CH bonds is found to be intermediate between that of singlet fluorenylidene[10] and singlet phenylcarbene,[11] both

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[5] Meijer, E. W.; Nijhuis, S.; van Vroonhaven, F. C. B. M. *J. Am. Chem. Soc.* **1988**, *110*, 7209.

[6] The irreversibility of ISC is demonstrated by the very different product ratios obtained by direct- and triplet-photosensitized photolysis of 1. Similar results have been obtained in toluene. The irreversibility of ring expansion (3 → 2S) has been demonstrated by Poe by laser flash photolysis. Poe, R. W. M. Sc. Thesis, The Ohio State University, 1989. The ring expansion reaction of singlet (pentafluorophenyl)nitrene 2S was discovered by Banks, who isolated a dimer of ketenimine 3. See: Banks, R. E.; Venayak, N. D. *J. Chem. Soc., Chem. Commun.* **1980**, 900.

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[9] Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868.

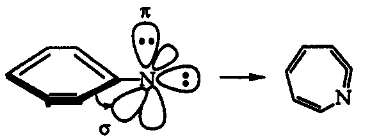
[10] Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990, p 239.

of which have lifetimes of only ≈1 ns in alkanes and ground-state singlet carbenes (in which the carbene center is stabilized by a heteroatom substituent) that show no tendency to insert into CH bonds of alkanes.[12]

The only activation parameters reported for a bond insertion reaction of a singlet carbene is that of phenylchlorocarbene[13] and triethylsilane with $E_a = 2.76$ kcal/mol and $A = 10^{8.48\pm0.43}$ $M^{-1}s^{-1}$. If we assume then that $A = 10^9$ M^{-1} s^{-1} for the insertion of **2S** into a CH bond we find that $A = 10^{4-6}$ s^{-1} for singlet to triplet nitrene intersystem crossing. Thus, the rate of **2S** → **2T** ISC must be many thousands of times slower than that found in aryl carbenes where ISC is on the order of 10^9 s^{-1}. Because the rates of radiationless transitions are fastest when the interconverting states are very close in energy,[14] the slow rate of aryl nitrene ISC can be explained as a consequence of a much larger singlet–triplet energy gap in (pentafluorophenyl)nitrene than is present in aryl carbenes. Consistent with this fact is that the singlet–triplet splitting in NH is 35 kcal/mol,[15] whereas that of CH_2 is 9.5 kcal/mol.[16] The singlet–triplet splittings of aryl and diarylcarbenes remain as yet unknown along with that of (pentafluorophenyl)nitrene. However, Brauman and Drzaic[17] have reported that the singlet–triplet gap in phenylnitrene is only 4.3 kcal/mol.

Ring Expansion. Assuming that ring expansion of **2S** has a normal Arrhenius preexponential factor for a unimolecular rearrangement (10^{13} s^{-1}) and recognizing that $k_{isc} \gg k_{EXP}$ in *n*-butane at −78 °C then using the Arrhenius parameters of ISC just deduced we find that the ring expansion reaction of **2S** must traverse a barrier of ≥6.3 kcal/mol. Using similar logic the barrier to ring expansion of parent singlet phenyl nitrene was deduced to be only 3 ± 1 kcal/mol.[8] This allows us to estimate the lifetime of **2S** in an inert solvent at 25 °C as 1–10 ns, or at least 100 times longer than that of singlet phenylnitrene at this temperature. Thus, the prevalence of CH insertion reactions in the (pentafluorophenyl)nitrene singlet is due to a slower rate of the competing ring expansion reaction in the fluorinated aryl nitrene.

This immediately raises the question of how fluorine retards the rate of ring expansion in the singlet aryl nitrene. One possibility is that the rearrangement of singlet phenylnitrene to azacycloheptatetra-1,2,4,6-ene is more exothermic and consequently faster than the isomerization of **2S** → **3**. Alternatively, the electronic configuration of the molecular orbitals of the singlet aryl nitrene may also influence the rate of ring expansion. To our knowledge, ab initio MO calculations of phenylnitrene have not been reported, although Braumann and Drzaic[17] have quoted an unpublished 3-21G* calculation of Catledge.[18] It seems likely that it is the π^2 configuration of singlet phenylnitrene that expands to the ketenimine by sliding a pair of electrons into the adjacent, empty σ orbital. We believe that the π^2 configuration of **2S** leading to ring expansion may be less accessible in **2S** than in singlet phenylnitrene due to differential stabilization of the $^1(\sigma,\pi)$ and $^1(\sigma^2)$ configurations of the fluorinated arylnitrene. These configurations may well be stabilized by both π back-bonding of the nonbonding electrons of fluorine into an empty π orbital of the nitrene nitrogen, and by stabilization of the filled σ orbital on nitrogen by delocalization onto fluorine. The dramatic ability of fluorine to lower the energies of σ orbitals has been amply documented by photoelectron spectroscopy.[19] These results point to the need for high-quality MO calculations of **2S**, **2T**, **3**, and the parent system.



Experimental Section

General Procedures. Melting points were recorded on an Electrothermal capillary melting point apparatus and are uncorrected. ^1H NMR spectra were recorded either on a Varian EM-390L (90-MHz) or a Bruker AM-250 (250-MHz) instrument. ^{19}F NMR spectra were recorded on a Bruker NR-80 (75-MHz) instrument. High-field ^1H NMR and ^{19}F NMR spectra were obtained by Mr. Carl Engelman. ^1H NMR chemical shifts are reported in units of ppm relative to tetramethylsilane (0 ppm) and ^{19}F NMR chemical shifts are reported in units of ppm relative to $CFCl_3$ (0 ppm). Infrared spectra were recorded on a Perkin-Elmer Model 457 infrared spectrophotometer or a Perkin-Elmer 1710 infrared fourier transform spectrometer. Mass spectra and exact masses were obtained on a VG 70-250S or a Kratos MS-30 mass spectrometer by Mr. Dick Weisenberger of the OSU Campus Chemical Instrumentation Center.

Tetrahydrofuran was dried by distillation over sodium-benzophenone. 2-Methyltetrahydrofuran was distilled over CaH_2 and diethylamine over BaO before use. Toluene, benzene, dichloromethane (all SpectroGrade Mallinckrodt), 3-methylpentane, cyclopentane, cyclohexane, and 2,3-dimethylbutane (Aldrich) were used without further purification. Butane (Matheson) was used directly from a cylinder without purification.

Gas chromatographic analyses were performed either on a Hewlett-Packard 5830A gas chromatograph equipped with a flame ionization detector and a 6 ft × $^1/_8$ in. column (5% SE-30, Chromosorb W-HP 80/100 or 5% OV-17, Chromosorb W-HP 80/100) or a Perkin-Elmer 8500 gas chromatograph equipped with a split/splitless injector, a flame ionization detector, and a 30 m × 0.254 mm J & W Scientific fused silica capillary column (5% DB-1701, 0.25 μm). GC/MS spectra were obtained on a Finnegan 4021 gas chromatograph/mass spectrometer by Mr. David Chang and Ms. Kathy Ault of the OSU Campus Chemical Instrumentation Center.

Samples for product studies were prepared by syringing 0.5 mL of solution into 6-mm Pyrex tubes that were prewashed with ammonium hydroxide and oven-dried. The solutions were then degassed using two to three freeze–pump–thaw cycles and then sealed under vacuum. Samples were kept at the temperatures indicated by either one of the following methods: (a) by keeping the samples in baths in Pyrex or quartz dewars or (b) keeping the samples in an evacuated quartz dewar through which warm or cold gas is flowed. The nitrogen gas is flowed through a coil that is immersed in a constant temperature bath. Photolyses were performed at λ ≈ 350 nm using 2 Southern New England RPR 3500-Å lamps.

The identities of the products formed after photolyses of samples were determined by GC/MS and by coinjection of authentic samples. The yields of the products were determined by using an internal standard.

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[11] Admasu, A.; Platz, M. S. Unpublished research at The Ohio State University.

[12] Moss, R. A.; Turro, N. J. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 213.

[13] The Arrhenius parameters for the insertion of singlet phenylchlorocarbene into the Si–H bond of triethylsilane are $E_a = 2.76$ kcal/mol and $A = 10^{8.48\pm0.43}$ M^{-1} s^{-1}.

[14] Michl, J.; Bonačič-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; Wiley: New York, 1990, Chapters 2 and 3.

[15] Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1048.

[16] Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* **1976**, *65*, 4323.

[17] Drzaic, P. S.; Braumann, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443.

[18] Catledge (see ref 17) has ordered the electronic configurations of phenylnitrene as $^3(\sigma,\pi) < '(\sigma,\pi) < '(\sigma^2) < '(\pi^2)$.

[19] (a) Bastide, J.; Hall, D.; Heilbronner, E.; Maier, J. P.; Plevey, R. G. *J. Electron Spectr. Rel. Phenom.* **1979**, *16*, 205. (b) Heilbronner, E. *Molecular Spectroscopy*; Inst. Petr. London: London, **1976**, p 422. (c) Robin, M. B.; *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1974. (d) Eland, J. H. D. *Photoelectron Spectroscopy*; Butterworths: London, 1974.

Photolysis of Pentafluorophenyl Azide 1 in *n*-Butane. Samples of 1 in butane were prepared in the following manner. Using a 15-in. pipet, azide 1 (4–8 mg) was transferred to the bottom of a 10-mm heavy-walled Pyrex tube. The tube was purged with N_2 and cooled to −78 °C, and $\sim$1 mL of *n*-butane was condensed in the tube and then sealed with a torch. After the seal cooled, the mixture was slowly warmed to room temperature by first immersing the tube in an ice bath for 10 min and then removing the tube from the ice bath. The mixture was then shaken to dissolve azide 1.

The samples of 1 in *n*-butane were photolyzed at 350 nm for 4 h at 25, 0, −10, −30, −50, and −78 °C. All the samples were brought to −78 °C before the tubes were opened, and the butane was allowed to warm slowly. To the residue of each sample was added 10 mL of a solution of PhI (5.4×10^{-3} M, internal standard) in acetone and the resulting solutions were analyzed by GC.

Triplet-Sensitized Photolysis of Pentafluorophenyl Azide 1 in Butane. A sample of azide 1 (6.5 mg) and 4-methoxyacetophenone (16 mg, sensitizer) in $\approx$1 mL of *n*-butane was photolyzed at $\lambda > 350$ nm for 4 h at room temperature and then kept in the dark overnight. Butane was removed from the solution, and 1.0 mL of a solution of PhI (5.4×10^{-3} M, internal standard) in acetone was added to the residue and the sample analyzed by GC.

Photolysis of Pentafluorophenyl Azide 1 in 2,3-Dimethylbutane. Samples of 1 (2.26×10^{-2} M) in 2,3-dimethylbutane were photolyzed at 350 nm for 4 h at 25, 0, −25, −50, and −78 °C. The first two samples were kept in the dark at 25 and 0 °C, respectively, overnight and the last three samples at −78 °C overnight before they were brought to room temperature. To each sample was added 10 μL of a solution of 0.25 M PhI (internal standard) in acetone, and the resulting solutions were analyzed by GC.

N-(1,1,2-Trimethylpropyl)pentafluoroaniline 6 was isolated on a preparative scale experiment. Azide 1 (307 mg, 1.5 mmol) was dissolved in 50 mL of 2,3-dimethylbutane. The solution was cooled to and photolyzed at 0 °C for 4 h at 350 nm. The reaction mixture was concentrated and passed through a 15 cm × 2 cm column of neutral alumina. The first fraction passed was 200 mL of cyclohexane, which eluted unreacted azide, followed by 200 mL of cyclohexane/ethyl acetate (98:2, v/v). A yellow band eluted that gave 48 mg (13% yield) of 6 as a yellow oil: IR (neat, cm^{-1}) 3422, 3367, 2971, 2880, 2655, 2438, 1516, 1470, 1177, 1149, 1101 (CF); ^{1}H NMR (CDCl$_3$, δ) 1.0023 (d, J = 6.8 Hz, 6 H), 1.0950 (s, 6 H), 1.8160 (septet, J = 6.8 Hz, 1 H), 3.0087 (br, 1 H); ^{19}F NMR (CDCl$_3$, δ) −153.802 to −154.076 (m, 2 F), −168.158 to −169.637 (m, 3 F); *m*/*e* calculated for $C_{12}H_{14}F_5N$ (M^+) 267.1046, found 267.1055.

Decafluoroazobenzene (5).[20] A suspension of pentafluoroaniline (2.5 g, 14 mmol) in 90 mL of a 10.25% NaOCl solution was stirred vigorously at room temperature overnight (15 h). The mixture was extracted with three 35-mL portions of ether, and the combined extracts were washed with five 25-mL portions of demineralized water to remove chloride ions. The extracts were then dried over $MgSO_4$ and concentrated to give a red-orange solid. Recrystallization from 95% ethanol gave 526 mg (21% yield) of 5 as red-orange crystals: mp 140–141 °C (lit.[21] mp 142–143 °C); IR (CCl$_4$, cm^{-1}) 1258, 1150, 1039, 1006, 983 (CF); ^{19}F NMR (CDCl$_3$, δ) −151.6852 to −152.5076 (m, 3 F), −164.5177 to −165.3232 (m, 2 F); *m*/*e* calculated for $C_{12}F_{10}N_2$ (M^+) 361.9901, found 361.9884.

***N*-(2-Butyl)pentafluoroaniline (4).** This material was prepared by reaction of hexafluorobenzene and *sec*-butylamine in 15% yield as a colorless oil: bp 45–47 °C (0.35 mmHg); IR (neat, cm^{-1}) 3410 (–NH–), 2980, 2940, 2880 (aliphatic CH), 1520 (–NH–), 1150, 1125 (CF); ^{1}H NMR (CDCl$_3$, δ) 0.9534 (t, J = 7.4 Hz, 3 H), 1.1598 (d, J = 6.3 Hz, 3 H), 1.3711–1.6229 (m, 2 H), 3.2145–3.2429 (br, 1 H), 3.5113–3.6597 (m, 1 H); ^{19}F NMR (CDCl$_3$, δ) −163.3050 to −163.6134 (m, 2 F), −168.6573 to −169.3800 (m, 2 F), −176.3176 (t, t, J = 21.8, 6.3 Hz, 1 F); *m*/*e* calculated for $C_{10}H_{10}F_5N$ (M^+) 239.0733, found 239.0735.

***N*-Cyclopentylpentafluoroaniline.** This material was prepared from cyclopentylamine and hexafluorobenzene in 31% yield as a colorless oil: bp 60.5 °C (0.35 mmHg); IR (neat, cm^{-1}) 3430 (–NH–), 2970, 2880 (aliphatic CH), 1520, 1280 (–NH–), 1190 (CF); ^{1}H NMR (CDCl$_3$, δ) 1.4151–1.5081 (m, 2 H), 1.5668–1.7936 (m, 4 H), 1.9067–2.0277 (m, 2 H), 3.3927 (br, 1 H), 3.9909–4.0975 (m, 1 H); ^{19}F NMR (CDCl$_3$, δ) −163.7217 to −164.0386 (m, 2 F), −168.6592 to −169.3837 (m, 2 F), −176.5175 (t, t, J = 21.9 Hz, 6.4 Hz, 1 F); *m*/*e* calculated for $C_{11}H_{10}F_5N$ (M^+) 251.0733, found 251.0737.

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Supplementary Material Available: General experimental details, gas chromatograms of 26, and ^{1}H and ^{9}F NMR spectra of 44, 45, and 47 (13 pages). Ordering information is given on any current masthead page.

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A General Procedure for the Fluorodenitration of Aromatic Substrates[1]

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The synthesis of several fluoroaromatic compounds by a new procedure of fluorodenitration of nitroarenes is reported. The methodology is based on the principle that the nitrite ion, generated during the fluorodenitration processes and responsible for most of the undesired side reactions, can be trapped with a suitable reagent, e.g., phthaloyl difluoride or tetrafluorophthaloyl difluoride. The yields of fluoro compounds thus obtained are good to excellent, and the procedure is of general application.

The nucleophilic aromatic displacement of a nitro group plays an important role in the synthesis of substituted benzenes.[2,3] The nitro functionality can readily be introduced in an aromatic ring and easily replaced by a number of nucleophiles. In fact, the ability of the nitro group as leaving group is, in many cases, comparable with that of fluorine and much better than that of chlorine or

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[1] Part of this work is the subject of the Italian Patent Appl. 22,440 19 Dec. 1990 by Scorrano, G.; Passudetti, M.; and Prato, M.

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