of *p*-toluenesulfonic acid (50 mg) was heated to reflux in a Dean-Stark apparatus for 4 h to remove water. After the reaction, the dry benzene layer was evaporated to obtain the olefin. The olefin was further purified by column chromatography on silica gel (hexane). The respective yields are shown in Table I. In the case of low boiling alkenes, the yields were obtained by GC analysis with internal standards.

Preparation of Carbocations. SbF_5 was freshly distilled before use. To SbF_5 dissolved in a 3-fold excess amount of SO_2ClF at either dry ice/acetone temperature (-78 °C) or pentane/liquid nitrogen slush (ca. -130 °C) was slowly added with vigorous stirring a cooled slurry or solution of the appropriate precursor in SO_2ClF, resulting in an approximately 10-15° solution of the ion. The solutions were then studied by ^{13}C NMR spectroscopy.

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Registry No. 1 (R = *t*-Bu), 815-24-7; 1 (R = Ph), 938-16-9; 1 (R = H), 630-19-3; 2 (R = *t*-Bu), 30436-14-7; 2 (R = Ph), 769-57-3; 2 (R = H), 513-35-9; 5 (R = *t*-Bu), 41902-42-5; 5 (R = Ph), 15656-90-3; 5 (R = H), 14609-79-1; 8, 14804-25-2; 9, 17603-15-5; 11, 19252-53-0; 14, 16804-70-9; 17, 700-58-3; 18, 38172-64-4; 19, 30545-23-4; 20, 125280-72-0; 21, 108-94-1; 22, 75-97-8; 23, 3419-66-7; 24, 5857-68-1; *t*-$Bu_2C(Me)OH$, 5857-69-2; $(CH_3)_2CHC^+(CH_3)_2$, 17603-18-8; 2-*tert*-butyl-2-adamantanol, 38424-20-3; 3-*tert*-butyl-3-diadamantanol, 125280-73-1; 1-*tert*-butyl-1-cyclohexanone, 20344-52-9.

Anomalous Reaction of Pentafluorophenacyl Bromide with Hexamethylenetetramine. Structure of the Product[1]

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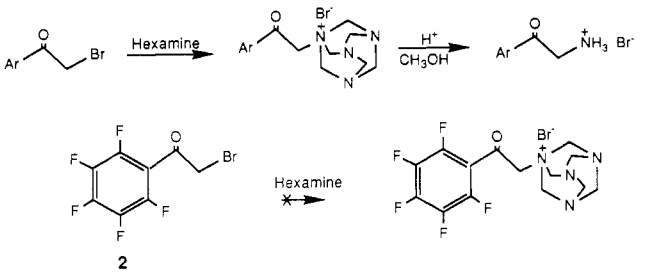
The title compounds condense in chloroform to yield tetrafluorobenzo[*b*]-1,3,5,7-tetraazatetracyclo-[7.3.1^{3,7}.1^{5,9}.0^{1,9}]tetradecan-10-one (1), a reaction proposed to involve both an ortho fluorine elimination and two Stevens type rearrangements. Structural assignment of the fluorescent product was based upon ^1H, ^{13}C, ^{19}F, and ^{15}N NMR spectra and a complete X-ray crystallographic determination. Additional studies supported the proposed mechanism and allowed improvements and modifications of the Delepine reaction as applied to phenacyl halides.

While preparing a series of substituted phenacylamine hydrochlorides by the Delepine synthesis[2] (Scheme I), it was noted that pentafluorophenacyl bromide (2) behaved anomolously. First, the condensation of the latter compound with hexamethylenetetramine (hexamine) in chloroform yielded a fluorescent, yellow salt (3) rather than the expected nonfluorescent, white or colorless salt. Second, the room temperature hydrolysis step in methanolic hydrochloric acid failed to cleave the initial bromide adduct, only transforming it to the corresponding chloride salt. Third, the adduct was not a quaternary ammonium salt as it readily furnished a stable, crystalline, free-base (1), which could be reconverted to the chloride or to other salts. Elemental analyses of the free base and of its various salts indicated that the compound had the formula $C_{14}H_{12}F_4N_4O\cdot(HX)$.

Besides the expected hexamine addition, attack on the pentafluorophenyl ring with loss of a fluoride had also occurred. Although displacement of the para or one of the ortho fluorine atoms seemed most logical, this could not be concluded unambiguously as 2-fluorophenacyl bromide (4) and hexamine behaved normally in the Delepine synthesis, yielding 2-fluorophenacylamine hydrochloride (5, no involvement of the ortho fluorine) (Scheme II). No reaction was observed between pentafluoroacetophenone (6) and hexamine in chloroform after 6 days at room temperature (Scheme II).

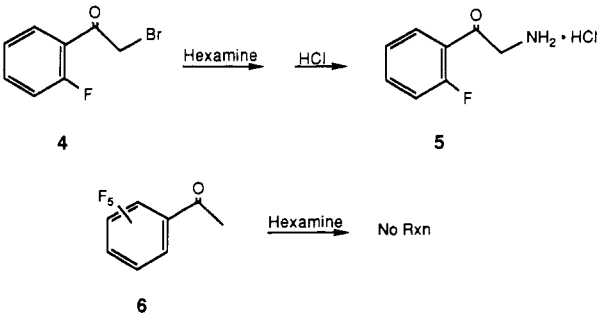
The structure of the unknown compound has now been elucidated by NMR studies (proton, carbon, fluorine, and nitrogen) and confirmed by a complete X-ray crystallographic structure determination. This paper summarizes the structure-determination studies and presents experimental investigations in support of a mechanism (Scheme III) by which the product, tetrafluorobenzo[*b*]-1,3,5,7-tetraazatetracyclo[7.3.1^{3,7}.1^{5,9}.0^{1,9}]tetradecan-10-one (1), is proposed to form. Literature precedents exist for both the intramolecular cyclization reaction[3] and the Stevens-type

Scheme I



2

Scheme II

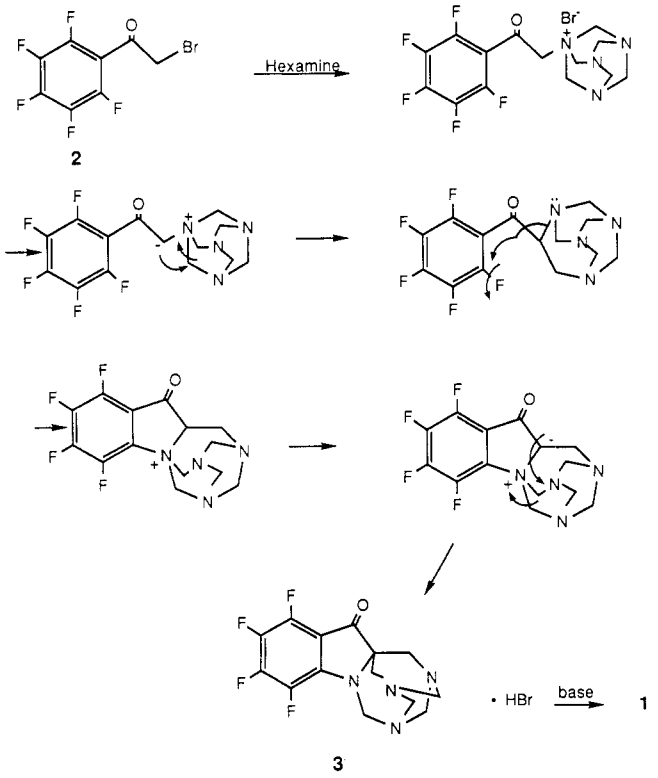


4 5 6

(1) Preliminary results presented at the 192nd ACS National Meeting, Anaheim, CA, September 7-12, 1986.

(2) Delepine, M. *Compt. Rend.* **1895**, *120*, 501. Long, L. M.; Troutman, H. D. *J. Am. Chem. Soc.* **1949**, *71*, 2473.

Scheme III



rearrangements[4] invoked by our proposed mechanism.

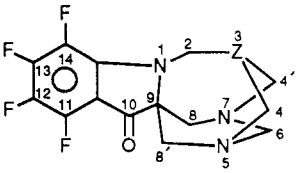
Results and Discussion

NMR Studies. A preliminary examination of the ^1H NMR spectra (see Table I) of the product indicated that the hexamine skeleton was left almost intact. The existence of two AB spin systems, each with integrated intensities of four protons, and one AB spin system with an integrated intensity of two, must be caused by an insertion into or addition onto the hexamine cage, rendering the pairs of geminal protons inequivalent. The observed geminal coupling constants of between 13.2 and 14.4 Hz are reasonable. The farthest downfield signal (two protons integrated intensity) is split into a doublet with a coupling of 4.3 Hz. All ^1H homodecoupling experiments had no effect on this coupling, indicating that a long range ^{19}F–^1H interaction was responsible.

A combination of ^1H coupled and ^1H decoupled ($\{^1H\}^{13}C$) NMR (see Table I) data (acetone-d_6 solution) was used to assign the $\{^1H\}^{13}C$ spectrum. The doublet at 194.9 ppm was assigned as a carbonyl carbon exhibiting a long-range ^{19}F–^{13}C coupling of 3.9 Hz. The resonance at 75.2 ppm was of lower intensity than all other aliphatic carbon resonances and showed no ^1H–^{13}C direct coupling in the ^1H coupled ^{13}C spectrum. The remaining ^{13}C resonances at 73.7, 71.1, 69.5, and 59.3 ppm all exhibited triplet multiplicity in the ^1H coupled ^{13}C NMR spectrum. Peak intensities were utilized in assigning these CH_2 (methylene) resonances. The resonances at 73.7 and 59.3 ppm were approximately twice the height of the resonance at 71.1 ppm, thus indicating that the more intense peaks both arose from symmetry related carbons (see ^1H assignments in Table I). Finally, the carbon resonance at 69.5 ppm in the $\{^1H\}^{13}C$ spectrum appeared as a doublet, again indicating a long-range ^{19}F–^{13}C coupling of 8.8 Hz. The aromatic carbon resonances were not assigned as all signals were of low intensity and displayed complex ^{19}F–^{13}C coupling patterns.

(3) Hudlicky, M. *Isr. J. Chem.* **1978**, *17*, 80.
(4) Vysochin, V. I.; Shishkin, G. V. *Khim. Geterotsikl. Soedin.* **1985**, no. 5, 664.

Table I. NMR Assignments (^1H, ^{13}C, ^{19}F, and ^{15}N) for Compounds 1 and 17a–c



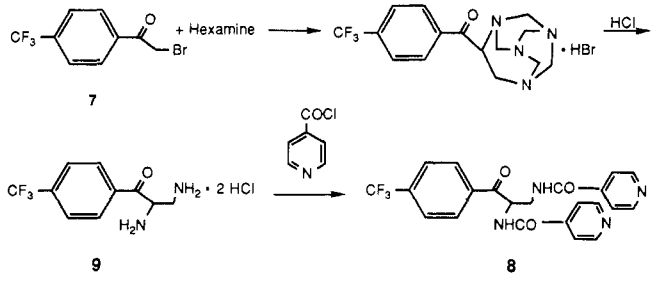
compound	nucleus	assignment δ, ppm	assignment J, Hz
1 (Z = N)	H_2	4.87	$^5J_{H-F}$ = 4.4
	$H_{4,4'}$	3.91, 4.75	J_{H-H} = 10.1
	H_6	4.07, 4.38	J_{H-H} = 13.7
	$H_{8,8'}$	2.89, 3.60	J_{H-H} = 12.9
	C_2	69.5	$^4J_{F-C}$ = 8.8
	$C_{4,4'}$	73.7	
	C_6	71.1	
	$C_{8,8'}$	59.3	
	C_9	75.2	
	C_{10}	194.9	$^3J_{F-C}$ = 3.9
	N_1	-269.6	
	N_3	-326.9	
	$N_{5,7}$	-343.8	
	F_{11}	-143.2	
	F_{12}	-176.0	
	F_{13}	-147.1	
	F_{14}	-163.2	
17a (Z = C-Br)	H_2	4.40	$^5J_{H-F}$ = 3.7
	$H_{4,4'}$	3.46, 4.04	J_{H-H} = 14.1
	H_6	4.05	
	$H_{8,8'}$	2.91, 3.57	J_{H-H} = 13.4
17b (Z = C-NH_2)	H_2	3.82	$^5J_{H-F}$ = 4.1
	$H_{4,4'}$	3.19	
	H_6	3.96	
	$H_{8,8'}$	2.87, 3.54	J_{H-H} = 14.3
17c (Z = C-NO_2)	H_2	4.66	$^5J_{H-F}$ = 3.1
	$H_{4,4'}$	3.73, 4.06	J_{H-H} = 13.2
	H_6	4.13	
	$H_{8,8'}$	3.15, 3.49	J_{H-H} = 14.0

The ^1H coupled ^{15}N NMR spectrum (see Table I) showed only three resonances. The relative intensity ratios indicate that one of the resonances (-343.8 ppm) is probably due to two symmetry-related nitrogens in the molecule. The ^{15}N NMR resonances all fall within the range expected for tertiary amines, with the peak at -269.6 ppm being at the downfield extreme. The severe deshielding of the latter is perhaps due to its proximity with the fluoro-aromatic group.

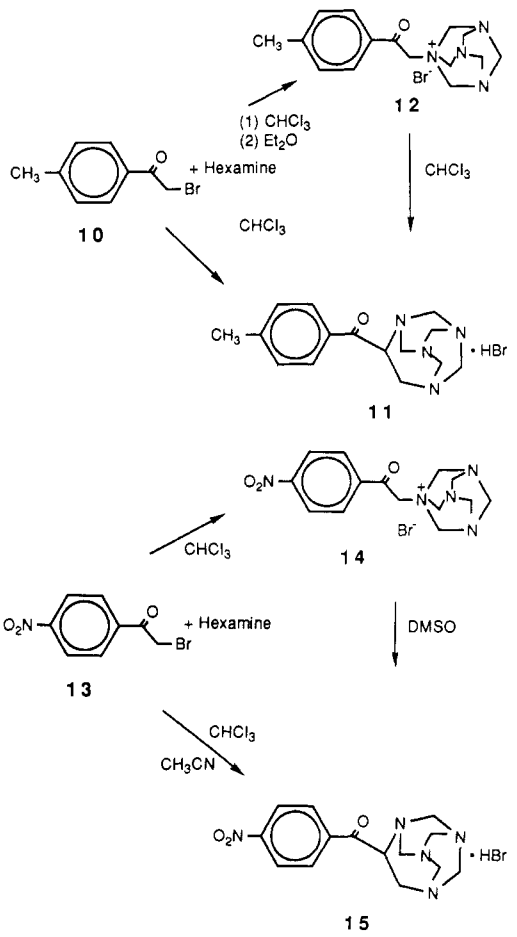
The ^{19}F NMR spectra (see Table I) are quite complex, indicating extensive ^{19}F–^{19}F coupling. There are only four resonances in the spectrum, clearly indicating that one aromatic fluorine is displaced under the reaction conditions. The ^{19}F NMR assignments were made using standard ortho > para > meta substituent effects in addition to the ortho effect of neighboring F substituents, which lead to about to 20 ppm upfield shift for each ortho fluorine. Additionally, we assume that the fluorine at position 14 couples to C(2) and to the methylene protons on C(2). The ^1H–^{19}F coupling of 4.3 Hz is observed in the ^{19}F NMR associated with the peak centered at -163.2 ppm.

A detailed NMR spectral analysis of the hexamine adduct led us to a number of its structural features and the tentative structure assignment of 1. Most significantly, the compound retains a fairly symmetrical hexamine unit (see X-ray section) as evidenced by the ^1H, ^{13}C, and ^{15}N NMR data. The compound also retains an aromatic ring with only four fluorine substituents. The carbonyl group

Scheme IV



Scheme V



is still bound to the aromatic ring as evidenced by a ^{19}F–^{13}C coupling. A particularly intriguing and diagnostic feature of the ^{13}C NMR spectrum was the quaternary carbon resonance at 75.2 ppm. Additionally, the resonance at 59.3 ppm, which we assigned to two carbons derived from the hexamine cage, is considerably upfield for a hexamine type carbon. These data indicated a ring expansion/insertion into the hexamine cage. The unexpected fluorescent nature of 1, either as a solid or in solution, and the novel mechanistic aspects of its formation led us to undertake a single-crystal X-ray structure determination to see if there were any unusual structural features.

X-ray Studies. The derived structure indicates that the reactions leading to the formation of **1** resulted in the opening of the hexamine ring structure to give an altered cage system containing two seven-membered rings and two six-membered rings. The eight C–N bonds in the two six-membered rings range from 1.454 to 1.474 Å with a mean value of 1.462 (8) Å. This compares well with 1.469 Å expected for an sp^3 C bonded to a three-coordinate N (sp^3).[5,6] The average C–N bond in hexamine itself is 1.476 Å.[7] Both of the six-membered rings of the hexamine part of **1** have chair conformations. The axial N(3)–C(12) bond is short at 1.422 (4) Å, whereas the N(1)–C(12) is slightly long at 1.477 (3) Å. The N(1)–C(8) bond at 1.469 (3) Å is as expected. The slightly shortened C(1)–N(1) bond [1.355 Å] and C(6)–C(7) bond [1.462 Å] may indicate some charge delocalization into the five-membered ring. The bonds about N(1) and C(7) are coplanar.[8] The C(7)–O(1) bond length is normal for a carbonyl. The mean C–F bond length in **1** is 1.346 (2) Å. The aromatic C–C bond lengths range from 1.360 to 1.404 Å with a mean value of 1.384 (20) Å, which is similar to the 1.372 seen for C–C bonds in other fluorinated aromatic systems.[5]

A best-plane calculation through N(3), C(10), and C(8), the plane that bisects the two six-membered rings, indicates that pairs of atoms across that plane, i.e., C(9) and C(13), N(2) and N(4), and C(11) and C(14), are symmetrically displaced away from the plane. C(12) and N(1) also lie in that plane with H(12A) and H(12B) symmetrically displaced on opposite sides of the plane. This plane, however, is at an angle of about 10° to the plane of the aromatic ring.

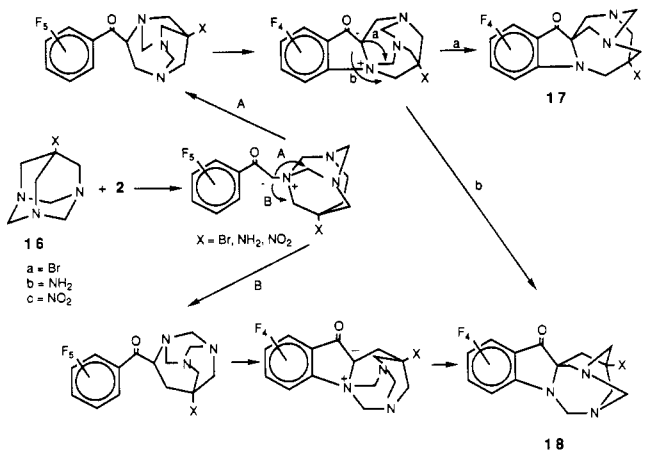
Synthesis and Mechanism Studies. In the course of examining several other substrates in attempted Delepine reactions, we also failed to obtain the expected products. When 4-(trifluoromethyl)phenacyl bromide (**7**) was carried through the Delepine procedure and the resulting intermediate treated with isonicotinoyl chloride, we obtained a product (**8**), which contained two pyridine nuclei per benzene ring. As the reaction of the bromide **7** with hexamine required several days for the salt to precipitate from solution, the expected "normal" intermediate hexamine adduct apparently had sufficient time to undergo a nitrogen Stevens rearrangement. Upon hydrolysis, this intermediate provides a carbon-homologated diamine product (**9**) instead of a phenacyl amine (Scheme IV).

An NMR examination of the products from other attempted, but "failed," Delepine reactions indicated the probable formation of "Stevens-rearranged" intermediates. For example, in the case of 4-methylphenacyl bromide (**10**), the initial hexamine salt must be soluble as what eventually precipitates apears to be the rearranged product (**11**). If, however, shortly after mixing 4-methylphenacyl bromide with hexamine in chloroform, one adds ether, a solid rapidly precipitates, which according to NMR is the desired primary adduct (**12**, Scheme V). The reaction of 4-nitrophenacyl bromide (**13**) with hexamine in chloroform occurs normally and rapidly, precipitates the expected, nonrearranged hexamine salt **14**. If, however, the reaction is carried out in acetonitrile/chloroform, then the initial adduct remains in solution until a Stevens-type rearrangement has occurred, yielding **15**. When the "normal" salt **14** is redissolved in DMSO and allowed to stand, it also undergoes the Stevens rearrangement to **15** (Scheme V).

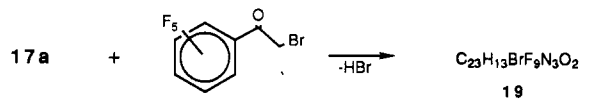
In our proposed mechanism for the formation of **1**, the first Stevens-type rearrangement involves one of three symmetrically identical carbon atoms. In the second rearrangement, there is participation by one of two symmetry-related carbon atoms, and thus the overall reaction sequence only allows for the formation of one product.

(5) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.
(6) Sorriso, S. In *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*; Patai, S., ed.; John Wiley & Sons: New York, 1982; Supplement F, Part 1, Chapter 1.
(7) Becka, L. N.; Cruickshank D. W. J. *Proc. R. Soc. London, Ser. A* **1963**, *273*, 435.
(8) Dahl, T. *Acta Crystallogr.* **1985**, *C41*, 931.

Scheme VI



Scheme VII



One can imagine an analogous mechanism for the reaction of pentafluorophenacyl bromide (**2**) and 7-substituted 1,3,5-triazaadamantanes (**16a–c**).[9] The substitution of a hexamine nitrogen atom by a carbon atom introduces an asymmetry factor, however, which in theory could result in the formation of two different products, **17** and **18** (Scheme VI).

In an effort to test the preceeding possibility and to investigate an extension of the reaction to other polyaza compounds, we did examine the reaction of **2** with several triazaadamantane derivatives.

The reaction of **2** with 7-bromo-1,3,5-triazaadamantane (**16a**) proved to be the most complicated case examined. The precipitate formed in this reaction was neutralized, affording a mixture of free bases consisting of **16a** plus one additional material exhibiting fluorescence (TLC). They were readily separated by chromatography, and the ^1H NMR spectrum of the new material was relatively simple and allowed for a straightforward assignment of the more symmetrical structure **17a** (Scheme VII). Workup of the original chloroform mother liquors provided not only additional quantities of **2** and **17a** but also another material tentatively identified as a 2:1 phenacyl to hexamine reaction product (**19**) derived from a combination of **2** and **17a** (Scheme VI). There are at least six possible structures which agree with the spectral and analytical data (see the Experimental Section for details). The ^1H NMR spectrum of the original crude reaction mixture contained unassigned peaks, which could perhaps be ascribed to a structure such as **18**; however, this compound was never isolated.

The reactions of **2** with 7-amino- and 7-nitro-1,3,5-triazaadamantane (**16b** and **16c**) proceeded in a similar manner except that no quaternary "double" adducts were isolated. Again, while the ^1H NMR analysis of crude reaction mixtures indicated the possible formation of different isomers, only the symmetrical products, **17b** and **17c**, respectively, were isolated.

Conclusions

The abnormal reaction between pentafluorophenacyl bromide (**2**) and hexamethylenetetramine yielding title compound **1** is reasonably explained by a combination of Stevens-type rearrangements and an intramolecular ring closure. Not only does **1** have a uniquely interesting structure, but also the noteworthy property of being highly fluorescent. Analogous reactions between **2** and various triazaadamantanes provided the corresponding cage molecules **17a–c**, which also exhibited fluorescence.

We have also demonstrated that if the initial hexamine adduct of the Delepine reaction sequence remains in solution, then a subsequent Stevens-type rearrangement can occur. Hydrolysis of the resulting intermediate generates a carbon-extended diamine and represents an unusual synthetic transformation. Thus, by manipulation of intermediate solubilities, the reaction of phenacyl halides with hexamethylenetetramine can be controlled to provide either phenacyl amines or 1-aroylethylenediamines.

Experimental Section

Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

NMR Spectroscopy. NMR samples were dissolved in $CDCl_3$ or CD_3COCD_3, and spectra were recorded on an NT-200 WB instrument or on an IBM AFNR-80 instrument. ^1H NMR spectra were recorded with a spectrometer frequency of 200.24 or 80.13 MHz and a sweep width of 15 ppm. Chemical shifts were referenced to the residual protonated solvent peaks. ^{13}C NMR spectra were recorded under ^1H coupled and ^1H decoupled conditions on our NT-200 instrument operating at a spectrometer frequency of 50.35 MHz and were referenced to the solvent resonances. ^{19}F NMR spectra were recorded with a spectrometer frequency of 188.38 MHz and referenced to an external sample of C_6F_6 in CD_3COCD_3 at −164.9 ppm relative to $CFCl_3$ at 0 ppm. ^{15}N NMR spectra were recorded on the NT-200 spectrometer operating at 20.28 MHz in the ^1H coupled mode. The spectra were referenced to an external solution of CH_3NO_2 in CD_3COCD_3. In each case, ^1H, ^{13}C, ^{19}F, and ^{15}N, free-induction decays were acquired until such time as the signal to noise ratios allowed for interpretation of the spectra. In general, 30° pulse widths were employed along with 5–10-s recycle times. Thus, ^1H and ^{19}F spectra with sufficient S/N could be obtained in minutes, whereas, ^{15}N and ^{13}C spectra required 12 h or more.

X-ray Crystal Structure Determination. Compound **1** crystallized as slightly opaque yellow-orange rod-shaped crystals from benzene in space group $P\bar{1}$ (as indicated by precession and Weissenberg photographs). Unit cell parameters are a = 6.864 (1), b = 9.671 (2), c = 11.063 (2) Å; α = 106.89 (2), β = 106.63 (2), γ = 98.80 (2)°, and were obtained from a least-squares fit of 25 computer-centered (Nicolet R3) reflections with 2θ values ranging from 9 to 34° (Mo Kα). At room temperature, intensity data were obtained at 8°/min with monochromated Mo Kα on a Nicolet R3 for octants $h\bar{k}l$, $h\bar{k}\bar{l}$, $hk\bar{l}$, hkl from 4 to 55° 2θ. Three check reflections (1,1,1), (5,0,0), and (2,3,−9) were monitored every 93 reflections; the check reflections were constant with variations of about ±2%. A total of 2997 unique data were obtained of which 2037 with $|F_o| > 4\sigma(F)$ were considered observed and used in refinement. Data were corrected for Lorentz and polarization effects, but no absorption corrections were applied (μ = 1.42 cm^{-1}). Phase solution was obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined with unconstrained thermal parameters but geometrically constrained as "riding" on their adjacent C atoms. Refinement was with SHELXTL's blocked-cascade algorithm and weights, $w = 1/[\sigma_F^2 + 0.0003F^2]$. The final refinement cycles had maximum shift/esd ratios of less than 0.1; the final difference Fourier map had peaks and troughs of +0.25 to −0.30 e$^-$/Å^3. Final agreement factors are R = 0.051, goodness of fit = 1.64. All calculations were done with SHELXTL.[10] Other tables appear in the supplementary material.

Synthesis. Pentafluorophenacyl Bromide (2). Pentafluoroacetophenone (21.0 g, 0.1 mol) (Trans-World Chemicals), 37 g of cupric bromide, 100 mL of chloroform, and 100 mL of ethyl

(9) Galik, V.; Safar, M.; Kafka, Z.; Landa, S. *Collect. Czech. Chem. Commun.* **1975**, *40*, 442.

(10) SHELXTL, version 4.1, Nicolet XRD, Sept 1984.

acetate were stirred and heated at reflux for 4 h. After cooling, the precipitated cuprous bromide was filtered and washed twice with chloroform. The combined filtrates were combined and freed of solvent on a rotary evaporator; the remaining oil was swirled with 40–50 mL of chloroform, refiltered to remove more cuprous bromide, and the filtrate reevaporated a second time to yield 25.5 g, of crude pentafluorophenacyl bromide. Based on the ^{1}H NMR spectrum, this oil contained about 70% of the desired monobromide, some of the fluorinated phenacyl dibromide, and the balance starting material. Longer reaction times generally increased the amount of dibromide without significantly increasing the yield of monobromide.

Tetrafluorobenzo[*b*]-1,3,5,7-tetraazatetracyclo-[7.3.1^{3,7}.1^{5,9}.0^{1,9}]tetradecan-10-one (1). A solution of 6.0 g of hexamethylenetetramine in 65 mL of chloroform was treated at room temperature with 16.0 g of crude **2** in 30 mL of chloroform. A bright yellow solid soon began to precipitate, and the solution developed a yellowish green fluorescence. After 24 h the solid was removed, washed twice with chloroform, and once with ether; the yield was 7.4 g (approximately 45% as the hydrobromide salt). An additional 3.4 g (21%) was obtained when the mother liquors stood for 4 weeks. Another run on a larger scale gave a 56% yield in the first crop.

The 3.4 g of salt was slurried in 25 mL of water and chilled in an ice bath, and the solution was saturated with potassium carbonate. The free base was extracted into methylene chloride (3 × 25 mL); the combined extracts were dried over solid anhydrous potassium carbonate, filtered, and evaporated, giving 2.3 g (97%) of a yellow glassy resin. Recrystallization from benzene furnished yellow-orange crusts and blades; mp 208–209.5 °C. IR (Nujol mull): 1700, 1660 cm^{-1}. Fluorescence (excitation), max (nm): ethanol 490 (412, 230). Anal. Calcd for $C_{14}H_{12}F_4N_4O$: C, 51.22; H, 3.69; F, 23.15; N, 17.07; mol wt 328.3. Found: C, 51.78, 51.50; H, 3.94, 3.62; F, 23.55, 23.75; N, 16.97, 16.79; mol wt (C_6H_6), 343.

Perchlorate Salt of 1. The perchlorate salt was obtained as yellow needles from methanol; it decomposed at about 225 °C when plunged into a preheated bath. If heated from 200 °C, the sample got progressively darker and more amorphous but did not melt. Fluorescence (excitation), max (nm): ethanol, 492 (412, 230). Anal. Calcd for $C_{14}H_{12}F_4N_4O\cdot HClO_4$: C, 39.22; H, 3.06; Cl, 8.27; F, 17.73; N, 13.07. Found: C, 39.08; H, 3.00; Cl, 8.46; F, 17.54; N, 12.62.

Hydrochloride Salt of 1. Bright yellow needles and grains of the hydrochloride crystallized from 95% ethanol–ether; the crystals began to darken at about 220 °C, became very black at 245–250 °C, but still retained their integrity at 300 °C. Anal. Calcd for $C_{14}H_{12}F_4N_4O\cdot HCl\cdot H_2O$: C, 43.93; H, 3.95; F, 19.85; N, 14.64. Found: C, 43.20; H, 3.47; F, 20.32; N, 14.32.

If 4.3 g of crude yellow salt obtained in the original condensation was dissolved in 40 mL of methanol, cooled in an ice bath, treated with 5.5 mL of concentrated hydrochloric acid, and the solution allowed to stand at room temperature for 5.5 h, 3.1 g of the hydrochloride crystallized. Only when such solutions stood for several days did ammonium salts begin to form (in one case ammonium bifluoride was detected). Formaldehyde was slowly evolved, and ammonium salts formed when some of **1**·HBr was digested with 2 N hydrochloric acid on the steam bath for 7 h. A red amorphous solid, mp 325 °C, precipitated.

2-Fluorophenacylamine Hydrochloride (5). 2-Fluoroacetophenone (25 g) was converted to the phenacyl bromide with 65 g of cupric bromide in 320 mL of 1:1 chloroform–ethyl acetate in the same manner as above; 36.7 g of oil (theory, 38.2 g). All of this product in 100 mL of chloroform was filtered into a solution of 24 g of hexamethylenetetramine in 300 mL of chloroform. The white precipitate, which formed immediately, was filtered after 16 h, washed three times with chloroform, and dried; yield was 47.1 g. (When the mother liquors were allowed to stand at 25 °C for several days, the solution became yellow and a weak fluorescence developed; however, only unreacted hexamethylenetetramine was isolated.) All of the adduct was slurried in 450 mL of methanol, chilled in an ice bath, and treated portionwise with 63 mL of concentrated hydrochloric acid. Complete solution was reached after stirring at room temperature for 5 h. After 3 days the supernatant was decanted from 9.1 g of ammonium salts and evaporated. Extraction of the residue with one 250-mL and two 200-mL portions of boiling absolute ethanol left 7.7 more grams of ammonium salts; cooling the extracts to 25 °C gave 12.3 g of the title compound after filtering, washing once with very cold ethanol, ethanol–ether, and finally ether; mp 197–202 °C with bubbling. (Another 12.3 g of the phenacyl hydrochloride mixed with ammonium salts was obtained when ether was added to the ethanolic mother liquors.) Two recrystallizations from acidified water (6 g/15 mL plus 9 drops concentrated hydrochloric acid) furnished white plates, decomposing at 205–208 °C. ^{1}H NMR (DMSO-d_6, 60 MHz): δ 4.46 (d, 2 H), 7.3–8.3 (m, 4 H), 8.64 (br s, 2 H). Anal. Calcd for $C_8H_9ClFNO\cdot 2H_2O$: C, 42.58; H, 5.81; Cl, 15.71; F, 8.42; N, 6.21. Found: C, 42.68; H, 4.28; Cl, 17.11; F, 8.22; N, 6.34.

1,2-Diamino-1-(4-(trifluoromethyl)benzoyl)ethane Dihydrochloride (9). 4-(Trifluoromethyl)phenacyl bromide (13.0 g, 49 mmol) in 40 mL of chloroform was added to 7.1 g of hexamine dissolved in 100 mL of chloroform. After 5 days at 25 °C, the solid was filtered, washed twice with chloroform, and dried; the yield was 3.1 g. ^{1}H NMR indicated that this solid was hexamine hydrobromide. Thirty milliliters of ether were added to the combined mother liquors; a yellow-orange gum precipitated. After chilling to 5 °C, the supernatant was decanted and the gum triturated twice with ether and then vacuum dried; the yield was 11.3 g. All of this gum was dissolved in 125 mL of methanol and treated with 19 mL of concentrated hydrochloric acid, and the solution was allowed to stand at 25 °C for 5 days. The crystalline solid was filtered and washed twice with 20 mL of 1:1 methanol–ether and then with ether; the yield was 2.8 g, mp 222–224 °C dec. Recrystallization from methanol–ether gave a white powder, mp 223–225 °C. An additional 2.6 g (36% combined yield), mp 209–211 °C, was obtained by evaporating the methanolic mother liquors to a paste on a rotary evaporator, chilling to 5 °C, filtering, and washing the cake three times with 13-mL portions of 3 N hydrochloric acid cooled to −15 °C. ^{1}H NMR (DMSO-d_6): δ 9.09 (br s, 6, NH_3^+), 7.93 and 8.44 (AB, 4, ArH, J = 8.2 Hz), 5.40–5.70 (m, 1, CH), 3.15–3.55 (m, 2, CH_2). Anal. Calcd for $C_{10}H_{13}Cl_2F_3N_2O$: C, 39.36; H, 4.29; F, 18.68; N, 9.18. Found: C, 39.25; H, 4.29; F, 19.41; N, 9.08.

Diisonicotinoyl Diamide of 9 (8). Treatment of **9** (2.4 g) with isonicotinoyl chloride (0.7 g) in 20 mL of dry pyridine at room temperature (8 days) furnished the diamide, mp 227.5–228.5 °C, after recrystallization from acetonitrile. ^{1}H NMR (DMSO-d_6): δ 9.25 (d, 1, NH, J = 7.5 Hz), 8.85 (dd, 1, NH, $J_1 = J_2$ = 5 Hz), 8.56–8.69 (m, 4, py), 7.81 and 8.10 (AB, 4, ArH, J = 8.2 Hz), 7.62–7.70 (m, 2, py), 7.51–7.59 (m, 2, py), 5.63–5.78 (m, 1, CH), 3.67–4.03 (m, 2, CH_2). Anal. Calcd for $C_{22}H_{17}F_3N_4O_3$: C, 59.71; H, 3.87; F, 12.83; N, 12.66. Found: C, 59.67; H, 3.74; F, 13.13; N, 12.67.

(4-Nitrophenacyl)hexaminium Bromide (14). When 2.44 g (0.01 mol) of 4-nitrophenacyl bromide in 25 mL of chloroform was added to 1.4 g (0.01 mole) of hexamine in 25 mL of chloroform, the unrearranged hexaminium salt began to crystallize immediately. After 2 h the yield of salt was quantitative, mp 142–144 °C dec. ^{1}H NMR (fresh solution; DMSO-d_6): δ 8.22 and 8.42 (AB, 4, ArH, J = 9.1 Hz), 8.31 (s, 0.8, $CHCl_3$), 5.48 (s, 6, CH_2N^+), 4.96 (s, 2, $COCH_2$), 4.65 (s, 6, CH_2N). Anal. Calcd for $C_{14}H_{18}BrN_5O_3\cdot 0.8CHCl_3$: C, 37.05; H, 3.95; Br, 16.66; N, 14.60. Found: C, 36.91; H, 4.07; Br, 16.61; N, 14.64. When dried at 108 °C, pump limit, for 24 h, the weight loss was 17.74% (theory 19.91%). Anal. Calcd for $C_{14}H_{18}BrN_5O_3\cdot 0.17CHCl_3$: Br, 19.75; N, 17.31. Found: Br, 19.77; N, 17.34.

8-(4-Nitrobenzoyl)-1,3,5,7-tetraazatricyclo[5.2.1^{1,5}.1^{3,7}]undecane Hydrobromide (15). Hexamine (1.4 g, 0.01 mol) was dissolved in 40 mL of 1:1 chloroform–acetonitrile and treated with 2.44 g (0.01 mol) of 4-nitrophenacyl bromide in 30 mL of acetonitrile. The mixture was stirred at ambient temperature for 4 days. The tan solid was filtered, washed with chloroform, and dried; the yield was 2.5 g, mp 163–165 °C. Recrystallization from dry acetonitrile did not change the melting point; tan crusts. ^{1}H NMR (DMSO-d_6): δ 8.19 and 8.34 (AB, 4, ArH, J = 9.2 Hz), 5.48 (t, 1, CH, J = 8.4 Hz), 3.2–4.9 (m, 12, CH_2). Anal. Calcd for $C_{14}H_{18}BrN_5O_3$: C, 43.76; H, 4.72; Br, 20.81; N, 18.23. Found: C, 43.83; H, 4.80; Br, 20.57; N, 18.40.

3-Bromotetrafluorobenzo[*b*]-1,5,7-triazatetracyclo-[7.3.1^{3,7}.1^{5,9}.0^{1,9}]tetradecan-10-one (17a). 7-Bromo-1,3,5-triazaadamantane[9] (1.14 g, 5.2 mmol), 2.1 g of 70% pentafluoro-

phenacyl bromide (2), and 30 mL of chloroform were heated at reflux with stirring for 21 h. A white solid began to precipitate within 10 min; the solution gradually turned yellow then orange. After cooling the solid was filtered, washed three times with chloroform, and dried; yield was 1.1 g, mp 215–220 °C (chloroform filtrate contained pentafluorophenacyl bromide adduct of **17a**, see below). This solid was slurried with 25 mL of ethanol, cooled in an ice bath, treated with 1 g of potassium carbonate in 5 mL of water, diluted with 20 mL of water, and extracted three times with methylene chloride. From the latter solution, 0.8 g of free bases were recovered; TLC on silica gel indicated only two compounds, a yellow fluorescent material and starting bromotriazaadamantane. Chromatography on 20 g of silica gel using chloroform furnished 0.33 g of the fluorescent component; recrystallization from *n*-hexane gave bright yellow, feathery needles and blades, mp 198–200 °C. NMR (see Table I). Analysis of CI mass spectrum revealed M/I + 1 = 406. High-resolution EI spectrum reveals a match for parent minus Br, $C_{15}H_{12}N_3O_1F_4$, which is within 6.1 ppm of the calculated mass. Anal. Calcd for $C_{15}H_{12}BrF_4N_3O$: C, 44.35; H, 2.98; Br, 19.67; F, 18.71; N, 10.35. Found: C, 44.60; H, 3.20; Br, 19.54; F, 18.67; N, 10.35.

Pentafluorphenacyl Bromide Adduct of 17a (19). The original chloroform mother liquors and washings from the preparation of **17a** were combined and evaporated giving 1.9 g of a viscous orange oil. This was extracted three times with 20-mL portions of *n*-hexane as follows: heat to boiling, cool to ambient, decant the supernatant (the hexane-insoluble residue contained additional quantities of **17a** and **19**, see below). Evaporation of the combined extracts gave 0.7 g of an oil mixed with solid; slurrying with 10 mL of *n*-hexane and chilling to 5 °C yielded a yellow solid. Recrystallization from chloroform/*n*-hexane gave a pale yellow powder, mp 213–214 °C dec. Analysis of CI mass spectrum indicate M/I + 1 = 614. High-resolution analysis reveals a match for parent minus bromine $C_{23}H_{13}N_3O_2F_9$, which is within 7.3 ppm of the calculated mass. ^1H and ^{13}C NMR results are consistent with a C_9N_3 cage molecule and two inequivalent carbonyl units. Anal. Calcd for $C_{23}H_{13}BrF_9N_3O_2$: C, 44.97; H, 2.13; Br, 13.01; F, 27.84; N, 6.84. Found: C, 45.30; H, 2.27; Br, 13.10; F, 27.44; N, 6.90.

Recovery of Additional 17a and 19. The 1.2 g of hexane-insoluble residue (from isolation of **19** above) was converted to free bases; 0.88 g, mp 189–195 °C. An additional 0.12 g of the adduct **19** was isolated by dissolving this mixture in 6 mL of chloroform, chilling to 5 °C, filtering through a cold frit, and washing once with chloroform chilled in a dry ice–acetone bath. Recrystallization from 30 mL of 1:1 acetonitrile–absolute ethanol furnished pale-yellow, small, flat needles, mp 212–213 °C dec. Chromatography of the mother liquors on 15 g of silica gel with chloroform as eluent gave an additional 0.15 g of **19** followed by 0.23 g of **17a**.

3-Aminotetrafluorobenzo[*b*]-1,5,7-triazatetracyclo-[7.3.1^{3,7}.1^{5,9}.0^{4,9}]tetradecan-10-one (17b). This compound was made similarly from 7-amino-1,3,5-triazaadamantane and pentafluorophenacyl bromide; bright yellow pills after recrystallization from 8:5 cyclohexane–*n*-hexane; mp 194–196 dec. NMR (see Table I). Anal. Calcd for $C_{15}H_{14}F_4N_4O$: F, 22.20; N, 16.37. Found: F, 21.91; N, 16.46.

3-Nitrotetrafluorobenzo[*b*]-1,5,7-triazatetracyclo-[7.3.1^{3,7}.1^{5,9}.0^{1,9}]tetradecan-10-one (17c). A solution of 1.46 g of 7-nitro-1,3,5-triazaadamantane[9] in 75 mL of chloroform was treated with 2.4 g of 70% pentafluorophenacyl bromide. A turbidity and fluorescence developed within 15 min; after standing for 4 days at ambient temperature much yellow solid had crystallized. After 18 days the solid (hydrobromide salt of 7-nitro-1,3,5-triazaadamantane) was removed by filtration and washed with chloroform. The combined chloroform washes and mother liquors were stirred with 20 mL of ethanol plus 40 mL of water and made basic with solid potassium carbonate. The organic phase was separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were dried before evaporating to leave 2.25 g of a yellow semisolid. Slurrying with 30 mL of chloroform and chilling to 5 °C gave 0.38 g of yellow solid, mp 265–270 °C dec; recrystallization from benzene furnished pale yellow plates, mp 277–278 °C dec. An additional 1.05 g of product was obtained by chromatography of the chloroform solution on 70 g of silica gel, using chloroform as eluent. Recrystallization from benzene gave pale yellow needles, mp 278–279 °C dec. NMR (see Table I). Anal. Calcd for $C_{15}H_{12}F_4N_4O_3$: C, 48.39; H, 3.25; F, 20.41; N, 15.05. Found: C, 48.74; H, 3.48; F, 20.57; N, 14.70.

Registry No. 1, 124562-72-7; 1·$HClO_4$, 124581-13-1; 1·HCl, 124562-74-9; 1·HBr, 124562-82-9; **2**, 5122-16-7; **4**, 655-15-2; **5**, 93102-96-6; **7**, 383-53-9; **8**, 124562-75-0; **9**, 124562-76-1; **13**, 99-81-0; **14**, 88260-40-6; **15**, 124562-77-2; **16a**, 51706-46-8; **16b**, 14707-75-6; **16c**, 14612-28-3; **16c**·HBr, 66570-68-1; **17a**, 124562-78-3; **17b**, 124562-79-4; **17c**, 124562-81-8; **19**, 124562-80-7; *o*-FC_6H_4Ac, 450-95-3; pentafluoroacetophenone, 652-29-9; pentafluorophenacyl dibromide, 124562-73-8; hexamine, 100-97-0; isonicotinyl chloride, 14254-57-0.

Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

Photolysis of Vinyl Halides. Reaction of Photogenerated Vinyl Cations with Cyanate and Thiocyanate Ions

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The title reaction was conducted in a two-phase system of dichloromethane and water using a tetrabutylammonium halide as a phase-transfer catalyst. The reaction of the photogenerated arylvinyl cations with cyanate ion gave only isoquinolone derivatives, whereas the reaction with thiocyanate ion afforded products derived from S attack, vinyl thiocyanates, and products derived from N attack, vinyl isothiocyanates or thioisoquinolones. The ambident nature of thiocyanate ion is compared with the reaction of benzyl bromides.

Most early studies on vinyl cations[1] have dealt with mechanistic aspects of their generation and behavior. Recently there has been an increasing number of synthetic applications of reactions involving vinyl cations.[1a] Al-

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