(22). A solution of propionaldehyde (2.9 g, 0.05 mol) and nitroethane (3.75 g, 0.05 mol) was mechanically stirred for 5 min at 0 °C, while cooling with an ice bath. After the addition of chromatographic alumina (Carlo Erba RS, activity I, 10 g) and stirring for 30 min at 0 °C, the mixture was allowed to stand at rt for 20 h. CH_2Cl_2 (60 mL) was added, and the mixture was stirred and heated at 40 °C for 7 h. The mixture was then filtered, and the alumina was washed with CH_2Cl_2 (3 × 30 mL). The organic layer was evaporated and purified by distillation to give 3.68 g (64%) of **22**: bp_{10} 66 °C (lit.[12] bp_{20} 85 °C); IR (film) ν 1650 (C=C), 1510 cm^{-1} (NO_2); ^1H NMR δ 1.12 (t, 3 H, J = 7.6 Hz), 2.1–2.4 (m, 2 H), 2.17 (s, 3 H), 7.12 (t, 1 H, J = 7.5 Hz). Anal. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.02; H, 7.99; N, 12.05.

(*E*)-2-Nitro-5-phenyl-2-pentene (12): yield 6.5 g (68%); $bp_{0.07}$ 163 °C; IR (film) ν 1670, 1600 (C=C), 1515 cm^{-1} (NO_2); ^1H NMR δ 2.08 (s, 3 H), 2.55 (q, 2 H, J = 7.4 Hz), 7.1–7.4 (m, 5 H). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.93; H, 6.97; N, 7.45.

(*E*)-2-Nitro-1-cyclohexyl-1-heptene (24): yield 8.1 g (72%); oil; IR (film) ν 1665 (C=C), 1520 cm^{-1} (NO_2); ^1H NMR δ 0.9 (t, 3 H, J = 7 Hz), 1.2–1.6 (m, 19 H), 2.18–2.35 (m, 2 H), 6.97 (d, 1 H, J = 10.8 Hz). Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.41; H, 10.13; N, 6.38.

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Registry No. (*R**,*S**)-**1**, 82978-02-7; (*R**,*R**)-**1**, 82978-01-6; **2**, 27748-48-7; (*R**,*S**)-**3**, 138751-71-0; (*R**,*R**)-**3**, 138751-72-1; **4**, 68837-74-1; (*R**,*S**)-**5**, 138668-08-3; (*R**,*R**)-**5**, 138668-21-0; **6**, 138668-09-4; **7**, 127811-20-5; **8**, 138668-10-7; (*R**,*S**)-**9**, 138668-11-8; (*R**,*R**)-**9**, 138668-22-1; **10**, 138668-12-9; (*R**,*S**)-**11**, 138668-13-0; (*R**,*R**)-**11**, 138668-23-2; **12**, 138668-14-1; **13**, 3156-74-9; **14**, 27675-37-2; **15**, 2224-39-7; **16**, 127143-69-5; (*R**,*S**)-**17**, 138668-15-2; (*R**,*R**)-**17**, 138668-24-3; **18**, 138668-16-3; (*R**,*S**)-**19**, 138668-17-4; (*R**,*R**)-**19**, 138668-25-4; **20**, 138668-18-5; (*R**,*S**)-**21**, 138668-19-6; (*R**,*R**)-**21**, 138668-26-5; **22**, 27748-50-1; (*R**,*S**)-**23**, 138693-75-1; (*R**,*R**)-**23**, 138668-27-6; **24**, 138668-20-9; propionaldehyde, 123-38-6; alumina, 1344-28-1; nitroethane, 79-24-3; 3-phenylpropanal, 104-53-0; cyclohexanecarboxaldehyde, 2043-61-0; 1-nitrohexane, 646-14-0.

Synthesis of Perfluorodiamantane by Aerosol Direct Fluorination

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Syntheses of organic cage hydrocarbons with novel structural carbon frameworks are an interesting and active field of research in organic chemistry.[1] Many novel cage hydrocarbons such as adamantane,[2] cubane,[3] and dodecahedrane[4] have been successfully synthesized. However, far fewer perfluorinated cage hydrocarbons are known. The synthesis of perfluoroadamantane by aerosol direct fluorination was reported several years ago by our group.[5] We report the synthesis of perfluorodiamantane by aerosol direct fluorination.

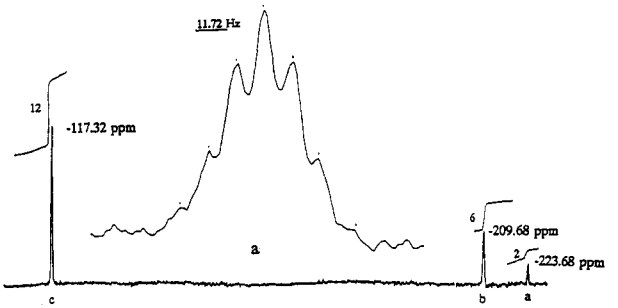

Figure 1. The ^{19}F NMR spectrum of perfluorodiamantane.

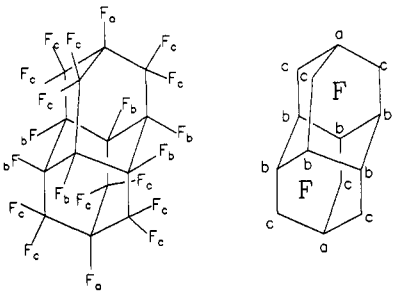

Figure 2. The structure and ^{19}F magnetic environments of perfluorodiamantane.

In 1965, Schleyer et al. first reported the synthesis of congressane,[6] which was later named diamantane. Although mono-, di-, and tetrafluorodiamantane have been prepared from the corresponding bromodiamantanes,[7,8] syntheses of higher fluorinated diamantanes have not to our knowledge been reported.

Results and Discussion

The perfluorination of diamantane was carried out in an improved aerosol reactor described elsewhere.[9] Briefly, this method involves the condensation of the starting material onto the surfaces of microscopic nucleating sodium fluoride preaerosol particles injected at a rate of 10–100 mg/h (0.4–4 mmol/h). The particulates so formed are fluorinated while traversing a concentration gradient of fluorine gas. The heat released during the fluorination is dissipated into the particulates and also efficiently removed by the external cooling system. As a result of the low temperature, condensed phase, and the relatively low acidity ($HF:F^-$, 25:1 to 2.5:1) produced by the injected fluoride ion, cationic rearrangements caused by super acidic endogenous hydrogen fluoride and fragmentation of the hydrocarbon frameworks can be all but eliminated during the fluorination. This is an especially important consideration in cage compounds. The low yield is most probably due to the difficulty in trapping the highly stable aerosol. Losses due to inefficient product capture are supported by the insufficient amounts of side products collected and the lack of residues deposited in the reactor.

The sole isolated product displayed the expected molecular ion, m/z 548, with accurate ^{13}C isotope peaks. The thermal electrons produced by negative chemical ionization (electron attachment) mass spectrometry produce anions by attachment to the fluorocarbon molecules with minimal fragmentation and excellent molecular ion intensities. The parent peak at m/z 548 not only was the base peak, but

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its intensity was much greater than that of any other ion. Minimal fragmentation in the mass spectrum suggests unusual stability of the diamantane structure and its anion. The ^{19}F NMR spectrum of *F*-diamantane consists of three resonances at −117.32, −209.68, and −223.68 ppm relative to internal $CFCl_3$ with ratio of 6:3:1 (Figure 1). This is consistent with the structure of *F*-diamantane which has three groups of chemically equivalent fluorine atoms. The chemical shifts of the secondary fluorine (F_s) and the axial tertiary fluorine (F_a) are close to those of *F*-adamantane[5] since they are in a similar magnetic environment (Figure 2). Also like *F*-adamantane a very simple infrared spectrum reflects the high symmetry of the *F*-diamantane structure. Besides the C–C and C–F stretching bands (at 1300 vs, 1272 w, 1052 m, 968 s cm^{-1}), there is only one other absorption of very weak intensity (at 822 cm^{-1}). The Raman spectrum has bands at 1336 w, 1327 w, 1314 m, 1292 s, 1200 w, 685 m, and 544 s cm^{-1}. Diamantane belongs to D_{3d} point group which has a center of symmetry, vibrations that are infrared active are not Raman active, and vice versa.[10] This was confirmed by our infrared and Raman spectral analysis of perfluorodiamantane. A detailed analysis and calculations relating to the infrared and Raman spectra will be reported later.

Experimental Section

The perfluorination was carried out on an improved reactor, and detailed procedures have been described elsewhere.[9] The products were characterized by a vapor-phase infrared spectrum recorded on a Bio-Rad FTS-7 SPC 3200 spectrometer and a Raman spectrum recorded on a Ramanor HG-2S Spectrophotometer manufactured by Jobin Yvon Instrument, SA. The negative chemical ionization (electron attachment) mass spectrum was recorded on a VG.ZAB-EQ mass spectrometer. Samples were introduced into the source via the reference inlet to a pressure of 10^{-6} Torr and diluted with nitrogen gas to 10^{-5}–10^{-4} Torr and bombarded with 70 eV electrons. The ^{19}F FTNMR spectrum was recorded on a JEOL FX90Q (omniprobe) in $CFCl_3$ as both solvent and internal standard; elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Diamantane was prepared according to literature procedures[11] and purified by column chromatography using hexane as eluant and alumina as stationary phase. The product (mp 230 °C, lit.[6] mp 236–237 °C) was contaminated with an isomeric material comprising approximately 22% by GLC. DSC of the unsealed diamantane sample shows sublimation (heat flow) begins about 62 °C and increases almost linearly to 125 °C where rapid heat gain occurs. Sublimation at 85 °C gives slow steady sublimation of about 0.08 g/h.

Aerosol Fluorination of Diamantane. Diamantane 77% (0.50 g, 2.66 mmol) was loaded into the hydrocarbon evaporator. Referring to the aerosol fluorinator components described in Figure 1 in ref 9, the following specific fluorination conditions were used: preaerosol furnace (>1050 °C), main carrier, 500 mL/min He; hydrocarbon evaporator (85 °C), primary hydrocarbon carrier, 170 mL/min He, secondary hydrocarbon carrier, 500 mL/min He; module 1 (−18 °C), inlet 1-1, 170 mL/min He, 8 mL/min F_2; inlet 1-2, 170 mL/min He, 52 mL/min F_2; module 2 (−10 °C), inlet 2-1, 170 mL/min He, 38 mL/min F_2; inlet 2-2, 170 mL/min He, 6 mL/min F_2. All helium carrier gas flows were initiated except the primary hydrocarbon carrier gas. When the preaerosol (NaF) furnace reached 1050 °C, fluorine flow was initiated. When all gas flows were stable and required temperatures were reached, the dewar around the product trap was filled with liquid N_2. The valve controlling the primary hydrocarbon carrier gas was opened, and the evaporator was heated to 85 °C at which temperature diamantane sublimes slowly. After 5 h, the reaction was stopped. The product trap was connected to the vacuum line and pumped for 18 h to effect maximum transfer. Following trap to trap fractionation, 0.12 g of crude product was collected as a white solid in the −22 °C trap. About 0.10 g of starting material was recovered from the evaporator of the reactor. Pure perfluorodiamantane (0.10 g, 8.0 % yield) was obtained by dissolving the fractionated product (77.2% GLC purity) in $CF_2ClCFCl_2$ (R-113) and separating on a Fluorosilicone QF-1 column (7 m × $^3/_8$ in.). The column temperature was 180 °C and retention time was 17.5 min. Anal. Calcd for $C_{14}F_{20}$: C, 30.68; F, 69.32; H, 0.00. Found: C, 30.75; F, 69.78; H, 0.00.

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Synthesis of Ant Venom Alkaloids from Chiral β-Enamino Lactones: (3*S*,5*R*,8*S*)-3-Heptyl-5-methylpyrrolizidine

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A large number of substituted piperidines and pyrrolidines have been reported as constituents from the venoms of ants in the related genera *Monomorium* and *Solenopsis*, many of which display significant biological activity.[1] Although the relative configurations of these compounds have been determined by racemic syntheses, their absolute configurations have not been yet established, probably owing to the scarcity of natural material. We report here the enantiospecific synthesis of (3*S*,5*R*,8*S*)-3-heptyl-3-methylpyrrolizidine (1), which is the only known bicyclic alkaloid from a *Solenopsis* species, as well as being the only known natural 3,5-dialkylpyrrolizidine.[2]

The first asymmetric synthesis was described by Takano et al.[3a] from a chiral epoxide, the second by Husson et al.,[3b] by utilizing a chiral 2-cyano-6-oxazolopiperidine synthon, and the third by Momose et al.[3c] from alanine. The relative stereochemistries at C-3, C-5, and C-8 of pyrrolizidine 1 have been well established in both syntheses, yet the reported optical rotations are contradictory: the synthetic alkaloid 1 was stated to be levorotatory in the work of Takano and dextrorotatory in the syntheses of Husson and Momose for the same reported absolute configurations. Here we present a new strategy for the synthesis of such compounds.

Results and Discussion

Our approach includes the reductions of the iminium **2** to induce the formation of the last asymmetric carbon C-3 and of the imino alcohol **3** to form the C-8 atom with a *S*-configuration from the chiral pyrrolidinone **4d** (Scheme I).

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