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AEROSOL DIRECT FLUORINATION-SYNTHESIS OF
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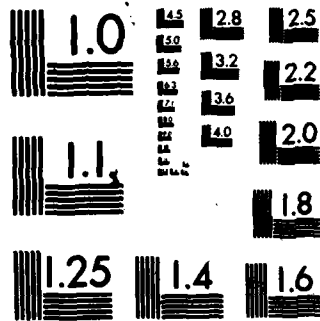
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AEROSOL DIRECT FLUORINATION-SYNTHESIS OF PERFLUOROADAMANTANE
THE PENULTIMATE STEP

by

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Department of Chemistry
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ABSTRACT

The aerosol direct fluorination technique has been successfully employed to convert adamantane to perfluoroadamantane in 28% overall yields based on input. Although physical losses in the reactor reduced yields the major (74.4%) product collected was perfluoroadamantane. Fragmentation and ring-opening proved to be insignificant as was the proportion of 1-hydrilpenta-decafluoroadamantane.



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Aerosol Direct Fluorination-Synthesis of Perfluoroadamantane-

The Penultimate Step

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Knoxville, Tennessee 37996-1600

The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation.¹ The application of this process to alkanes, ethers, cycloalkanes, ketals and ketones has been demonstrated.^{1,2} We report here the extension of the process to the synthesis of perfluoro-adamantane via direct fluorination of adamantane, a feat not realized by other direct fluorination methods, nor by indirect fluorination methods to any significant degree.

Due to the current interest in fluorocarbons as synthetic blood substitutes,³ the fluorination of adamantane and substituted adamantane systems has been attempted. Moore and Driscoll, employing a CoF_3 method involving the recycling of partially fluorinated materials through a reactor, have successfully produced perfluoro-1-methyladamantane, perfluoro-1,3-dimethyladamantane and perfluoro-1,3,5,7-tetramethyladamantane, from 1-trifluoromethyl-adamantane, 1,3-bis(trifluoromethyl)adamantane and 1,3-bis(trifluoromethyl)-5,7-dimethyladamantane, respectively.⁴ Lagow, et. al., reported the successful direct fluorination of 1,3-difluoro-5,7-dimethyladamantane, 1,3-dimethyl-5,7-bis(trifluoromethyl)-adamantane, and 1-adamantamine to the perfluorinated analogs.⁵

The direct fluorination of adamantane to the perfluoro product has remained elusive however; whereas substituted adamantane systems have been successfully perfluorinated, direct fluorination of adamantane itself has previously led only to the production of 1-hydrilpentadecafluoroadamantane in

low yields.⁷ The penultimate substitution would not take place even in pure fluorine under "vigorous" conditions.⁵ At the present time the only other method for the production of perfluoroadamantane, other than via the aerosol direct fluorination method presented here, appears in a recent patent application; wherein adamantane in methylcyclohexane was contacted with a CoF_3 bed at 275° to produce 1-hydrilpentadecafluoroadamantane and perfluoroadamantane (no yields given).⁸

Results and Discussion

The major product collected from the aerosol direct fluorination of adamantane was perfluoroadamantane; of the products collected, F -adamantane comprised 74.4% of the total by weight. Based on input of adamantane, the yield of F -Adamantane was 28%. The aerosol system is dependent on the generation of a particulate aerosol which is ideally crystalline, of uniform size and with little tendency to aggregate. If the conditions for producing the aerosol are ideal, percent yields based on throughputs and product percent distributions will differ by only a few percent; as molecules deviate from this ideality, the percent yields based on throughput fall due to physical losses within the aerosol generator and initial reaction stage (see Reference 1). Due to the relatively low volatility of adamantane these losses are significant, resulting in significant amounts of unreacted adamantane settling throughout the reactor. The majority of material traversing the reactor however is seen to be upwards of 70% perfluorinated, and it is likely that modifications to allow higher carrier flows through the reactor would result in a significant increase in the amounts of material reaching the collection point. The difficulty of vacuum line transfers of the perfluorinated material also leads to significant losses in material isolated.

Previously fluorinations of adamantane and its substituted derivatives have resulted in significant ring opening. Lagow et. al. have attributed this tendency to the fact that : "As hydrogens are replaced by fluorine, the remaining positions become increasingly acidic and the resultant tendency toward carbanion formation may lead to carbon-carbon bond cleavage, especially at the bridge head positions,"⁵ This building up in positive charge, reduction in electron density, or increased acidity is likely to be the cause of the difficulty in obtaining perfluorination as well. The reluctance of fluorine to attack cations, a phenomenon reported by Bartlett, supports this conclusion.⁶ Moreover, Moore and Driscoll report that for the CoF_3 fluorination of 1,3-dimethyladamantane, the major products are ring-opened species.⁴ In an attempt to reduce this ring-opening, two bridgehead fluorines were incorporated into the molecule prior to exhaustive fluorination over CoF_3 ; however, fluorination of the resulting 1,3-difluoro-5,7-dimethyladamantane over CoF_3 again yielded primarily ring-opened species. Lagow was able to successfully direct-fluorinate 1,3-difluoro-5,7-dimethyladamantane to the perfluoro compound, but again the majority of products (70%) consisted of ring-opened species.⁵ The problem of ring-opening does appear to be reduced somewhat by substitution of hydrogen and/or alkyl groups on the adamantane structure by fluorine and/or perfluoroalkyl groups prior to fluorination. Thus Lagow was able to produce $\underline{\text{F}}$ -1,3-dimethyladamantane (26%) and $\underline{\text{F}}$ -1,3,5,7-tetramethyladamantane (4.2%) from 1,3-difluoro-5,7-dimethyladamantane and 1,3-dimethyl-5,7-bis(trifluoromethyl)adamantane, respectively; while Moore and Driscoll prepared $\underline{\text{F}}$ -1-methyladamantane (65%), $\underline{\text{F}}$ -1,3-dimethyladamantane (60%), and $\underline{\text{F}}$ -1,3,5,7-tetramethyladamantane (10%) from 1-(trifluoromethyl)adamantane, 1,3-bis(trifluoromethyl)adamantane, and 1,3-bis(trifluoromethyl)-5,7-dimethyladamantane, respectively.^{4,5}

In contrast to the above methods, aerosol fluorination of adamantane resulted in no significant amount of ring-opening; the major product was the perfluorinated species, the remainder of materials being partially fluorinated adamantanes, as evidenced by mass spectral analysis of a mixture of the non-volatile products. These results indicate the potential value of the direct aerosol method for the synthesis of perfluorinated materials useful as potential blood substitutes. Also the lack of problems with ring-opening suggests the possibility of the production of perfluorinated alkyladamantanes directly from the hydrocarbon analogs.

Experimental

The basic aerosol fluorinator design and a basic description of the process is presented elsewhere.¹ A modified aerosol generator (Figure 1) was adapted to a sublimator loaded with solid adamantane and heated to 150°C. Workup of products, following removal of hydrogen fluoride, consisted of vacuum line fractionation, infrared assay of fractions, gas chromatographic separation of components using a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh, acid washed chromosorb P conditioned at 225°C (12 hrs). Following gas chromatographic separation (Bendix Model 2300, subambient multi-controller) products were collected, transferred to the vacuum line, assayed and characterized by vapor phase infrared spectrophotometry (PE 1330), electron impact (70 eV) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980A MS, 5934A Computer) and ¹H and ¹⁹F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in CDCl₃ with 1% CFC1₃ internal standard. Elemental Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

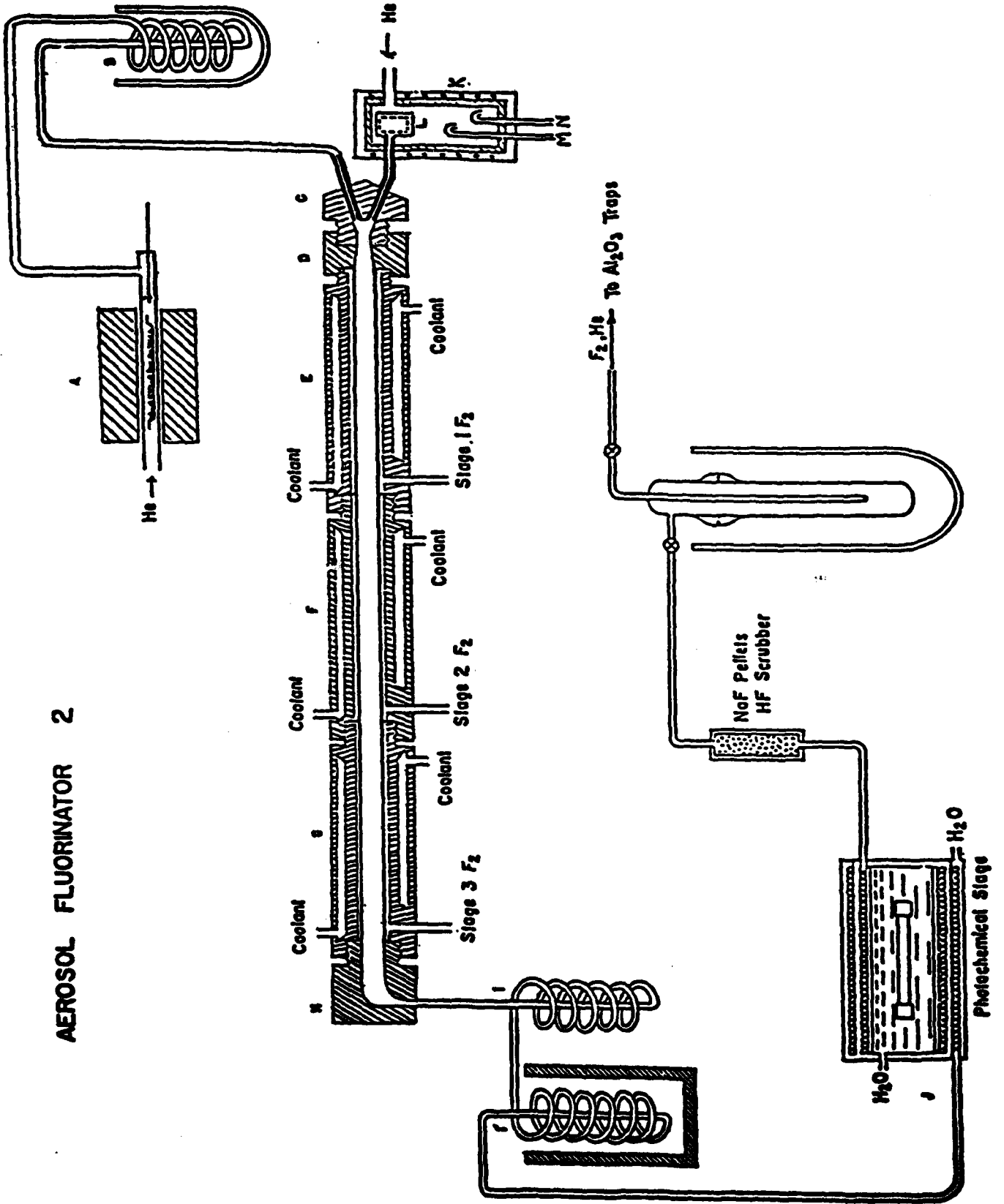
Aerosol Fluorination of Adamantane - Adamantane (Aldrich) 99+% was used

as received. Adamantane (1.39g, 11.2 μ moles) was loaded into the sublimator. The main helium carrier flow (Figure 1) was set at 600 cc/m. This flow is directed through the nucleating particle, NaF, furnace (A), the liquid nitrogen heat exchanger (B) and enters one side of the aerosol generator (C) where it is mixed in the aerosol generator (C) with the hydrocarbon carrier containing the adamantane vapor. The hydrocarbon carrier consists of one upper, primary (150 cc/m) and two lower, secondary (20 cc/m) helium flows entering into the sublimator (K) at the top (L) and bottom (M,N) of the sublimator body (K) respectively. The reactor modules (E,F,G) were cooled to -30°C , -20°C and ambient (-10°C) while the copper coil (I) preceding the photochemical stage (J) was heated to 100°C . Fluorine flows into the reactor modules were 20 cc/m, 50 cc/m and zero respectively. The photochemical lamp was ignited and the sublimator was then heated to 150°C . After 7 hours the reaction was stopped. Upon opening the reactor, 1.23 g of unreacted adamantane was recovered (0.300, 2.2 μ moles reacted); 0.361 g of crude product was collected, dissolved in perfluoropentane and separated on the fluorosilicone QF-1 column (70° , 15 min; $30^{\circ}\text{C}/\text{min}$ to 180°) producing 0.259, (74%) of F-Adamantane, a 28% yield based on theoretical input. It should be noted that significant quantities of unfluorinated adamantane were found inside the reactor. Elemental analyses for $\text{C}_{10}\text{F}_{16}$ require: $\% \text{C} = 28.32\%$, $\% \text{F} = 71.68\%$, $\% \text{H} = 0.0\%$, found: $\% \text{C} = 28.60\%$, $\% \text{F} = 71.88\%$, $\% \text{H} = 0.0\%$. The fluorine-19 nmr consists of a pentet of intensity 12 at -121.20 ppm and a near symmetrical multiplet of -13 prominent diminishing maxima of intensity 4 at -223.53 ppm relative to internal CFCl_3 , a coupling constant of 6 hertz is a best fit. A reproduction of the ^{19}F nmr spectra and a complete characterization; EI-MS, IR (2 pages); are available as Supplementary Material, ordering information is given on any current masthead page.

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AEROSOL FLUORINATOR 2

FIGURE 1



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APPENDIX I

Supplementary Material

Characterization of F-Adamantane

SUPPLEMENTAL MATERIAL

PAGE 1

CHARACTERIZATION OF F-ADAMANTANEInfrared (cm^{-1}): 1295(s), 1280(vs), 960(s), 645(w), 595(w)Mass Spectra [m/e (int.) Formula]:^a

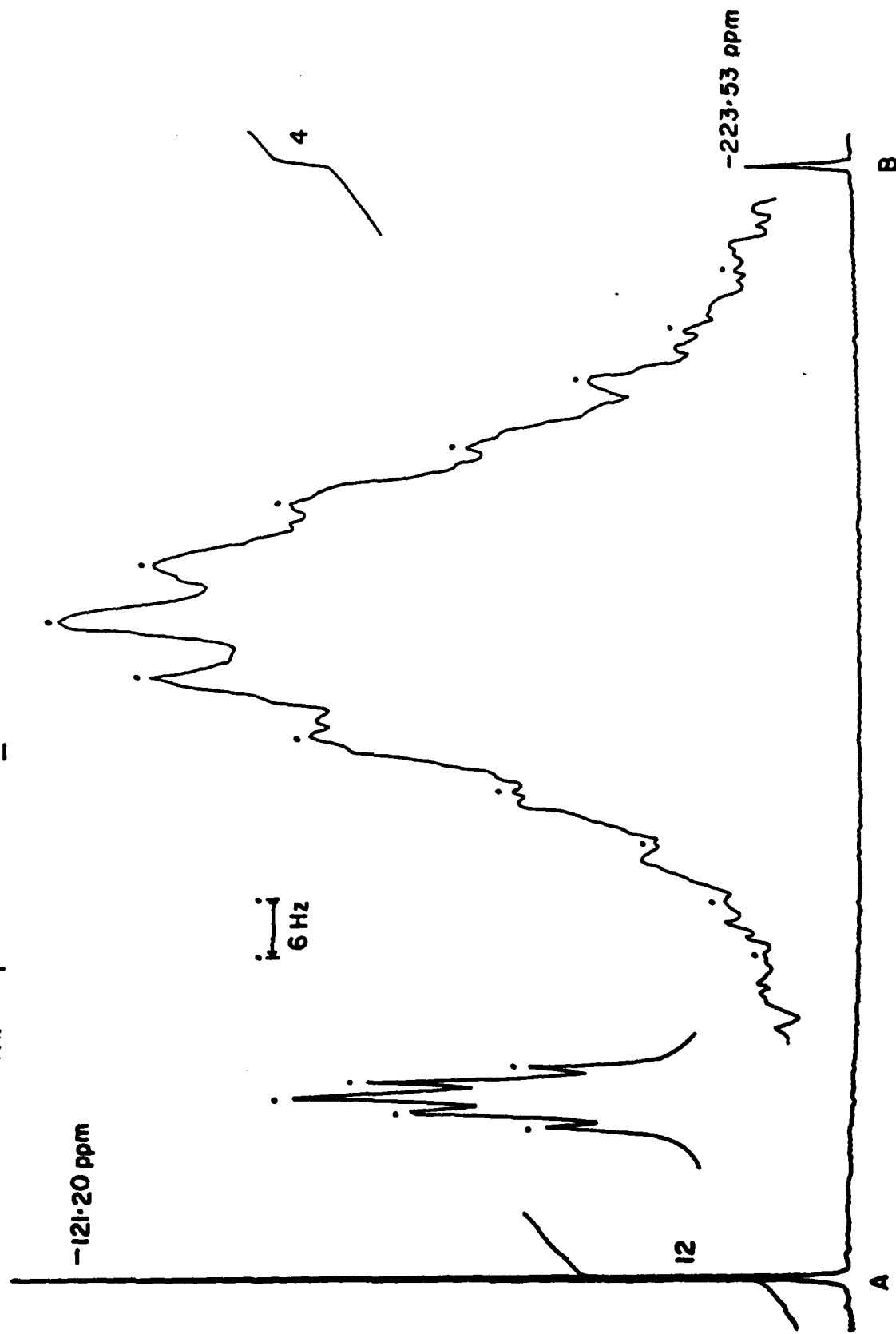
424(1) $\text{C}_{10}\text{F}_{16}$, M; 406(2) $^{13}\text{C}_9\text{F}_{15}$; 405(15) $\text{C}_{10}\text{F}_{15}$, M-F; 355(1) C_9F_{13} ;
 317(1) C_9F_{11} ; 305(2) C_8F_{11} ; 286(2) C_8F_{10} ; 267(3) C_8F_9 ; 255(7) C_7F_9 ; 236(3) C_7F_8 ;
 224(1) C_6F_8 ; 219(1) C_4F_9 ; 217(3) C_7F_7 ; 206(7) $^{13}\text{C}_5\text{F}_7$; 205(100) C_6F_7 ;
 193(1) C_5F_7 ; 186(5) C_6F_6 ; 174(1) C_5F_6 ; 162(2) C_4F_6 ; 155(9) C_5F_5 ; 143(3) C_4F_5 ;
 131(42) C_3F_5 ; 124(3) C_4F_4 ; 119(3) C_2F_5 ; 117(3) C_5F_3 ; 112(2)(C_3F_4 ; 100(2) C_2F_4 ;
 93(7) C_3F_3 ; 69(24) CF_3

^{19}F nmr $\phi\text{CFCl}_3 = 0.0\text{ppm}^b$	Integral	
$\phi = -121.20$ ppm, p	12	
$\phi = -223.53$ ppm, mult.	4	$J_{\text{CF}_2-\text{CF}} = 6$ Hz

<u>Elemental Analysis</u>	%C	%F	%H
Calc. for $\text{C}_{10}\text{F}_{16}$:	28.32	71.68	0.00
Found	28.60	71.88	0.00

^aElectron Impact at 70 eV.^bSee figure 1.

^{19}F nmr Spectrum of F-Adamantane



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