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REACTION OF PERFLUOROTRIMETHYLAMINE WITH ANTIMONY PENTAFLUORIDE. SYNTHESIS AND X-RAY STRUCTURE OF A PERFLUORINATED HEXAHYDRO-TRIAZINEDIONE DERIVATIVE

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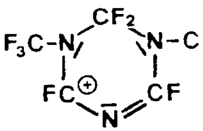
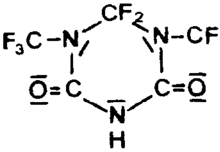
SUMMARY

Perfluorotrimethylamine and SbF_5 at an elevated temperature slowly eliminate CF_4 to form the cation (III). (III) is also obtained from the reaction of CF_3NCF_2 with SbF_5 in nearly quantitative yield. The hexahydrotriazinedione (IV) has been obtained by hydrolysis of (III). The constitution and structure of (IV) are established by X-ray crystallography.


(III)


(IV)

INTRODUCTION

Perfluorotrialkyl amines $(R_f)_3N$ are generally resistent against chemical attack [1]. Among the few reactions they undergo are the degradation by $AlCl_3$ at high temperature [2] and the insertion of SO_3 into a CF bond [3]. Perfluorotrimethylamine (I), which is insoluble in common fluorinated solvents, apparently resists treatment with strong Lewis acids.

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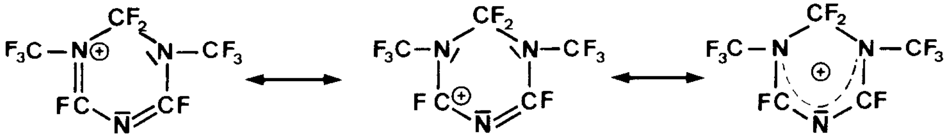
The obvious inertness of (I) stimulated the search for reactants that are sufficiently powerful to attack either at the nitrogen or carbon atom. In the following we report on the reaction of (I) and, for comparison, $(CF_3)_2NC_2F_5$ (II) with SbF_5 and describe the independent synthesis and the result of an x-ray structure analysis of one of the reaction products, which was undertaken to establish its structure and gain some insight into the reaction pathway.

RESULTS and DISCUSSION

Reaction of $(CF_3)_3N$ and $(CF_3)_2NC_2F_5$ with SbF_5

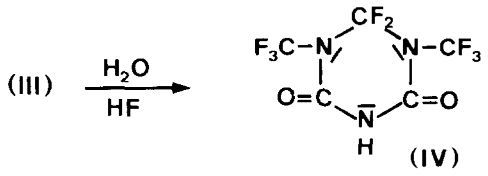
Mixtures of (I) and SbF_5 form two liquid phases, (I) being poorly soluble in the heavier SbF_5 layer. After several weeks at room temperature, the upper layer disappears, and the ^{19}F NMR spectrum reveals, besides CF_4 and starting material, the formation of a new product (III) in nearly quantitative yield. Its ^{19}F NMR spectrum (Table 1) comprises three signals in a 1:1:3 intensity ratio which, by decoupling experiments, are shown to belong to a $A_3A'_3M_2XX'$ spin system. At the same time a broad singlet due to SbF_6^- (or $Sb_2F_{11}^-$) appears. It is concluded that (III) is a cation which is derived from tetrahydrotriazine.



(IIIa) (IIIb) (IIIc)

(III) can be described with several mesomeric structures (IIIa) to (IIIc). Dissolved in SbF_5, this cation is stable up to 90°C before fragmentation begins yielding CF_4. This stability may be a result of the possible electron delocalization implied by formula (IIIc).

Hydrolysis of (III) in acidic solution affords a crystalline material poorly soluble in water which, from analyses, mass and ^{19}F NMR spectra, has the constitution (IV). Its structure was confirmed by the single crystal x-ray investigation reported below.

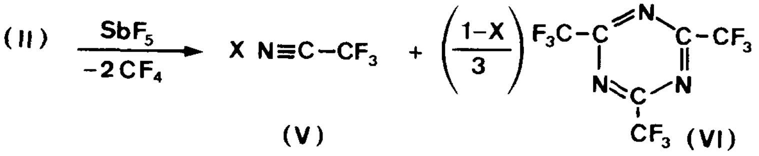


(1)

The cyclic amide of octafluoro-2,4-dimethyl-2,4-diaza-glutaric acid (IV) is poorly soluble in water and undergoes rapid decomposition with alkali.

Under similar conditions, perfluoro-dimethylethylamine (II) is much more reactive than (I). With SbF_5 at room temperature, CF_4 is formed within few days, and in the ^{19}F NMR spectrum two singlets at -56.8 and -72.5 ppm occur which belong to volatile species. These were isolated by fractional condensation in vacuo, and their physical properties, their infrared [4], Raman [5] and mass spectra [6] were identical with those of CF_3CN (V) and perfluoro-2,4,6-trimethyl-s-triazine (VI).

The replacement of one F atom in (I) by a CF_3 group directs the reaction with SbF_5 to entirely different products (2):



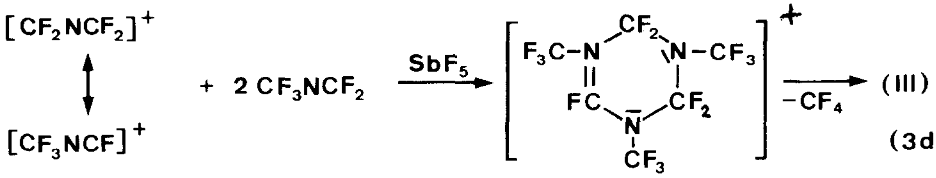
(2)

Obviously the cation $\left[(CF_3)_2NCFCF_3\right]^+$, which is easily formed in a first step, readily undergoes complete cleavage of the F_3C-N bonds, while the cation $\left[(CF_3)_2NCF_2\right]^+$ formed from (I) eliminates only one single CF_4 molecule when treated with SbF_5. The probable reaction pathway involves a cyclotrimerization of CF_3NCF_2 which may be formed according to eqn. (3):

$$(CF_3)_3N + SbF_5 \rightleftharpoons [(CF_3)_2NCF_2]^+ SbF_6^- \qquad (3a)$$

$$[(CF_3)_2NCF_2]^+ SbF_6^- \longrightarrow CF_4 + SbF_5 + CF_3NCF_2 \qquad (3b)$$

$$CF_3NCF_2 + SbF_5 \rightleftharpoons [CF_2NCF_2]^+ SbF_6^- \qquad (3c)$$



(3d)

This reaction mechanism requires that perfluoroazapropene (VII) should undergo a similar cyclotrimerization according to steps (3c) and (3d).

CF_3NCF_2 is known to add fluoride ions, and dimerization products of this anion have been isolated (4) [7]:

$$CF_3NCF_2 \xrightarrow{F^-} \left[CF_3NCF_3\right]^- \xrightarrow{(VII)} (CF_3)_2NCFNCF_3 \quad (4)$$

Fragmentation of (VII) has been reported in the reaction with SbF_5, and no other products than CF_4 have been identified [7]. At room temperature, (VII) and SbF_5 in fact react rapidly, and treatment of the intermediate complex with an excess of SbF_5 at 60°C for several hours converts this complex to (III), which can be hydrolyzed to yield (IV).

This evidence supports the participation of (VII) in the reaction sequence (3), and in contact with SbF_5, (I) may be considered as source for (VII). Since however (VII) is easier accessible than (I) [8], the former is a preferable starting material for the synthesis of (III) and (VI).

Attempts to replace SbF_5 by other Lewis acids have failed so far. No reaction occured when (I) was treated with AsF_5, PF_5 and BF_3. Weak complex formation was observed between (VII) and AsF_5, but no cyclotrimerization was found even on prolonged heating of this complex. Further investigations into the 1:1 adducts of (VII) with Lewis acids are in progress.

EXPERIMENTAL AND SPECTRA

3,5-Bis(trifluoromethyl)-4,4-difluoro-hexahydrotriazenedione (IV)

a) SbF_5 (Merck) and $CF_3)_3N$ were condensed into a glass ampoule in a 4:1 molar ratio and heated to 60°C for 30 days. CF_4 and unreacted (I) were removed in vacuo, the non-volatile residue was hydrolysed with water and after cooling the precipitate was collected. (IV) was dried and recrystallized from CH_3OH or benzene, mp. 148°. b) (IV) was alternatively prepared by heating SbF_5 and (VII) in a 2:1 molar ratio to 60°C for 6 hours and similar work-up. The intermediate (III) was formed in yields of 85% and 95% respectively from (I) and (VII). The hydrolysis was apparently not quantitative, (IV) being obtained in an overall yield of ca. 50%.

$C_5HF_8N_3O_2$, mw 287.01. Calculated / found; % C, 20.91/21.53; %H, 0.35/0.41; % F, 52.95/51.5; % N, 14.64/14.97.

Spectra

The mass spectrum was measured with a VARIAN MAT 311 A spectrometer operating at 70 eV. The following fragments, arranged in the order of decreasing intensity, were observed:

69 (CF_3^+), 44 (CO_2^+), 40 ($H_2F_2^+$), 111 (CF_3NCO^+), 92 (CF_2NCO^+), 178 ($CF_3NCNCF_3^+$), 159 ($CF_2NCNCF_3^+$), 114 (CF_3NCF^+), 133 ($CF_3NCF_2^+$), 287 (M^+).

IR (KBr pellet, cm^{-1}) 1770/1746/1460 (ν CO, amide), 1396, 1348, 1237, 1204, 1157.

Raman (crystal, cm^{-1}) 1780/1754 (ν CO, amide) 687 ($\delta_s CF_3$).

^{19}F NMR spectra were obtained of (III) in SbF_5 and of (IV) in CH_3OH solution respectively with a Varian EM 390 instrument operating at 84.67 MHz. The ^{13}C NMR spectrum of (IV) in CH_3OH was measured with a Varian CFT 80 spectrometer at 20.0 MHz. The ^{19}F spectrum of (III) is displayed in Fig. 1. The NMR parameters of (III) and (IV) are set out in Table 1.

TABLE 1

NMR spectra of (III) and(IV)

		(III)	(IV)
^{19}F			
δ (CF_3)	[ppm]	-51.0[a]	-54.0[b]
δ (CF_2)	[ppm]	-33.5	-48.9
δ (CF)	[ppm]	-13.5	-
$^4J(FF)(F_3CNCF_2)$	[Hz]	13.5	15.2
$^4J(FF)(FCNCF_2)$	[Hz]	4.1	
$^4J(FF)(F_3CNCF)$	[Hz]	~19.8[c]	
$^6J(FF)(F_3CNCNCF)$	[Hz]	~ 0.5[c]	
$^4J(FF)(FCNCF)$	[Hz]	~22.5[c]	
^{13}C			
δ (CO)	[ppm]		143.6[d]
δ (CF_3)	[ppm]		119.8
δ (CF_2)	[ppm]		115.5
$^1J(CF)$ (CF_3)	[Hz]		269.9
$^1J(CF)$ (CF_2)	[Hz]		258.6
$^3J(CF)$ ($CNCF_2$)	[Hz]		2.8

[a] From CCl_3F against internal CF_4, δ = -62.5 ppm. [b] From internal CCl_3F. [c] Estimated from simulation. [d] From TMS.

TABLE 2

Details of the structure analysis [a]

Cell data: a = 10.300(1), b = 6.769(8), c = 13.902(1) Å
β = 104.486(8)°, Space group: $P2_1/c$, Z = 4,
R = 0.073, (R_w = 0.09).
167 parameters and 1770 reflections, of
which 1185 where considered observed (2 σ).

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[a] Information may be obtained from Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, B.R.D. on submission of the name of the authors and the literature reference.

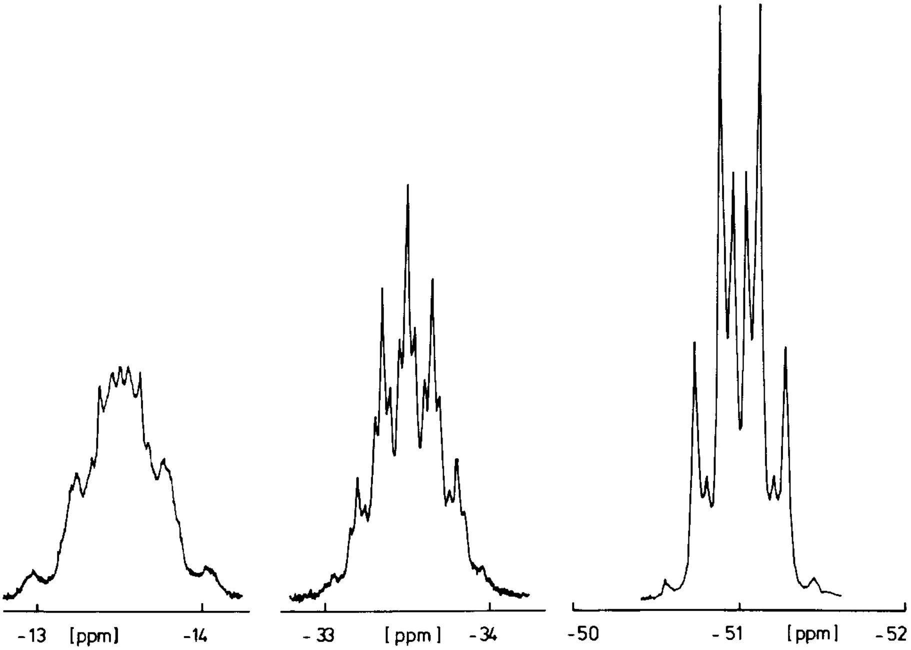

Fig. 1. ^{19}F NMR spectrum of (III).

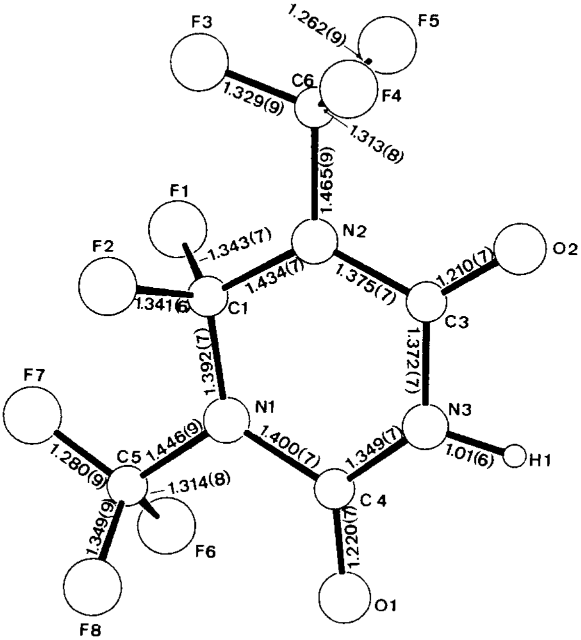

Fig. 2. The structure of (IV).

X-RAY STRUCTURE ANALYSIS

The structure of (IV) has been elucidated by x-ray diffraction from 1770 diffracted intensities collected on a Nonius CAD-4 diffractometer. Pertinent information about the unit cell, data collection and subsequent refinement of the structure is given in Table 2. The structure of the molecule is shown in Figure 2, and bond distances and angles are given in Table 3.

TABLE 3

Bond distances in (Å) and bond angles in (°) of IV

F1-C1	1.343(7)	O2-C3	1.210(7)
F2-C1	1.341(6)	N1-C1	1.329(7)
F3-C6	1.329(9)	C1-N2	1.434(7)
F4-C6	1.313(8)	N2-C3	1.375(7)
F5-C6	1.262(9)	C3-N3	1.372(7)
F6-C5	1.314(8)	N3-C4	1.349(7)
F7-C5	1.280(9)	C4-N1	1.400(7)
F8-C5	1.349(9)	N1-C5	1.446(9)
O1-C4	1.220(7)	N2-C6	1.465(9)
N1-C1-N2	113.0(5)	F1-C1-F2	104.9(4)
C1-N2-C3	124.3(5)	F8-C5-F7	110.2(6)
N2-C3-N3	115.4(5)	F7-C5-F6	107.6(6)
C3-N3-C4	125.7(5)	F6-C5-F8	106.3(6)
N3-C4-N1	115.3(5)	F5-C6-F4	108.7(6)
C4-N1-C1	125.1(5)	F5-C6-F3	107.6(6)
		F4-C6-F3	108.2(6)

The central 1.3.5-triazane ring is essentially planar (± 0.05 Å) with both carbon atoms of the trifluoromethyl groups at N1 and N2 and O2 located exactly in the plane. O1, on the other hand, lies 0.2 Å out of the plane and it is interesting to note that the adjacent C-N distances [C4-N1, C4-N4] are different from those for O2 [C3-N2, C3-N3] (Table 3).

Bond distances within the cyclic framework compare favourably with those given for similar molecules [9]. Some of the F-C bond lengths appear to be artificially shortened and this may be a result of large thermal motion or rotational disorder of the fluorine atoms in these groups.

ACKNOWLEDGEMENTS

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