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FORMATION OF THE PERFLUORO-2,6-DIMETHYL-2,4,6-TRIAZA-HEPT-3,4-DIENIUM ION BY TRIMERIZATION OF PERFLUORO-AZAPROPENE

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SUMMARY

The reaction of CF_3NCF_2 with SbF_5, from which previously a cyclotrimer has been obtained, can be directed to selectively yield the acyclic trimeric cation (III) if carried out in SO_2 as a solvent. The derivatives (V) and (VII) were obtained when (III) was treated with $F^{\ominus}$ and $(C_2H_5)_2O$, respectively, while (VIII) and (IX) were formed by hydrolysis of (III). (VI) was obtained from (V) and BCl_3. All compounds were isolated, characterized analytically and investigated by infrared, Raman, mass and NMR spectroscopy.

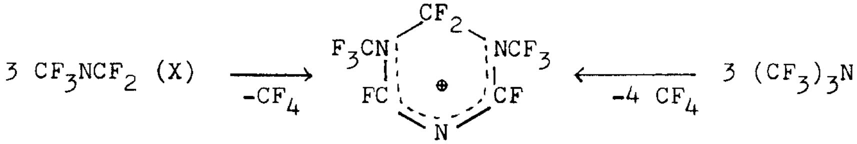
$[(CF_3)_2NCFNCFN(CF_3)_2]^+$ (III) $(CF_3)_2NCFNCF_2N(CF_3)_2$ (V)

$(CF_3)_2NCClNCCl_2N(CF_3)_2$ (VI) $(CF_3)_2NC(OC_2H_5)NCF_2N(CF_3)_2$ (VII)

$(CF_3)_2NCFNCON(CF_3)_2$ (VIII) $(CF_3)_2NCONH_2$ (IX)

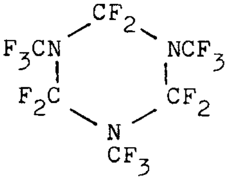
INTRODUCTION

Recently we have described the formation of the cation (I) by treatment of perfluorotrimethylamine and perfluoro-azapropene (X) with neat SbF_5 [1]. Both reaction pathways involve a cyclotrimerization with concomittant elimination of CF_4:



(I)

The hydrolysis of (I) was shown to yield a hexahydrotriazinedione derivative. Some of our results were independently confirmed by Knunyants et al.[2] who observed the formation of 18 % of the cyclotrimer (IV) along with the dimer $(CF_3)_2NCFNCF_3$ (XI), 23 %, and 36 % of the linear trimer (V) when treating (X) and SbF_5 for 2 hours at ~20°C.



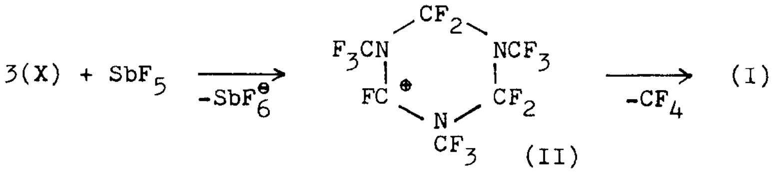
(IV)

$(CF_3)_2NCF_2NCFN(CF_3)_2$ (V)

In the following we report on investigations directed towards the selective synthesis of (V), its chemical properties and the formation and characterization of several of its derivatives.

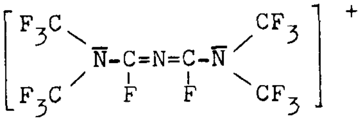
THE REACTION OF CF_3NCF_2 WITH SbF_5

In the reaction of (X) with an excess of neat SbF_5, the cation of the cyclotrimer (II) is formed as an intermediate; it eliminates CF_4 to form the stable cation (I) (1):



(II) (1)

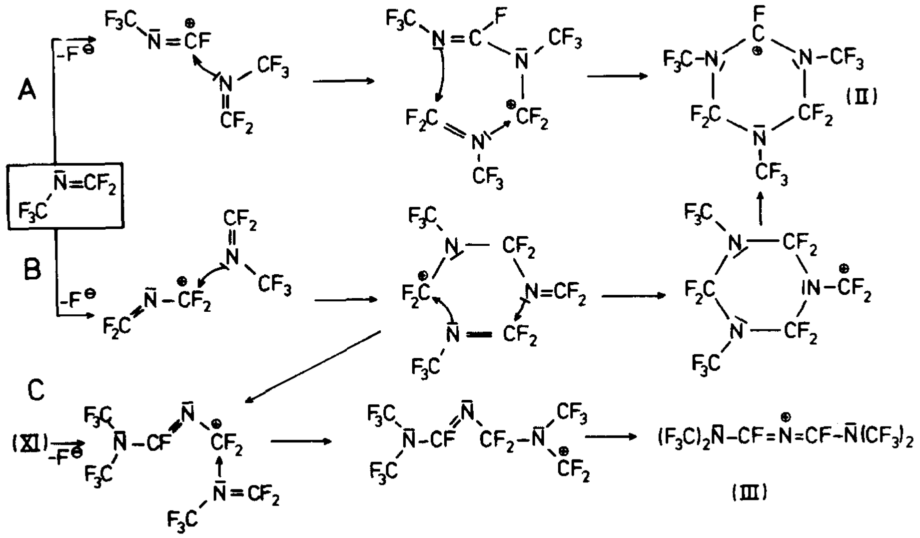
If however this reaction is carried out in SO_2 as a solvent, only small quantities (<10 %) of (II) are formed. Under these conditions, the $Sb_2F_{11}^{\ominus}$ salt of (II) is sufficiently stable to be characterized by its ^{19}F NMR spectrum. The 6 : 4 : 3 : 1 intensity ratio and the qualitative and quantitative coupling pattern confirm the constitution of (II). The major product, which is formed in a yield of 90 %, was shown to be the isomeric noncyclic cation (III).



$$\left[(F_3C)_2\bar{N}-\underset{F}{C}=N=\underset{F}{C}-\bar{N}(CF_3)_2\right]^+$$

(III)

The cation (III) is selectively formed when the dimer of (X), $(CF_3)_2NCFNCF_3$ (XI) [3], dissolved in SO_2/SbF_5, is treated with (X). This is the pathway of choice if (III) and its derivatives are required in high purity. Obviously (II) and (III) are formed from (X) <u>via</u> a common intermediate (routes A and B, Scheme 1) while pathway C is selectively directed towards (III).



Scheme 1

The reaction of (X) with SbF_5 proceeds preferentially *via* route A if an excess of SbF_5, which may act as solvent, is present. In solution, pathway B is preferred. The results reported by Knunyants *et al.* [2] are in agreement with scheme 1 if it is assumed that the reaction simultaneously follows routes A and B, unreacted (X) serving as a solvent.

CHEMICAL PROPERTIES OF (III)

Both cations (II) and (III) add fluoride ions if treated with carefully dried KF in SO_2 solution according to eqn. 2 and 3. The $SO_2F^{\ominus}$ anion is apparently the reactive species because KF did not react in the absence of SO_2.

$$\text{(II)} \quad + F^{\ominus} \quad \xrightarrow{SO_2} \quad \text{(IV)} \qquad (2)$$

$$\text{(III)} \quad + F^{\ominus} \quad \xrightarrow{SO_2} \quad \text{(V)} \qquad (3)$$

The similar vapour pressures of isomers (IV) and (V) prevented their separation by fractional distillation. Pure material was however obtained by selective synthesis of (V) via (XI) and by making use of the different chemical reactivity of (IV) and (V). Thus, the CF_2 groups of (IV) are less readily attacked by Lewis acids than the CF and CF_2 groups respectively of (V). In contrast to (IV), (V) forms a poorly volatile complex with AsF_5 which can be dissolved in SO_2 to form the cation (III). At room temperature, BCl_3 selectively attacks (V) according to (4):

$$\text{(V)} \quad + \quad BCl_3 \longrightarrow BF_3 \quad + \quad (CF_3)_2NCCl_2NCClN(CF_3)_2 \text{ (VI)} \qquad (4)$$

In the presence of KSO_2F, (III) cleaves diethyl ether according to eqn. (5):

$$\text{(III)} \quad + \quad Sb_2F_{11}^{\ominus} \quad + \quad 2\text{ KF} \quad + \quad C_2H_5OC_2H_5 \quad \xrightarrow{SO_2}$$

$$2\text{ KSbF}_6 \quad + \quad C_2H_5F \quad + \quad (CF_3)_2NC(OC_2H_5)NCF_2N(CF_3)_2 \text{ (VII)} \qquad (5)$$

Two by-products, (VIII) and, in traces, (IX), were formed in the course of reaction (5). They were isolated and identified as hitherto unknown urea derivatives. They are obviously formed by hydrolysis of (III).

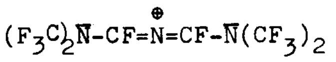
$(CF_3)_2NCFNC(O)N(CF_3)_2$ (VIII) $(CF_3)_2NC(O)NH_2$ (IX)

SPECTRA AND EXPERIMENTAL

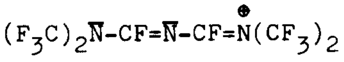
All new compounds were characterized by elemental analyses, IR, Raman (Table 1), NMR and mass spectra. The vibrational spectra exhibit the diagnostic frequencies of the expected group vibrations. The phase dependence of $\nu(C{=}O)$ of (IX) which is due to hydrogen bridging in the solid state should be particularly mentioned.

^1H and ^{19}F NMR Spectra

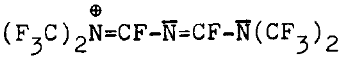
The NMR spectra are set out in Table 2. The ^{19}F NMR spectra are of first order except for (III) and (IV). Due to the very limited number of resolved features, no attempts to simulate their complicated spin systems seemed justified. The ^{19}F NMR spectra of (III) recorded at 84.67 and 282.4 MHz turned out to be temperature dependent. At 30°C the low frequency spectrum shows two resonances in a 1 : 6 ratio for the CF and CF_3 groups. Upon cooling the signal of the CF_3 groups is split into two signals with an intensity ratio of 1 : 1. In the high frequency spectrum coalescence is observed close to 300 K. The nonequivalence of the CF_3 groups due to hindered rotation of the $N(CF_3)_2$ groups suggests that the tertiary nitrogen atoms participate in the central allenic π system (A) by means of the resonance structures B and C.



$(F_3C)_2\overline{N}\text{-}CF{=}\overset{\oplus}{N}{=}CF\text{-}\overline{N}(CF_3)_2$ (A)



$(F_3C)_2\overline{N}\text{-}CF{=}\overline{N}\text{-}CF{=}\overset{\oplus}{N}(CF_3)_2$ (B)



$(F_3C)_2\overset{\oplus}{N}{=}CF\text{-}\overline{N}{=}CF\text{-}\overline{N}(CF_3)_2$ (C)

TABLE 1

Physical properties, analyses and vibrational spectra

		(IV)	(V)	(VI)	(VII)	(VIII)	(IX)
bp [°C]		94	93	157	136	98	66 (mp)
Formula		$C_6F_{15}N_3$	$C_6F_{15}N_3$	$C_6Cl_3F_{12}N_3$	$C_8H_5F_{14}N_3O$	$C_6F_{13}N_3O$	$C_3H_2F_6N_2O$
mw (calc.)		399.00	399.00	448.36	425.04	377.00	196.02
calc/found	%C	18.05/18.2	18.05/18.1		22.59/22.0	19.10/19.3	18.37/17.6
	%H				1.19/1.2		1.03/1.1
	%Cl			23.72/23.8			
	%F	71.42/71.4	71.42/71.3	50.85/50.7	62.58/61.7	65.51/65.9	58.15/58.1
	%N	10.53/10.3	10.53/10.6	9.37/9.4	9.89/10.1	11.15/11.3	14.29/14.6
Selected skeletal vibrations, $IR_g/Raman_{l,s}$ [cm^{-1}]							
ν(C=N)			1768vs/1758m	1688vs/1680m	1705vs/1700m	1758vs/1740vs	
ν(C=O)						1785s/1760vs	1800s/1713m
ν(Ring)		-/273vs					
ν(CCl)				-/362vs			
ν(CF)		1245vs/- 1388vs/- 1398vs/-	1170vs/- 1220vs/- 1240vs/- 1350vs/- 1396vs/-	1222vs/- 1240vs/- 1285vs/- 1335vs/- 1363vs/-	1215vs/- 1230vs/- 1315vs/- 1345vs/-	1160vs/- 1226vs/- 1308vs/- 1354vs/- 1396vs/-	1160s/- 1289vs/- 1345vs/-
$\delta_s(CF_3)$		-/757vs	768w/766vs	753m/752vs	764m/780vs	-/774vs	772m/782vs

TABLE 2

NMR spectra. (II) = $F^{C}C(NCF_3^{A}CF_2^{D})_2NCF_3^{B\oplus}$; (V) = $(CF_3^{B})_2NCF^{C}NCF_2^{D}N(CF_3^{A})_2$;
(VII) = $(CF_3^{B})_2NC(OC_2H_5)NCF_2^{D}N(CF_3^{A})_2$; (VIII) = $(CF_3^{B})_2NCF^{C}NCON(CF_3^{A})_2$

	$(II)^{a}$	$(III)^{b}$	$(IV)^{c}$	$(V)^{c}$	$(VI)^{c}$	$(VII)^{c}$	$(VIII)^{c}$	$(IX)^{d}$
$^{19}F^{e}$								
$\delta(CF)$ [ppm]	-39.2^{C}	-1.2		-18.9^{C}			-22.0^{C}	
$\delta(CF_2)$[ppm]	-55.0^{D}		-61.9	-58.8^{D}		-58.8^{D}		
$\delta(CF_3)$[ppm]	-48.4^{A}	-53.1	-53.4	-54.4^{A}	-50.7	-54.0^{A}	-55.0^{A}	-56.7
	-50.4^{B}	-55.1		-56.1^{B}	-54.9	-56.9^{B}	-55.9^{B}	
$^{4}J(FF)$ [Hz]	26.8^{AC}			14.1^{BC}			14.5^{BC}	
	5.5^{CD}			18.1^{CD}				
	13.6^{AD}			12.1^{AD}		12.0^{AD}		
	13.5^{BD}							
$^{6}J(FF)$ [Hz]				1.7^{AC}		4.2^{BD}		
$^{8}J(FF)$ [Hz]					0.9			
$^{1}H^{f}$								
$\delta(NH_2)$[ppm]								6.1
$\delta(CH_3)$[ppm]						1.38		
$\delta(CH_2)$[ppm]						4.43		
$^{3}J(HH)$[Hz]						7.0		

[a] In neat SbF_5. [b] At 282.4 MHz in SO_2 at 236 K. [c] Neat liquids against CF_3COOCH_3, -76.2 ppm from $CFCl_3$, as internal standard. [d] In $CDCl_3$. [e] At 84.67 MHz from $CFCl_3$, positive sign = high frequency. [f] From TMS.

Mass Spectra

The EI mass spectra obtained at 70 eV are listed in Table 3 in the order of decreasing intensity. The masses of the fragments, in particular the M^+ and $(M-F)^+$ peaks, confirm the suggested constituents.

Perfluoro-2,6-dimethyl-2,4,6-triaza-hept-3,4-dienium ion (III)

9.2 g (69 mmole) (XI) [4] are condensed into a mixture prepared from 10 g (46 mmole) SbF_5 and 10 g SO_2 in a glass ampoule equipped with a PTFE valve. After 2 days at 25°C, the formation of (III) is complete. The solution is concentrated and cooled to -30°C. (III) is obtained as $Sb_2F_{11}^{\ominus}$ salt in a yield of ca. 70 %.

Perfluoro-1,3,5-trimethyl-1,3,5-triaza-cyclohexane (IV) and 1,1,1,7,7,7-hexafluoro-2,6-bis(trifluoromethyl)-3,5-trichloro-2,4,6-triaza-hept-3-ene (IV)

15 ml SO_2 are condensed on 2.7 g KF which had been dried at 300°C, the mixture stirred for 12 hours at 25°C and the above-mentioned solution of (III) added, shaken for 2 days, and volatile products pumped off. (IV) and (V) in a ca. 8 : 2 ratio are condensed in a -55°C trap, total yield ~6 g (~65 %). This mixture is treated for 12 hours at 25°C with an amount of BCl_3 equimolar to (V) and worked up by standard vacuum techniques. (IV) and (VI) are collected in -55 and -20°C traps respectively in quantitative yield.

Perfluoro-2,6-dimethyl-2,4,6-triaza-hept-2-ene (V)

6 g (22.5 mmole) (XI) are dissolved in 19.5 ml SO_2/SbF_5 1:1 and 3 g (X) added. After work up as described, (V) is obtained in a yield of 70 %.

1,1,1,5,5,7,7,7-octafluoro-2,6-bis(trifluoromethyl)-3-ethoxy-2,4,6-triaza-hept-3-ene (VII) and Perfluoro-2,6-dimethyl-2,4,6-triaza-hept-3-ene-5-one (VIII)

A solution of (III) is prepared as described above. SO_2 is partly removed and a suspension of an equimolar amount of dried KF and an excess of diethylether in SO_2 is added.

TABLE 3

EI mass spectra, m/e arranged in the order of decreasing intensity[a]

(IV)	114 $(CF_3NCF)^+$, 69 $(CF_3)^+$, 133 $(CF_3NCF_2)^+$, 247 $((CF_3)_2NCF_2NCF)^+$, 266 $((CF_3)_2NCFNCF_3)^+$, 202 $((CF_3)_2NCF_2)^+$, 159 $(CF_3NCNCF_2)^+$, 380 $(M - F)^+$
(V)	69 $(CF_3)^+$, 114 $(CF_3NCF)^+$, 247 $((CF_3)_2NCF_2NCF)^+$, 202 $((CF_3)_2NCF_2)^+$, 159 $(CF_3NCNCF_2)^+$, 133 $(CF_3NCF_2)^+$, 266 $((CF_3)_2NCFNCF_3)^+$, 380 $(M - F)^+$, 292 $((CF_3)_2NCFNCNCF_3)^+$
(VI)	69 $(CF_3)^+$, 130/132 $(CF_3NCCl)^+$, 412/414/416 $(M - Cl)^+$, 85/87 $(CF_2Cl)^+$, 114 $(CF_3NCF)^+$, 199/201 $((CF_3)_2NCCl)^+$
(VII)	92 $(CF_2NCO)^+$, 114 $(CF_3NCF)^+$, 45 $(C_2H_5O)^+$, 69 $(CF_3)^+$, 202 $((CF_3)_2NCF_2)^+$, 245 $((CF_3)_2NCF_2NCOH)^+$, 361 $((CF_3)_2NCNCFN(CF_3)_2)^+$, 225 $((CF_3)_2NCFNCO)^+$, 273 $((CF_3)_2NCNCNCF_3)^+$, 292 $(CF_3NCNCFN(CF_3)_2)^+$, 180 $((CF_3)_2NCO)^+$, 137 $(CF_3NCNCO)^+$, 134 $(CF_3NHCF_2)^+$, 159 $(CF_3NCFNCF)^+$, 377 $(M-C_2H_5F)^+$, 425 $(M)^+$
(VIII)	69 $(CF_3)^+$, 225 $((CF_3)_2NCFNCO)^+$, 137 $(CF_3NCNCO)^+$, 92 $(CF_2NCO)^+$, 114 $(CF_3NCF)^+$, 180$((CF_3)_2NCO)^+$, 247 $((CF_3)_2NCF_2NCF)^+$, 202 $((CF_3)_2NCF_2)^+$, 159 $(CF_3NCFNCF)^+$, 292 $(CF_3NCNCFN(CF_3)_2)^+$, 358 $(M - F)^+$
(IX)	69 $(CF_3)^+$, 134 $(CF_3NHCF_2)^+$, 114 $(CF_3NCF)^+$, 133 $(CF_3NCF_2)^+$, 92 $(CF_2NCO)^+$, 111 $(CF_3NCO)^+$, 196 $(M)^+$

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[a] Varian MAT 311 A, 70 eV.

After shaking for 12 hours at 25°C, the mixture is worked up by fractional condensation *in vacuo*. (VII) and (VIII) are collected in a -50°C trap, yield 50 %, and separated by fractional distillation, the (VII) : (VIII) ratio ranging from >9 : 1 to 7 : 3 depending on the residual moisture of the reagents.

N,N-Bis(trifluoromethyl)-urea (IX) was obtained in poor yield (~10 %) when (III) · $Sb_2F_{11}^{\ominus}$ was added to ice water/diethylether, the ethereal phase dried with Na_2SO_4, the ether removed *in vacuo*, (IX) collected in a -20°C trap and purified by sublimation at 30°C/2 Torr.

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