Polyfluoroalkyl Derivatives of Nitrogen. Part XLII.¹ Reaction of N-Bromobistrifluoromethylamine with 1H-Pentafluoropropene and Some Further Studies on the Thermal Rearrangement of NN-Bistrifluoromethylvinylamines

By George L. Fleming, Robert N. Haszeldine,* James R. McAllister, and Anthony E. Tipping, Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

N-Bromobistrifluoromethylamine reacts with a 95:5 mixture of cis- and trans-1H-pentafluoropropene under freeradical conditions to give a high yield of a mixture of erythro- and threo-2-bromo-1,2,3,3,3-pentafluoro-NNbistrifluoromethylpropylamine in the ratio 62:38. Dehydrobromination of the erythro-isomer affords a mixture of cis- and trans-1,2,3,3,3-pentafluoro-NN-bistrifluoromethylprop-1-envlamine in the ratio 38:62 whereas the threo-isomer yields the cis-olefin exclusively. The static pyrolysis of perfluoro-(NN-dimethylvinylamine) at 500 °C affords perfluoro-2-azapent-2-ene in reasonable yield, together with hexafluoroethane and other decomposition products. Pyrolysis in the presence of an excess of toluene gives trifluoromethane and only a low yield of the azapent-2-ene. Similarly 1.2-difluoro-NN-bistrifluoromethylvinylamine affords 4H-octafluoro-2-azapent-2ene on pyrolysis, but 2-bromo-1,2-difluoro-NN-bistrifluoromethylvinylamine and NN-bistrifluoromethylvinylamine give mainly decomposition products.

N-bromobistrifluoromethylamine (I) reacts with a variety of olefins, both symmetrical and unsymmetrical, under free-radical conditions (u.v., sunlight, or thermal) to afford 1:1 adducts in high yield; 2-5 the chain carrier is believed to be the $(CF_2)_2N$ radical. More recently ionic additions of (I) to olefins susceptible to electrophilic attack, e.g. but-2-ene ⁶ and propene,⁷ have been observed.

We report here the reactions of (I) with 1H-pentafluoropropene (II) under free-radical conditions, carried out as part of a general investigation ⁸ into the chemistry

of this olefin; radical addition of trifluoroiodomethane and hydrogen bromide have previously been studied.8

Reaction of a 95:5 cis-trans-mixture of (II) with the N-bromo-amine (I) (2:1 molar ratio) in the vapour phase in weak sunlight gave unchanged olefin (55% 2-bromo-1,2,3,3,3-pentafluoro-NN-bistrirecovered), fluoromethylpropylamine (III) (85%), 2-bromo-2,3,3,3tetrafluoro-NN-bistrifluoromethylpropylamine (IV) (4%), a mixture of erythro- and threo-1,2-dibromo-1,2,3,3,3-pentafluoropropane (V) [7% based on olefin,

{CF ₃ } ₂ N·CHF·CFBr·CF ₃	$(CF_3)_2 N \cdot CH_2 \cdot CFBr \cdot CF_3$			
(111)	(IV)			
CF₃·CFBr·CHFBr	(CF3 2N·N(CF3)2			
(V)	(I <u>V</u>)			

12% based on N-bromo-amine (I)], and tetrakistrifluoromethylhydrazine (VI) (14%).

The 1:1 adduct was separated by g.l.c. into its two

¹ Part XLI, R. E. Banks, R. N. Haszeldine, P. Mitra. T. Myerscough, and E. Smith, J. Macromol. Sci., 1974, A8(8), 1325. ² J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, J. Amer.

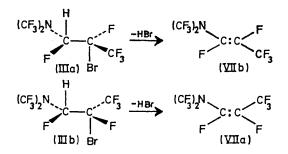
Chem. Soc., 1958, 80, 3604. R. N. Haszeldine and A. E. Tipping, J. Chem. Soc., 1965,

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⁴ E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, J. Chem. Soc. (C), 1968, 796.

stereoisomers, present in the ratio 53:32, which were identified on the basis of the products formed from each on dehydrobromination with potassium hydroxide. The major adduct isomer on dehydrobromination afforded 1,2,3,3,3-pentafluoro-NN-bistrifluoromethylprop-1-enylamine (100%) as a 38 : 62 mixture of *cis*- (VIIa) and *trans*-(VIIb) isomers; the minor adduct afforded cis-olefin (VIIa) (78%) exclusively.

A trans-E2 elimination of hydrogen bromide from the threo-like isomer (where threo-like and erythro-like are designated from a consideration of the group sizes on each of the asymmetric carbon atoms) would yield cis-olefin (VIIa) whereas the *erythro*-like isomer would yield the trans-olefin (VIIb). The major adduct is thus considered to be the erythro-like isomer (IIIa) and the minor adduct the threo-like isomer (IIIb).



The elimination from isomer (IIIa) is not completely of the trans-E2 type since olefin (VIIb) is not formed exclusively. The preponderance of *cis*-olefin (VIIa) formed in both reactions suggests that perhaps it is the thermodynamically more stable olefin even though it is the least sterically favoured olefin. In this respect it is interesting that dehydrobromination of a 1:1

⁵ G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, J.C.S. Perkin I, 1972, 1877.

M. G. Barlow, G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, J. Chem. Soc. (C), 1971, 2744.

D. H. Coy, G. L. Fleming, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, J.C.S. Perkin I, 1972, 1880. ⁸ R. N. Haszeldine, J. R. McAllister, and A. E. Tipping,

J.C.S. Perkin I, 1974, 1303.

mixture of erythro- and threo-(CF₃)₂N·CFBr·CHF·N(CF₃)₂ under comparable conditions gave exclusively the cisisomer of the olefin $(CF_3)_2N \cdot CF \cdot CF \cdot N(CF_3)_2$.⁵ In contrast dehydrobromination of the compound $(CF_3)_2$ N·CH₂· $CHBr \cdot N(CF_3)_2$ gave only the *trans*-isomer of the olefin $(CF_3)_2$ N·CH:CH·N $(CF_3)_2$.4

It has been postulated previously ⁹ that the cis-CF:CF grouping has greater electronic stabilising effect than than the trans-CF:CF grouping; the present results are in agreement with this.

The structure of the unexpected product (IV) was established by mass spectrometry and n.m.r. spectroscopy. The mass spectrum showed peaks at m/e 266 $[(M - Br)^+]$ and 195 and 193 (CF₃·CFBr·CH₂⁺) in addition to a base peak at m/e 166 [(CF₃)₂N·CH₂⁺]; compounds which contain a (CF₃)₂N·CH₂ grouping have been observed ¹⁰ previously to contain base or very intense peaks at m/e 166 in their spectra. The n.m.r. spectra showed the presence of (CF₃)₂N, CFBr, CH₂, and CF_3 groups on the basis of the observed chemical shifts and coupling constants and the coupling (7.8 Hz) between the CF₃ and CFBr fluorines was strong evidence that the grouping CF₃·CFBr was present.

The formation of product (IV) is best accounted for by the presence of a small amount of 2,3,3,3-tetrafluoropropene (VIII) in the reactant olefin (II). Free-radical reaction of the N-bromo-amine (I) with this olefin would be expected to take place via exclusive $(CF_3)_2N$ radical attack on the terminal CH₂ group.

$$(CF_3)_2 N \cdot + CH_2 : CF \cdot CF_3 \longrightarrow (CF_3)_2 N \cdot CH_2 \cdot CF \cdot CF_3 \xrightarrow{(CF_3)_2 NBr} (IV)$$

$$(VIII)$$

The olefin (II) was prepared from hexafluoropropene by hydrogenation over palladium [to give (IX)] followed by dehydrofluorination.¹¹ Hydrogenolysis of the adduct (IX) would afford 1,2,3,3,3-pentafluoropropane (X),

which on treatment with potassium hydroxide would be expected to afford the olefin (VIII). Such further reduction occurs in the presence of a nickel catalyst,¹² but has not been reported previously for the palladium catalyst.

The dibromide (V) was identified by a comparison of its spectral data (i.r., n.m.r.) with those of an authentic sample prepared by reaction of bromine with the olefin (II).⁸ The hydrazine (VI) was also identified spectroscopically.3

The only 1:1 adduct detected in the products was that formed via exclusive $(CF_3)_2N$ radical attack on the terminal CHF group in the olefin (II), i.e. (III). Initial $(CF_3)_2$ N· radical attack on hexafluoropropene occurs to

the extent of 96% on the CF_2 group and 4% on the CF_3 CF group.¹³ The proportion of attack on the CF_3 ·CF group in the olefin (II) would be expected to be less than 4%because a CF₂ group can stabilise a lone electron to a greater extent than can a CHF group $[(CF_3)_2N \cdot radical$ attack on CHF: CF_2 occurs in the ratio 78 : 22³]. Thus the adduct, (CF₃)₂N·CF(CF₃)·CHFBr, formed via (CF₃)₂N· radical attack on the CF3 CF group of the olefin (II), was expected to be present in the products in a trace amount only.

If the addition of the amine (I) to the olefin (II) had been exclusively trans-stereospecific then the adducts (IIIa and b) would have been formed in the ratio 95:5 (the cis-trans-ratio of reactant olefin) rather than the ratio 62:38 (1.7:1) observed. The additions of hydrogen bromide and trifluoroiodomethane to the olefin (II) gave adducts resulting from trans- and cis-addition in the ratios 2.3:1 and 1.4:1, respectively.⁸ Since all three addends have relatively weak element-halogen bonds it is possible that the ratios represent to some degree the amount of interaction in the intermediate radical (XI) tending to aid chain-transfer from the opposite side of the molecule. If this is correct then the effectiveness of

$$x + (II) \longrightarrow CHF \xrightarrow{CF \cdot CF_3} \xrightarrow{XY} CHF \xrightarrow{CF \cdot CF_3}$$

X for such interaction lies in the order $Br > N(CF_3)_2 >$ CF₃.

Reaction of (I) with the olefin (II) did not take place under ionic conditions (-78 °C, dark); this is as expected because the olefin (II) is not susceptible to electrophilic attack.

Thermal Rearrangement.-It has been reported previously 14 that flow pyrolysis of the olefins (CF₃)₂N·CF: CF_2 (XII) and $(CF_3)_2$ N·CF:CFCl (XIII) at *ca*. 600 °C gave the rearrangement products perfluoro-2-azapent-2ene (XIV) (55%) and 4-chloro-octafluoro-2-azapent-2ene (XV) (51%), respectively, together with decomposition products which included hexafluoroethane.

$$CF_3 \cdot N : CF \cdot CF_2 \cdot CF_3$$
 $CF_3 \cdot N : CF \cdot CF \cdot CF \cdot CF_3$
(XIV) (XV)

Flow pyrolysis of the vinylamine (XII) in the presence of an excess of toluene afforded the rearrangement product (XIV) (46%) and trifluoromethane (31%); hexafluoroethane was not detected.¹⁴ This result was interpreted on the basis that the rearrangement involved mainly an intramolecular mechanism and did not occur to any large extent *via* free-radical intermediates.

In the present work the static pyrolyses of the vinyl-

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 ¹³ G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, J.C.S.

W. A. Sheppard and C. M. Sharts, 'Organic Fluorine Chemistry,' Benjamin, New York, 1969, p. 31.
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 D. Sianesi and R. Fontanelli, Ann. Chim. (Italy), 1965, 55, 376. 850.

Perkin I, 1971, 3833.

¹⁴ R. N. Haszeldine and A. E. Tipping, J. Chem. Soc. (C), 1968, 398.

amines (XII), (XVI), and (XVII) and the flow pyrolyses of the vinylamines (XVI) and (XVIII) have been investigated. The results obtained from the static pyrolyses

(CF3)2N·CF:CHF	(CF3)2N·CH:CH2	(CF) ₃ N·CF:CFBr		
(XVI)				

of the vinylamine (XII) are compared in Table 1 with those previously reported ¹⁴ for flow pyrolysis. A reasonable conversion of the olefin (XII) into the rearrangement product (XIV) occurs at a temperature *ca*. 100 °C lower in the static pyrolysis than in the flow pyrolysis. The major difference between the flow and static pyrolyses is the yield of (XIV) obtained in the presence of an excess of toluene. In the latter experiment fluoroform (70%) was formed [this accounts for 81% of the CF₃ Free-radical attack on the terminal CF_2 group of the olefin (XII) by the CF_3 radical is to be expected because

Initiation
$$(CF_3)_2 N \cdot CF: CF_2 \longrightarrow CF_3 \cdot + CF_3 \cdot N \cdot CF: CF_2 \longrightarrow decomposition products including CF_3 \cdot Propagation CF_3 \cdot + (XII) \longrightarrow CF_3 \cdot CF_2 \cdot CF \cdot N(CF_3)_2 \longrightarrow (XIV) + CF_3 \cdot \downarrow e^{tc.}$$

Termination $2CF_3 \cdot - C_2F_6$

$$CF_3 + R \rightarrow CF_3R$$

SCHEME 1

it is reported ¹⁴ that bromine atoms formed from hydrogen bromide attack this position [reaction (i)]. The

 TABLE 1

 Pyrolysis of perfluoro-(NN-dimethylvinylamine)

			Products (%)				
	Pyrolysis		Reactant recovered	(X	(IV)	~	- \
Type	time (min)	Temp. (°C)	(%)	Conv.	Yield	C ₂ F ₆ †	CHF ₃ †
Static	60	450	87	5	40	44	
Static	40	500	36	29	44	42	
Static *	30	500	63	5	14		70
Flow		595	16	46	55	‡	
Flow *		610	60	18	46	•	31

* Excess of toluene present. \dagger Yields based on vinylamine not recovered on the basis that vinylamine (1 mol) can give C_2F_6 (1 mol) or CHF₃ (2 mol). \ddagger Not determined.

groups in the olefin (XII) not recovered or rearranged]; in the flow reaction a lower yield of fluoroform (31%) was obtained (equivalent to 57% of the CF₃ groups in decomposed olefin). Thus the scavenging of trifluoromethyl radicals by toluene (CF₃· + PhCH₃ \longrightarrow CHF₃ + PhCH₂· \longrightarrow PhCH₂·CH₂Ph, *etc.*) was more effective in the static than in the flow pyrolysis, although hexafluoroethane, formed by combination of trifluoromethyl radicals, was not observed in either reaction.

In the flow reactions in the absence and presence of toluene the comparable yields of (XIV) obtained were taken as indicating that the rearrangement occurred to an appreciable extent by an intramolecular mechanism. The results from the static experiment contrast with this in that the much decreased yield of (XIV) obtained from the reaction in the presence of toluene suggests that the rearrangement is mainly free-radical.

These two results may be reconciled as follows. The rearrangement does occur mainly by a free-radical mechanism, but the different results obtained are a direct result of differences in the scavenging efficiency of the toluene for trifluoromethyl radicals in the two experiments, far better mixing of the reactants being achieved in the static pyrolysis. The CF_3 radicals when formed are scavenged by either the toluene or unchanged vinylamine (XII), the reactions occurring in the absence of toluene being as illustrated (Scheme 1; where \mathbb{R}^* is any radical present in the system). The better the mixing of the toluene and olefin the more efficient will be the suppression of the chain reaction by removal of CF_3^* radicals from the system as trifluoromethane.

alternative free-radical mechanism (ii) put forward previously,¹⁴ is considered either not to operate or to be a minor reaction pathway.

$$(XII) + Br \cdot \longrightarrow (CF_3)_2 N \cdot \dot{C}F \cdot CF_2 Br \xrightarrow{HBr} (CF_3)_2 N \cdot CHF \cdot CF_2 Br \quad (i)$$

$$CF_{3}\cdot\dot{N}\cdot CF: CF_{2} \xrightarrow{heat} CF_{3}\cdot + \qquad \diamondsuit \qquad (XIV) \qquad (ii) \\ CF_{3}\cdot_{2}N\cdot CF: CF_{2} \xrightarrow{heat} CF_{3}\cdot + \qquad \diamondsuit \qquad (XIV) \qquad (ii)$$

Since some rearrangement was observed to occur in the static pyrolysis in the presence of toluene it is possible that an intramolecular rearrangement does take place to some extent. Alternatively it may indicate that even in this reaction the vinylamine (XII) does scavenge CF_3 ·radicals to some extent.

$$\begin{array}{c} \mathsf{CF}_3 & \mathsf{N} & \mathsf{CF} \\ & \mathsf{I} & \mathsf{I} \\ & \mathsf{CF}_3 & \mathsf{CF}_2 \end{array} (XIV)$$

The results obtained from both flow and static pyrolysis of the vinylamine (XVI) are shown in Table 2. As observed with the vinylamine (XII) reasonable yields of the rearranged product, 4H-octafluoro-2-azapent-2-ene (XIX), are obtained either by flow or by static pyrolysis but the latter may be used at a temperature *ca.* 100 °C lower. Little, if any, hexafluoroethane is observed in these reactions and the major decomposition product is $(XVI) \longrightarrow CF_3 + CF_3 \cdot N \cdot CF : CHF \longrightarrow decomposition products$

 $\mathsf{CF}_3^{} + (X \forall I) \longrightarrow \mathsf{CF}_3^{} \cdot \mathsf{CHF} \cdot \dot{\mathsf{CF}} \cdot \mathsf{N} (\mathsf{CF}_3^{})_2^{} \longrightarrow \mathsf{CF}_3^{} \cdot \mathsf{CHF} \cdot \mathsf{CF} : \mathsf{N} \cdot \mathsf{CF}_3^{} + \mathsf{CF}_3^{} \cdot$

(XIX)

Scheme 2

the vinylamine (XVI) decomposed are recovered as trifluoromethane. Trifluoromethane (*ca.* 80% based on olefin decomposed) is also the major by-product from the reactions carried out in the absence of toluene [the

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a vacuum system to avoid contamination with air or moisture.

Products were separated by fractional condensation *in vacuo* or by g.l.c. [Pye model 104 or Perkin-Elmer F21 machine; columns packed with Celite impregnated with dinonyl phthalate (DNP) (10% by weight) unless stated otherwise] and were identified by molecular weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer fitted with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60.0 MHz for ¹H and 56.46 MHz for ¹⁹F or a Varian HA 100 instrument operating at 100.0 MHz for ¹H and 94.1 MHz for ¹⁹F, tetramethylsilane as internal reference for ¹H and trifluoroacetic acid as external reference for ¹⁹F), and mass spectrometry (A.E.I. MS902 machine).

1H-Pentafluoropropene (II) was prepared (84%) as a

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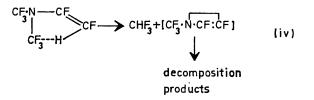
Pyrolysis of 1,2 difluoro-NN-bistrifluoromethylvinyla	umine (XVI)
	Products (%)

		i iouucis (/0)				
		Reactant recovered	(XIX)			
Time (min)	Temp. (°C)	(%)	Conv.	Yield	CHF ₃	C_2F_6
(1.37 s) †	610	44	36	64	t	t
(1.34 s) †	630	73	45	15	85 §	•
` 60 ´ '	400	91			v	
30	500	38	38	57	30	
60	520	19	11	13	74	
	$(1.37 s) \dagger (1.34 s) \dagger 60 \\ 30$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{ccc} & & & & & \\ \hline \text{Time (min)} & \text{Temp. (°C)} & (\%) \\ (1.37 \text{ s}) \dagger & 610 & 44 \\ (1.34 \text{ s}) \dagger & 630 & 73 \\ 60 & 400 & 91 \\ 30 & 500 & 38 \end{array}$	$\begin{array}{c cccc} & & & & & & & & & & & & & & & & & $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

* Excess of toluene present. † Contact time. ‡ Not determined. § Based on vinylamine (1 mol) giving fluoroform (2 mol).

yield in these reactions in the absence of toluene is based on olefin decomposed: olefin $(1 \text{ mol}) \longrightarrow \text{CHF}_{3}(1 \text{ mol})]$. It is unlikely that this product arises by a vinylic

hydrogen abstraction reaction (iii), and it is more probable that it is formed by an intramolecular elimination *via* a cyclic five-membered transition state (iv).



Flow pyrolysis of the bromo-olefin (XVIII) at 620 °C gave unchanged olefin (69%) and only a low yield (4%) of a compound tentatively identified as the rearrangement product 4-bromo-octafluoro-2-azapent-2-ene, CF₃·N: CF·CFBr·CF₃. Extensive decomposition of the olefin also occurred to give a mixture of products which included hexafluoroethane and bromotrifluoromethane. Similarly the vinylamine (XVII) also decomposed extensively on static pyrolysis at 520 °C (30 min); unchanged olefin (28%) was recovered and trifluoromethane (ca. 10%) was the only volatile major product identified.

95:5 mixture of the *cis*- and *trans*-isomers by hydrogenation of hexafluoropropene over palladium-alumina and dehydrofluorination of the resultant adduct.¹¹ N-Bromobistrifluoromethylamine (I) was prepared as described previously ^{3,15} and was handled *in vacuo* outside the vacuum system. The vinylamines (XII),¹⁴ (XVI),¹⁴ (XVII),⁴ and (XVIII) ⁵ were prepared by standard methods in good yield.

Reaction of N-Bromobistrifluoromethylamine with 1H-Pentafluoropropene.-A mixture of the N-bromo-amine (1.97 g, 8.5 mmol) and 1H-pentafluoropropene (2.06 g, 15.6 mmol), mixed in the vapour phase in a Pyrex bulb (ca 5 l) and kept in weak sunlight (12 h), gave a mixture (1.24 g), 8.6 mmol; M, 144) which was shown by i.r. spectroscopy and g.l.c. (6 m column at 25 °C) to contain unchanged olefin (1.06 g, 8.0 mmol, 55% recovered), tetrakistrifluoromethylhydrazine (VI) (0.18 g, 0.6 mmol, 14%) contaminated with traces of NN-bistrifluoromethylamine and perfluoro-2-azapropene, and a higher-boiling fraction (2.73 g) which was separated by g.l.c. (6 m column at 60 °C) into its five components identified as (i) threo-2-bromo-1,2,3,3,3-pentafluoro-NN-bistrifluoromethylpropylamine (IIIb) (0.87 g, 2.4 mmol, 32%) (Found: C, 16.8; H, 0.4; N, 3.7%; M, 362. C₅HBrF₁₁N requires C, 16.5; H, 0.3; N, 3.8%; M, 364), b.p. (isoteniscope) 75.0 °C; m/e 346 and 344 [1%, $(M - F)^+$] and 69 (100%, CF₃⁺); ¹H n.m.r. band for C(F_a)₃·CF_bBr·CHF_c·N- $[C(F_d)_3]_2$ at τ 4.11 (dd, CHF, $J_{H,c}$ 43.2, $J_{H,b}$ 17.4 Hz) and ¹⁹F n.m.r. bands at -21.0 (6F, s, F_d), 2.0 (3F, dd, F_a, $J_{a,c}$ 14.1, $J_{a,b}$ 7.3 Hz), 67.0 (1F, complex, F_c) and 76.0 p.p.m. (1F, complex, F_b); (ii) erythro-2-bromo-1,2,3,3,3-pentafluoro-

¹⁵ H. J. Emeléus and B. W. Tattershall, Z. anorg. Chem., 1964, **827**, 147.

NN-bistrifluoromethylpropylamine (IIIa) (1.47 g, 4.0 mmol, 53%) (Found: C, 16.5; H, 0.4; N, 3.9%; M, 365), b.p. (isoteniscope) 86.1 °C; m/e 346 and 344 [1%, $(M - F)^+$], and 69 (100%, CF_3^+); ¹H n.m.r. band for $C(F_a)_3$ · CF_bBr · CHF_c·N[C(F_d)₃]₂ at τ 3.67 (dd, CHF, $J_{\rm H,c}$ 42.3, $J_{\rm H,b}$ 13.5 Hz) and ¹⁹F n.m.r. bands at -21.4 (6F, ddq, F_d, $J_{\rm d,b}$ 14.4, $J_{\rm d,c}$ 9.0, $J_{d,a}$ 2.0 Hz), 2.0 (3F, ddsep, F_a, $J_{a,b}$ 9.3, $J_{a,c}$ 5.1 Hz, $J_{a,d}$), 62.0 (1F, ddsepq, F_c , $J_{c,H}$, $J_{c,b}$ 14.1 Hz, $J_{c,d}$, $J_{c,a}$), and 80.4 p.p.m. (1F, nonq, F_b , $J_{b,d} \simeq J_{b,H} \simeq J_{b,c} = ca$. 14 Hz, $J_{b,a}$; (iii) 2-bromo-2,3,3,3-tetrafluoro-NN-bistrifluoromethylpropylamine (IV) (0.10 g, 0.3 mmol, 4%); m/e 266 $[3\%, (M - Br)^+]$, 195 and 193 (37%, $CH_2 \cdot CFBr \cdot CF_3^+$), 166 [100%, (CF₃)₂N·CH₂], and 69 (74%, CF₃⁺); ¹H n.m.r. band for $C(F_a)_3 \cdot CF_b Br \cdot CH_2 \cdot N[C(F_c)_3]_2$ at $\tau 6.17$ (d, CH_2 , $J_{H,b}$ 17.3 Hz) and ¹⁹F n.m.r. bands at -20.3 (6F, dq, F_c, $J_{c.b}$ 9.5, J_{c.a} 1.5 Hz), 5.5 (3F, dsep, F_a, J_{a,b} 7.8 Hz), and 52.8 p.p.m. (1F, tdec, F_b); and (iv) a mixture of erythro- and threo-1,2dibromo-1,2,3,3,3-pentafluoropropane (V) (0.15 g, 0.5 mmol, 7%) which was identified ⁸ by i.r. and n.m.r. spectroscopy and g.l.c. retention time.

Reaction did not occur when a mixture of the N-bromoamine and the olefin (2:3 molar ratio) was kept in the dark at -78 °C (16 h).

Reaction of threo-2-Bromo-1,2,3,3,3-pentafluoro-NN-bistrifluoromethylpropylamine (IIIb) with Potassium Hydroxide. —A mixture of the amine (0.26 g, 1.0 mmol) and powdered dry potassium hydroxide (5 g), heated at 40 °C (30 min) in vacuo, gave unchanged amine (0.03 g, 0.1 mmol, 9% recovered) and cis-1,2,3,3,3-pentafluoro-NN-bistrifluoromethylprop-1-enylamine (VIIa) (0.20 g, 0.7 mmol, 78%) (Found: M, 280. Calc. for C₅F₁₁N: M, 283), λ_{max} , 5.76m μ m (C·C str.); ¹⁹F n.m.r. bands for C(Fa)₃·CFb·CFo·N-[C(Fd)₃]₂ at -18.1 (6F, s, Fd). -6.6 (3F, tsep, Fa, Ja,b \approx $J_{a,c} = 9.8, J_{a,d} ca. 1.0 Hz$), 22.3 (1F, complex, Fc), and 67.0 p.p.m. (1F, dqsep, Fb, Jb_bc 21.2, Jb_ba 9.9, Jb_bd 1.5 Hz).

Reaction of erythro-2-Bromo-1,2,3,3,3-pentafluoro-NNbistrifluoromethylpropylamine (IIIa) with Potassium Hydroxide.—Reaction of the amine (0.47 g, 1.3 mmol) with potassium hydroxide (5 g), as in the previous experiment, gave a mixture (0.36 g, 1.3 mmol, 100%) (Found: M, 281. Calc. for $C_5F_{11}N$: M, 293) of cis- and trans-1,2,3,3,3-pentafluoro-NN-bistrifluoromethylprop-1-enylamine (VII) shown by n.m.r. spectroscopy to contain the isomers in the ratio 38:62; ¹⁹F n.m.r. bands for trans-C(Fa)₃·CF_b·CF₀·N-[C(Fd)₃]₂ at -17.8 (6F, s, Fd), -5.6 (3F, dd, Fa, $J_{a,c}$ 21.7, $J_{a,b}$ 9.6 Hz), 37.8 (1F, dqsep, F_c, $J_{c,b}$ 130.5, $J_{c,a}$, $J_{c,d}$ ca. 1.0 Hz), and 79.9 p.p.m. (1F, dqsep, Fb, $J_{b,c}$, $J_{b,a}$, $J_{b,d}$ ca. 1.0 Hz).

Pyrolysis of Perfluoro-(NN-dimethylvinylamine) (XII).—(a) At 450 °C. Pyrolysis of the vinylamine (0.85 g, 3.7 mmol) in a steel autoclave (ca. 60 ml) in vacuo at 450 °C (1 h), gave (i) material non-condensable at -196 °C (0.14 mmol), (ii) hexafluorethane (0.22 mmol, 44%), and (iii) a mixture (0.78 g, 3.4 mmol, 92%) of unchanged vinylamine (XII) and perfluoro-2-azapent-2-ene (XIV) which, when treated with bromine (0.8 g) in vacuo at room temperature (56 h), yielded 1,2-dibromo-1,2,2-trifluoro-NN-bistrifluoromethylethyl-

amine (1.26 g, 3.2 mmol, 87%) and perfluoro-2-azapent-2-ene (XIV) (0.05 g, 0.2 mmol, 5% conversion, 40% yield) (Found: M, 233. Calc. for C₄F₉N: M, 233), the i.r. and n.m.r. spectra of which were identical with those reported.¹⁴

(b) At 500 °C. The vinylamine (1.30 g, 5.6 mmol), treated as in (a) at 500 °C (40 min), gave (i) material non-condensable at -196 °C (ca. 0.18 mmol); (ii) hexafluoro-

ethane (0.22 g, 1.6 mmol; M, 136) shown by i.r. spectroscopy to be contaminated with silicon tetrafluoride and which, on hydrolysis with aqueous sodium hydroxide (5% w/v, 5 ml) *in vacuo*, gave hexafluoroethane (0.21 g, 1.5 mmol, 42%); and (iii) a mixture (0.83 g, 3.6 mmol, 64%; M, 233) which, when treated with bromine (as in the previous experiment), afforded 1,2-dibromo-1,2,2-trifluoro-NN-bistrifluoromethylethylamine (0.79 g, 2.0 mmol, 36%) and perfluoro-2-azapent-2-ene (XIV) (0.36 g, 1.6 mmol, 29% conversion, 44% yield).

(c) With an excess of toluene. A mixture of the vinylamine (0.58 g, 2.5 mmol) and toluene (2.02 g, 22.0 mmol), heated in the autoclave in vacuo at 500 °C (30 min), gave (i) material non-condensable at -196 °C (ca. 0.22 mmol); (ii) a mixture (0.10 g, 1.4 mmol; M, 72) of trifluoromethane, silicon tetrafluoride, and unknown material with i.r. bands at 4.4w, 5.4w, and 8.1w µm, and which on hydrolysis with aqueous sodium hydroxide (5% w/v, 5 ml) in vacuo, gave trifluoromethane (0.09 g, 1.3 mmol, 70%; M, 70) contaminated with the same unknown material; (iii) a mixtute (0.39 g, 1.7 mmol, 68%; M, 232) of unchanged olefin (XII) and a small amount of rearranged material (XIV) and which, on hydrolysis with aqueous sodium hydroxide (5% w/v, 5 ml) in vacuo, gave unchanged vinylamine (XII) (0.36 g, 1.57 mmol, 63% recovered); and (iv) unchanged toluene (1.86 g, 20.0 mmol; M, 93) contaminated with unknown material with i.r. bands at 7.25w, 7.42w, 7.80m, 7.99w, 8.24m, 10.10w, and 10.80w µm.

Pyrolysis of 1,2-Difluoro-NN-bistrifluoromethylvinylamine (XVI).—(a) Flow. The vinylamine (1.94 g, 9.0 mmol), passed in vacuo at low pressure (1-2 mmHg) through a platinum tube (40 cm heated length, 1 cm i.d.) at 610 °C (40 min; contact time 0.23 s), gave (i) a small amount of material noncondensable at -196 °C; (ii) a mixture (ca. 5 gas ml) of hexafluoroethane, trifluoromethane, silicon tetrafluoride, trifluoromethyl isocyanate, and carbonyl fluoride (i.r.); and (iii) a mixture (1.80 g, 8.4 mmol, 93%) (Found: M, 214. Calc. for C_4HF_8N : M, 215) of unchanged olefin (XVI) and 4H-octafluoro-2-azapent-2-ene (XIX) which condensed at -95 °C. The -95 °C fraction was re-passed several times through the platinum tube at 600 °C (total time 4 h, contact time 1.37 s), with separation after each pass, to afford (i) a mixture (0.17 g, 1.6 mmol; M, 105) of the same decomposition products; (ii) a -95 °C fraction (1.55 g, 7.2 mmol, 80%) (Found: M, 215); and (iii) a trace of higher boiling material. Separation of the -95 °C fraction by g.l.c. (10 m Kel-F 10 oil at 25 °C) gave unchanged vinylamine (XVI) (0.86 g, 4.0 mmol, 44% recovered) and 4H-octafluoro-2-azapent-2-ene (XIX) (0.69 g, 3.2 mmol, 64% yield, 36% conversion) (Found: C, 22.6; H, 0.6; N, 6.3%; M, 215. C4HF8N requires C, 22.3; H, 0.5; N, 6.5%; M, 215), b.p. (isoteniscope) 30.5 °C; i.r. band at 5.65s (C.N str.) µm; m/e 215 (4% M^+) and 69 (100%, CF₃⁺); ¹⁹F n.m.r. bands for C(F_a)₃. $N:CF_b \cdot CHF_c \cdot C(F_d)_3$ at -58.6br (1F, s, F_b), -19.5 (3F, d, F_a , $J_{a,b}$ 14.4 Hz), 1.3 (3F, dt, F_d, $J_{d,c}$ 12.8, $J_{d,H} \simeq J_{d,b} = 5.5$ Hz), and 132.3 p.p.m. (1F, dquin, F_c , $J_{c,H}$ 44.8, $J_{c,b} \simeq J_{c,d}$ = 12.8 Hz) and ¹H n.m.r. band at τ 4.48 (dquin, $J_{\rm H,c}$ 44.8, $J_{\mathrm{H,b}} \simeq J_{\mathrm{H,d}} = 5.5 \,\mathrm{Hz}$).

(b) Static at 500 °C. The vinylamine (1.60 g, 7.4 mmol), heated in the autoclave *in vacuo* at 500 °C (30 min), gave (i) material non-condensable at -196 °C (*ca.* 0.14 mmol), (ii) trifluoromethane (0.10 g, 1.4 mmol, 30%; M, 72), and (iii) a mixture (1.20 g, 5.6 mmol, 76%; M, 217) of unchanged vinylamine (XVI) (0.60 g, 2.8 mmol, 38% recovered) and 4H-octafluoro-2-azapent-2-ene (XIX) (0.60 g, 2.8 mmol, 57%, 38% conversion) as determined by g.l.c. (as before).

A reaction carried out at 400 °C (1 h) gave unchanged vinylamine (XVI) (91%).

(c) Static at 520 °C. The vinylamine (1.00 g, 4.7 mmol), treated as in the previous experiment at 520 °C (1 h), gave (i) material non-condensable at -196 °C (ca. 0.27 mmol), (ii) trifluoromethane (0.20 g, 2.8 mmol, 74%; M, 72) contaminated with a trace of silicon tetrafluoride (i.r.), (iii) a mixture which was shown by g.l.c. (as before) to contain unchanged vinylamine (XVI) (0.19 g, 0.9 mmol, 19%) and 4H-octafluoro-2-azapent-2-ene (XIX) (0.12 g, 0.5 mmol, 13%, 11% conversion), and (iv) a trace of higher boiling material (ca. 2 gas ml) which decomposed in the system to form silicon tetrafluoride.

(d) Flow with an excess of toluene. A mixture of the vinylamine (0.65 g, 3.02 mmol) and toluene (3.00 g, 33.0 mmol), pyrolysed as in experiment (a) in vacuo at ca. 4 mmHg and 630 °C (6 h; contact time 1.34 s), gave (i) trifluoromethane (0.10 g, 1.4 mmol; M, 72) contaminated with traces of silicon tetrafluoride, carbonyl fluoride, and trifluoromethyl isocyanate (i.r.), (ii) a mixture (0.50 g, 2.32 mmol, 76%) shown by g.l.c. (as before) to contain unchanged vinylamine (XVI) (0.47 g, 2.20 mmol, 72%) and 4H-octa-fluoro-2-azapent-2-ene (XIX) (0.03 g, 0.12 mmol, 15%, 4% conversion), and (iii) a higher boiling fraction (3.00 g, 32.6 mmol; M, 92) shown by i.r. spectroscopy to be mainly toluene.

Pyrolysis of 2-Bromo-1,2-difluoro-NN-bistrifluoromethylvinylamine (XVIII).— The vinylamine (1.20 g, 4.1 mmol), passed through the pyrolysis tube at 1—2 mmHg and 620 °C and the —120 °C fraction re-passed a further three times through the tube (total time 3 h; contact time 2.2 s) with separation after each pass, gave (i) a mixture (0.25 g, 1.8 mmol; M, 140) of bromotrifluoromethane, trifluoromethyl isocyanate, hexafluoroethane, carbonyl fluoride, and silicon tetrafluoride (i.r.), and (ii) a mixture (0.85 g, 3.0 mmol, 73%) which was shown by g.l.c. (as before) to contain unchanged vinylamine (XVIII) (0.80 g, 2.85 mmol, 69%) and an unknown component possibly 4-bromo-octafluoro-2-azapent-2ene [0.05 g, 0.15 mmol, 12%, 4% conversion; λ_{max} , 5.67m µm (C.N str.)].

Pyrolysis of NN-Bistrifluoromethylvinylamine (XVIII).— The vinylamine (1.10 g, 6.1 mmol), heated in the autoclave at 520 °C (30 min), gave (i) nitrogen (0.54 mmol), (ii) trifluoromethane (0.05 g, 0.71 mmol; M, 72) contaminated with traces of carbonyl fluoride and trifluoromethyl isocyanate (i.r.), (iii) unchanged vinylamine (XVII) (0.31 g, 1.7 mmol, 28% recovered; M, 180) shown by i.r. spectroscopy to be contaminated with a small amount of an unknown component (i.r. bands at 8.00 and 12.50 µm), and (iv) a higher boiling fraction (0.10 g).

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