

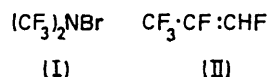
Polyfluoroalkyl Derivatives of Nitrogen. Part XLII.¹ Reaction of *N*-Bromobistrifluoromethylamine with 1*H*-Pentafluoropropene and Some Further Studies on the Thermal Rearrangement of *NN*-Bistrifluoromethylvinylamines

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N-Bromobistrifluoromethylamine reacts with a 95 : 5 mixture of *cis*- and *trans*-1*H*-pentafluoropropene under free-radical conditions to give a high yield of a mixture of *erythro*- and *threo*-2-bromo-1,2,3,3,3-pentafluoro-*NN*-bistrifluoromethylpropylamine 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-enylamine 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 4*H*-octafluoro-2-azapent-2-ene on pyrolysis, but 2-bromo-1,2-difluoro-*NN*-bistrifluoromethylvinylamine and *NN*-bistrifluoromethylvinylamine give mainly decomposition products.

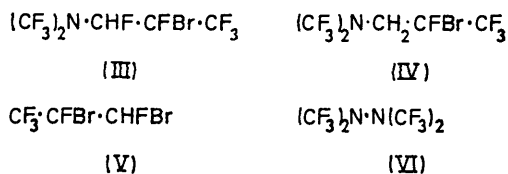
N-BROMOBISTRIFLUOROMETHYLAMINE (I) reacts with a variety of olefins, both symmetrical and unsymmetrical, under free-radical conditions (u.v., sunlight, or thermal) to afford 1 : 1 adducts in high yield; ²⁻⁵ the chain carrier is believed to be the (CF₃)₂N· radical. More recently ionic additions of (I) 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 1*H*-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% recovered), 2-bromo-1,2,3,3,3-pentafluoro-*NN*-bistrifluoromethylpropylamine (III) (85%), 2-bromo-2,3,3,3-tetrafluoro-*NN*-bistrifluoromethylpropylamine (IV) (4%), a mixture of *erythro*- and *threo*-1,2-dibromo-1,2,3,3,3-pentafluoropropane (V) [7% based on olefin,



12% based on *N*-bromo-amine (I)], and tetrakis(trifluoromethyl)hydrazine (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 S. Smith, *J. Macromol. Sci.*, 1974, **A8**(8), 1325.

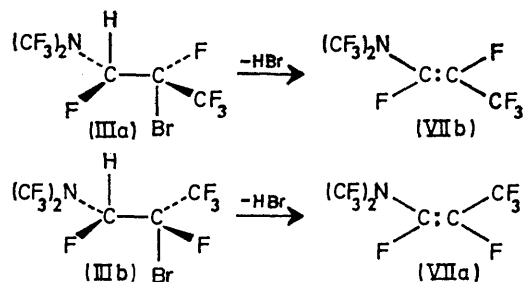
² J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.

³ R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, 1965, 6141.

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.

⁶ M. G. Barlow, G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 2744.

⁷ D. H. Coy, G. L. Fleming, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 1880.

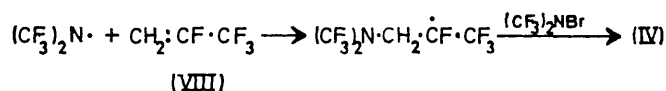
⁸ R. N. Haszeldine, J. R. McAllister, and A. E. Tipping, *J.C.S. Perkin I*, 1974, 1303.

mixture of *erythro*- and *threo*-(CF₃)₂N·CFBr·CHF·N(CF₃)₂ under comparable conditions gave exclusively the *cis*-isomer of the olefin (CF₃)₂N·CF:CF·N(CF₃)₂.⁵ In contrast dehydrobromination of the compound (CF₃)₂N·CH₂·CHBr·N(CF₃)₂ gave only the *trans*-isomer of the olefin (CF₃)₂N·CH:CH·N(CF₃)₂.⁴

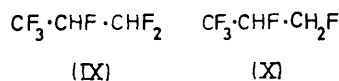
It has been postulated previously⁹ that the *cis*-CF:CF grouping has greater electronic stabilising effect than than the *trans*-CF:CF grouping; the present results are in agreement with this.

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 observed¹⁰ 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 CF₃ 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 (CF₃)₂N· radical attack on the terminal CH₂ group.



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 (CF₃)₂N· radical attack on the terminal CHF group in the olefin (II), *i.e.* (III). Initial (CF₃)₂N· radical attack on hexafluoropropene occurs to

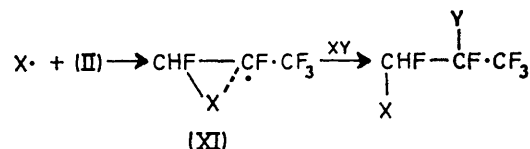
⁹ W. A. Sheppard and C. M. Sharts, 'Organic Fluorine Chemistry,' Benjamin, New York, 1969, p. 31.

¹⁰ J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 1096.

¹¹ D. Sianesi and R. Fontanelli, *Ann. Chim. (Italy)*, 1965, **55**, 850.

the extent of 96% on the CF₂ group and 4% on the CF₃·CF group.¹³ The proportion of attack on the CF₃·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 [(CF₃)₂N· radical attack on CHF:CF₂ 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.

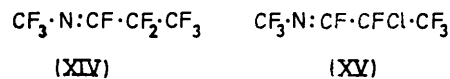
If the addition of the amine (I) to the olefin (II) had been exclusively *trans*-stereospecific then the adducts (IIIa and b) would have been formed in the ratio 95:5 (the *cis*-*trans*-ratio of reactant olefin) rather than the ratio 62:38 (1.7:1) observed. The additions of hydrogen bromide and trifluoriodomethane 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 for such interaction lies in the order Br > N(CF₃)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 previously¹⁴ that flow pyrolysis of the olefins (CF₃)₂N·CF:CF₂ (XII) and (CF₃)₂N·CF:CFCl (XIII) at *ca.* 600 °C gave the rearrangement products perfluoro-2-azapent-2-ene (XIV) (55%) and 4-chloro-octafluoro-2-azapent-2-ene (XV) (51%), respectively, together with decomposition products which included hexafluoroethane.



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-

¹² I. L. Knunyants, G. L. Mysor, and M. P. Krasuskaya, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 1958, 906.

¹³ G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J.C.S. Perkin I*, 1971, 3833.

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

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_b·Br·CHF_c·N[C(F_d)₃]₂ at τ 3.67 (dd, CHF, $J_{H,c}$ 42.3, $J_{H,b}$ 13.5 Hz) and ¹⁹F n.m.r. bands at -21.4 (6F, ddq, F_d , $J_{d,b}$ 14.4, $J_{d,c}$ 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 , $J_{b,d} \approx J_{b,H} \approx J_{b,c} = ca.$ 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 ·CFBr·CF₃⁺), 166 [100%, (CF_3)₂N·CH₂⁺], and 69 (74%, CF_3^+); ¹H n.m.r. band for C(F_a)₃·CF_b·Br·CH₂·N[C(F_c)₃]₂ at τ 6.17 (d, CH₂, $J_{H,b}$ 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-1,2-dibromo-1,2,3,3,3-pentafluoropropane (V) (0.15 g, 0.5 mmol, 7%) which was identified⁸ 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} , 5.76 μ m (C:C str.); ¹⁹F n.m.r. bands for C(F_a)₃·CF_b·CF_c·N[C(F_d)₃]₂ at -18.1 (6F, s, F_d), -6.6 (3F, tsep, F_a , $J_{a,b} \approx J_{a,c} = 9.8$, $J_{a,d}$ *ca.* 1.0 Hz), 22.3 (1F, complex, F_c), and 67.0 p.p.m. (1F, dqsep, F_b , $J_{b,c}$ 21.2, $J_{b,a}$ 9.9, $J_{b,d}$ 1.5 Hz).

Reaction of erythro-2-Bromo-1,2,3,3,3-pentafluoro-NN-bistrifluoromethylpropylamine (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 C₅F₁₁N: 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(F_a)₃·CF_b·CF_c·N[C(F_d)₃]₂ at -17.8 (6F, s, F_d), -5.6 (3F, dd, F_a , $J_{a,c}$ 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, F_b , $J_{b,c}$, $J_{b,a}$, $J_{b,d}$ *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) hexafluoroethane (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-bistrifluoromethylethylamine (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 μ m, 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 mixture (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 μ m.

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 non-condensable 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 C₄HF₈N: 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.) μ m; m/e 215 (4% M^+) and 69 (100%, CF_3^+); ¹⁹F n.m.r. bands for C(F_a)₃·N:CF_b·CHF_c·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, $J_{d,H} \approx J_{d,b} = 5.5$ Hz), and 132.3 p.p.m. (1F, dqin, F_c , $J_{c,H}$ 44.8, $J_{c,b} \approx J_{c,d} = 12.8$ Hz) and ¹H n.m.r. band at τ 4.48 (dqin, $J_{H,c}$ 44.8, $J_{H,b} \approx J_{H,d} = 5.5$ 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 4*H*-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 4*H*-octafluoro-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-bis(trifluoromethyl)vinylamine (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-2-ene [0.05 g, 0.15 mmol, 12%, 4% conversion; λ_{\max} 5.67 μm (C \cdot N str.)].

Pyrolysis of NN-Bis(trifluoromethyl)vinylamine (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 (XVIII) (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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