Polyfluoroalkyl Derivatives of Nitrogen. Part XLIII.[1] Reactions of *N*-Bromobis(trifluoromethyl)amine with 1-Fluoropropene under Free-radical and under Ionic Conditions

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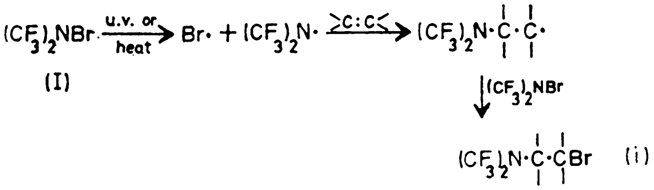
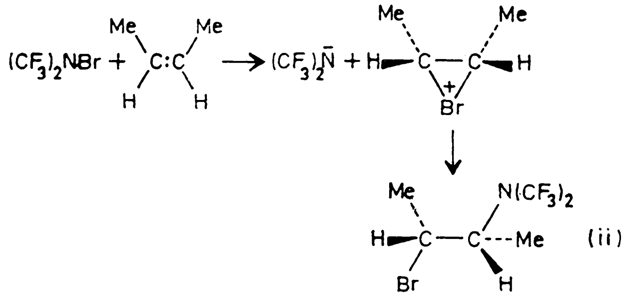
Photochemical reaction of *N*-bromobis(trifluoromethyl)amine with 1-fluoropropene in the vapour phase gives a mixture of the 1 : 1 adducts 2-bromo-1-fluoro-*NN*-bis(trifluoromethyl)propylamine and 2-bromo-2-fluoro-1-methyl-*NN*-bis(trifluoromethyl)ethylamine in the ratio 46 : 54. Under conditions conducive to the formation of ionic intermediates (−78 °C in the dark in the liquid phase), stereospecific *anti*-addition to the olefin takes place and the 1 : 1 adducts are formed in the ratio 90 : 10 (*cis*-isomer) and 77 : 23 (*trans*-isomer). All the adducts undergo dehydrobromination by *anti*-elimination to give the corresponding (*E*)- or (*Z*)-olefins, except for (1*R*,2*S*)-2-bromo-1-fluoro-*NN*-bis(trifluoromethyl)propylamine, which undergoes mainly *syn*-elimination to afford a mixture of (*E*)- and (*Z*)-1-fluoro-*NN*-bis(trifluoromethyl)prop-1-enylamine in the ratio 82 : 18.

THE reactions of *N*-bromobis(trifluoromethyl)amine with olefins have been widely investigated and two distinct modes of addition are believed to occur. Under free-radical conditions (u.v. or thermal), addition generally takes place readily to electron-rich or electron-deficient olefins to give 1 : 1 adducts in high yield, and the $(CF_3)_2N\cdot$ radical is considered to be the chain-propagating species [2,3] [equation (i)].



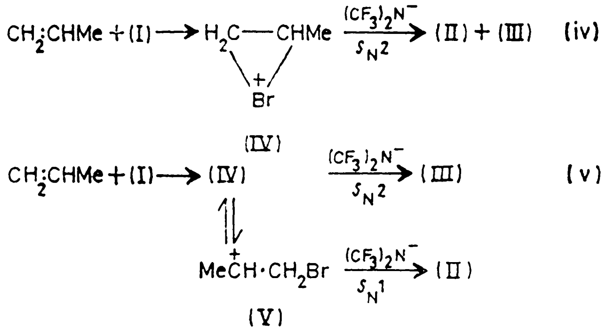
Under ionic conditions (liquid phase in the dark at low temperature) reaction of the *N*-bromo-amine (I) with *cis*- or *trans*-but-2-ene gave products resulting from exclusive *anti*-addition; these reactions were interpreted as involving initial electrophilic attack of (I) polarised as $\overset{\delta-}{(CF_3)_2N}-\overset{\delta+}{Br}$ [4] [equation (ii)].



However, addition of the *N*-bromo-amine (I) to propene under ionic conditions at −78 °C gave the 1 : 1 adducts (II) and (III) [equation (iii)] in the ratio 60 : 40; addition under free-radical conditions gave the same adducts in the ratio 9 : 91.[5]

$$\text{(I)} + CH_2{:}CHMe \longrightarrow \underset{\text{(II)}}{(CF_3)_2N{\cdot}CHMe{\cdot}CH_2Br} + \underset{\text{(III)}}{(CF_3)_2N{\cdot}CH_2{\cdot}CHMeBr} \quad \text{(iii)}$$

The reaction under ionic conditions was interpreted as involving either bidirectional nucleophilic attack on the intermediate cyclic bromonium ion (IV) [equation (iv)] or attack on a mixture of the cyclic bromonium ion (IV) and the open-chain carbocation (V) [equation (v)], but it was not possible to differentiate between these alternatives.



The reactions of the *N*-bromo-amine (I) with allyl chloride and allyl bromide in the dark at −78 °C also resulted in bidirectional addition.[6]

In the present work *cis*- and *trans*-1-fluoropropene (VIa and b) [7-9] have been synthesised and their reactions with the *N*-bromo-amine (I) under free-radical and ionic conditions have been studied to determine if bidirectional radical and ionic addition to this olefin takes place and, if possible, to determine the mechanism of ionic addition.

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[1] Part XLII, G. L. Fleming, R. N. Haszeldine, J. R. McAllister, and A. E. Tipping, *J.C.S. Perkin I*, 1975, **1633**.

[2] R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, 1965, **6141**.

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

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

[6] D. H. Coy, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J.C.S. Perkin I*, 1973, 1062.

[7] F. Casas, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1964, 3655.

[8] P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Amer. Chem. Soc.*, 1955, **77**, 2783.

[9] R. A. Beaudt and J. D. Baldeschwieler, *J. Mol. Spectroscopy*, 1962, **9**, 30.

The isomers (VIa and b), in the ratio 70 : 30, were obtained by the new route shown in equation (vi). Attempted dehydrofluorination of the precursor, $EtCHF_2$, with potassium hydroxide was unsuccessful, as was the attempted preparation of the alternative precursor, EtCHFCl, by fluorination of 1,1-dichloropropane with antimony(III) fluoride.

$$\underset{}{EtCHO} \xrightarrow{SF_4} \underset{(41\%)}{EtCHF_2} \xrightarrow[690\,°C,\ ca.\ 10\ mmHg]{flow\ pyrolysis} \underset{(VI)}{CH_3{\cdot}CH{:}CHF}\ (53\%) \quad (vi)$$

Photochemical reaction of a mixture of the olefin isomers (VIa and b) in the ratio 70 : 30 and the *N*-bromo-amine (I) (1 : 1 molar ratio) gave *NN*-bis(trifluoromethyl)-amine (3%), a mixture (88%) of four 1 : 1 adducts (A—D) in the ratio 24 : 22 : 27 : 27, and a small amount of higher-boiling material. The adducts were identified on the basis of their mass and n.m.r. spectra and the olefins obtained on dehydrobromination. Adducts A and B gave similar n.m.r. spectra, showed base peaks at *m*/*e* 184 {$[(CF_3)_2N{\cdot}CHF]^+$} in their mass spectra, and on dehydrobromination afforded 1-fluoro-*NN*-bis(trifluoromethyl)prop-1-enylamine (VII), thus showing that they were both isomers of 2-bromo-1-fluoro-*NN*-bis(trifluoromethyl)propylamine (VIII). Adducts C and D gave similar n.m.r. spectra, showed strong peaks at *m*/*e* 180 {$[(CF_3)_2N{\cdot}CHMe]^+$} in their mass spectra, and on dehydrobromination afforded 2-fluoro-1-methyl-*NN*-bis(trifluoromethyl)vinylamine (IX), thus showing that they were isomers of 2-bromo-2-fluoro-1-methyl-*NN*-bis(trifluoromethyl)ethylamine (X).

$(CF_3)_2N{\cdot}CF{:}CHMe$

(VII)

$(CF_3)_2N{\cdot}CHF{\cdot}CHBrMe$

(VIII)

$(CF_3)_2N{\cdot}CMe{:}CHF$

(IX)

$(CF_3)_2N{\cdot}CHMe{\cdot}CHFBr$

(X)

The stereochemical structures of the four adducts (A—D) were determined by (i) the stereochemistry of the olefins formed on dehydrobromination, (ii) a consideration of the vicinal H,H and H,F n.m.r. coupling constants (Table 1), and (iii) the observation that only adducts B and C were formed by addition of the *N*-bromo-amine (I) to the *cis*-olefin (VIa) under ionic conditions (see later).

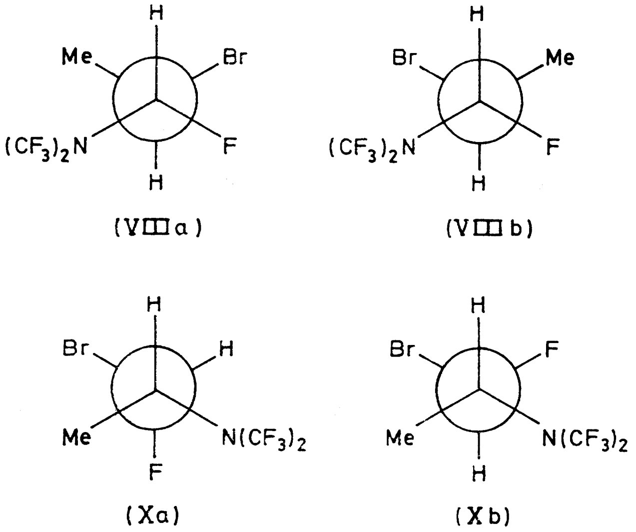
TABLE 1

N.m.r. coupling constant for the adducts

Adduct	J_{HH}/Hz	Assignment	J_{HF}/Hz	Assignment
A	9.6	*anti*	6.3	*gauche*
B	10.8	*anti*	1.6	*gauche*
C	6.9	*gauche*	12.6	*anti*
D	8.8	*anti*	7.0	*gauche*

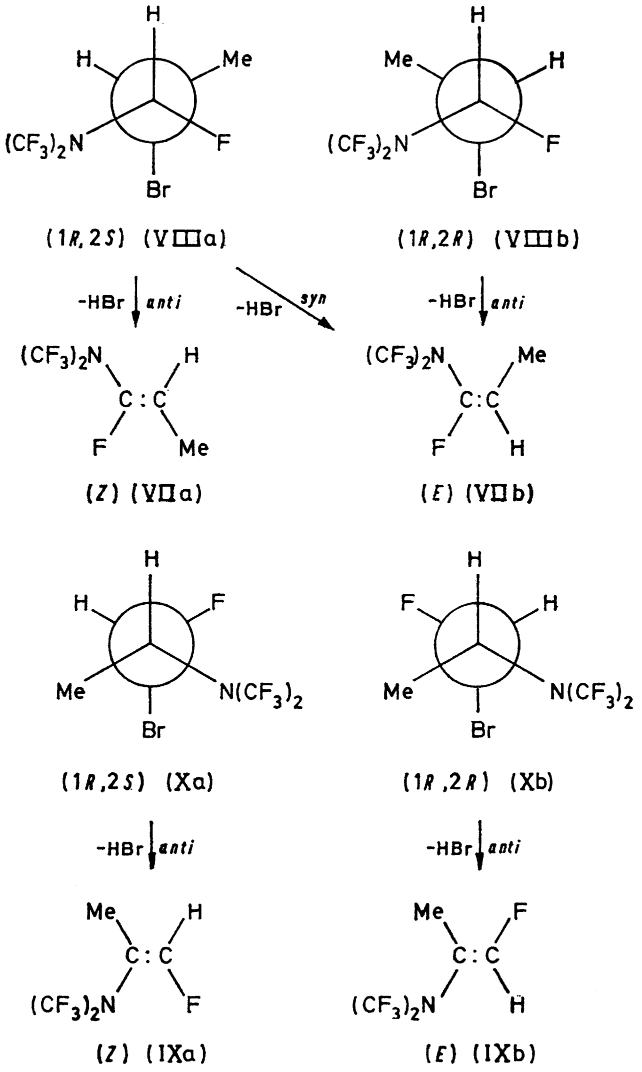
Adduct B gave the (*E*)-isomer of the olefin (VII) (96%) on dehydrobromination, as expected for *anti*-elimination from the (1*R*,2*R*)-isomer (VIIIb), whereas adduct A gave a mixture (96%) of the (*E*)- (VIIb) and (*Z*)- (VIIa) isomers of the olefin (VII) in the ratio 82 : 18. The (*Z*)-isomer of the olefin (VII) would be expected to arise by *anti*-elimination of hydrogen bromide from the (1*R*,2*S*)-adduct isomer (VIIIa). However, the olefin mixture formed shows that the elimination is not stereospecific and either that *syn*-elimination from adduct (VIIIa) is favoured or that elimination involves an *E*1cB mechanism in which, surprisingly, the favoured olefin is the (*E*)-isomer with the bulky $(CF_3)_2N$ and CH_3 groups *cis*. The addition of the bromo-amine (I) to the *cis*-olefin (VIa) under ionic conditions gave isomer B and not isomer A, and so isomer B is the product of *anti*-addition, *i.e.* the (1*R*,2*R*)-isomer (VIIIb), which confirms the assignments made.

Adducts C and D underwent dehydrobromination stereospecifically to give the (*Z*)- (99%) and (*E*)- (97%) isomers (IXa) and (IXb), respectively, as expected for *anti*-elimination from the (1*R*,2*S*)- (Xa) and (1*R*,2*R*)- (Xb) adduct isomers, respectively. These assignments were confirmed by the observation that addition of (I) to the *cis*-olefin (VIa) under ionic conditions gave adduct C and not adduct D and by the n.m.r. coupling constants shown in Table 1. These conclusions, coupled with the n.m.r. evidence shown in Table 1, indicated that the preferred conformations for the four adducts are as shown in Scheme 1.

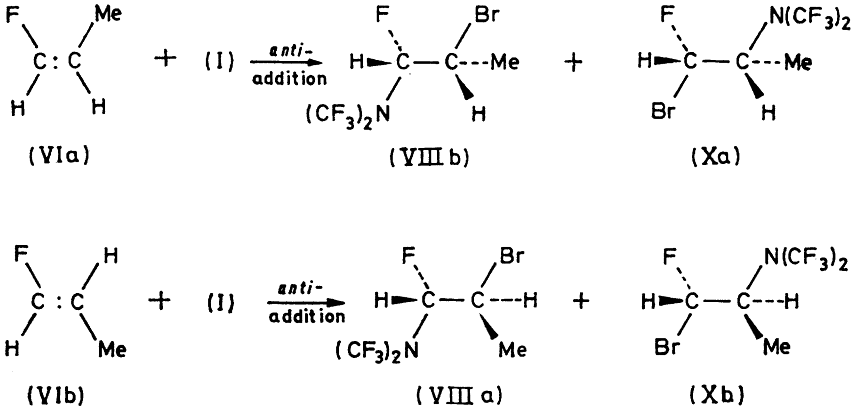


SCHEME 1

The preferred conformations of adducts (Xa and b) are, as expected, those in which the bulky $(CF_3)_2N$ and Br groups are *anti*, and the preferred conformations of adducts (VIIIa and b) are those in which the $(CF_3)_2N$



group is *anti* to the bulky bromine atom and the bulky methyl group, respectively.



SCHEME 2

The 1 : 1 adducts (VIII) and (X) are formed in reasonably high yield (88%) and so the adduct ratio 46 : 54 is meaningful and represents the relative amounts of initial $(CF_3)_2N\cdot$ radical attack at each end of the double bond in olefin (VI) (Scheme 2). The very different results obtained for addition under ionic conditions (see later) mean that it is unlikely that significant addition *via* a competing ionic pathway is taking place under photochemical conditions. It has been found previously that $(CF_3)_2N\cdot$ radical attack on vinyl fluoride[10] and propene[5] occurs to the extent of *ca.* 90—95% on the terminal CH_2 group in both olefins. These results also indicated that a fluorine atom and a methyl group stabilise an adjacent lone electron to a similar degree and they are thus consistent with the present observations.

The free-radical addition is not *anti*- or *syn*-stereospecific since an olefin ratio [(VIa) : (VIb)] of 70 : 30 gave the adducts (VIIIa and b) and (Xa and b) in *ca.* 50 : 50 ratio in each case.

The formation of *NN*-bis(trifluoromethyl)amine (3%) and a high-boiling residue in the reaction indicates that allylic hydrogen abstraction and perhaps telomerisation reactions are also taking place.

The reaction of the *N*-bromo-amine (I) with an excess of a mixture of olefins (VIa and b) (ratio 76 : 24) in the liquid phase in the dark at −78 °C gave a mixture (97%) of the adducts (VIIIa) (22%), (VIIIb) (61%), (Xa) (7%), and (Xb) (7%), in the ratio 23 : 63 : 7 : 7, together with the excess of olefin (VIa and b) (ratio 84 : 16). The recovered olefin ratio is as expected from reaction involving bidirectional *anti*-addition of (I) to the olefins (VIa and b) as shown in Scheme 2.

The exclusive *anti*-addition was confirmed by reaction of the *N*-bromo-amine (I) with an excess of the *cis*-olefin (VIa) under comparable conditions, which gave the adducts (VIIIb) (70%) and (Xa) (9%) in the ratio 89 : 11, and, surprisingly, the compound $MeCHBr\cdot CHF_2$ (XI) (13%); the recovered olefin was exclusively the *cis*-isomer (VIa).

These results are consistent with bidirectional nucleophilic attack on intermediate cyclic bromonium ions (XIIa and b), formed by electrophilic attack by (I) on the olefins (VIa and b), respectively [equations (vii) and (viii)].

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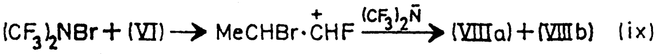
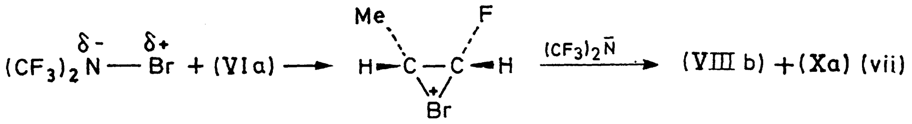
[10] J. Freear and A. E. Tipping, *J. Chem. Soc.* (*C*), 1969, 1955.

Ionic addition of hydrogen bromide to the olefin (VI) gives 1-bromo-1-fluoropropane exclusively, indicating that the carbocation $MeCH_2\cdot\overset{+}{C}HF$ is more stable than the alternative $CH_2F\cdot\overset{+}{C}HMe$.[11] Therefore if an open-chain carbocation were involved in the reaction of the olefin (VI) with the *N*-bromo-amine (I) it would be expected to have structure (XIII) and react to give a mixture of adducts (VIIIa and b) [equation (ix)]. The absence of the adduct (VIIIa) in the products from the reaction of (I) with the *cis*-olefin (VIa) indicates that the carbocation (XIII) is not formed.

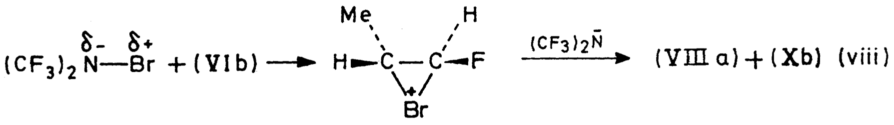


$$(CF_3)_2NBr + (VI) \longrightarrow MeCHBr\cdot\overset{+}{C}HF \xrightarrow{(CF_3)_2\bar{N}} (VIIIa) + (VIIIb) \quad (ix)$$

(XIII)



(XIIa)



(XIIb)

of the anion $(CF_3)_2N^-$ to give fluoride ion and perfluoro-2-azapropene, $CF_3\cdot N{:}CF_2$, which was also observed in the products, followed by nucleophilic attack of fluoride ion on the CHF group of the cyclic bromonium ion intermediate (XIIa); it is possible that fluoride ion attack on the CHMe group in the ion (XIIa) also took place, but the product from such attack, CHFMe·CHFBr, would be expected in low yields only and could have remained undetected. Similar BrF adducts have been observed previously in the products from the reactions of the bromo-amine (I) with certain fluoro-olefins, *e.g.* vinyl fluoride.[10]

TABLE 2

Adduct isomer ratios obtained from ionic addition of *N*-bromobis(trifluoromethyl)amine to olefins at −78 °C

Olefin	Adducts		Ratio
$CH_2{:}CHMe$	$(CF_3)_2N\cdot CH_2\cdot CHBrMe$ (III)	$(CF_3)_2N\cdot CHMe\cdot CH_2Br$ (II)	40 : 60
$CH_2{:}CH\cdot CH_2Cl$	$(CF_3)_2N\cdot CH_2\cdot CHBr\cdot CH_2Cl$	$(CF_3)_2N\cdot CH(CH_2Cl)\cdot CH_2Br$	66 : 34
$CH_2{:}CH\cdot CH_2Br$	$(CF_3)_2N\cdot CH_2\cdot CHBr\cdot CH_2Br$	$(CF_3)_2N\cdot CH(CH_2Br)_2$	85 : 15
cis-$CHF{:}CHMe$	$(CF_3)_2N\cdot CHF\cdot CHBrMe$ (VIII)	$(CF_3)_2N\cdot CHMe\cdot CHFBr$ (X)	89 : 11
cis-$CHF{:}CHMe$	(VIII)	(X)	90 : 10
+			
trans-$CHF{:}CHMe$	(VIII)	(X)	77 : 23

The present results thus indicate strongly that the observed bidirectional addition of the *N*-bromo-amine (I) to propene,[5] allyl chloride,[6] and allyl bromide [6] at −78 °C in the dark also involves cyclic bromonium ion intermediates which undergo bidirectional nucleophilic attack. The adduct ratios obtained from reaction of these olefins and olefin (VI) with the *N*-bromo-amine (I) at −78 °C in the dark are shown in Table 2.

It is not clear why the reaction of (I) with the *cis*-olefin (VIa) under ionic conditions gave some of the adduct (XI) whereas none was detected in the reaction with the mixture of *cis*- (VIa) and *trans*- (VIb) olefins. Compound (XI) is considered to arise by decomposition

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. Products were separated either by repeated fractional distillation *in vacuo* or by preparative-scale g.l.c. [Perkin-Elmer F21 or Pye 104 machine; columns packed with trixylyl phosphate (TXP), Kel-F 10 oil, or a fluorinated silicone oil (QF1) on Celite]. The identities of products were established by molecular-weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 56.46 MHz for ^{19}F and 60.0 MHz for ^{1}H or Varian HA 100 spectrometer operating at 94.1 MHz for ^{19}F and 100.0 MHz for ^{1}H; external trifluoroacetic

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[11] R. N. Haszeldine, I-ud-D. Mir, and A. E. Tipping, unpublished results.

acid and internal tetramethylsilane as the respective references), and mass spectrometry (A.E.I. MS902 spectrometer).†

Preparation of 1-*Fluoropropene*.—A mixture of propionaldehyde (50.0 g, 1.1 mol) and sulphur tetrafluoride (118.8 g, 1.1 mol) was heated in a rocked stainless steel autoclave (*ca.* 500 cm^3) at 50 °C (16 h) and the volatile product was bubbled through aqueous sodium hydroxide (1M; 2 000 cm^3), dried by passage through two tubes containing potassium hydroxide pellets and phosphorus pentaoxide, respectively, and identified as 1,1-difluoropropane (27.84 g, 0.347 mol, 41%) (Found: *M*, 79. Calc. for $C_3H_6F_2$: *M*, 80). The difluoropropane (5.45 g, 68.2 mmol), passed *in vacuo* at *ca.* 10 mmHg through a silica tube (75 cm; 1.5 cm i.d.) packed with silica chips and heated at 690 °C, gave (i) impure silicon tetrafluoride and (ii) a mixture (68.0 mmol) of 1-fluoropropene, propyne, and carbonyl fluoride, which was bubbled *in vacuo* through traps containing ammoniacal copper(I) chloride and aqueous potassium hydroxide (5% v/v), and the resultant material was dried by passage over phosphorus pentaoxide. The product was identified as 1-fluoropropene (VI) (2.13 g, 35.5 mmol, 53%) (Found: C, 60.3; H, 8.5; F, 31.1%; *M*, 60. Calc. for C_3H_5F: C, 60.0; H, 8.3; F, 31.6%; *M*, 60), b.p. −18 to −22 °C, present as a mixture of the *cis*- (VIa) and *trans*- (VIb) isomers in the ratio 70 : 30 as shown by n.m.r. spectroscopy and g.l.c. (4 m Kel-F 10 oil at 22 °C); the isomers were separated by g.l.c. (10 m QF1 at −23 °C) and the n.m.r. spectra of the separated isomers were identical with those reported.[9]

Reaction of 1-*Fluoropropene with* N-*Bromobis*(*trifluoromethyl*)*amine*.—(a) *Photochemical*. A mixture of the olefin (0.52 g, 8.89 mmol) and the *N*-bromo-amine (2.1 g, 9.05 mmol), mixed *in vacuo* in the vapour phase in a Pyrex bulb (*ca.* 5 dm^3) and irradiated (18 h) *ca.* 15 cm from a Hanovia S500 medium-pressure u.v. lamp, gave a mixture (0.08 g, 0.46 mmol) of unchanged *N*-bromo-amine (0.05 g, 0.22 mmol, 3% recovered), *NN*-bis(trifluoromethyl)amine (0.03 g, 0.22 mmol, 3%), and perfluoro-2-azapropene (0.02 mmol) as shown by i.r. spectroscopy and g.l.c. (4 m Kel-F 10 at 22 °C) and a mixture (2.26 g, 7.74 mmol, 88%) of four 1 : 1 adducts (A—D) in the ratio 24 : 22 : 27 : 27 as shown by g.l.c. (7.5 m TXP at 70 °C). The four products were separated by g.l.c. (as above) and were identified as (1R,2S)-2-*bromo*-1-*fluoro*-NN-*bis*(*trifluoromethyl*)*propylamine* * (VIIIa) (0.54 g, 1.86 mmol, 21%) (Found: C, 20.7: H, 1.8; F, 45.5; N, 4.5%; M^+, 292. $C_5H_5BrF_7N$ requires C, 20.6; H, 1.7; F, 45.6; N, 4.8%; *M*, 292), b.p. (Siwoloboff) 104—105 °C; (1R,2R)-2-*bromo*-1-*fluoro*-NN-*bis*(*trifluoromethyl*)*propylamine* * (VIIIb) (0.50 g, 1.70 mmol, 19%) (Found: F, 45.6; N, 4.8%; M^+, 292), b.p. (Siwoloboff) 103—104 °C; (1R,2S)-2-*bromo*-2-*fluoro*-1-*methyl*-NN-*bis*(*trifluoromethyl*)*ethylamine* * (Xa) (0.61 g, 2.09 mmol, 24%) (Found: C, 20.8; H, 1.7; F, 45.2%), b.p. (Siwoloboff) 103—104 °C; and (1R,2R)-2-*bromo*-2-*fluoro*-1-*methyl*-NN-*bis*(*trifluoromethyl*)*ethylamine* * (Xb) (0.61 g, 2.09 mmol, 24%) (Found: C, 20.7; H, 1.8; F, 45.5; N, 4.7%), b.p. (Siwoloboff) 110—111 °C.

A small amount (0.25 g) of unidentified higher-boiling material was recovered from the reaction tube.

(b) *In the dark*. A mixture of the olefin (1.10 g, 18.3 mmol) (*cis* : *trans* 76 : 24) and the *N*-bromo-amine (3.0 g, 12.9 mmol), maintained (17 h) at −78 °C in the dark *in vacuo* in a Pyrex ampoule (*ca.* 100 cm^3), gave (i) a mixture (9.04 mmol) which was shown by i.r. spectroscopy and g.l.c. (4 m Kel-F 10 at 22 °C) to consist of unchanged 1-fluoropropene (0.47 g, 7.78 mmol, 43% recovered) (*cis* : *trans* ratio 84 : 16) and small amounts of *NN*-bis(trifluoromethyl)amine, perfluoro-2-azapropene, and an unknown component with an i.r. band at 5.67 µm and (ii) a mixture (3.05 g) shown by g.l.c. (7.5 m TXP at 70 °C) to contain compounds (VIIIa) (0.70 g, 2.40 mmol, 22%), (VIIIb) (1.91 g, 6.54 mmol, 61%), (Xa) (0.21 g, 0.73 mmol, 7%), and (Xb) (0.21 g, 0.73 mmol, 7%) in the ratio 23 : 63 : 7 : 7. In a second experiment a mixture of the *cis*-isomer (VIa) (0.32 g, 5.26 mmol) and the *N*-bromo-amine (0.82 g, 3.50 mmol), treated as described in the first experiment (36 h), gave (i) unchanged *cis*-olefin (0.12 g, 1.95 mmol, 37% recovered), (ii) a fraction (0.60 mmol) consisting mainly of perfluoro-2-azapropene, together with a small amount of *NN*-bis(trifluoromethyl)amine, and (iii) a mixture (0.84 g, 3.07 mmol) which was separated by g.l.c. (6 m TXP at 80 °C) into its three components, identified as compounds (VIIIb) (0.68 g, 2.33 mmol, 70%) and (Xa) (0.09 g, 0.305 mmol, 9%) and 2-bromo-1,1-difluoropropane (XI) (0.07 g, 0.434 mmol, 13%) in the ratio 76 : 10 : 14.

Dehydrobromination of the 1 : 1 *Adducts*.—(a) (1R,2S)-2-*Bromo*-1-*fluoro*-NN-*bis*(*trifluoromethyl*)*propylamine* (VIIIa). A mixture of the adduct (0.32 g, 1.10 mmol) and powdered potassium hydroxide (6 g), heated *in vacuo* at 40 °C (30 min) and occasionally shaken, gave a volatile fraction (0.223 g, 1.06 mmol, 96%) (Found: C, 28.6; H, 2.0; N, 6.7%; *M*, 211. Calc. for $C_5H_4F_7N$: C, 28.4; H, 1.9; N, 6.6%; *M*, 211) which was shown by n.m.r. spectroscopy to be a mixture of (*E*)-1-fluoro-*NN*-bis(trifluoromethyl)prop-1-enylamine (VIIb) (0.18 g, 0.87 mmol, 79%) and the (*Z*)-isomer (VIIa) (0.04 g, 0.19 mmol, 17%); τ[(*Z*)-isomer] 5.32 [1 H, dq, vinylic H, $J_{H,F}$(*trans*) 25.2, $J_{H,Me}$(*gem* (7.2Hz] and 8.78 (3 H, mult, CH_3), δ_F −18.0 [6F, d $(CF_3)_2N$, $J_{CF_3,F}$(*gem*) 4.0 Hz] and 19.4 (1F, dmult, vinylic F).

(b) (1R,2R)-2-*Bromo*-1-*fluoro*-NN-*bis*(*trifluoromethyl*)-*propylamine* (VIIIb). A mixture of the adduct (0.67 g, 2.29 mmol) and powdered potassium hydroxide (6 g), treated as in (a), gave (E)-1-*fluoro*-NN-*bis*(*trifluoromethyl*)-*prop*-1-*enylamine* * (VIIa) (0.46 g, 2.21 mmol, 96%) (Found: C, 28.7; H, 1.8; F, 62.7; N, 6.8%; *M*, 211. Calc. for $C_5H_4F_7N$: C, 28.4; H, 1.9; F, 63.0; N, 6.6%; *M*, 211), b.p. (isoteniscope) 43.1 ± 0.5 °C; $\lambda_{max.}$ 5.80s µm (>C:C< str.).

(c) (1R,2S)-2-*Bromo*-2-*fluoro*-1-*methyl*-NN-*bis*(*trifluoromethyl*)*ethylamine* (Xa). A mixture of the adduct (0.186 g, 0.638 mmol) and powdered potassium hydroxide (5 g), treated as in (a), gave (Z)-2-*fluoro*-1-*methyl*-NN-*bis*(*trifluoromethyl*)*vinylamine* * (IXa) (0.133 g, 0.634 mmol, 99%) (Found: C, 28.6; H, 2.1%; *M*, 211. Calc. for $C_5H_4F_7N$: C, 28.4; H, 1.9%; *M*, 211), b.p. (isoteniscope) 38.4 ± 0.5 °C; $\lambda_{max.}$ 5.85s µm (>C:C< str.).

(d) (1R,2R)-2-*Bromo*-2-*fluoro*-1-*methyl*-NN-*bis*(*trifluoromethyl*)*ethylamine* (Xb). A mixture of the adduct (0.526 g, 1.80 mmol) and powdered potassium hydroxide (6 g), treated as in (a), gave (E)-2-*fluoro*-1-*methyl*-NN-*bis*(*trifluoromethyl*)*vinylamine* * (IXb) (0.369 g, 1.75 mmol, 97%) (Found: C, 28.5; H, 2.1%; *M*, 211), b.p. 37.6 ± 0.5 °C; $\lambda_{max.}$ 5.88m µm (>C:C< str.).

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† Spectral data for compounds marked with an asterisk are available as Supplementary Publication No. SUP 21573 (8 pp.). For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.