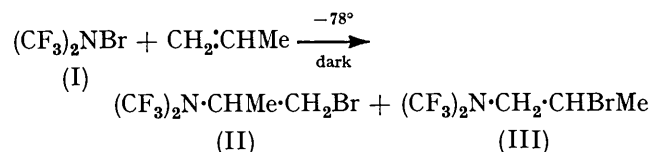# Polyfluoroalkyl Derivatives of Nitrogen. Part XXXVIII.[1] Reaction of N-Bromobistrifluoromethylamine with Allyl Chloride; Preparation of NN-Bistrifluoromethylprop-2-enylamine [2]
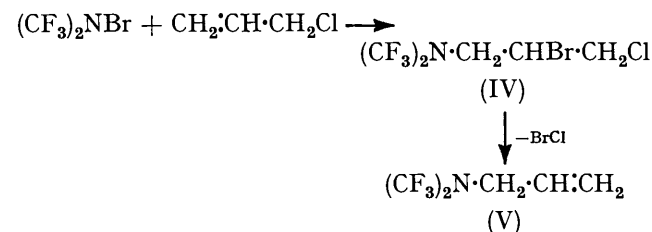
By David H. Coy, Robert N. Haszeldine,* Michael J. Newlands, and Anthony E. Tipping, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Reaction of N-bromobistrifluoromethylamine with allyl chloride at −78° in the dark gives the 1 : 1 adducts 2-bromo-3-chloro-NN-bistrifluoromethylpropylamine and 1-bromomethyl-2-chloro-NN-bistrifluoromethylethylamine in the ratio 66 : 34; at room temperature in the vapour phase in light the same adducts are formed in the ratio 90 : 10. Dehydrohalogenation of the former adduct gives mainly cis- and trans-3-chloro-NN-bistrifluoromethylprop-1-enylamine and 2-bromo-NN-bistrifluoromethylprop-2-enylamine, together with a small amount of NN-bistrifluoromethylpropadienylamine; the latter adduct affords a mixture of 3-chloro- and 3-bromo-2-(NN-bistrifluoromethylamino)propene with the former olefin predominating. Dehalogenation of the 2-bromo-3-chloro-compound gives NN-bistrifluoromethylprop-2-enylamine in good yield.

PREVIOUS papers have described the reaction of the N-halogenobistrifluoromethylamines, $(CF_3)_2NX$ (X = Cl, Br, or I), with various olefins under free-radical and ionic conditions.[1,3,4] It was observed that the reaction of the N-bromo-amine (I) with propene [1] at −78° in the dark gave a mixture of the adducts (II) and (III) in the ratio 60 : 40, and it was suggested that the adducts were both formed by an ionic mechanism, i.e. free-radical intermediates were not involved.

$$(CF_3)_2NBr + CH_2\!:\!CHMe \xrightarrow[\text{dark}]{-78°}$$
$$(I)$$
$$(CF_3)_2N\!\cdot\!CHMe\!\cdot\!CH_2Br + (CF_3)_2N\!\cdot\!CH_2\!\cdot\!CHBrMe$$
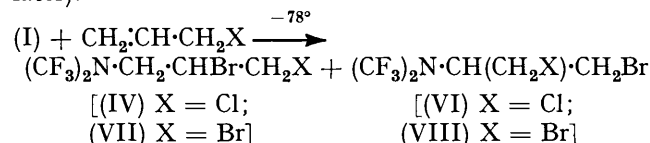$$\text{(II)} \qquad\qquad\qquad \text{(III)}$$

In a continuation of this study the reactions of the bromo-amine (I) with allyl chloride and allyl bromide under conditions favouring ionic intermediates have been studied. The reaction with allyl chloride under free-radical conditions has also been investigated since the expected major adduct (IV) should be a suitable precursor for the preparation of NN-bistrifluoromethylprop-2-enylamine (V).

$$(CF_3)_2NBr + CH_2\!:\!CH\!\cdot\!CH_2Cl \longrightarrow$$
$$(CF_3)_2N\!\cdot\!CH_2\!\cdot\!CHBr\!\cdot\!CH_2Cl$$
$$\text{(IV)}$$
$$\downarrow -\text{BrCl}$$
$$(CF_3)_2N\!\cdot\!CH_2\!\cdot\!CH\!:\!CH_2$$
$$\text{(V)}$$

The reaction with allyl chloride in the dark at −78° gave a mixture (88%) of 2-bromo-3-chloro-NN-bistrifluoromethylpropylamine (IV) and 1-bromomethyl-2-chloro-NN-bistrifluoromethylethylamine (VI) in the ratio 66 : 34. Bistrifluoromethylamine (10%) was also obtained. A corresponding reaction with allyl bromide gave bistrifluoromethylamine (ca. 23%), a mixture (49%) of the 1 : 1 adducts 2,3-dibromo-NN-bistrifluoromethylpropylamine (VII) and 1-bromomethyl-2-bromo-NN-bistrifluoromethylethylamine (VIII) in the ratio 85 : 15, and a large amount of a viscous non-volatile residue.

We were unable to separate the pair of adducts from either reaction by g.l.c. on a variety of columns, and the structures were determined by n.m.r. spectroscopy and, in the case of the allyl chloride adducts (IV) and (VI), also by dehydrohalogenation. The allyl bromide adduct (VII) was also prepared by an unambiguous route (see later).

$$(I) + CH_2\!:\!CH\!\cdot\!CH_2X \xrightarrow{-78°}$$
$$(CF_3)_2N\!\cdot\!CH_2\!\cdot\!CHBr\!\cdot\!CH_2X + (CF_3)_2N\!\cdot\!CH(CH_2X)\!\cdot\!CH_2Br$$
$$\text{[(IV) X = Cl;} \qquad\qquad \text{[(VI) X = Cl;}$$
$$\text{(VII) X = Br]} \qquad\qquad \text{(VIII) X = Br]}$$

Previously reported reactions of the bromo-amine (I) with olefins at −78° in the dark are consistent with an ionic mechanism, e.g. trans-addition to the but-2-enes [5] as compared with non-stereospecific addition under free-radical conditions [4] and the direction of addition to

[1] Part XXXVII, D. H. Coy, G. L. Fleming, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, J.C.S. Perkin I, 1972, 1880.
[2] Presented in part (by A. E. T.) at the Sixth International Fluorine Symposium, Durham, 1971.

[3] G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, J. Chem. Soc. (C), 1971, 3833, and references contained therein.
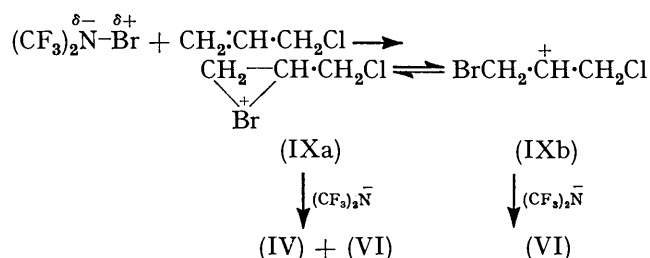[4] G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, J.C.S. Perkin I, 1972, 1877.
[5] M. G. Barlow, G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, J. Chem. Soc. (C), 1971, 2744.

NN-bistrifluoromethylvinylamine to give exclusively the adduct $[(CF_3)_2N]_2CH\cdot CH_2Br$ as compared with the adduct $(CF_3)_2N\cdot CH_2\cdot CHBr\cdot N(CF_3)_2$ formed under free-radical conditions.[6] It thus seems probable that the adducts formed at $-78°$ in the dark during the present investigation are also formed *via* ionic intermediates.

As in the case of propene, electrophilic attack of compound (I) on allyl chloride is postulated to involve formation of a cyclic bromonium ion (IXa), which is possibly in equilibrium with the linear carbonium ion (IXb). The involvement of the linear carbonium ion

$$(CF_3)_2\overset{\delta-}{N}-\overset{\delta+}{Br} + CH_2\overset{\cdot}{:}CH\cdot CH_2Cl \longrightarrow$$

$$\underset{\underset{Br}{\diagdown\overset{+}{\diagup}}}{CH_2-CH\cdot CH_2Cl} \rightleftharpoons BrCH_2\cdot \overset{+}{C}H\cdot CH_2Cl$$

<div align="center">

(IXa)   (IXb)

$\downarrow_{(CF_3)_2\bar{N}}$ $\downarrow_{(CF_3)_2\bar{N}}$

(IV) + (VI)   (VI)

</div>

(IXb) is considered unlikely, however, because reaction of the bromo-amine (I) with *cis*-1-fluoropropene at $-78°$ in the dark affords only the adducts (X) and (XI) formed by bidirectional *trans*-addition to the olefin.[7] Adducts (X) and (XI) are best explained in terms of bidirectional $(CF_3)_2\bar{N}$ ion attack on a cyclic bromonium ion intermediate; $(CF_3)_2\bar{N}$ ion attack on a linear carbonium ion intermediate would be expected to give the adducts (XI) and (XII).
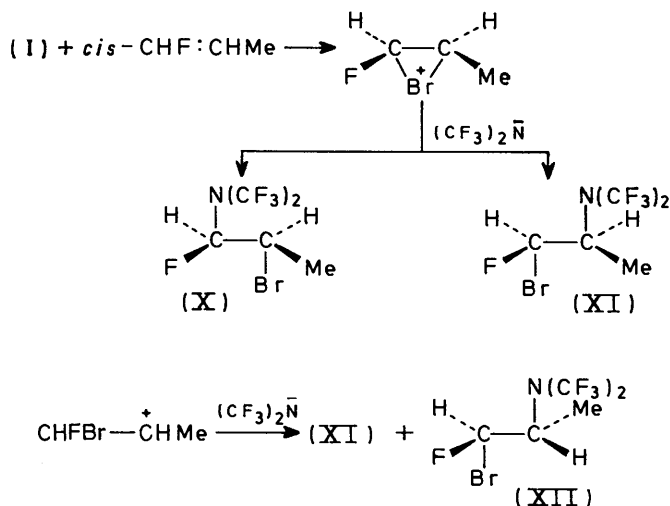
The bistrifluoromethylamine is considered to arise by proton abstraction from one of the intermediates or products by the anion $(CF_3)_2N$, *e.g.*
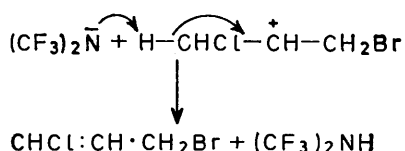
[6] E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1968, 796.

A lower yield of adducts (49%) and a correspondingly higher yield of bistrifluoromethylamine were obtained from the allyl bromide reaction as compared with the allyl chloride reaction. The greater proportion of the adduct (VII) formed by $(CF_3)_2\bar{N}$ ion attack on the CH_2 group of the cyclic brominium ion in the allyl bromide reaction as compared with that (IV) formed in the allyl chloride reaction is probably a consequence of the greater steric inhibition to attack at the central carbon atom arising from an adjacent CH_2Br than from a CH_2Cl group.

The reaction of the bromo-amine (I) with allyl chloride under radical conditions gave a mixture (81%) of the adducts (IV) and (VI) in the ratio 90 : 10 and bistrifluoromethylamine (18%) contaminated with perfluoro-2-azapropene. The bistrifluoromethylamine is probably formed by $(CF_3)_2N\cdot$ radical abstraction of allylic hydrogen.

Radical attack of both the $(CF_3)_2N\cdot$[1] and $CF_3\cdot$ radicals[8] on propene occurs to the extent of 90% on the CH_2 group and 10% on the CHMe group, and the attack of $CF_3\cdot$ radicals on allyl chloride is also predominantly on the terminal CH_2 group;[9] other radicals, *e.g.* $CCl_3\cdot$,[10] are reported to react similarly.

Dehydrobromination of a mixture of adducts (IV) and (VI) with solid potassium hydroxide *in vacuo* afforded unchanged (IV) (7%), unchanged (VI) (6%), and a mixture of seven unsaturated products. The products from adduct (IV) were *cis*-3-chloro-*NN*-bistrifluoromethylprop-1-enylamine (XIIIa) (43%), the corresponding *trans*-olefin (XIIIb) (16%), 2-bromo-*NN*-bistrifluoromethylprop-2-enylamine (XIV) (26%), a compound thought to be either *cis*- or *trans*-3-chloro-*NN*-bistrifluoromethylprop-2-enylamine (XV) (*ca.* 2%), which
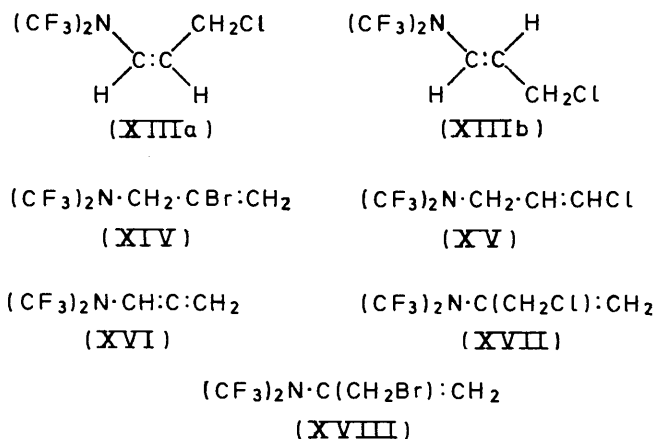
was not characterised, and *NN*-bistrifluoromethylpropadienylamine (XVI) (*ca.* 5%). Adduct (VI) gave

[7] R. N. Haszeldine, I. U. D. Mir, and A. E. Tipping, unpublished results.

[8] R. N. Haszeldine, D. W. Keen, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1970, 414.

[9] R. N. Haszeldine, K. Leedham, and B. R. Steele, *J. Chem. Soc.*, 1954, 2040.

[10] M. S. Kharasch and M. Sage, *J. Org. Chem.*, 1949, **14**, 537; W. A. Skinner, E. Bishop, D. Teiser, and J. D. Johnstone, *ibid.*, 1958, **23**, 1710.

3-chloro-2-(NN-bistrifluoromethylamino)propene (XVII) (73%) and 3-bromo-2-(NN-bistrifluoromethylamino)-propene (XVIII) (15%).
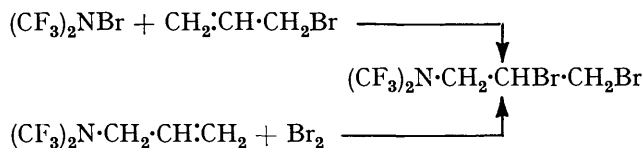
The compounds (XIV) and (XVIII) were identical with the two adducts formed by the reaction of the bromo-amine (I) with allene,[11] and the diene (XVI) has been prepared previously by dehydrobromination of the olefin (XIV) [11] and of a mixture of cis- and trans-2-bromo-NN-bistrifluoromethylprop-1-enylamine.[12]

Thus the adduct (IV) is dehydrobrominated more readily than it is dehydrochlorinated (ratio 61 : 26), and dehydrobromination occurs almost exclusively from the $(CF_3)_2N \cdot CH_2 \cdot CHBr-$ grouping to give a mixture of (XIIIa) and (XIIIb) in which the former, cis-isomer surprisingly predominates. The direction of dehydrobromination observed may be explained by the expected greater acidity of the hydrogen atoms in the $(CF_3)_2N \cdot CH_2$ group as compared with those in the CH_2Cl group. The adduct (VI) is similarly dehydrobrominated more readily than it is dehydrochlorinated (ratio 73 : 15).

Reaction of a mixture of the adducts (IV) and (VI) (ratio 90 : 10) with zinc dust in ethanol gave the expected olefin (V) [80% based on (IV)] and, surprisingly, propene [16% based on (IV)]. The propene could arise via hydrogenolysis of adduct (IV) to give bistrifluoromethyl-amine and 1-chloro-2-bromopropane followed by de-halogenation of the latter. The bistrifluoromethylamine is probably decomposed by reaction with the solvent.

$$(IV) \longrightarrow (CF_3)_2NH + CH_3 \cdot CHBr \cdot CH_2Cl \xrightarrow[EtOH]{Zn} CH_2 \vdots CH \cdot CH_3$$
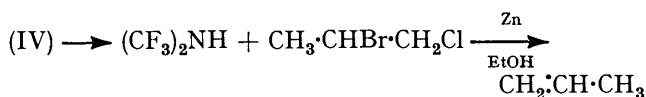
Reaction of olefin (V) with bromine gave the corresponding dibromide, the ^{19}F n.m.r. spectrum of which was identical with that of the major adduct (VII) formed in the reaction of the bromo-amine (I) with allyl bromide.

$$(CF_3)_2NBr + CH_2 \vdots CH \cdot CH_2Br \longrightarrow$$
$$(CF_3)_2N \cdot CH_2 \cdot CHBr \cdot CH_2Br$$
$$(CF_3)_2N \cdot CH_2 \cdot CH \vdots CH_2 + Br_2 \longrightarrow$$

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 116, 154B, or 451 Fraktometer). 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 spectrometer operating at 56·46 MHz for ^{19}F and 60·0 MHz for ^1H or Varian HA100 spectrometer operating at 100·0 MHz for ^1H; external trifluoroacetic acid and internal tetramethylsilane as the respective references), mass spectrometry (A.E.I. MS/902 spectrometer), and g.l.c.

Reactions of N-Bromobistrifluoromethylamine (I).—
(a) With allyl chloride in the liquid phase in the dark. The N-bromo-amine (4·80 g, 20·68 mmol) and allyl chloride (1·67 g, 22·12 mmol), sealed in a Pyrex ampoule (ca. 20 ml) which was kept at −78° in the dark (24 h), gave (i) bistrifluoromethylamine (0·30 g, 2·0 mmol, 10%; M, 148) contaminated with a small amount of perfluoro-2-aza-propene (i.r.), (ii) unchanged allyl chloride (0·075 g, 1·5 mmol, 7% recovered), and (iii) a higher-boiling volatile fraction (5·60 g, 18·18 mmol, 88%) (Found: C, 19·7; H, 1·7; N, 4·8. Calc. for $C_5H_5BrClF_6N$: C, 19·6; H, 1·6; N, 4·5%), b.p. 148° (Siwoloboff), shown by ^{19}F n.m.r. spectroscopy to be a mixture of 2-bromo-3-chloro-NN-bistrifluoromethylpropylamine (IV) (3·70 g, 12·00 mmol, 58%) and 1-bromomethyl-2-chloro-NN-bistrifluoromethyl-ethylamine (VI) (1·90 g, 6·18 mmol, 30%), present in the ratio 66 : 34 and which were not separated on a variety of g.l.c. columns.

A viscous non-volatile residue (0·36 g), i.r. $\lambda_{max.}$ 5·5— 5·9br μm ($>C \vdots C<$ str.), was also obtained.

(b) With allyl chloride in the vapour phase in daylight. The N-bromo-amine (3·00 g, 12·93 mmol) and allyl chloride (1·20 g, 15·53 mmol), rapidly vaporised into a Pyrex bulb (5 l) and exposed to daylight (3 h), gave (i) a mixture (0·32 g, 2·28 mmol, 18%; M, 140) of bistrifluoromethyl-amine and perfluoro-2-azapropene, (ii) unchanged allyl chloride (0·18 g, 2·40 mmol, 16% recovered), and (iii) a mixture (3·22 g, 10·45 mmol, 81%) of 2-bromo-3-chloro-NN-bistrifluoromethylpropylamine (IV) and 1-bromo-methyl-2-chloro-NN-bistrifluoromethylethylamine (VI) present in the ratio 90 : 10 (n.m.r.). A small amount of a non-volatile liquid coated the inside of the flask.

(c) With allyl bromide. The N-bromo-amine (2·00 g, 8·62 mmol) and allyl bromide (1·30 g, 10·74 mmol), sealed in a Pyrex ampoule (ca. 20 ml) which was allowed to warm from −78° in the dark (24 h), gave (i) a mixture (0·29 g, 2·00 mmol, 23%; M, 145) of bistrifluoromethylamine and perfluoro-2-azapropene, (ii) unchanged allyl bromide (0·31 g, 0·87 mmol, 8% recovered), (iii) a higher-boiling volatile fraction (1·50 g, 4·20 mmol, 49%) (Found: C, 17·1; H, 1·5; N, 3·8. Calc. for $C_5H_5Br_2F_6N$: C, 17·0; H, 1·4; N, 4·0%), shown by n.m.r. spectroscopy to be a mixture of 2,3-dibromo-NN-bistrifluoromethylpropylamine (VII) (1·28 g, 3·58 mmol, 42%) and 1-bromomethyl-2-bromo-NN-bistri-fluoromethylethylamine (VIII) (0·22 g, 0·62 mmol, 7%) present in the ratio 85 : 15, and (iv) a viscous non-volatile residue (1·10 g).

Reaction of the N-Bromo-amine–Allyl Chloride 1 : 1 Adduct Isomers with Zinc in Ethanol.—A mixture of 2-bromo-3-chloro-NN-bistrifluoromethylpropylamine (IV) (2·97 g, 9·62 mmol) and 1-bromomethyl-2-chloro-NN-bistrifluoro-methylethylamine (VI) (0·33 g, 1·07 mmol) was slowly added (30 min) to a stirred suspension of activated zinc (6·0 g) in refluxing ethanol (8 ml) and the resultant mixture was refluxed (1 h). The volatile products were propene (0·07 g, 1·67 mmol, 16%) and NN-bistrifluoromethylprop-2-enyl-amine (V) (1·40 g, 7·25 mmol, 80% based on the major reactant isomer) (Found: C, 31·2; H, 2·6; N, 7·1%; M, 190. $C_5H_5F_6N$ requires C, 31·1; H, 2·7; N, 7·2%; M, 193), b.p. 48° (Siwoloboff); $\lambda_{max.}$ 6·06w ($>C \vdots C<$ str.) μm; m/e 193 (100%, M^+), 192 [35, $(M - H)^+$], 165 [66,

[11] D. H. Coy, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, Chem. Comm., 1970, 456.
[12] J. Freear and A. E. Tipping, J. Chem. Soc. (C), 1969, 1955.

$(CF_3)_2N\cdot CH^+]$, 78 (45, $CF_2\cdot N\cdot CH_2^+$), 69 (83, CF_3^+), and 41 (34, $C_3H_5^+$); τ 3·89—4·9 (3H, complex, $CH_2\dot{:}CH$) and 6·19 (2H, d, J 4·5 Hz, $CH_2\cdot N$), ^{19}F n.m.r. δ −20·9 (s) p.p.m.

Reaction of NN-Bistrifluoromethylprop-2-enylamine with Bromine.—The olefin (0·40 g, 2·08 mmol) and bromine (0·48 g, 3·00 mmol), sealed in a Pyrex tube (*ca.* 20 ml) were shaken in daylight (30 min). The excess of bromine was removed by shaking *in vacuo* with mercury to give 2,3-*dibromo-NN-bistrifluoromethylpropylamine* (VII) (0·70 g, 1·98 mmol, 95%) (Found: C, 17·0; H, 1·5; N, 3·7. $C_5H_5Br_2F_6N$ requires C, 17·0; H, 1·4; N, 4·0%), b.p. 165° (Siwoloboff); τ 6·50—6·70 (4H, complex, CH_2 and CH_2Br) and 5·98 (1H, tm, J *ca.* 10 Hz, CHBr), ^{19}F n.m.r. δ −19·5 (s) p.p.m.; *m/e* 355, 353, and 351 (trace, M^+), 274 and 272 [15%, $(M - Br)^+$], 166 [100, $(CF_3)_2N\cdot CH_2^+$], 78 (36, $CF_2\cdot N\cdot CH_2^+$), and 69 (45, CF_3^+).

Reaction of the N-Bromo-amine–Allyl Chloride 1 : 1 *Adduct Isomers with Potassium Hydroxide.*—A mixture of 2-bromo-3-chloro-*NN*-bistrifluoromethylpropylamine (IV) (4·95 g, 16·04 mmol) and 1-bromomethyl-2-chloro-*NN*-bistrifluoromethylethylamine (VI) (2·55 g, 8·27 mmol), heated under reflux under reduced pressure (3·0 cmHg) over a large excess of dry, powdered potassium hydroxide (3 h) gave a mixture (0·52 g, 1·69 mmol) of unchanged 1 : 1 adducts, shown by n.m.r. spectroscopy to contain adduct (IV) (0·43 g, 1·39 mmol, 7% recovered) and adduct (VI) (0·09 g, 0·30 mmol, 6% recovered), and a lower-boiling fraction (4·76 g, 20·24 mmol, 89·5%), which was shown by g.l.c. (8 m Fluorosilicone FS1 oil and 8 m Kel-F 10 oil at 100°) to consist of seven components. The components were separated by g.l.c. and were identified, in order of retention time, as (i) *NN*-bistrifluoromethylpropadienylamine (XVI) [11,12] (0·13 g, 0·67 mmol, 5%), (ii) 3-*chloro-2-(NN-bis-trifluoromethylamino)propene* (XVII) (1·31 g, 5·77 mmol, 73%) (Found: C, 26·2; H, 1·8; N, 5·8%; M, 226. $C_5H_4ClF_6N$ requires C, 26·3; H, 1·8; N, 6·1%; M, 227·5), b.p. 87° (Siwoloboff); $\lambda_{max.}$ 5·99m ($\diagup C\dot{:}C\diagdown$ str.) μm; *m/e* 229 and 227 (75%, M^+), 178 [99, $(M - CH_2Cl)^+$], 90 (31, $CF_2\cdot N\cdot C_2H_2^+$), 77 and 75 (37, $C_3H_4Cl^+$), 69 (100, CF_3^+), and 39 (24, $C_3H_3^+$); τ 4·15 (1H, s, H *cis* to CH_2Cl), 4·33 (1H, t, J 2·1 Hz, H *trans* to CH_2Cl), and 5·96 (2H, d, CH_2Cl), ^{19}F n.m.r. δ −20·7 p.p.m., (iii) cis-3-*chloro-NN-bistrifluoro-methylprop-1-enylamine* (XIIIa) (1·43 g, 6·30 mmol, 43%) (Found: C, 26·4; H, 1·5; N, 6·1%; M, 224), b.p. 90° (Siwoloboff); $\lambda_{max.}$ 6·10m ($\diagup C\dot{:}C\diagdown$ str.) μm; *m/e* 229 and 227 (3%, M^+), 192 [100, $(M - Cl)^+$], 77 (10, $CF_2\cdot N\cdot CH^+$), 77 and 75 (36, $C_3H_4Cl^+$), and 69 (40, CF_3^+); τ [for $(CF_3)_2N\cdot CH_a\dot{:}CH_b\cdot C(H_c)_2Cl$] 4·18 (1H, dt, J_{ab} 7·5, J_{cb} 5·7 Hz, H_b), 4·48 (1H, dt, J_{ca} 1·5 Hz, H_a), and 6·00 (2H, dd, H_c), ^{19}F n.m.r. δ −19·0 p.p.m., (iv) 2-bromo-*NN*-bistrifluoro-

methylprop-2-enylamine (XIV) [11] (1·05 g, 3·84 mmol, 26%), (v) trans-3-*chloro-NN-bistrifluoromethylprop-1-enylamine* (XIIIb) (0·53 g, 2·31 mmol, 16%) (Found: C, 26·6; H, 2·0; N, 6·2%; M, 225), b.p. 98° (Siwoloboff); $\lambda_{max.}$ 6·11m ($\diagup C\dot{:}C\diagdown$ str.) μm; *m/e* 229 and 227 (5%, M^+), 192 [100, $(M - Cl)^+$], 77 and 75 (54, $C_3H_4Cl^+$), and 69 (77, CF_3^+); τ [for $(CF_3)_2N\cdot CH_a\cdot CH_b\dot{:}C(H_c)_2Cl$] 3·78 (1H, dt, J_{ab} 12·1, J_{cb} 6·0 Hz, H_b), 4·09 (1H, d, H_a), and 6·22 (2H, d, H_c), ^{19}F n.m.r. δ −19·5 p.p.m., (vi) an unidentified component (0·05 g, 0·19 mmol, 2%) thought to be either cis- or trans-3-chloro-*NN*-bistrifluoromethylprop-2-enylamine (XV), and (vii) 3-bromo-2-(*NN*-bistrifluoromethylamino)propene (XVIII) [11] (0·26 g, 1·16 mmol, 15%).

N.m.r. Spectra.—The spectra of the isomeric olefins cis- and trans-$(CF_3)_2N\cdot CH\dot{:}CH\cdot CH_2Cl$ and $(CF_3)_2N\cdot C(CH_2Cl)\dot{:}CH_2$ were assigned on the basis that *trans*-H,H couplings are larger than *cis*-H,H couplings, which are larger than *gem*-H,H couplings. The ^1H n.m.r. spectra of the *N*-bromo-amine adducts with allyl chloride and allyl bromide were complex but the ^{19}F spectra of both mixtures showed two broad singlets at −19·6 and −23·6 p.p.m. (allyl chloride adducts) and −19·5 and −23·5 p.p.m. (allyl bromide adducts). The lower-field bands were assigned to the adducts $(CF_3)_2N\cdot CH(CH_2X)\cdot CH_2Br$ (X = Cl or Br) and the higher-field bands to the adducts $(CF_3)_2N\cdot CH_2\cdot CHBr\cdot CH_2X$ by comparison with the observed ^{19}F n.m.r. chemical shifts in the propene adducts $(CF_3)_2N\cdot CHMe\cdot CH_2Br$ (−22·5 p.p.m.) and $(CF_3)_2N\cdot CH_2\cdot CHBrMe$ (−19·3 p.p.m.).[1] These assignments were confirmed by the separate synthesis of the adduct $(CF_3)_2N\cdot CH_2\cdot CHBr\cdot CH_2Br$ and by the results obtained on dehydrohalogenation of the mixture of allyl chloride adduct isomers. The adduct ratios were thus obtained by repeated integrations of the *ca.* −19·5 and −23·5 p.p.m. ^{19}F n.m.r. bands.

Mass Spectra.—The spectra were all in agreement with the proposed structures.

The base peak for the adduct $(CF_3)_2N\cdot CH_2\cdot CHBr\cdot CH_2Br$ was at *m/e* 166 [$(CF_3)_2N\cdot CH_2^+$], but surprisingly the olefin $(CF_3)_2N\cdot CH_2\cdot CH\dot{:}CH_2$ only showed a weak peak at *m/e* 166. However, the olefin, besides showing the molecular ion as base peak in its spectrum, also gave a strong peak at $M - 1$ and a corresponding strong peak was observed at *m/e* 165 assigned to $(CF_3)_2N\cdot CH^+$. The olefins cis- and trans-$(CF_3)_2N\cdot CH\dot{:}CH\cdot CH_2Cl$ both gave weak parent peaks in their spectra with the base peaks at *m/e* 192, formed by loss of chlorine from the parent, but in contrast the isomeric olefin $(CF_3)_2N\cdot C(CH_2Cl)\dot{:}CH_2$ showed a strong parent peak, only a relatively weak peak at *m/e* 192, and an extremely strong peak at *m/e* 178 due to loss of CH_2Cl.