

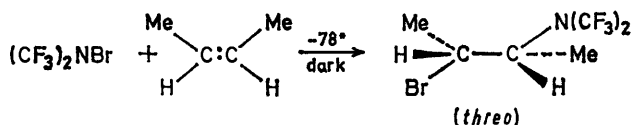
## Polyfluoroalkyl Derivatives of Nitrogen. Part XXXVII.<sup>1</sup> Reaction of *N*-Bromobistrifluoromethylamine with Propene under Ionic and Free-radical Conditions<sup>2</sup>

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Photochemical reaction of *N*-bromobistrifluoromethylamine with propene in the vapour phase gives the 1:1 adducts 2-bromo-*NN*-bistrifluoromethylpropylamine and 2-bromo-1-methyl-*NN*-bistrifluoromethylethylamine in the ratio 91:9; *N*-chlorobistrifluoromethylamine gives the corresponding chloro-adducts in the ratio 90:10. Reaction of the *N*-bromo-amine in the liquid phase in the dark at  $-78^\circ$  and at  $-140^\circ$  gives the same adducts in the ratio 40:60 and 55:45, respectively; the presence of acetone as solvent, air, or hydroquinone has no effect on the isomer ratio at  $-78^\circ$ . 2-Bromo-*NN*-bistrifluoromethylpropylamine dehydrobrominates readily to afford a mixture of *cis*- and *trans*-*NN*-bistrifluoromethylprop-1-enylamine in high yield and 2-bromo-1-methyl-*NN*-bistrifluoromethylethylamine gives 2-(*NN*-bistrifluoromethylamino)propene. Reaction of the *N*-bromo-amine with isobutene at  $-78^\circ$  or  $-140^\circ$  gives mainly bistrifluoromethylamine and brominated material.

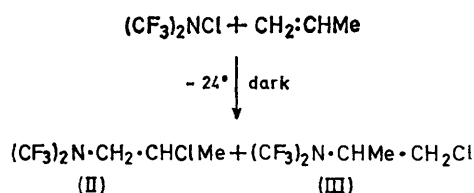
REACTIONS of the *N*-halogenobistrifluoromethylamines,  $(\text{CF}_3)_2\text{NX}$  (I) [(Ia), X = Cl; (Ib), X = Br; (Ic), X = I] with olefins under ionic conditions have been reported recently, *i.e.*, the reactions of (Ia) with *trans*-but-2-ene<sup>3</sup> and propene,<sup>4</sup> (Ib) with *NN*-bistrifluoromethylvinylamine<sup>5</sup> and *cis*- or *trans*-but-2-ene,<sup>3</sup> and (Ic) with vinyl fluoride.<sup>4</sup>

The but-2-ene reactions proceeded at  $-78^\circ$  and gave products resulting from exclusive *trans*-addition, *e.g.*,



Such reactions were interpreted<sup>3</sup> as involving initial electrophilic attack of the *N*-halogenoamine polarised as  $(\text{CF}_3)_2\overset{\delta-}{\text{N}}-\overset{\delta+}{\text{X}}$ .

With the unsymmetrical olefins only the reaction of (Ia) with propene, which proceeded at  $-24^\circ$  but not at  $-78^\circ$ , gave appreciable amounts of two isomeric 1:1 adducts,<sup>4</sup> *i.e.*



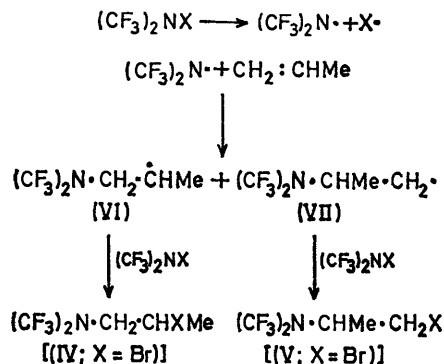
The expected ionic adduct (III) was the major product (59%) but an appreciable amount (39%) of the unexpected adduct (II) was also formed.

The products (II) and (III) were considered to be formed either by a bidirectional ionic addition mechanism or by competing ionic and free-radical mechanisms.<sup>4</sup>

In order to obtain more information on such additions to propene under ionic conditions, the more reactive amine (Ib) has been allowed to react with the olefin at both  $-78^\circ$  and  $-140^\circ$  in the dark. The reactions of

(Ia) and (Ib) with propene under free-radical conditions and of (Ib) with isobutene under ionic conditions have also been investigated.

The photochemical reaction of (Ib) with propene (vapour phase) gave a mixture (94%) of the 1:1 adducts 2-bromo-*NN*-bistrifluoromethylpropylamine (IV) and 2-bromo-1-methyl-*NN*-bistrifluoromethylethylamine (V) in the ratio 91:9. Similarly photochemical reaction of (Ia) with propene (vapour phase) gave a mixture (96%) of the 1:1 adducts (II) and (III) in the ratio 90:10. These results suggest that initial  $(\text{CF}_3)_2\text{N}\cdot$  radical attack on the  $\text{CH}_2$  and  $\text{CHMe}$  groups in propene occurs in the ratio 90:10.



The secondary radical (VI) is thus, as expected, more stable than the primary radical (VII).

In the Table are shown the ratios of 1:1 adducts formed from reaction of the *N*-halogenoamines and trifluoriodomethane with certain olefins under free-radical conditions. From the Table it can be seen that for the olefins  $\text{CHF}:\text{CF}_2$  and  $\text{CH}_2:\text{CHF}$  the ratios of bidirectional  $(\text{CF}_3)_2\text{N}\cdot$  radical addition closely parallel those of  $\text{CF}_3\cdot$  radical addition. The ratio (91:9) observed in the present work for  $(\text{CF}_3)_2\text{N}\cdot$  radical addition to propene also closely parallels that observed for  $\text{CF}_3\cdot$  radical addition.

<sup>3</sup> M. G. Barlow, G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 2744.

<sup>4</sup> G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 3829.

<sup>5</sup> E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 796.

<sup>1</sup> Part XXXVI, G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, preceding paper.

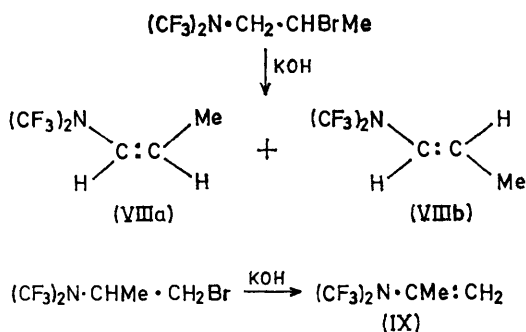
<sup>2</sup> Presented in part at the Sixth International Fluorine Symposium, Durham, 1971.

The similar ratios obtained for attack by either radical on vinyl fluoride and propene (*ca.* 90–95% on the CH<sub>2</sub> groups) suggest that a fluorine atom and a methyl group

Radical additions to olefins				
Addend	Conditions	1 : 1 Adduct yield (%)	Ratio of attack	Ref.
CHF=CF <sub>2</sub>				
(CF <sub>3</sub> ) <sub>2</sub> NCl	140°	99	78 22	6
(CF <sub>3</sub> ) <sub>2</sub> NCl	u.v.	96	87 13	6
(CF <sub>3</sub> ) <sub>2</sub> NBr	Daylight	95	78 22	7
(CF <sub>3</sub> ) <sub>2</sub> NI	u.v.	93	74 26	6
CF <sub>3</sub> I	u.v.	85	80 20	8
CH <sub>2</sub> =CHF				
(CF <sub>3</sub> ) <sub>2</sub> NCl	u.v.	96	95 5	6
(CF <sub>3</sub> ) <sub>2</sub> NBr	Daylight	98	94 6	9
(CF <sub>3</sub> ) <sub>2</sub> NI	u.v.	98	93 7	6
CF <sub>3</sub> I	200°	96	90 10	10
CF <sub>3</sub> I	u.v.	91	96 4	11
CH <sub>2</sub> =CHMe				
CF <sub>3</sub> I	200°	99	89 11	10

stabilise an adjacent lone electron to a similar degree. Thus it is to be expected that (CF<sub>3</sub>)<sub>2</sub>N• or CF<sub>3</sub>• radical addition to the olefin CHF:CHMe would result in bidirectional attack in a *ca.* 1 : 1 ratio.

The structures of the adducts (IV) and (V) were established by their mass and n.m.r. spectra and by their dehydrobromination to give a mixture (96%) of *cis* (VIIIa)- and *trans* (VIIIb)-*NN*-bistrifluoromethylprop-1-enylamine in the ratio 36 : 64, and 2-(*NN*-bistrifluoromethylamino)propene (IX) (97%), respectively. The mass and n.m.r. spectra of the olefins were in full agreement with the proposed structures.



Reaction of (Ib) with a slight excess of propene in the liquid phase in the dark at -78° gave a mixture (94%) of the adducts (IV) and (V) in the ratio 40 : 60. An identical ratio of products was obtained from reaction of (Ib) with propene at -78° in the dark (i) with acetone present as solvent (98% yield), (ii) with hydroquinone present as a radical inhibitor (96% yield), and (iii) with dry air present (90% yield).

These results suggest that at -78° in the dark adduct (IV) is not formed by a free-radical process, as does the observation that reaction of (Ib) with propene at -140°

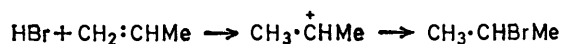
<sup>6</sup> G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 3833.

<sup>7</sup> R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, 1965, 6141.

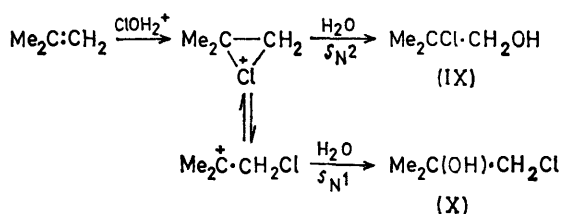
<sup>8</sup> R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1957, 2800.

gave (IV) and (V) in the ratio 55 : 45; it would be expected that if (IV) had been formed by a radical process it would be present in lower yield in the products of reaction at -140 than in reaction at -78°. In support of this all other successful reactions of (Ib) with olefins at -78° in the dark have given the expected ionic products exclusively. Thus the formation of adducts (IV) and (V) by reaction at -78 or -140° probably takes place by an ionic mechanism.

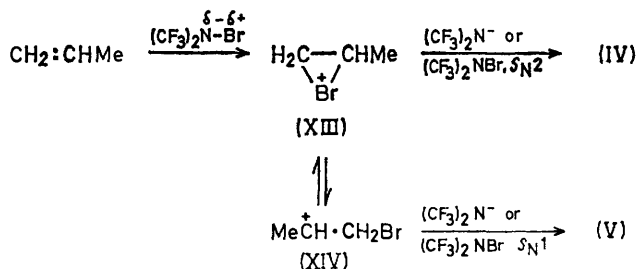
Previous electrophilic additions to propene have been observed to give exclusively a single 1 : 1 adduct, the direction of addition being in accordance with the intermediate formation of the more stable secondary rather than the alternative primary carbonium ion, *e.g.*,<sup>12</sup>



However, in the reaction of hypochlorous acid with isobutene the expected adduct (X) and the unexpected adduct (XI) are formed in the ratio 85 : 5 together with the allylic chloro-olefin CH<sub>2</sub>:CMe·CH<sub>2</sub>Cl (XII) (10%). It was postulated that the adducts arose by the following reaction scheme.



If a comparable mechanism is operative in reaction of (Ib) with propene then the difference in ratio of the adducts (IV) and (V) obtained at -78° (40 : 60) and -140° (55 : 45) can be explained on the basis that opening of the cyclic bromonium ion (XIII) to the open-chain carbonium ion (XIV) is less preferred at -140 than at -78°.



Predominant, if not exclusive, attack on the cyclic bromonium ion (XIII) at the CH<sub>2</sub> group is to be expected because of the inductive and steric effects of the methyl group.

An alternative is that the open-chain carbonium ion

<sup>9</sup> J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1969, 1955.

<sup>10</sup> R. N. Haszeldine, D. W. Keen, and A. E. Tipping, *J. Chem. Soc. (C)*, 1970, 414.

<sup>11</sup> R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 1216.

<sup>12</sup> M. S. Kharasch and F. R. Mayo, *J. Amer. Chem. Soc.*, 1933, 55, 2531.

(XIV) is not formed and that the products (IV) and (V) result from bidirectional  $S_N2$  attack on the ion (XIII). At present it is not possible to differentiate between the two alternatives, and indeed both could be occurring simultaneously.

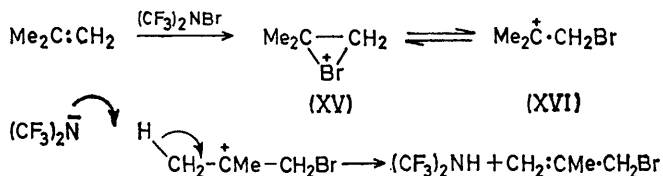
The above evidence suggests, but does not prove, that the analogous reaction of the amine (Ia) with propene at  $-24^\circ$ ,<sup>4</sup> also involves bidirectional ionic addition.

Reaction of (Ib) with isobutene at  $-78$  or at  $-140^\circ$  gave as major products bistrifluoromethylamine (84 and 86%, respectively) and brominated material. The i.r. spectrum of the brominated material showed weak bands in the  $7.0$ – $8.5$   $\mu\text{m}$  region (C–F str.) and suggests the presence of a small amount (maximum *ca.* 15%) of adduct.

The brominated material probably consists mainly of the olefin  $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\text{Br}$  and the difference in mode of reaction with isobutene as compared with propene is considered to be a measure of the increased number of allylic hydrogen atoms in the former olefin (6) as compared with the latter (3).

The formation of olefin (XII) in the reaction of hypochlorous acid with isobutene has been shown to arise by loss of a proton from the open-chain carbonium ion intermediate.<sup>13</sup>

If an analogous reaction is occurring in the present case then loss of a proton from the carbonium ion (XVI) is faster than nucleophilic attack on the cyclic bromonium ion (XV) to give adduct and the equilibrium that exists between (XVI) and (XV) is displaced. The proton loss from (XVI) probably involves attack by  $(\text{CF}_3)_2\text{N}^-$  acting as a base.



## EXPERIMENTAL

Techniques used were as described previously.<sup>1,5</sup> *N*-Bromo- and *N*-chloro-bistrifluoromethylamine were prepared by the reaction of mercuric bistrifluoromethylamide with bromine<sup>7,14</sup> and chlorine,<sup>7</sup> respectively. Detailed i.r. and mass spectral data for compounds marked with an asterisk are deposited with the W.L.L. as a Supplementary Publication (SUP. No. 20413, 7 pp.).†

*Reactions of N-Bromobistrifluoromethylamine.*—(a) *With propene in the liquid phase at  $-78^\circ$  in the dark.* The *N*-bromo-amine (3.40 g, 15.00 mmol) and propene (0.67 g, 15.95 mmol), sealed in a Pyrex ampoule (*ca.* 20 ml) at  $-196^\circ$  and maintained at  $-78^\circ$  in the dark (24 h), gave (i) unchanged propene (0.05 g, 1.19 mmol, 7% recovered), (ii) bistrifluoromethylamine (0.09 g, 0.58 mmol), and (iii) a higher-boiling fraction (3.80 g, 13.87 mmol, 94%) (Found: *M*, 275. Calc. for  $\text{C}_5\text{H}_6\text{BrF}_6\text{N}$ : *M*, 274) which was separ-

ated by g.l.c. (8m Fluorosilicone FS1 oil at  $110^\circ$ ) into its two components present in the ratio 40 : 60. The minor component was identified as 2-bromo-*NN*-bistrifluoromethylpropylamine\* (1.52 g, 5.55 mmol, 38%) (Found: C, 22.2; H, 2.3; N, 4.9%; *M*, 271.  $\text{C}_5\text{H}_6\text{BrF}_6\text{N}$  requires C, 21.9; H, 2.2; N, 5.1%; *M*, 274), b.p.  $103^\circ$  (Siwoloff);  $^1\text{H}$  n.m.r. bands for  $(\text{CF}_3)_2\text{N}\cdot\text{CH}_2\cdot\text{CHBrMe}$  at  $\tau$  6.06 (complex, 1H), 6.67 (complex AB, 2H), and 8.31 (d, 3H, Me; *J*, 6.1 Hz) and  $^{19}\text{F}$  n.m.r. band at 19.3 p.p.m. to low field of external reference  $\text{CF}_3\cdot\text{CO}_2\text{H}$ . The major component was identified as 2-bromo-1-methyl-*NN*-bistrifluoromethylethylamine\* (2.28 g, 8.32 mmol, 56%) (Found: C, 22.2; H, 2.4; N, 5.0%; *M*, 270), b.p.  $107^\circ$  (Siwoloff);  $^1\text{H}$  n.m.r. bands for  $(\text{CF}_3)_2\text{N}\cdot\text{CHMe}\cdot\text{CH}_2\text{Br}$  at  $\tau$  6.24 (complex, 1H), 6.60 (complex AB, 2H,  $\text{CH}_2\text{Br}$ ), and 8.50 (d, 3H, Me; *J*, 6.9 Hz) and  $^{19}\text{F}$  n.m.r. band at 22.5 p.p.m. (s) to low field of reference.

(b) *With propene in the liquid phase at  $-140^\circ$  in the dark.* The *N*-bromo-amine (0.50 g, 2.15 mmol) and propene (0.13 g, 3.09 mmol), reacted in a Pyrex ampoule (*ca.* 10 ml) at  $-140^\circ$  in the dark (6 h), gave unchanged propene (0.039 g, 0.93 mmol, 30% recovered) and a higher-boiling fraction (0.57 g, 2.08 mmol, 96%) (Found: *M*, 274) which was identified by g.l.c. (as before) and n.m.r. as a mixture of the 1 : 1 adducts 2-bromo-*NN*-bistrifluoromethylpropylamine and 2-bromo-1-methyl-*NN*-bistrifluoromethylethylamine in the ratio 55 : 45.

(c) *With propene in the liquid phase at  $-78^\circ$  in the dark in the presence of other compounds.* The *N*-bromo-amine and propene, allowed to react at  $-78^\circ$  in the dark (6 h) with (i) the reaction mixture open to dry air, (ii) an excess of hydroquinone *in vacuo*, and (iii) an excess of acetone as solvent *in vacuo*, gave the 1 : 1 adducts 2-bromo-*NN*-bistrifluoromethylpropylamine and 2-bromo-1-methyl-*NN*-bistrifluoromethylethylamine in the ratio 40 : 60 (g.l.c. and n.m.r.) in 90, 96, and 98% yield, respectively.

(d) *With propene in the vapour phase under photochemical conditions.* The *N*-bromo-amine (1.27 g, 5.47 mmol) and propene (0.38 g, 9.05 mmol), mixed in the vapour phase in a Pyrex bulb (5 l) whilst being irradiated with a 300-W tungsten filament lamp (1 h), gave (i) unchanged propene (0.15 g, 3.56 mmol, 39% recovered), (ii) a trace of bistrifluoromethylamine, and (iii) a mixture (1.41 g, 5.14 mmol, 94%) shown by g.l.c. (as before) and n.m.r. spectroscopy to consist of 2-bromo-*NN*-bistrifluoromethylpropylamine and 2-bromo-1-methyl-*NN*-bistrifluoromethylethylamine in the ratio 91 : 9.

(e) *With isobutene in the liquid phase in the dark.* The *N*-bromo-amine (3.70 g, 15.94 mmol) and isobutene (0.89 g, 15.94 mmol), sealed in a Pyrex ampoule (*ca.* 20 ml) at  $-196^\circ$ , underwent an immediate violent reaction when placed in a bath in the dark at  $-78^\circ$ . The products were (i) bistrifluoromethylamine (2.00 g, 13.42 mmol, 84%) (Found: *M*, 149. Calc. for  $\text{C}_2\text{HF}_6\text{N}$ : *M*, 153), (ii) a higher-boiling fraction (2.10 g) which was shown to be a mixture of brominated products containing a small amount of fluorinated material (weak i.r. bands from 7.10 to 9.00  $\mu\text{m}$ , C–F str.), and (iii) a non-volatile viscous residue (0.51 g).

In a second experiment carried out at  $-140^\circ$  in the dark (30 min) the same products were formed and bistrifluoromethylamine (86%) was isolated.

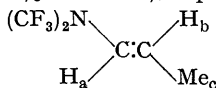
† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are supplied as full page copies).

<sup>13</sup> P. B. de la Mare and A. Salama, *J. Chem. Soc.*, 1956, 3337.  
<sup>14</sup> H. J. Emelús and B. W. Tattershall, *Z. anorg. Chem.*, 1964, 327, 147.

*Reaction of the N-Bromo-amine-Propene 1:1 Adduct Isomers with Potassium Hydroxide.*—A mixture of 2-bromo-*NN*-bistrifluoromethylpropylamine (1.68 g, 6.11 mmol) and 2-bromo-1-methyl-*NN*-bistrifluoromethylethylamine (2.52 g, 9.16 mmol), refluxed under reduced pressure (10 cm) over a large excess of dry, powdered potassium hydroxide (24 h), gave a mixture (1.40 g, 5.09 mmol, 33%) of recovered reactants, which was shown by g.l.c. (8m Fluorosilicone FS1 oil at 110°) to contain unchanged 2-bromo-*NN*-bistrifluoromethylpropylamine (0.05 g, 0.15 mmol, 2.5% recovered) and 2-bromo-1-methyl-*NN*-bistrifluoromethylethylamine (1.35 g, 4.94 mmol, 54% recovered), and a lower-boiling fraction (1.89 g, 9.79 mmol, 97%), which was shown by g.l.c. (8m Fluorosilicone FS1 oil at 45°) to contain (i) 2-(*NN*-bistrifluoromethylamino)propene\* (0.79 g, 4.09 mmol, 97%) (Found: C, 30.9; H, 2.7; N, 7.3%; *M*, 190. C<sub>5</sub>H<sub>5</sub>F<sub>6</sub>N requires C, 31.1; H, 2.7; N, 7.2%; *M*, 193), b.p. 40° (Siwoloboff); <sup>1</sup>H n.m.r. bands for (CF<sub>3</sub>)<sub>2</sub>N·CMe:CH<sub>2</sub> at τ 4.79 (s, 2H) and 8.11 (s, 3H) and <sup>19</sup>F n.m.r. band at 20.4 p.p.m. to low field of reference, (ii) *cis*-*NN*-bistrifluoromethylprop-1-enylamine\* (0.40 g, 2.07 mmol, 35%) (Found: C, 31.2; H, 2.7; N, 7.4%; *M*, 191), b.p. 45° (Siwoloboff);

<sup>1</sup>H n.m.r. bands for 
$$\begin{array}{c} (\text{CF}_3)_2\text{N} \\ \diagdown \\ \text{C}:\text{C} \\ \diagup \\ \text{H}_a \end{array} \begin{array}{c} \text{Me}_c \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H}_b \end{array}$$
 at τ 4.08 (dq,

1H, H<sub>b</sub>; *J*<sub>a-b</sub>, 6.1; *J*<sub>c-b</sub>, 6.0 Hz), 4.31 (dsep, 1H, H<sub>a</sub>; *J*<sub>F-a</sub>, 1.3 Hz), and 8.29 (d, 3H, H<sub>c</sub>) and <sup>19</sup>F n.m.r. band at 18.1 p.p.m. (s) to low field of reference, (iii) *NN*-bistrifluoromethylprop-2-enylamine (<1%), and (iv) *trans*-*NN*-bistrifluoromethylprop-1-enylamine\* (0.70 g, 3.63 mmol, 61%) (Found: C, 31.3; H, 2.7; N, 7.3%; *M*, 189), b.p. 49° (Siwoloboff); <sup>1</sup>H n.m.r. bands for



at τ 3.97 (dq, 1H, H<sub>b</sub>; *J*<sub>a-b</sub>, 11.9; *J*<sub>c-b</sub>, 6.0 Hz), 4.29 (dsep, 1H, H<sub>a</sub>; *J*<sub>F-a</sub>, 1.2 Hz), and 8.32 (d, 3H, H<sub>c</sub>) and <sup>19</sup>F n.m.r. band at 18.7 p.p.m. to low field of reference.

*Reaction of N-Chlorobistrifluoromethylamine with Propene.*—The *N*-chloro-amine (4.24 g, 22.7 mmol) and propene (1.15 g, 25.0 mmol), mixed in the vapour phase in a Pyrex bulb (2 l) whilst being irradiated with a Hanovia S500 u.v. lamp (1 h), gave unchanged propene (0.14 g, 3.0 mmol, 12% recovered), contaminated with a trace of bistrifluoromethylamine (i.r.), and a mixture (5.08 g, 21.8 mmol, 96%) (Found: *M*, 233. Calc. for C<sub>6</sub>H<sub>8</sub>ClF<sub>6</sub>N: *M*, 233) which was separated by g.l.c. (6m Silicone MS550 oil at 70°) into its two components 2-chloro-*NN*-bistrifluoromethylpropylamine (4.57 g, 19.6 mmol, 86%) and 2-chloro-1-methyl-*NN*-bistrifluoromethylethylamine (0.51 g, 2.2 mmol, 10%) as identified by a comparison of their i.r. and n.m.r. spectra with those reported previously.<sup>4</sup>

*Nuclear Magnetic Resonance Spectra.*—The spectra of the adducts (CF<sub>3</sub>)<sub>2</sub>N·CHMe·CH<sub>2</sub>Br and (CF<sub>3</sub>)<sub>2</sub>N·CH<sub>2</sub>·CHBrMe were similar to those of the corresponding *N*-chloro-amine adducts (CF<sub>3</sub>)<sub>2</sub>N·CHMe·CH<sub>2</sub>Cl and (CF<sub>3</sub>)<sub>2</sub>N·CH<sub>2</sub>·CHClMe reported previously,<sup>4</sup> except for the small upfield shift of the protons in the CH<sub>2</sub>X and CHX groups on replacement of chlorine by bromine. The olefins formed by dehydrobromination of the adducts were distinguished from each other by the magnitude of the olefinic H-H coupling constants, *J*<sub>trans</sub> > *J*<sub>cis</sub> > *J*<sub>gem</sub>.

*Mass Spectra.*—The spectra were all in full agreement with the proposed structures and the only surprising feature was the presence of a strong rearrangement peak at *m/e* 166 [(CF<sub>3</sub>)<sub>2</sub>N·CH<sub>2</sub><sup>+</sup>] in the spectra of the olefins *cis*- and *trans*-(CF<sub>3</sub>)<sub>2</sub>N·CH:CHMe. Normally this peak is only present in the spectra of compounds which contain the (CF<sub>3</sub>)<sub>2</sub>N·CH<sub>2</sub>- group when invariably it is the base peak.

[1/2227 Received, 23rd November, 1971]