

1145. *Perfluoroalkyl Derivatives of Nitrogen. Part XVII.¹ The Reaction of N-Bromobistrifluoromethylamine with Olefins*

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N-Bromobistrifluoromethylamine reacts with tetrafluoroethylene, trifluoroethylene, 1,1-difluoroethylene, *cis*-1,2-difluoroethylene, ethylene, hexafluoropropene, chlorotrifluoroethylene, or 1,2-dichlorodifluoroethylene under mild conditions, to give the 1 : 1 adducts in high yield. The (CF₃)₂N group becomes attached only to the CF₂ groups of chlorotrifluoroethylene or hexafluoropropene, and only to the CH₂ group of 1,1-difluoroethylene, whereas trifluoroethylene gives the isomers (CF₃)₂N·CHF·CF₂Br (78%) and (CF₃)₂N·CF₂·CHFBr (22%). Hexafluorocyclobutene and octafluorobut-2-ene require more drastic conditions, and give the olefin dibromide and tetrakis-trifluoromethylhydrazine rather than addition of the *N*-bromo-compound.

N-CHLOROBISTRIFLUOROMETHYLAMINE, postulated as an intermediate in the reaction of bistrifluoromethylhydroxylamine with phosphorus pentachloride,² was prepared with *N*-bromobistrifluoromethylamine by reaction of mercuric bistrifluoromethylamide with chlorine or bromine in carbon tetrachloride solution.³ Modifications in technique developed during the present work have given some improvement in the yields (98%) of these *N*-halogeno-amines.

The reaction of the *N*-bromo-amine with hexafluoropropene was described earlier,³ and others⁴ have shown recently that it reacts with ethylene, acetylene, or tetrafluoroethylene. The research now presented has been concerned initially with addition to symmetrical olefins which range in type from those activated towards electrophilic attack (ethylene) to those activated towards nucleophilic attack (tetrafluoroethylene, 1,2-dichlorodifluoroethylene, hexafluorocyclobutene, octafluorobut-2-ene); 1,2-difluoroethylene, which is not especially sensitive to either type of ionic attack, was also studied. These olefins vary greatly in their susceptibility towards free-radical attack. The ready formation of the 1 : 1 adducts with ethylene and with tetrafluoroethylene was confirmed, although the boiling point of the ethylene adduct reported earlier⁴ would seem to be appreciably in error. The direction of addition of *N*-bromobistrifluoromethylamine to the unsymmetrical olefins 1,1-difluoroethylene, hexafluoropropene, chlorotrifluoroethylene, 1,1-dichlorodifluoroethylene, and trifluoroethylene was then studied in order to deduce whether the bromo-compound reacted *via* ionic or radical intermediates.

The results of these addition reactions are summarised in Table 1. Reaction with ethylene or with the fluorohydroethylenes occurred readily in Dreadnought tubes exposed to normal dull Manchester daylight at 25°; reaction with the chlorofluoroethylenes or with hexafluoropropene required a reaction temperature of 100° in the dark, but in all these cases the yields of the 1 : 1 adducts were 86—96%. The olefins containing the -CF₂·CF·CF·CF₂- group did not afford a 1 : 1 adduct, but underwent bromination when heated or irradiated with the *N*-bromo-compound. Small amounts (<1%) of the dibromides were detected in most of the other reactions. Formation of tetrakis-trifluoromethylhydrazine is also noteworthy.

The 1 : 1 adducts were examined by gas-liquid chromatography which showed that, to the extent of at least 95% and possibly exclusively, only one adduct was obtained from hexafluoropropene and from chlorotrifluoroethylene, and that trifluoroethylene gave two 1 : 1 adducts in a 78 : 22 ratio. Mass- and n.m.r.-spectroscopic investigations of the pure

¹ Part XVI, R. E. Banks, M. G. Barlow, and R. N. Haszeldine, *J.*, 1965, 4714.

² R. N. Haszeldine and B. J. H. Mattinson, *J.*, 1957, 1741.

³ J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.

⁴ H. J. Emeléus and B. W. Tattershall, *Z. anorg. Chem.*, 1964, **327**, 147.

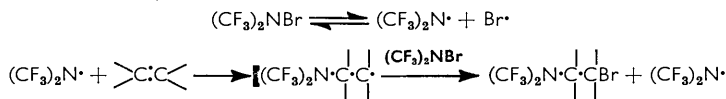
1 : 1 adducts were all consistent with the structures shown, and in the case of the unsymmetrical olefins were clearly against structures for the 1 : 1 adducts involving addition of the *N*-bromo-amide to the double bond in the opposite direction to that shown in Table I.

TABLE I
Reaction of *N*-bromobistrifluoromethylamine with olefins

Olefin	Conditions	Reaction time (hr.)	Products	Yield (%)
CF ₂ :CF ₂	25°, light	0·5	(CF ₃) ₂ N·CF ₂ ·CF ₂ Br	96
CH ₂ :CF ₂	25°, light	0·5	(CF ₃) ₂ N·CH ₂ ·CF ₂ Br	95
CH ₂ :CH ₂	25°, light	0·5	(CF ₃) ₂ N·CH ₂ ·CH ₂ Br	95
<i>cis</i> -CHF:CHF	25°, light	0·5	(CF ₃) ₂ N·CHF·CHFBr	96
CHF:CF ₂	25°, dark	160	(CF ₃) ₂ N·CHF·CF ₂ Br (77%) (CF ₃) ₂ N·CF ₂ ·CHFBr (23%)	15
			(CF ₃) ₂ N·CHF·CF ₂ Br (78%) (CF ₃) ₂ N·CF ₂ ·CHFBr (22%)	
CHF:CF ₂	25°, light	1·0	(CF ₃) ₂ N·CF ₂ ·CFClBr	95
CF ₂ :CFCl	25°, light	24	(CF ₃) ₂ N·CF ₂ ·CFClBr	92
	100°, dark	24		
CFCl:CFCl	100°, dark	24	(CF ₃) ₂ N·CFCl·CFClBr	92
CF ₃ :CF:CF ₂	100°, dark	24	(CF ₃) ₂ N·CF ₂ ·CFBr·CF ₃	86
CF ₂ :CF:CF·CF ₂	100°, dark	96	(CF ₃) ₂ N·N(CF ₃) ₂	40
			CF ₂ ·CFBr·CFBr·CF ₂	41
CF ₃ :CF:CF·CF ₃	100°, dark then u.v.	48	(CF ₃) ₂ N·N(CF ₃) ₂	91
		168	CF ₃ ·CFBr·CFBr·CF ₃	86

Mechanism of the addition reaction. The dark reactions are relatively rapid, and although they are greatly accelerated by light, this alone cannot distinguish between an ionic reaction, a free-radical reaction, or both occurring simultaneously. Ionic addition to ethylene could involve Br⁺ attack, and to tetrafluoroethylene (CF₃)₂N⁻ attack. An ionic reaction involving these ions would be consistent with the direction of addition involved in the formation of the compound (CF₃)₂N·CF₂·CFBr·CF₃ from hexafluoropropene, and in particular, would explain why this olefin did not give even traces of the isomer (CF₃)₂N·CF(CF₃)·CF₂Br; free-radical addition reactions with hexafluoropropene have hitherto given 4—50% of the compound formed *via* radical attack on the CF group.⁵ Nucleophilic attack by (CF₃)₂N⁻ would also lead to the correct direction of addition to chlorotrifluoroethylene.

The results from some of the other olefins can best be explained by radical addition, however, and although there is no compelling evidence against a mixed mechanism, particularly for the dark reactions, on balance radical attack by (CF₃)₂N· seems preferable, leading to a chain reaction:



Radical addition to the CH₂ group of 1,1-difluoroethylene to give the product shown in Table I, then agrees with other radical additions to this olefin,⁶ and it should be particularly noted that by analogy with other ionic additions to 1,1-difluoroethylene,⁷ nucleophilic attack *via* (CF₃)₂N⁻ would have given the compound (CF₃)₂N·CF₂·CH₂Br and not the isomer actually obtained. The 1,1-difluoroethylene reaction thus provides strong evidence for a radical reaction. The reaction with chlorotrifluoroethylene is also consistent with radical attack, which is known to occur on the CF₂ group.⁸

⁵ G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J.*, 1963, 1083; J. F. Harris, *J. Amer. Chem. Soc.*, 1962, **84**, 3148.

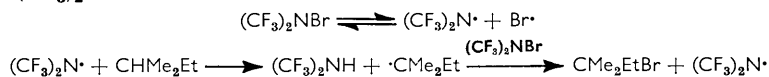
⁶ R. N. Haszeldine and B. R. Steele, *J.*, 1954, 923; G. W. Cross, R. N. Haszeldine, and M. J. Newlands, unpublished results.

⁷ R. N. Haszeldine and J. E. Osborne, *J.*, 1956, 61.

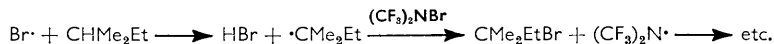
⁸ R. N. Haszeldine and B. R. Steele, *J.*, 1953, 1952; J. Brown and R. N. Haszeldine, unpublished results.

The trifluoroethylene reaction is also best interpreted as involving radical intermediates. Nucleophilic attack by $(\text{CF}_3)_2\text{N}^-$ would lead to a predominance of the isomer $(\text{CF}_3)_2\text{N}\cdot\text{CF}_2\text{-CHFBr}$, since the olefin is known⁹ to be polarised as $\text{CHF}:\overset{\delta-}{\text{C}}\overset{\delta+}{\text{CF}_2}$ during ionic attack; the slow dark reaction is also at variance with known fast ionic additions. The 78 : 22 isomer distribution (Table I) is very similar to that found for $\text{CF}_3\cdot$ attack (80 : 20;⁹ 74 : 26¹⁰) or $\text{CH}_3\cdot\text{S}\cdot$ attack (75 : 25;¹¹ 78 : 22¹⁰), with similar predominance of attack on the CHF group.

Photochemical reaction of *N*-bromobistrifluoromethylamine with isopentane gave bistrifluoromethylamine (97%), and hydrogen bromide was not detected. This is clearly consistent with free-radical chain bromination *via* homolytic fission of *N*-bromo-compound followed by $(\text{CF}_3)_2\text{N}\cdot$ attack:

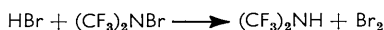


Hydrogen abstraction by the bromine atom would also give the $\cdot\text{CMe}_2\text{Et}$ radical and thence 2-bromo-2-methylbutane, with generation of a $(\text{CF}_3)_2\text{N}\cdot$ radical to begin a chain reaction of the above type:



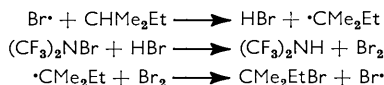
If this were the only means of interpreting the reaction, strong evidence would be available for the formation of $(\text{CF}_3)_2\text{N}\cdot$ radicals from *N*-bromobistrifluoromethylamine. However, two other explanations must be considered.

Hydrogen bromide liberated by bromine atom attack would be oxidised immediately to bromine, just as hydrogen chloride is oxidised to chlorine by *N*-chlorobistrifluoromethylamine:²

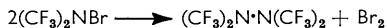


The bromine so produced could yield two bromine atoms on photolysis, each setting up a reaction sequence of the above type. This branching kinetic chain involving bromine atoms could play an important or dominant role in the formation of bistrifluoromethylamine, particularly if the kinetic reaction chain first considered, involving $(\text{CF}_3)_2\text{N}\cdot$ as chain carrier, is short. Both schemes require that $(\text{CF}_3)_2\text{N}\cdot$ radicals are generated and that they can abstract hydrogen from isopentane, and hence support the postulate that homolytic *N*-Br fission occurs during the olefin addition reactions.

However, the following third reaction scheme can account for the products without formation of $(\text{CF}_3)_2\text{N}\cdot$ radicals to any significant extent. If the $\cdot\text{CMe}_2\text{Et}$ radical, generated by bromine atom attack as above, has a marked preference to abstract a bromine atom from a bromine molecule rather than from *N*-bromobistrifluoromethylamine, a long kinetic chain for the sequence:



would account for the high yield of $(\text{CF}_3)_2\text{NH}$ and absence of hydrogen bromide. The low initial concentration of bromine atoms required to initiate this sequence could arise by photolysis of hydrogen bromide, which may be present by reaction of the *N*-bromo-amine with traces of moisture in the reaction vessel, or by initial photolysis of the *N*-bromo-compound. Photolytic decomposition of the type:

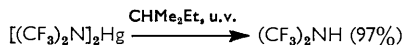


⁹ R. N. Haszeldine and B. R. Steele, *J.*, 1957, 2800.

¹⁰ R. N. Haszeldine and B. Higginbottom, unpublished results.

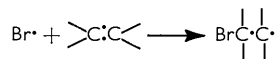
cannot play a major role, since 97% of the $(\text{CF}_3)_2\text{N}$ groups are accounted for as bistrifluoromethylamine, and tetrakis(trifluoromethyl)hydrazine was not detected as a product. Similarly, loss of $(\text{CF}_3)_2\text{N}\cdot$ radicals by dimerisation cannot occur to any extent.

The photochemical reaction products of *N*-bromobistrifluoromethylamine with isopentane thus do not prove conclusively that homolytic fission of the N-Br bond occurs and that the $(\text{CF}_3)_2\text{N}\cdot$ radical is the chain carrier. However, the fact that $(\text{CF}_3)_2\text{N}\cdot$ radicals are efficient in abstracting hydrogen from isopentane (shown by the following):



and with no loss of $(\text{CF}_3)_2\text{N}\cdot$ radicals by dimerisation, together with the observation⁴ that photolysis of *N*-bromobistrifluoromethylamine alone yields tetrakis(trifluoromethyl)hydrazine, presumably by dimerisation of $(\text{CF}_3)_2\text{N}\cdot$ radicals, gives support to the postulate of free radicals as intermediates in the isopentane reaction with $(\text{CF}_3)_2\text{N}\cdot$ as the chain carrier. The conditions used, the high yields, and the products, are certainly not consistent with heterolytic N-Br fission followed by nucleophilic attack by $(\text{CF}_3)_2\text{N}^-$ or electrophilic attack by Br^+ .

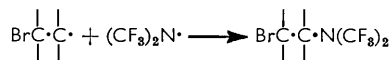
If the olefin addition reactions with *N*-bromobistrifluoromethylamine involve bromine atom attack



the next step would have to involve either a displacement reaction



unusual in radical chemistry,¹² or a highly specific radical combination



The radical-combination route seems unlikely, since the concentration of $(\text{CF}_3)_2\text{N}\cdot$ radicals must be very low, and tetrakis(trifluoromethyl)hydrazine is not formed during the successful addition reactions, yet the yields of 1 : 1 adducts are high.

If it is assumed that the olefin addition reactions with *N*-bromobistrifluoromethylamine involve $(\text{CF}_3)_2\text{N}\cdot$ attack, the qualitative relative reactivities: $\text{CF}_2\cdot\text{CF}_2$, $\text{CH}_2\cdot\text{CF}_2$, $\text{CH}_2\cdot\text{CH}_2$, $\text{CHF}\cdot\text{CHF} > \text{CHF}\cdot\text{CF}_2 > \text{CF}_3\cdot\text{CF}\cdot\text{CF}_2$, $\text{CF}_2\cdot\text{CFCl}$, $\text{CFCl}\cdot\text{CFCl} > \text{CF}_3\cdot\text{CF}\cdot\text{CF}\cdot\text{CF}_3$, $\overline{\text{CF}_2\cdot\text{CF}\cdot\text{CF}\cdot\text{CF}_2}$ are in agreement with those observed for other free-radical additions to these olefins. The difficulty of radical addition to olefins containing the $-\text{CF}_2\cdot\text{CF}\cdot\text{CF}\cdot\text{CF}_2-$ unit, noted earlier,¹¹ leads to the formation of the olefin dibromide by dimerisation of the $(\text{CF}_3)_2\text{N}\cdot$ radical and formation of free bromine which is known to brominate these olefins under free-radical conditions.^{7,13} Control reactions with hexafluorocyclobutene confirmed the ready bromination and showed also that tetrakis(trifluoromethyl)hydrazine would not add photochemically to this olefin.

Radical electrophilicity. It is tempting to argue that the exclusive one-way addition of *N*-bromobistrifluoromethylamine to hexafluoropropene implies that the $(\text{CF}_3)_2\text{N}\cdot$ radical is less electrophilic than the $\text{CF}_3\cdot$, $\text{MeSiH}_2\cdot$, $\text{SiH}_3\cdot$, $\text{CF}_3\cdot\text{CH}_2\cdot\text{S}$, $\text{PH}_2\cdot$, or $\text{SF}_5\cdot$ radicals, which attack the CF_2 group in $\text{CF}_3\cdot\text{CF}\cdot\text{CF}_2$ to the extent of 80, 76, 60, 70, 45, 66, and 50%, respectively,^{5,14,15} during radical addition reactions. In this sense, the $(\text{CF}_3)_2\text{N}\cdot$ radical would be comparable with the $\text{Me}_3\text{Si}\cdot$, $\text{Me}_2\text{SiH}\cdot$, and $\text{MeS}\cdot$ radicals,⁵ with 96, 95, and 91%

¹¹ J. F. Harris and F. W. Stacey, *J. Amer. Chem. Soc.*, 1961, **83**, 840.

¹² C. Walling, "Free Radicals in Solution," Wiley, New York, 1957, p. 240.

¹³ T. J. Brice, J. D. LaZerte, L. J. Hals, and W. H. Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 2698.

¹⁴ R. N. Haszeldine, *J.*, 1953, 3559; J. Brown and R. N. Haszeldine, unpublished results.

¹⁵ J. R. Case, N. H. Ray, and H. L. Roberts, *J.*, 1961, 2070.

addition to the $\overset{\cdot}{\text{C}}\text{F}_2$ of hexafluoropropene, respectively. That this picture is oversimplified is immediately shown by the results with the olefin $\overset{\delta-}{\text{C}}\text{H}\text{F}:\overset{\delta+}{\text{C}}\text{F}_2$, since, as noted earlier, $(\text{CF}_3)_2\text{N}\cdot$ addition to the CF_2 group occurs to much the same extent as does $\text{CF}_3\cdot$ addition. Other factors, *e.g.*, differences in the steric requirements of the radicals and of the olefins, make such comparisons of radical electrophilicity dangerous, particularly when the lone electron is located on quite different atoms—carbon, nitrogen, sulphur, silicon, etc.

The photochemical reaction of *N*-chlorobistrifluoromethylamine with chlorotrifluoroethylene gave complex products from which a 1 : 1 adduct could not be isolated. Since free chlorine, 1,2,2-trichlorotrifluoroethane, and tetrakis(trifluoromethyl)hydrazine were not detected, it is clear that both $(\text{CF}_3)_2\text{N}\cdot$ radicals and chlorine atoms attack the olefin, and the complex products arise through telomerisation encouraged by increased difficulty in chain transfer by attack on the *N*-halogen bond.

EXPERIMENTAL

The olefins were prepared and purified by known methods, or were commercial samples adequately purified. The *N*-halogenobistrifluoromethylamines react with mercury and with moisture, and were therefore manipulated in a special vacuum system and stored in sealed Pyrex ampoules in the dark. All reaction vessels were thoroughly dried, but nevertheless small amounts of bistrifluoromethylamine and perfluoro(methylenemethylamine) were often found to be present in the reaction products.

Reactions were carried out in 300-ml. Dreadnought tubes, and products were separated by distillation *in vacuo* into a low-boiling olefin fraction and a 1 : 1-adduct fraction, both of which were analysed by gas-liquid chromatography (g.l.c.), infrared (i.r.) spectroscopy, and mass spectrometry (A.E.I. M.S.2H instrument). Perkin-Elmer 154B or 451 instruments were used for gas-liquid chromatography, and were calibrated with known mixtures of pure compounds, with nitrogen as carrier gas. The 2 m. \times 4 mm. i.d., columns were packed with dodecyl phthalate (30%) on Celite and were operated at 100° for analysis of the 1 : 1-adduct fraction, and were packed with Fluorolube (30%) on Celite and operated at room temperature for analysis of the olefin fractions; 4 m. \times 4 mm. i.d., columns packed with dodecyl phthalate (30%) and operated at room temperature were also used for the olefin analysis. The g.l.c. trace for the 1 : 1-adduct fraction normally showed only two minor peaks (total <1% by area; one of them attributed to the dibromide of the olefin) other than the 1 : 1-adduct peak; purification was effected by repeated distillation or by g.l.c.

N-Bromobistrifluoromethylamine.—Carbon tetrachloride (75 ml.), bromine (19.0 g., 0.119 mole), and mercuric bistrifluoromethylamide³ (31.6 g., 0.063 mole), sealed in a 350-ml. Dreadnought tube and shaken for 1 hr. at 20° gave a volatile fraction (*ca.* $\frac{1}{3}$ of the total volume) which was stripped from the solvent by condensation *in vacuo* into a trap cooled to -196° , then distilled through a 15-cm. glass-helices-packed column to give *N*-bromobistrifluoromethylamine (27.1 g., 0.117 mole, 98%), b. p. 21.5—22.5° (lit.,³ 22°). Its i.r. spectrum was identical with that reported,³ except that the 9.80- μ band, described as a main band, was weak.

Reaction of N-Bromobistrifluoromethylamine.—(a) *With tetrafluoroethylene.* The bromo-compound (2.85 g., 12.3 mmoles) and olefin (2.66 g., 26.6 mmoles), shaken in daylight at 25° (0.5 hr.) gave unchanged olefin, 2-bromotetrafluoroethylbistrifluoromethylamine (3.89 g., 11.8 mmoles, 96%) (Found: C, 14.7; N, 4.3%; *M*, 332. Calc. for $\text{C}_4\text{BrF}_{10}\text{N}$: C, 14.5; N, 4.2%; *M*, 332), and a fraction (<1%) containing 1,2-dibromotetrafluoroethane.

(b) *With 1,1-difluoroethylene.* The bromo-compound (3.91 g., 16.9 mmoles) and 1,1-difluoroethylene (1.87 g., 29.2 mmoles) treated as in (a), gave unchanged olefin and 2-bromo-2,2-difluoroethylbistrifluoromethylamine (4.72 g., 16.0 mmoles, 95%) (Found: C, 16.3; H, 0.7; N, 4.9%; *M*, 295. $\text{C}_4\text{H}_2\text{BrF}_8\text{N}$ requires C, 16.3; H, 0.7; N, 4.7%; *M*, 296).

(c) *With ethylene.* The olefin (0.56 g., 20.1 mmoles) and the bromo-compound (4.04 g., 17.4 mmoles) similarly gave unchanged olefin, 2-bromoethylbistrifluoromethylamine (4.33 g., 16.6 mmoles, 95%) (Found: C, 18.7; H, 1.4; N, 5.2%; *M*, 260. Calc. for $\text{C}_4\text{H}_4\text{BrF}_6\text{N}$: C, 18.5; H, 1.5; N, 5.4%; *M*, 260), and traces of ethylene dibromide.

(d) *With cis-1,2-difluoroethylene.* Free-radical reaction of hydrogen bromide with trifluoroethylene gave the isomers $\text{CHF}_2\cdot\text{CHFBr}$ and $\text{CH}_2\text{F}\cdot\text{CF}_2\text{Br}$ in 98% yield; ⁹ dehalogenation gave *cis*- and *trans*-1,2-difluoroethylene, which on distillation yielded pure *cis*-1,2-difluoroethylene

(42%). The olefin (2.29 g., 35.7 mmoles) and *N*-bromobistrifluoromethylamine (7.00 g., 30.2 mmoles) reacted to give unchanged olefin and 2-bromo-1,2-difluoroethylbistrifluoromethylamine (8.58 g., 29.0 mmoles, 96%) (Found: C, 16.3; H, 0.7; N, 4.5%; *M*, 296. $C_4H_2BrF_8N$ requires C, 16.3; H, 0.7; N, 4.7%; *M*, 296).

(e) *With trifluoroethylene*. The bromo-compound (3.03 g., 13.1 mmoles) and trifluoroethylene (1.43 g., 17.4 mmoles), shaken at room temperature for 1 hr. gave unchanged olefin and a fraction of higher b. p. (3.91 g., 12.45 mmoles, 95%; *M*, 312) separated by g.l.c. into 2-bromo-1,1,2-trifluoroethylbistrifluoromethylamine (22% of the 1:1-adduct mixture) (Found: C, 15.5; H, 0.5; N, 4.6%; *M*, 313. C_4HBrF_9N requires C, 15.3; H, 0.3; N, 4.5%; *M*, 314) and 2-bromo-1,2,2-trifluoroethylbistrifluoromethylamine (78% of the 1:1-adduct mixture) (Found: C, 15.5; H, 0.4; N, 4.4%; *M*, 312).

A similar reaction mixture, kept in the dark at room temperature for 7 days, gave the 1:1-adduct mixture in 15% yield and with similar isomer ratio (23:77).

(f) *With chlorotrifluoroethylene*. The olefin (3.12 g., 26.7 mmoles) and the bromo-compound (3.16 g., 13.6 mmoles), shaken at 25° for 24 hr., gave an intense yellow solution, and reaction was therefore completed at 100° for 24 hr. to give (i) a mixture of unchanged olefin and *N*-bromo-compound (1.89 g., 15.3 mmoles; *M*, 123.5), (ii) 2-bromo-2-chlorotrifluoroethylbistrifluoromethylamine (4.36 g., 12.5 mmoles; 92%) (Found: C, 13.9; N, 3.9%; *M*, 349. C_4BrClF_9N requires C, 13.8; N, 4.0%; *M*, 348), and (iii) small amounts (1%) of materials with higher b. p.

(g) *With 1,2-dichlorodifluoroethylene*. The olefin (3.56 g., 26.8 mmoles), prepared as a *cis-trans* mixture by dechlorination of tetrachloro-1,2-difluoroethane, and the bromo-compound (2.95 g., 12.7 mmoles), heated at 100° for 24 hr., gave unchanged olefin and 2-bromo-1,2-dichlorodifluoroethylbistrifluoromethylamine (4.27 g., 11.7 mmoles, 92%) (Found: C, 13.2; N, 3.6%; *M*, 362. $C_4BrCl_2F_8N$ requires C, 13.2; N, 3.8%; *M*, 365).

(h) *With hexafluoropropene*. The olefin (4.10 g., 27.3 mmoles) and the bromo-compound (3.54 g., 15.3 mmoles), kept at 100° for 24 hr., gave unchanged olefin contaminated by *N*-bromo-compound (2.52 g., 16.2 mmoles; *M*, 156) and 2-bromohexafluoropropylbistrifluoromethylamine (5.04 g., 13.2 mmoles, 86%) (Found: C, 15.7; N, 3.8%; *M*, 382. Calc. for $C_5BrF_{12}N$: C, 15.7; N, 3.7%; *M*, 382).

(i) *With hexafluorocyclobutene*. The olefin (5.87 g., 36.3 mmoles) and the bromo-compound (2.15 g., 9.3 mmoles) heated at 100° for 96 hr. gave 1,2-dibromohexafluorocyclobutane (0.62 g., 1.9 mmoles, 41%) (Found: *M*, 323. Calc. for $C_4Br_2F_6$: *M*, 322) and a fraction (7.36 g.) of lower b. p. containing unchanged olefin, *N*-bromo-compound, and tetrakis(trifluoromethyl)hydrazine. Removal of the bromo-compound with 30% aqueous sodium hydroxide and further chromatographic analysis of the residue (6.10 g., 36.1 mmoles; *M*, 169) showed that the mixture originally contained unchanged olefin (5.54 g., 34.2 mmoles, 94%), *N*-bromobistrifluoromethylamine (1.26 g., 5.4 mmoles, 43%), and tetrakis(trifluoromethyl)hydrazine (0.56 g., 1.90 mmoles; 40%).

(j) *With octafluorobut-2-ene*. The olefin (5.35 g., 26.7 mmoles), prepared by dechlorination of 2,3-dichloro-octafluorobutane in 95% yield, and the bromo-compound (2.68 g., 11.6 mmoles), kept at 100° for 48 hr., gave 2,3-dibromo-octafluorobutane (0.38 g., 1.10 mmoles, 19%; *M*, 358) and a yellow more-volatile mixture (7.60 g.) which was sealed in a 300-ml. silica tube and irradiated with u.v. light (Hanovia S 500 lamp at 6 in.) for 7 days, to give a further quantity of 2,3-dibromo-octafluorobutane (1.42 g., 3.9 mmoles, 67%; *M*, 364), unchanged olefin (4.32 g., 21.6 mmoles, 81%), unchanged *N*-bromo-compound, and tetrakis(trifluoromethyl)hydrazine (1.63 g., 5.3 mmoles, 91%).

Bromine (2.40 g., 15.0 mmoles) reacted with hexafluorocyclobutene (1.60 g., 10.0 mmoles) in a 200-ml. tube at 100° (96 hr.) to give the dibromide (2.51 g., 7.8 mmoles, 78%) and unchanged olefin (0.34 g., 2.1 mmoles, 21%). A similar reaction mixture gave a 91% yield of the dibromide on irradiation [see (j) above] for 16 hr.

Tetrakis(trifluoromethyl)hydrazine (2.63 g., 8.6 mmoles) and hexafluorocyclobutene (1.69 g., 10.4 mmoles) were recovered unchanged after being heated at 100° (96 hr.). Irradiation [see (j)] of the mixture in a 400-ml. silica tube for 42 days gave a 98% recovery of the hydrazine, a 74% recovery of hexafluorocyclobutene, and a solid (0.40 g.) which was partly soluble in acetone and contained only 0.7% nitrogen.

Reaction of N-Bromobistrifluoromethylamine with Isopentane.—The bromo-compound (1.87 g., 8.1 mmoles) and isopentane (0.73 g., 10.2 mmoles) irradiated [see (j)] in a 350-ml.

silica tube for 4 days gave (i) a mixture (1.60 g., 13.3 mmoles; *M*, 120) of bistrifluoromethylamine and isopentane containing a 97% yield of the amine, (ii) a fraction of higher b. p. (0.82 g., 5.7 mmoles) (Found: *M*, 144. Calc. for C₅H₁₁Br: *M*, 151) and (iii) a mixture (0.04 g., 0.50 mmoles) of carbonyl fluoride and silicon tetrafluoride.

TABLE 2
Vapour-pressure data

Compound	Range measured	A	B	<i>L_v</i>	<i>T</i>	B. p.
(CF ₃) ₂ N·CH ₂ ·CH ₂ Br	50—83°	7.394	—1620	7400	21.7	85.6 *
(CF ₃) ₂ N·CH ₂ ·CF ₂ Br	40—75	7.848	—1753	8030	22.7	79.9
(CF ₃) ₂ N·CHF·CHFBr	41—75	7.714	—1690	7730	22.1	76.4
(CF ₃) ₂ N·CHF·CF ₂ Br	28—59	8.143	—1766	8180	24.4	62.4
(CF ₃) ₂ N·CF ₂ ·CHFBr	35—69	7.674	—1664	7620	22.0	74.0
(CF ₃) ₂ N·CF ₂ ·CF ₂ Br	16—56	7.593	—1574	7210	21.6	60.9
(CF ₃) ₂ N·CF ₂ ·CFCIBr	56—91	7.599	—1730	7920	21.6	93.5
(CF ₃) ₂ N·CFCl·CFCIBr	85—121	7.657	—1904	8720	21.7	125.6
(CF ₃) ₂ N·CF ₂ ·CFBr·CF ₃	51—78	7.326	—1580	7230	20.4	82.2 †

* Lit.,⁴ b. p. ca. 141°. † Lit.,³ b. p. 84°.

TABLE 3
¹⁹F N.m.r. spectra: assignments and chemical shifts

Compound	Group 1			Group 2			Group 3		
	Type	Intensity	Shift	Type	Intensity	Shift	Type	Intensity	Shift
(CF ₃) ₂ N—CH ₂ —CH ₂ Br	Singlet	—	—19.5	—	—	—	—	—	—
(CF ₃) ₂ N—CH ₂ —CF ₂ Br	Triplet	6	—19.7	—	—	—	Triplet of triplets	2	—21.9
(CF ₃) ₂ N—CHF—CHFBr	Doublet of doublets	6	—21.4	Complex	1	68.6	Complex	1	66.1
(CF ₃) ₂ N—CHF—CF ₂ Br	Quartet	6	—21.8	Complex	1	87.0	Complex	2	—15.7
(CF ₃) ₂ N—CClF—CFCIBr	Triplet	6	—26.1	Complex	1	14.0	Complex	1	—15.9
(CF ₃) ₂ N—CF ₂ —CF ₂ Br	Triplet of triplets	6	—24.6	Quintet of triplets	2	13.6	Quintet of triplets	2	—11.4
(CF ₃) ₂ N—CF ₂ —CHFBr	Triplet of doublets	6	—22.0	Complex	2	15.5	Complex	1	78.8
(CF ₃) ₂ N—CF ₂ —CFCIBr	Quartet	6	—25.3	Complex	2	9.8	Complex	1	—5.6
(CF ₃) ₂ N—CF ₂ —CFBr·CF ₃ *	Quartet of quartets	6	—24.5	Complex	2	14.0	Complex	1	—15.9
(CF ₃) ₂ N—Cl	Singlet	—	—12.5	—	—	—	—	—	—
(CF ₃) ₂ N—Br	Singlet	—	—16.2	—	—	—	—	—	—

All shifts are in p.p.m. relative to external CF₃·CO₂H; negative values are to low field.

* The CF₃ group shows a quartet of septets, of intensity 3 and chemical shift —0.8.

Photolysis of Mercuric Bistrifluoromethylamide in Isopentane.—The mercurial (2.07 g., 4.1 mmoles) and isopentane (0.72 g., 10.0 mmoles), sealed in a 250-ml. silica tube and shaken and irradiated (Hanovia S 500 lamp) for 14 days, gave bistrifluoromethylamine (1.13 g., 7.4 mmoles, 97%), isopentane (0.50 g., 7.3 mmoles, 73%), unchanged mercurial (0.16 g., 0.30 mmoles, 8%), and a residual black tar.

N-Chlorobistrifluoromethylamine.—A mixture of carbon tetrachloride (85 ml.), chlorine (6.45 g., 90.9 mmoles), and mercuric bistrifluoromethylamide (24.6 g., 48.7 mmoles), shaken at 25° in sunlight, gave *N*-chlorobistrifluoromethylamine (16.6 g., 88.6 mmoles, 98%), b. p. —9° to —7° (lit.,³ —9°). The *N*-chloro-compound did not react appreciably, if at all, with mercury at 25°.

Irradiation [see (*j*)] of the *N*-chloro-compound (5.36 g., 28.6 mmoles) and chlorotrifluoroethylene (4.16 g., 35.7 mmoles) in a 300-ml. silica tube (5 hr.), gave a non-volatile residue (1.18 g.), a mixture of unchanged reactants (6.20 g., 39.0 mmoles; *M*, 159), and a fraction (1.98 g.), of higher b. p. shown by g.l.c. to contain at least six components.

Vapour-pressure Equations.—The constants A and B for the vapour-pressure equation $\log_{10} p$ (mm.) = A + B/T, the b. p., latent heat of vaporisation, L_V (cal. mole⁻¹), and Trouton's constant T (cal. mol.⁻¹ deg.⁻¹) for the olefin adducts are shown in Table 2.

Nuclear Magnetic Resonance Spectra.—The data in Tables 3 and 4 were recorded on an A.E.I. R.S.2 instrument (60 mc./sec.) with trifluoroacetic acid and tetramethylsilane as external references.

TABLE 4
¹H N.m.r. data

Compound	Type of band
(CF ₃) ₂ N·CH ₂ ·CH ₂ Br	Both complex *
(CF ₃) ₂ N·CH ₂ ·CF ₂ Br	Triplet
(CF ₃) ₂ N·CHF·CF ₂ Br	Doublet of triplets
(CF ₃) ₂ N·CHF·CHFBr	Both complex *
(CF ₃) ₂ N·CF ₂ ·CHFBr	Doublet of doublets of doublets

* Close absorption of both the hydrogen-containing groups.

¹⁹F Chemical shifts which have been established for various groups are as follows:

Group	Chemical shift (p.p.m.)	Reference
(CF ₃) ₂ N·C<	ca. -20	16, 17
>N·CF ₂ ·C<	8.6 to 51.1	16
CF ₃ ·C<	0.0 to -19.7	16
CFCIBr·C<	0.5	18
CHFBr·C<	71.5 to 75.5	18
(CF ₃) ₂ N·F	-4.3	17
CF ₂ Br·C<	-13.0 to -22.0	18

TABLE 5
Main mass-spectral bands

Compound	Ions		
	Mass	Intensity	Assignment
(CF ₃) ₂ N·CH ₂ ·CH ₂ Br	259, 261	1.5	Parent
	166	100	(CF ₃) ₂ N·CH ₂ ⁺
(CF ₃) ₂ N·CH ₂ ·CF ₂ Br	109, 107	22	CH ₂ ·CH ₂ Br ⁺
	216	41	(CF ₃) ₂ N·CH ₂ ·CF ₂ ⁺
	166	65	(CF ₃) ₂ N·CH ₂ ⁺
	143, 145	34	CH ₂ ·CF ₂ Br ⁺
(CF ₃) ₂ N·CFCI·CFCIBr	129, 131	8	CF ₂ Br ⁺
	218	18	(CF ₃) ₂ N·CFCI ⁺
	211, 213	11	CFCI·CFCIBr ⁺
	145, 147	9	CFCIBr ⁺
(CF ₃) ₂ N·CF ₂ ·CHFBr	132	12	CFCI·CFCI ⁺
	202	69	(CF ₃) ₂ N·CF ₂ ⁺
	184	5	C ₃ HF ₇ N ⁺
	161, 163	29	CF ₂ ·CHFBr ⁺
(CF ₃) ₂ N·CF ₂ ·CFBr·CF ₃	82	10.5	CF ₂ ·CHF ⁺
	229, 231	26	CF ₂ ·CFBr·CF ₃ ⁺
	202	52	(CF ₃) ₂ N·CF ₂ ⁺
	129, 131	16.5	CF ₂ Br ⁺
(CF ₃) ₂ N·CHF·CHFBr	216	31.5	(CF ₃) ₂ N·CHF·CHF ⁺
	184	69	(CF ₃) ₂ N·CHF ⁺
	143, 145	20	CHF·CHFBr ⁺
	234	6	(CF ₃) ₂ N·CHF·CF ₂ ⁺
(CF ₃) ₂ N·CHF·CF ₂ Br	161, 163	15.5	CHF·CF ₂ Br ⁺
	146	14	CF ₂ ·N·CHF·CF ₂ ⁺
	129, 131	4	CF ₂ Br ⁺
	82	7	CF ₂ ·CHF ⁺
	202	42	(CF ₃) ₂ N·CF ₂ ⁺
	181, 179	26	CF ₂ ·CF ₂ Br ⁺
(CF ₃) ₂ N·CF ₂ ·CFCI·Br	131, 129	13	CF ₂ Br ⁺
	268, 270	12	(CF ₃) ₂ N·CF ₂ ·CFCI ⁺
	202	29	(CF ₃) ₂ N·CF ₂ ⁺
	195, 197	27	CF ₂ ·CFCI·Br ⁺
	145, 147	13	CFCI·Br ⁺

¹⁶ N. Muller, P. C. Lauterbur, and G. F. Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1807.

¹⁷ Unpublished data from this department.

¹⁸ J. Lee and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1959, **55**, 880; *ibid.*, 1958, **54**, 308.

Mass-spectral Data.—The intensities in the data shown in Table 5 are all relative to CF_3^+ intensity 100, except for the first compound.

The mass spectrum of the compound $(\text{CF}_3)_2\text{N}\cdot\text{CF}_2\cdot\text{CFBr}\cdot\text{CF}_3$ showed a strong peak which could be attributed to CF_2Br^+ , but since this peak also appears weakly in the spectra of the compounds $(\text{CF}_3)_2\text{N}\cdot\text{CFCl}\cdot\text{CFClBr}$ and $(\text{CF}_3)_2\text{N}\cdot\text{CF}_2\cdot\text{CFClBr}$, it is believed to arise *via* rearrangement in the spectrometer. The mass spectrum of compound $(\text{CF}_3)_2\text{N}\cdot\text{CHF}\cdot\text{CF}_2\text{Br}$ did not show a peak due to $(\text{CF}_3)_2\text{N}\cdot\text{CHF}^+$, unlike compound $(\text{CF}_3)_2\text{N}\cdot\text{CHF}\cdot\text{CHFBr}$ but quantitative dehydrobromination of the first compound to the vinylamine $(\text{CF}_3)_2\text{N}\cdot\text{CF}\cdot\text{CF}_2$ ¹⁹ proved its structure without doubt.

Infrared Spectra.—The spectra of the 1 : 1 adducts all showed a strong band between 9·9 and 10·3 μ assigned²⁰ to C-N stretching in the $(\text{CF}_3)_2\text{N}$ group: $(\text{CF}_3)_2\text{N}\cdot\text{CH}_2\cdot\text{CF}_2\text{Br}$, 10·10; $(\text{CF}_3)_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, 9·92; $(\text{CF}_3)_2\text{N}\cdot\text{CHF}\cdot\text{CF}_2\text{Br}$, 10·12; $(\text{CF}_3)_2\text{N}\cdot\text{CHF}\cdot\text{CHFBr}$, 10·30; $(\text{CF}_3)_2\text{N}\cdot\text{CF}_2\cdot\text{CF}_2\text{Br}$, 10·10; $(\text{CF}_3)_2\text{N}\cdot\text{CFCl}\cdot\text{CFClBr}$, 10·10; $(\text{CF}_3)_2\text{N}\cdot\text{CF}_2\cdot\text{CFClBr}$, 10·12; $(\text{CF}_3)_2\text{N}\cdot\text{CF}_2\cdot\text{CHFBr}$, 10·09; $(\text{CF}_3)_2\text{N}\cdot\text{CF}_2\cdot\text{CFBr}\cdot\text{CF}_3$, 10·11 μ .

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¹⁹ R. N. Haszeldine and A. E. Tipping, unpublished results.

²⁰ J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1960, **82**, 396.