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Fluorinated Acetylenes. Part I. The Preparation of NN-Bistrifluoromethylethynylamines

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NN-Bistrifluoromethylethynylamine, (CF₃)₉N·CCH, has been prepared in high yield by the reaction of N-bromobistrifluoromethylamine with acetylene, followed by dehydrobromination of the resultant 1 : 1-adduct, 2-bromo-NN-bistrifluoromethylvinylamine. The bromination of bistrifluoromethylvinylamine to give 1,2-dibromo-NNbistrifluoromethylethylamine and the dehydrobromination of this adduct, by way of the olefin 1-bromo-NN-bis trifluoromethylvinylamine, also gives the acetylene. N-Bromobistrifluoromethylamine reacts with NN-bistrifluoromethylethynylamine to give 1,2-di(bistrifluoromethylamino)-1-bromoethylene, (CF₃)₂N·CBr:CH·N(CF₃)₂, and this on dehydrobromination gives perfluoro-1,2-bisdimethylaminoacetylene in good yield. The thermal reaction of trifluoroiodomethane with NN-bistrifluoromethylethynylamine gives a mixture of cis- and trans-3,3,3-trifluoro-1-iodo-NN-bistrifluoromethylprop-1-enylamine which dehydroiodinates readily to 3,3,3-trifluoro-NN-bistrifluoromethylprop-1-ynylamine. Other routes to this latter acetylene, which involve the preparation of 3,3,3-trifluoro-NN-bistrifluoromethylprop-1-enylamine, were also investigated, but these were less satisfactory.

ACETYLENES which contain an amino- or substituted amino-group attached to the unsaturated centre have been little investigated. However, the reactions of lithio-dialkylamines with (i) alkoxyacetylenes,¹ (ii) unsaturated or saturated halogenohydrocarbons,² and (iii) phenyl halogenoacetylenes,³ have all been reported to give the corresponding aminoacetylenes, e.g.

> $R^{2}CC^{2}C^{2} + LiNR^{1} \rightarrow R^{2}CC^{2}C^{2}NR^{1}_{2}$ (where R^1 and R^2 are alkyl)

 $Bu^{t}CHBr \cdot CHFBr + LiNMe_{2} \longrightarrow Bu^{t}C:C \cdot NMe_{2}$

 $PhC:CCl + LiNR_2 \longrightarrow PhC:C·NR_2$

Treatment of NN-disubstituted amides with phosphorus pentachloride⁴ and dehalogenation of vicinal dihalides ⁵ have also been used to prepare amino-acetylenes, e.g.

 $Et_2N \cdot CO \cdot CH_2Br + PCl_5 \longrightarrow Et_2N \cdot CCBr$ Et_2N ·CCl:CClPh + BuⁿLi \longrightarrow Et_2N·C:CPh

At the present time few reactions of these compounds have been reported.

In the present work, various routes to the acetylenes $(CF_3)_2 N \cdot C:CH$ $(CF_3)_2$ N·C·C·CF₃ (I), (II), and $(CF_3)_2 N \cdot C: C \cdot N(CF_3)_2$ (III) have been investigated.

NN-Bistrifluoromethylethynylamine (I).--Two routes were investigated for the preparation of this compound:

(a)
$$(CF_3)_2 N \cdot CH: CH_2 \xrightarrow{Br_2} (CF_3)_2 N \cdot CHBr \cdot CH_2 Br \xrightarrow{KOH} (CF_3)_2 N \cdot CBr: CH_2 \xrightarrow{KOH} (CF_3)_2 N \cdot C: CH (IV)$$
 (I)

(b)
$$(CF_3)_2NBr + HC:CH \longrightarrow (CF_3)_2N\cdotCH:CHBr \longrightarrow (CF_3)_2N\cdotC:CH$$

In sequence (a), NN-bistrifluoromethylvinylamine was made in high yield (99%) by the dehydrobromination of the 1: 1-adduct (CF₃)₂N·CH₂·CH₂Br⁶ formed from the reaction of N-bromobistrifluoromethylamine with ethylene.^{7,8} Bromination of the vinylamine in daylight gave the dibromide (99%) and this compound when heated

- Union Carbide Corporation, Neth Pat. 6,415,095/1965.
- ³ Union Carbide Corporation, Neth. Pat. 6,415,094/1965.
- 4 Yu. Yu. Tsmur, Byul. Izobret., 1964, 22, 23.

under reflux over powdered potassium hydroxide gave 1-bromo-NN-bistrifluoromethylvinylamine (IV) (75%) and the acetylene (I) (19%). Further treatment of the olefin (IV) with potassium hydroxide gave (I) (94%).

In sequence (b) the reaction of N-bromobistrifluoromethylamine with acetylene has been reported⁷ to give 2-bromo-NN-bistrifluoromethylethenylamine. We found that these reactants in daylight give a mixture (96%) of two 1: 1-adducts with the *trans*-isomer as the major product (trans: cis, 72:28). The reaction of N-bromobistrifluoromethylamine with olefins in light or when heated has been reported ⁸ to be a free-radical reaction and the trans-isomer should predominate if any stereospecificity of addition occurs owing to the bulky substituents in the adduct or a rapid chain-transfer reaction.

$$(CF_{3})_{2}NBr \longrightarrow (CF_{3})_{2}N + Br + (CF_{3})_{2}N + HC:CH \longrightarrow (CF_{3})_{2}N + HC:CH \xrightarrow{(CF_{3})_{2}NBr} + + HC:CH \xrightarrow{(CF_{3})_{2}$$

Dehydrobromination of the mixture of cis- and trans-2-bromo-NN-bistrifluoromethylethenylamine with potassium hydroxide gave (I) (92%).

Thus, both routes were satisfactory for the preparation of acetylene (I), and sequence (b), because it is shorter was used for subsequent preparations.

3,3,3-Trifluoro-NN-bistrifluoromethylprop-1-ynylamine (II).—Three routes were investigated:

(a)
$$(CF_3)_2 N \cdot CH: CH_2 \xrightarrow{CF_3I} (CF_3)_2 N \cdot CHI \cdot CH_2 \cdot CF_3 \xrightarrow{KOH}$$

 $(CF_3)_2 N \cdot CH: CH \cdot CF_3 \xrightarrow{Br_2} (CF_3)_2 N \cdot CHBr \cdot CHBr \cdot CF_3 \xrightarrow{KOH}$
 $(CF_3)_2 N \cdot CBr: CH \cdot CF_3 \xrightarrow{KOH}$
 $(CF_3)_2 N \cdot CH: CBr \cdot CF_3 \xrightarrow{KOH}$ (II)

⁵ J. Ficini and C. Barbara, Bull. Soc. chim. France, 1964, 4, 871. ⁶ E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, J. Chem. Soc. (C), 1968, 796. ⁷ H. J. Emeléus and B. W. Tattershall, Z. anorg. Chem., 1964,

¹ P. P. Montijn, E. Harryvan, and L. Brandsma, Rec. Trav. chim., 1964, 83, 1211.

^{327, 147}

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

(b)
$$CF_3 \cdot CH:CH_2 \xrightarrow{(CF_4)_* NBr} \longrightarrow CF_3 \cdot CH:CH \cdot N(CF_3)_2 \xrightarrow{KOH} CF_3 \cdot CH:CH \cdot N(CF_3)_2$$

[and then as in (a)]
(c) $(CF_3)_2 N \cdot C:CH \xrightarrow{CF_4 I} (CF_3)_2 N \cdot CI:CH \cdot CF_3 \xrightarrow{KOH} (II)$

The addition of trifluoroiodomethane to bistrifluoromethylvinylamine at 200° gave a low yield (5%) of Dehydroiodination of the 1:1-adduct (V) with potassium hydroxide gave olefin (VII) (91%), identical with that formed in the above reactions and exclusively as one isomer (n.m.r.), with the bulky groups presumably oriented *trans* to each other. The olefin (VII) when treated with bromine under ionic conditions gave a dibromide (96%) (n.m.r. shows only one isomer). If olefin (VII) is indeed the *trans*-isomer, then ionic addition of bromine would give the *erythro*-dibromide.



1:1-adduct (V) and the major products were 3,3,3-trifluoro-NN-bistrifluoromethylpropylamine (VI) (46%) and 3,3,3-trifluoro-NN-bistrifluoromethylprop-1-enylamine (VII) (46%). The presence of the last two compounds in equimolar amounts can be explained in two ways: (i) the intermediate radical (VIII) disproportionates or (ii) the 1:1-adduct (V) initially formed eliminates hydrogen iodide to give olefin (VII) and the hydrogen iodide then reacts with undissociated (V) to produce the reduced compound (VI) and iodine.

$$CF_{3}I \xrightarrow{\Delta} CF_{3} \cdot + I \cdot$$

$$CF_{3} \cdot + (CF_{3})_{2}N \cdot CH:CH_{2} \longrightarrow$$

$$(CF_3)_2 N \cdot \dot{C} H \cdot CH_2 \cdot CF_3 \xrightarrow{CF_*I} (CF_3)_2 N \cdot CHI \cdot CH_2 \cdot CF_3$$
(VIII) (V)

$$\begin{array}{c} 2(CF_3)_2N \cdot \dot{C}H \cdot CH_2 \cdot CF_3 \longrightarrow \\ (CF_3)_2N \cdot CH_2 \cdot CH_2 \cdot CF_3 + (CF_3)_2N \cdot CH \cdot CH \cdot CF_3 \\ (VI) & (VII) \end{array}$$

However, when the adduct (V) was heated at 200° , only a small amount of decomposition occurred, and the adduct (90°_{0}) was recovered unchanged. The breakdown products contained olefin (VII) and an olefin with Treatment of this dibromide with potassium hydroxide gave the acetylene (II) (68%) and a mixture (19%) of the monobromo-olefins $CF_3 \cdot CBr: CH \cdot N(CF_3)_2$ and $CF_3 \cdot CH: CBr \cdot N(CF_3)_2$.

In sequence (b) the free-radical addition of N-bromobistrifluoromethylamine to 3,3,3-trifluoropropene went smoothly to give the 1 : 1 adduct $(CF_3)_2N\cdot CH_2\cdot CHBr\cdot CF_3$ (97%), but treatment of this product with potassium hydroxide gave only a low yield (6%) of the desired olefin (VII). The major products, 2-bromo-3,3-difluoro-NN-bistrifluoromethylprop-2-enylamine (IX) (24%) and 2-bromo-3,3,3-trifluoropropene (X) (34%), can be explained either by an E2 or by an E1 CB elimination reaction involving initial attack on the most acidic hydrogen atom, *i.e.* that in the \cdot CHBr·CF₃ group. In the case of the E1 CB mechanism the intermediate carbanion (XI) is stabilised by the -I effects of the bromine atom and the trifluoromethyl group.

$$(CF_3)_2N \cdot CH_2CHBr \cdot CF_3 \xrightarrow{OH^-} (CF_3)_2N \cdot CH_2 \cdot \overline{C}Br \cdot CF_3$$

(XI)

Decomposition of the carbanion then gives the observed major products.

$$(CF_{3})_{2}N \cdot CH_{2} \cdot \overbrace{CBr}^{\bullet} \cdot CF_{2} \cdot F \longrightarrow (CF_{3})_{2}N \cdot CH_{2} \cdot CBr : CF_{2} + F^{-}$$

$$(IX)$$

$$(CF_{3})_{2}N \cdot CH_{2} \cdot \overbrace{CBr}^{\bullet} \cdot CF_{3} \longrightarrow CH_{2} : CBr \cdot CF_{3} + (CF_{3})_{2}N^{-}$$

$$(X)$$

a band at 5.70 μ in its i.r. spectrum which could be due to the compound $(CF_3)_2$ N·CHI·CH:CF₂, formed by dehydrofluorination. Thus compounds (VI) and (VII) are probably formed in the original reaction by disproportionation of the intermediate radical (VIII).

A u.v.-initiated addition of trifluoroiodomethane to the vinylamine gave a higher yield (46%) of the 1 : 1-adduct (V), but compounds (VI) (22%) and (VII) (22%) were also formed.

This is the first time that elimination of a $(CF_3)_2N$ group has been observed in an attempted dehydrohalogenation reaction.

Sequence (c) was subsequently found to be the best of the three routes investigated. The thermally initiated addition of trifluoroiodomethane to the acetylene (I) gave a 1:1-adduct fraction (99%) shown by g.l.c. to consist of two components (1:1), the *cis*- and *trans*isomers (XIIa) and (XIIb).



Dehydroiodination of the mixture of olefins with potassium hydroxide went easily to give (II) (91%, 43%) conversion).

Perfluoro-1,2-bisdimethylaminoacetylene (III).— The acetylene was prepared in 94% overall yield by the free-radical addition of N-bromobistrifluoromethylamine to the acetylene (I) to give the adduct (XIII) (97%) followed by dehydrobromination.

$$(CF_{3})_{2}N \cdot (CF_{3})_{2}N \cdot \dot{C}:CH \longrightarrow \\ (CF_{3})_{2}N \cdot \dot{C}:CH \cdot N(CF_{3})_{2} \xrightarrow{(CF_{3})_{2}NBr} \rightarrow \\ (CF_{3})_{2}N \cdot CBr:CH \cdot N(CF_{3})_{2} \xrightarrow{KOH} (CF_{3})_{2}N \cdot C:C \cdot N(CF_{3})_{2} \\ (XIII)$$

The olefin (XIII) was shown to be exclusively one isomer (n.m.r.); this is presumably the one in which the aminogroups lie *trans* to each other.

Certain reactions of these acetylenes will be reported in due course.

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. N-Bromobistrifluoromethylamine, which reacts with mercury, was handled in a special vacuum apparatus attached to the main system. Reactions with this compound were carried out in carefully dried apparatus but the reaction products often contained small amounts of the hydrolysis products, bistrifluoromethylamine and perfluoro-2-azapropene. Products were separated either by repeated fractional distillation in vacuo or by preparativescale g.l.c. (Perkin-Elmer 116, 154B, or 451 Fraktometers). The identities of products were established by molecularweight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 56.46 Mc./sec. for ¹⁹F and 60.0 Mc./sec. for ¹H), mass spectrometry (A.E.I. MS/2H spectrometer with a resolution of 1 in 700). and g.l.c.

All reactions were carried out in Dreadnought tubes (300 ml.) unless stated to the contrary.

NN-Bistrifluoromethylvinylamine was prepared (93%) by the reaction of N-bromobistrifluoromethylamine with ethylene and dehydrobromination of the resultant 2-bromo-NN-bistrifluoromethylethylamine.⁶

Reaction of NN-Bistrifluoromethylvinylamine with Bromine. —The olefin (2·20 g., 12·3 mmoles) and bromine (2·66 g., 16·6 mmoles) were sealed in a Pyrex ampoule (20 ml.) and shaken in daylight (4 hr.); the excess of bromine was destroyed by shaking in vacuo with mercury. The products were (i) unchanged olefin (0·20 g., 1·1 mmoles, 9%) and (ii) 1,2-dibromo-NN-bistrifluoromethylethylamine (3·75 g., 11·1 mmoles, 99%) (Found: C, 14·4; H, 1·1; N, 4·4%; M, 336. $C_4H_3Br_2F_6N$ requires C, 14·2; H, 0·9; N, 4·1%; M, 339), b.p. 130·5—131·5°/749 mm.

Reaction of 1,2-Dibromo-NN-bistrifluoromethylethylamine

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with Potassium Hydroxide.—The dibromide (2·43 g., 7·20 mmoles), heated under reflux in vacuo over an excess of dry, powdered potassium hydroxide (30 min.), gave (i) unchanged dibromide (0·35 g., 1·03 mmoles, 14%), (ii) 1-bromo-NN-bistrifluoromethylvinylamine (IV) (1·20 g., 4·65 mmoles, 75%) (Found: C, 18·9; H, 0·9; N, 5·5%; M, 259. C₄H₂BrF₆N requires C, 18·6; H, 0·8; N, 5·4%; M, 258), and (iii) NN-bistrifluoromethylethynylamine (I) (0·21 g., 1·20 mmoles, 19%) (Found: C, 27·0; H, 0·6; N, 8·2%; M, 178. C₄HF₆N requires C, 27·1; H, 0·6; N, 7·9%; M, 177).

Reaction of 1-Bromo-NN-bistrifluoromethylvinylamine with Potassium Hydroxide.—The bromo-olefin (2.85 g., 11.0 mmoles), heated under reflux in vacuo over an excess of dry, powdered potassium hydroxide (0.75 hr.), gave (i) unchanged olefin (0.20 g., 0.78 mmole, 7%) and (ii) (I) (1.70 g., 9.6 mmoles, 94%).

Reaction of N-Bromobistrifluoromethylamine with Acetylene. —The N-bromo-amine (1.89 g., 8.13 mmoles) and acetylene (0.65 g., 25.0 mmoles) reacted in the vapour phase in a Pyrex flask (3 l.) at room temperature in daylight (3 days) to give (i) unchanged acetylene (0.45 g., 17.2 mmoles, 69%) and (ii) a higher-boiling fraction (2.01 g., 7.8 mmoles, 96%), separated by g.l.c. (2 m. dodecylphthalate at 88°) into two components: trans-2-bromo-NN-bistrifluoromethylethenylamine (1.45 g., 5.72 mmoles, 69%) (Found: C, 18.9; H, 1.0; N, 5.2%; M, 260. C₄H₂BrF₆N requires C, 18.6; H, 0.8; N, 5.4%; M, 258) and cis-2-bromo-NN-bistrifluoromethylethenylamine (0.56 g., 2.08 mmoles, 27%) (Found: C, 18.9; H, 1.0; N, 5.1%; M, 257).

Reactions of cis- and trans-2-Bromo-NN-bistrifluoromethylethenylamine with Potassium Hydroxide.—The bromo-compound (1.81 g., 7.02 mmoles), heated under reflux in vacuo over an excess of dry, powdered potassium hydroxide (20 min.), gave (I) (1.14 g., 6.45 mmoles, 92%) (Found: M, 178. Calc. for C₄HF₆N: M, 177).

Reaction of Trifluoroiodomethane with NN-Bistrifluoromethylvinylamine.--(a) Thermal. The olefin (1.90 g., 10.6 mmoles) and trifluoroiodomethane (8.82 g., 45.0 mmoles) were heated at 205° (22 hr.); the iodine formed in the reaction was removed by shaking with mercury. The products were (i) unchanged trifluoroiodomethane (6.50 g., 33.2 mmoles, 73%) shown by its i.r. spectrum to be contaminated with a small amount of trifluoromethane, (ii) a compound later identified as the 1:1-adduct, 3,3,3-trifluoro-1-iodo-NN-bistrifluoromethylpropylamine (0.20 g., 0.54 mmole, 5%), and (iii) a mixture (2.43 g., 9.8 mmoles; M, 248) separated by g.l.c. (4 m. silicone oil at 40°) into two com-3,3,3-trifluoro-NN-bistrifluoromethylprop-1-enylponents: amine (VII) (1.21 g., 4.9 mmoles, 46%) (Found: C, 24.4; H, 0.85; N, 5.7%; M, 245. C₅H₂F₉N requires C, 24.3; H, 0.8; N, 5.7%; M, 247) and 3,3,3-trifluoro-NN-bistrifluoromethylpropylamine (VI) (1.22 g., 4.9 mmoles, 46%) (Found: C, 23.9; H, 1.7; N, 5.4%; M, 246. C₅H₄F₉N requires C, 24.1; H, 1.6; N, 5.6%; M, 249).

(b) *Photolytic.* The olefin (1.82 g., 10.16 mmoles) and trifluoroiodomethane (2.52 g., 12.85 mmoles) were sealed in a silica tube (200 ml.) and irradiated at a distance of 6 in. from a Hanovia S. 500 lamp (72 hr.); the products were shaken with mercury to remove iodine. The products were (i) unchanged trifluoroiodomethane (0.75 g., 3.83 mmoles, 30%), (ii) a mixture shown by g.l.c. (4 m. silicone oil at 40°) to consist of (VII) (0.553 g., 2.24 mmoles, 22%) and (VI) (0.558 g., 2.24 mmoles, 22%), and (iii) 3,3,3-tri-fluoro-1-iodo-NN-bistrifluoromethylpropylamine (V) (1.75 g., 4.67 mmoles, 46%) (Found: C, $16\cdot3$; H, 0.9; N, $3\cdot6\%$;

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M, 374. C₅H₃F₉IN requires C, 16.0; H, 0.8; N, 3.7%; M, 375), b.p. (Siwoloboff) 111°/753 mm. A small amount of an involatile residue remained in the reaction tube; this was not examined further.

Pyrolysis of 3,3,3-Trifluoro-1-iodo-NN-bistrifluoromethylpropylamine.—The iodo-amine (0.078 g., 0.208 mmole), sealed in a Pyrex ampoule (5 ml.) and heated at 205° (21 hr.), gave (i) unchanged iodo-amine (0.071 g., 0.188 mmole, 90%), (ii) a fraction (0.032 g.) shown by g.l.c. (2 m. dodecylphthalate at 100°) to contain (VII) and an unknown component in the ratio 2:1, and (iii) traces of more volatile material. The i.r. spectrum of the mixture showed all the bands of (VII) and in addition a band at 5.70 μ (C=C str.).

Reaction of 3,3,3-Trifluoro-1-iodo-NN-bistrifluoromethylpropylamine with Potassium Hydroxide.—The iodo-amine (1·22 g., 3·26 mmoles), heated under reflux in vacuo over an excess of dry, powdered potassium hydroxide (30 min.), gave (VII) (0·73 g., 2·96 mmoles, 91%).

Reaction of Bromine with 3,3,3-Trifluoro-NN-bistrifluoromethylprop-1-enylamine.—The olefin (0.55 g., 2.23 mmoles), bromine (0.80 g., 5.0 mmoles), and aluminium tribromide (0.1 g.) were sealed in a Pyrex tube (10 ml.) and shaken in fluoromethylpropylamine (2·20 g., 6·7 mmoles, 97%) (Found: C, 18·5; H, 1·0; N, 4·4%; M, 330. $C_5H_3BrF_9N$ requires C, 18·3; H, 0·9; N, 4·3%; M, 328); g.l.c. (4 m. Kel-F oil at 90°) showed only one peak.

Reaction of 2-Bromo-3,3,3-trifluoro-NN-bistrifluoromethylpropylamine with Potassium Hydroxide.—The amine (5.61 g., 17.1 mmoles), heated under reflux in vacuo over an excess of dry, powdered potassium hydroxide (20 min.), gave (i) a mixture (2.50 g., 7.8 mmoles) separated by g.l.c. (5 m. silicone 10 oil at 95°) into two components: unchanged amine (1.62 g., 4.9 mmoles, 29%) and 2-bromo-3,3-difluoro-NN-bistrifluoromethylprop-2-enylamine (IX) (0.88 g., 2.9 mmoles, 24%) (Found: C, 19.75; H, 0.9; N, 4.2%; M, 307. $C_5H_2BrF_8N$ requires C, 19.5; H, 0.7; N, 4.5%; M, 308), (ii) (VII) (0.18 g., 0.73 mmole, 6%) (Found: M, 245. Calc. for C₅H₂F₂N: M, 247), and (iii) 2-bromo-3,3,3-trifluoropropene (X) ⁹ (0.72 g., 4.1 mmoles, 34%) (Found: C, 20.7; H, 1.1%; M, 175. Calc. for C₃H₂BrF₃: C, 20.6; H, 1.1%; M, 175); λ_{max} 3·23vw (C-H str.), 6·13m (C=C str.), 7·00m (C-H bend), 7·24m, 7·60s, 7·84vs, 8·48vs, and 9·22s (C-F str.), 10.70m, 10.78m and 12.00m, and 14.32m (CF₃ def.) µ; principal mass spectral peaks at m/e 176, 174 (base peak,

TABLE 1

Vapour pressure data

Range

	measured	А	В	L _v	Т	B.p.
(CF _a) _a N·C:CH	-44 to -2°	7.793	-1361	6230	$22 \cdot 5$	4 ∙0°
(CF ₃), N·C·C·CF ₃	4 - 20	7.281	-1302	5960	$20 \cdot 1$	$23 \cdot 0$
(CF_{3}) , $N \cdot C \cdot C \cdot N(CF_{3})$,	32 - 55	7.965	-1676	7670	$23 \cdot 3$	56.6
$(CF_3)_2 N \cdot CH: CH \cdot CF_3$ (trans)	14 - 46	7.460	-1471	6760	21.1	48.2
(CF ₃) ₂ N·CH ₂ ·CBr:CF ₂	63 - 94	7.635	-1765	8080	$21 \cdot 8$	98.2
(CF ₃),N·CBr·CH,	15 - 54	8.018	-1714	7850	23.5	60.7
(CF ₃), N·CH:CHBr (trans)	41 - 68	7.431	-1569	7180	20.8	71.8
(CF ₃), N·CH:CHBr (cis)	41 - 73	7.301	-1552	7100	20.2	78.1
$(CF_3)_{2}^{\circ}N \cdot CBr : CH \cdot N(CF_3)_{2}$ (trans)	75 - 98	7.391	-1683	7700	20.6	100.1
$(CF_3)_{\circ}N \cdot CI:CH \cdot CF_3(cis)$	7093	7.327	-1636	7490	20.3	$95 \cdot 1$
(CF ₃), N·CI:CH·CF ₃ (trans)	72 - 95	7.799	-1826	8360	$22 \cdot 5$	98 ·1
(CF ₃) ₂ N·CH ₃ ·CH ₃ ·CF ₃	17 - 60	7.726	-1622	7420	$22 \cdot 3$	61.8
$(CF_3)_2$ N·CH ₂ ·CHBr·CF ₃	69-92	7.732	-1785	8170	$22 \cdot 2$	95.2

the dark (12 hr.), and the excess of bromine was destroyed with mercury. The product was erythro-1,2-dibromo-3,3,3-trifluoro-NN-bistrifluoromethylpropylamine (0.87 g., 2.14 mmoles, 96%) (Found: C, 14.9; H, 0.8%. C₅H₂Br₂F₉N requires C, 14.7; H, 0.5%), b.p. 130°/773 mm. (Siwoloboff).

Reaction of 1,2-Dibromo-3,3,3-trifluoro-NN-bistrifluoromethylpropylamine with Potassium Hydroxide.-The dibromide (0.84 g., 2.06 mmoles), heated under reflux over an excess of dry potassium hydroxide (15 min.), gave (i) 3,3,3-trifluoro-NN-bistrifluoromethylprop-1-ynylamine (II)(0.32 g., 1.31 mmoles, 68%) (Found: C, 24.2; N, 5.5%; M, 247: C₅F₉N requires C, 24.5; N, 5.7%; M, 245), (ii) unchanged dibromide (0.05 g., 0.12 mmole, 10%), and (iii) an intermediate fraction (0.12 g., 0.37 mmoles, 19%) (Found: M, 323. Calc. for C₅HBrF₉N: M, 326) consisting of 1-bromo-3,3,3-trifluoro-NN-bistrifluoromethylprop-1-envlamine and 2-bromo-3,3,3-trifluoro-NN-bistrifluoromethylprop-1-enylamine; λ_{max} 5.96m and 6.07m (C=C str.), 7.38vs, 7.90vs, 8.45vs, and 9.02m (C-F str.), 10.11s and 10.46m (C-N str.), 11.70m and 12.27m (C-N-C bend), and 13.65m (triplet) and 14.06m (CF₃ def.) μ .

Reaction of N-Bromobistrifluoromethylamine with 3,3,3-Trifluoropropene.—The N-bromo-amine (1.60 g., 6.9 mmoles) and 3,3,3-trifluoropropene (1.48 g., 15.4 mmoles), shaken in daylight (3 hr.), gave (i) unchanged olefin (0.83 g., 8.6 mmoles, 56%) and (ii) 2-bromo-3,3,3-trifluoro-NN-bistri M^+ , $C_3H_2BrF_3^+$), 157, 155 ($C_3H_2BrF_2^+$, 9.6%), 131, 129 ($CBrF_2^+$, 11.5%), 107, 105 ($C_2H_2Br^+$, 19.5%), 95 ($C_3H_2F_3^+$, 29%), 81, 79 (Br^+ , 4.3%), 75 ($C_3HF_2^+$, 9.8%), 69 (CF_3^+ , 38%), 31 (CF^+ , 4.2%), and 26 ($C_2H_2^+$, 4.2%); ¹H n.m.r. CF_3 H_a

bands for $\begin{array}{c} CF_3 \\ Br \end{array}$ $C:C \\ H_b \\ H_b \end{array}$ at $\tau 2.99$ (H_a, doublet of

quartets) and $3\cdot44$ (H_b, doublet of quartets), and 19 F n.m.r. band at $7\cdot9$ p.p.m. to low field from external CF₃·CO₂H (*J* H(a)H(b), $2\cdot7$; *J* H(a)F, $1\cdot0$; *J* H(b)F $1\cdot4$ c./sec.).

Reaction of Trifluoroiodomethane with NN-Bistrifluoromethylethynylamine.—Trifluoroiodomethane (7.62 g., 38.9 mmoles) and NN-bistrifluoromethylethynylamine (1.58 g., 8.95 mmoles), heated at 215° (22 hr.), gave (i) unchanged trifluoroiodomethane (6.23 g., 31.8 mmoles, 82%), (ii) unchanged NN-bistrifluoromethylethynylamine (0.36 g., 2.05 mmoles, 23%), and (iii) a higher-boiling fraction (2.56 g., 6.85 mmoles, 99%) (Found: M, 370. Calc. for C₅HIF₉N: M, 373) shown by g.l.c. (4 m. dodecylphthalate at 130°) to consist of two components which were separated (g.l.c.) and identified as trans-3,3.3-trifluoro-1-iodo-NN-bistrifluoromethylprop-1-enylamine (XIIb) (1.28 g., 3.43 mmoles, 49.5%) (Found: C, 16.3; H, 0.5%; M, 370. C₅HIF₉N

⁹ R. N. Haszeldine, J. Chem. Soc., 1951, 2495.

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Table	2
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N.m.r. spectral data

			19F						
(CF ₃) ₂ N·C;CH	Group a	Type s	Intensity	Chemical shift (p.p.m.) 16·1	Group b	Type sep	Intensity	Chemical shift (τ) $7\cdot 26$	Coupling constants J (c./sec.) a-b, 0.6
(CF ₃) ₂ N·C•C·CF ₃	a	s	2	-19.1					
a b $(CF_3)_2 N \cdot C \cdot C \cdot N (CF_3)_2$	b a	s s	1	-26.8 -16.2					
$\begin{array}{ccc} a & a \\ (CF_3)_2 N \cdot CH_2 \cdot CH_2 \cdot CF_3 \\ a & b & c & d \end{array}$	a d	s t	$\frac{2}{1}$	$-18 \cdot 1 \\ -9 \cdot 2$	b c	Complex Complex	$\frac{2}{2}$	$\begin{array}{c} 6\cdot 45 \\ 7\cdot 50 \end{array}$	c−d, 10·2
$(CF_3)_2$ N·CH ₂ ·CHBr·CF ₃	ad	s d	$\frac{2}{1}$	-18.7	b	Complex	2	$6.20 \\ 5.75$	c-d 6.5
$(CF_3)_2$ N·CHBr·CH ₂ Br	a	s(br)	1	-21.7	b	dd Complex	$\frac{1}{2}$	$4.25 \\ 6.00$	C≕u, 0-5
(CF ₃) ₂ N·CHI·CH ₂ ·CF ₃	a	d	2	-16.2 and	b	dd	1	3.85	
a b c d	d	t	1	$-23.6 \\ -11.4$	с	Complex	2	6.80	c−d, 9·3
(CF₃)₂N•CHBr•CHBr•CF₃	a	d	2	18.0 and	b	d	1	4.27	b–c, 10·2
a b c d (CF2)2N Hc	đ	d	1	$-25 \cdot 2$ -12 \cdot 2	с	dq	1	5.18	c−d, 5·7
a C:C Br N(CF ₃) ₂	a b	s d	1 1	-19.6 -18.8	С	sep		3.36	b–c, 2·0
(CF ₃) ₂ N H _b a C:C Br H _c	a	S		- 19.6	b c	d d	1 1	3∙45 3∙59	b-c, 2·1
$(CF_3)_2 N \cdot CH_2 F_c$ C:C Br F ₄	a c d	s d d	6 1 1	$-rac{20\cdot 4}{7\cdot 2}$ 1 · 2	b	S		5.79	c−d, 29 ·9
$(CF_3)_2N$ H_c a C:C H_b CF_{3d}	a d	s dd	2 1	-20.4 -14.4	b c	dq dq	1 1	3·18 4·40	b–c, 15·6 b–d, 2·3 c–d, 6·3
$(CF_{a})_{2}N$ H _b a C:C	a C	s d	2 1	-22.6 -16.7	b	q		3.16	b-c, 6·6
$(CF_3)_2N$ CF_{3c} a $C:C$	a c	q dsep	2 1	20·1 15·4	b	q		3.20	ac, 2·4 bc, 6·4
$ \begin{array}{c} 1 \\ (CF_3)_2N \\ a \\ C:C \\ H \\ B_r \end{array} $	a	đ		20.1	b c	dsep dsep	1 1	3·52 3·32	bc, 18·2 b-a, 1·5 ca, 0·7
$(CF_{3})_{2}N$ Br a C:C H _b H _c	a	d		- 19-9	b c	dsep d	1 1	3·51 3·19	b–c, 5·5 b–a, 1·8

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Org.

	Table	3	
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Main mass spectral bands									
(CF₃)₂N•CHBr•CH₂Br	Mass 260, 258	Inty. 38	Assignment $C_4H_3BrF_6N^+$	$(CF_3)_2$ N•CH ₂ •CH ₂ •CF ₃	Mass 249	Inty. Trace	Assignment M^+		
	179 96	$\frac{33}{23}$	$(CF_3)_2 N \cdot CH \cdot CH_2^+$ CF_*N \cdot CH^+		$\frac{166}{134}$	100 11	$(CF_3)_2N \cdot CH_2^+$ C ₂ HF ₅ N ⁺		
	91 76	9·4	$CF_2 \cdot N \cdot CH \cdot CH_2^+$		97 96	$6.2 \\ 7.4$	$CF_3 \cdot CH_2 \cdot CH_2^+$		
	69	100	$C_{2}F_{2}R$		30 78	47	$C_2H_2F_2N^+$		
	64 50	$\frac{25}{3 \cdot 2}$	CF ₂ N ⁺ CF ₂ ⁺		77 69	$\frac{7 \cdot 4}{63}$	$C_{3}H_{3}F_{2}^{+}$ CF ₃ +		
	40	5.7	$C_2H_2N^+$		51	4.5	CHF ₂ ⁺		
(CFa) N·CHI·CHa·CFa	$\frac{27}{277}$	23 11	$C_2H_3^+$ (CF ₂) ₂ N·CH1 ⁺	(CF_a)_N·CH_a·CHBr·CF_	33 177, 175	6·0 26	CH ₂ r ⁺ CH ₂ ·CHBr·CF ₂ +		
(3/2	239	96 97	$(CF_3)_2$ N·CH·CH ₂ ·CF ₃ +	(166	100	$(CF_3)_2 N \cdot CH_2^+$		
	$\frac{218}{165}$	27 6·0	$(C_3 \Pi_3 \Gamma_2 \Pi N + (CF_3)_2 N \cdot CH^+$		96	9.3 10.0	CHBIF ⁺ CF ₃ ·N·CH ⁺		
	$\frac{158}{126}$	7.9 15	C ₄ HF ₅ N ⁺ C ₂ F ₂ N ⁺		95 78	9.9 30	$C_{3}H_{2}F_{3}^{+}$ CF ₂ ·N·CH ₂ +		
	96	47	$CF_3 \cdot N \cdot CH^+$		69 51	64	CF_3^+		
	83 69	100	$CF_3 CH_2^+$ CF_3^+		$\frac{31}{40}$	6.0	$C_{2}H_{2}$ ⁺ $C_{2}H_{2}N^{+}$		
CE \ N.CHP-CHP-CF	208 206	45	C H BrF N+	(CE) N.CH'CH.CE	27 947	6·9	$C_2H_3^+$ M+		
(CF ₃) ₂ N°CHDFCHDFCF ₃	257 255	40		(Cr ₃) ₂ N CH.CH Cr ₃	228	15	$C_5H_2F_8N^+$		
	$\frac{253}{247}$	11	CHBr·CHBr·CF ₃ ⁺ (CF ₃) ₂ N·CH·CH·CF ₃ ⁺		$\frac{159}{158}$	9·1 5·3	$C_4H_2F_5N^+$ $C_4HF_5N^+$		
	196	4·6	Č₄HF ₇ N+		140	9·7 4·4	$C_4H_2F_4N^+$ C HF N+		
	131, 129	2.8	CBr_{2^+}		96	13	CF ₃ ·N·CH+		
	127 96	3·6 17	C ₃ HF ₄ N ⁺ CF ₃ •N•CH ⁺		95 90	4·2 3·6	$C_3H_2F_3^+$ $C_3H_2F_2N^+$		
	69	100	CF ₃ ⁺		69	100	CF ₃ ⁺		
rans-(CF ₃) ₂ N•CH.CHBr	259, 257 240, 238	$\frac{100}{2 \cdot 1}$	M^+ CF ₂ ·N(CF ₃)·CH·CHBr+	<i>cis</i> -(CF ₃) ₂ N·CH.CHBr	259, 257 240, 238	100	M^+ CF ₂ ·N(CF ₃)·CH·CHBr ⁺		
	171, 169	34 4.4	CF ₂ ·N·CH·CHBr ⁺ C.HBrF. ⁺		171, 169 144 142	$31 \\ 4.5$	CF ₂ ·N·CH·CHBr+ C ₂ HBrF ₂ +		
	131, 129	2.3	$\operatorname{CBr}\mathbf{F}_{2}^{+}$		131, 129	2.4	$CBrF_2^+$		
	109	$2.8 \\ 27$	CH•CHBr+		109	$\frac{2\cdot 9}{21}$	CH·CHBr+		
	96 90	$\frac{25}{13}$	CF ₃ ·N·CH+ CF ₃ ·N·CH·CH+		96 90	9∙7 14	CF ₃ •N•CH+ CF ₂ •N•CH•CH+		
	69	84	CF_3^+		69	90	CF ₃ ⁺		
$(CF_3)_2N$ H	$\frac{373}{246}$	frace 61	M^+ (CF ₃) ₂ N•C•CH•CF ₃ +	$(CF_3)_2N$ CF_3	$\frac{373}{246}$	1 race 76	M^+ (CF ₃) ₂ N·C·CH·CF ₃ +		
Ċ:Ć	$\frac{221}{177}$	24 4·1	CF ₃ ·CH·CI+ C.HF.N+	Ċ:Ċ	$\begin{array}{c} 221 \\ 177 \end{array}$	$\frac{26}{5\cdot7}$	CF ₃ ·CH·CI+ C.HF ₂ N+		
Í ČF ₃	158	10	$C_4HF_5N^+$	í H	158	14	CHF ₅ N+		
	134	1·8 8·8	I^+		127	9.9			
	89 83	$2 \cdot 1 \\ 3 \cdot 5$	C ₃ HF ₂ N ⁺ CF ₂ N ⁺		89 83	$\frac{3 \cdot 3}{2 \cdot 8}$	$C_3HF_2N^+$ CF ₂ ·N ⁺		
	69 21	100	CF_3^+		75 69	1.6	$C_3 HF_2^+$		
(CF ₃) ₂ N·CBr:CH ₂	259, 257	2·3 17	M+	(CF ₃) ₂ N·CH ₂ ·CBr:CF ₂	309, 307	13	M^+		
	$178 \\ 134$	95 6·4	$(CF_3)_2 N \cdot C \cdot CH_2^+$ C_HF_N^+		176, 174	54	$C_3H_2BrF_3^+$ (CF_2)_2N•CH_2^+		
	131, 129	3.2	$\operatorname{CBrF}_{2^+}$		157, 155	37	$CH_2 \cdot CBr \cdot CF_2$		
	109	5·5 48	$CF_3 \cdot N \cdot C \cdot CH_2^+$ CBr · CH ₂ +		131, 129	12 7·0	CBr_{2^+} CBr·CH ₂ +		
	90 81 79	$\frac{26}{4.5}$	CF ₂ ·N·C·CH ₂ + Br ⁺		95 78	$9 \cdot 2 \\ 34$	CF ₃ ·NC ⁺ CF ₃ ·N·CH ₂ ⁺		
	69 40	100	CF ₃ ⁺		75	12	$C_3HF_2^+$		
(CF ₂), ·N·CBr:CH·N(CF ₂),	40 410, 408	0.8 19	M^+	(CF ₃),N·C : CH	177	29	M ⁺		
	391, 389 320	9.9 65	$C_{6}HBrF_{11}N_{2}^{+}$		158 89	2.5	$CF_2 \cdot N(CF_3) \cdot C \cdot CH^+$		
	246	7.9	$C_5HF_9N^+$		69 69	100	CF_2^+		
	191 146	9.9 5.6	$C_4HF_6N_2^+$ $C_3HF_5N^+$		50 39	$\frac{2 \cdot 2}{2 \cdot 7}$	CF_2^+ C_2HN^+		
	131, 129	$10 \\ 5.8$	$CBrF_{2}^{+}$		$\frac{31}{26}$	4·8 5·6	CF+ CN+		
	96	15	$CF_3 \cdot N \cdot CH^+$		$\overline{25}$	$2 \cdot 1$	C_2H^+		
(CF ₃) ₂ N·C:C·CF ₃	09 245	18	M^+	$(CF_3)_2 N \cdot C \cdot C \cdot N (CF_3)_2$	328	25	M^+		
,	$\frac{226}{157}$	6·9 7.0	$C_5F_8N^+$ CF.·N·C·C·CF.+		$\frac{309}{264}$	7.7 4.4	$C_6F_{11}N_2^+$ CrF10N ⁺		
	138	13	$C_4F_4N^+$		245	5.2	$C_5F_9N^+$		
	107 93	4∙5 1∙3	$C_3F_3N^{+}C_3F_3^{+}$		$\frac{226}{195}$	0·3 1·6	$C_5 \Gamma_8 N + C_4 F_7 N^+$		
	88 69	$\begin{array}{c} 0.7\\100\end{array}$	C ₃ F ₂ N ⁺ CF ₃		$\begin{array}{c} 152 \\ 121 \end{array}$	$3.7 \\ 2.9$	$(CF_3)_2N^+$ $CF_3\cdot NF_2$		
4C	50 31	1.4	CF_2^+		76 69	5·8	$C_2 \tilde{F}_2 N^+$ CF-+		
	01	- T .A	~.			T A A	~-3		

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requires C, 16.1; H, 0.3%; M, 373) and cis-3,3,3-trifluoro-1-iodo-NN-bistrifluoromethylprop-1-enylamine (XIIa) (1.28 g., 3.43 mmoles, 49.5%) (Found: C, 16.3; H, 0.5%; M, 371).

Reaction of 3,3,3-Trifluoro-1-iodo-NN-bistrifluoromethylprop-1-envlamine with Potassium Hydroxide.-The iodoamine (0.97 g., 2.60 mmoles), heated under reflux in vacuo over an excess of dry, powdered potassium hydroxide (30 min.), gave (i) unchanged iodo-compound (0.55 g., 1.50 mmoles, 57% and (ii) (II) (0.25 g., 1.02 mmoles, 91%) (Found: M, 246. Calc. for C₅F₉N: M, 245).

Reaction of N-Bromobistrifluoromethylamine with NN-Bistrifluoromethylethynylamine.-The N-bromo-amine (2.50 g.,

4.18 mmoles, 97%) (Found: C, 21.95; N, 8.5%; M, 326. $C_6F_{12}N_2$ requires C, 22.0; N, 8.5%; M, 328).

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 $[L_{v} \text{ (cal. mole}^{-1})]$, and Trouton's constant $[T(cal. mole^{-1} deg.^{-1})]$ for certain of the new compounds are shown in Table 1.

Nuclear Magnetic Resonance Spectra.—The data in Table 2 were recorded with trifluoroacetic acid as external reference for ¹⁹F and tetramethylsilane as internal reference for ¹H.

The hydrogen nuclei in the compound (CF₃)₂N·CBr:CH₂ are assigned by reference to the spectrum of vinyl bromide $^{\mathbf{10}}$

								Τ.	ABLE 4							
]	Infrared	1 spect	ra (µ)						
(I) 2·97m	(11)	(III)	(IV) 3-26vw	(VII) 3·17w 3·26w	(IX) 3·33w	(XIIa) 3·25w	(XIIb) 3·25w	(XIII) 3·26w	A† 3·22w 3·26w	B† 3·21w 3·26w	(V) 3·25w	(VI) 3·34w 3·36w	C† 3·26w 3·33w	D† 3·28w	E† 3·32w 3·35w	Assignment } C-H str.
4•58 m	4•33m		6·12s	5.91s	5·72s	6•06m	6·06m	6 ·1 3w	6·13w	6·13m						C:C str. C:C str.
6-86s			6·91m	6·94m	6.86m	7•08m	7•07w	6-96m	6·96m	7•00m	6·97m	6·77m 6·91m	6•99m	6·96m	6-82m 6-98m	C-H bend 16
7•34s	7∙07m 7∙40m	6·86s 7·3 4 m 7·42m	7·21s 7·37s 7·48vs	7∙26s 7∙45s	7∙30s 7∙45s	7.38vs	7·37s	7•42vs*	7•36s	7·35s 7·48s	7·30s 7·43vs	7·23s 7·40s	7∙15m 7∙46s	7•44vs	7∙28s 7∙42vs]
7.82s 8.21s	7·67s 7·84s 8·14s	7·71s 7·85s 8·20s	7.78vs 7.91s 8.31vs	7.77s 7.88s 8.33s	7∙66s 8∙05s	7.60s 7.84vs 8.02s 8.32s	7.64vs 7.84s 8.02s 8.32vs	7.78vs 8.10m 8.30vs*	7∙80s 8∙00m	7·78s	7.60s 7.89vs 8.06s 8.31c	7∙91s 8∙05s	7·70s 7·96m 8·18m	7.86vs 7.92vs 8.08s	7.84s 7.92s 8.02s	C. F. etc.
8·71m	8∙51s 8∙67m		0 0110	8-66s 8-80s	8.42s 8.71s 8.90m	8.55s	8.555s 8.80m	8·44s 8·58m	8·42s 8·75m	8.43s 8.50vs	8·53s 8·76s	8·42s 8·50s 8·71m	8-355 8-42s 8-60m 8-82m	8.74m	8-93c	C-r str.
9•32m	9·35m			9·35m	9·15m 9·47s	9·02s			9•07m	9∙08s	9·03m	9∙05m 9∙45m		0.092	0.992	
10·10s*	9.80m 10.09m	10·14s	9.64s 10.13s	10·10s	9·74m 10·05m 10·32m	10·13s	10•13s	10·11s	9·80w 10·17s	10·17s	9·78m 10·26s	9·82s 10·15m	9·79m 10·24m	9·71m 10·28s	9∙52m 10∙04s	} C-N str. 8,18,a-a
10·86w		10.90w	10.86s	10·57m 11·36m	10·84w 11·42m		11.25m	11.46m*	10-90s	10·90w	10 ·93w	10.64m	10.72w	10.97m	10.84m)
12·20w	11·93 m				12·15w	11·85m		11.85m	12·10w	12·13m	11•90w	11•67w*	11 2111	11 000	11 00%	C-N-C bend a.c.d
	12 ·96 m		12•67m*	12·46m		12·52m 13·02m	12·40m	13·27m	12·90m 13·17m	13·17s		12·61w 12·85w	12.80w		12-48w	
13·76s*	13·42m 13·75m	13·85s	13·49s	13.55m	14·00m	13·73m 13·90m	13·54m 13·89m	13.75s	14,990	14.25m	13-83m	14 40	13•73m	13.65m	13.88m	CF ₈ def.a, c
14·49s*	15·24 m	1 4·8 8m	14·50s 15·12m	11.9011	14·52m 15·26m	15·12m		14.80m	14-358 14-40s 14-95m	13·20m	14-10m	14·46m	14·30m 14·64m	14-35m	14·27m 14·88m	ر ا
		15.54m										10 Juni	75.420			

* Triplet. † A, trans-(CF₃)₂N·CH:CHBr; B, cis-(CF₃)₂N·CH:CHBr; C, (CF₃)₂N·CHBr·CH₂Br; D, (CF₃)₂N·CHBr·CF₃; E, (CF₃)₂N·CH₂-CHBr·CF₃.

^a A. H. Dinwoodie and R. N. Haszeldine, J. Chem. Soc., 1965, 1681. ^b J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, J. Amer. Chem. Soc., 1960, 82, 396. e R.N. Haszeldine and A. E. Tipping, J. Chem. Soc. (C), 1966, 1236. ^d A. H. Dinwoodie and R. N. Haszeldine, J. Chem. Soc., 1965, 1675.

10.8 mmoles) and NN-bistrifluoromethylethynylamine (2.75 g., 15.5 mmoles) reacted in the vapour phase in a Pyrex bulb (3 l.) at room temperature in daylight (48 hr.) to give (i) unchanged acetylene (0.92 g., 5.2 mmoles, 34%) shown by its i.r. spectrum to be contaminated with traces of bistrifluoromethylamine and trifluoromethyl isocyanate and (ii) 1,2-di(bistrifluoromethylamino)-1-bromoethylene (4.10 g., 10.0 mmoles, 97%) (Found: C, 17.3; H, 0.4; N, 6.8%; *M*, 409. $C_{6}HBrF_{12}N_{2}$ requires C, 17.6; H, 0.2; N, 6.9%; M, 409), probably the *trans*-isomer.

Reaction of 1,2-Di(bistrifluoromethylamino)-1-bromoethylene with Potassium Hydroxide.-The bromo-compound (2.10 g., 5.13 mmoles), heated under reflux in vacuo over an excess of dry, powdered potassium hydroxide (30 min.), gave (i) unchanged bromo-olefin (0.33 g., 0.81 mmole, 16%) and (ii) perfluoro-1,2-bisdimethylaminoacetylene (III) (1.37 g.,

¹⁰ C. N. Banwell and N. Sheppard, Mol. Phys., 1960, 3, 351. ¹¹ N. Muller, P. C. Lauterbur, and G. F. Svatos, J. Amer. Chem. Soc., 1957, 79, 1807.

¹² Unpublished data from this department.

¹³ E. G. Brame, Analyt. Chem., 1962, 34, 591.

in which the hydrogen trans to the bromine atom is found at a lower τ value than that *cis* to bromine.

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

Group	Chemical shift	Ref.
$(CF_3)_2 N \cdot C \leq$	-16 to -26 p.p.m.	6, 8, 11, 12
CF ₃ ·C	$0 \text{ to } -20^{-1}$	11, 12
$CF_2 = $	-10 to +50	12, 13
CHΞ	τ 7 to 8	14
$(CF_3)_2$ N·C H_2 ·	τ 5.8 to 6.7	12

The ¹⁹F chemical shift for the fluorine nuclei in the CF. group of the acetylene $(CF_3)_2$ N·C:C·CF₃ is at -26 p.p.m., in reasonable agreement with the shift of ca. -20 p.p.m. reported for hexafluorobut-2-yne.¹⁵ The fluorine nuclei $(CF_3)_2N$ groups \mathbf{in} the \mathbf{of} \mathbf{the} compounds $(CF_3)_2$ N·CHI·CH₂·CF₃ (CF₃)₂N·CHBr·CHBr·CF₃ and

¹⁴ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectra,' vol. 2, Pergamon, Oxford, 1966.
 ¹⁵ N. Muller and D. T. Carr, J. Phys. Chem., 1963, 67, 112.

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appeared as doublets in the ¹⁹F spectra and a similar observation has been reported for the compound $(CF_3)_2N\cdot CHBr\cdot CH_2\cdot N(CF_3)_2.^6$ This is owing to slow inversion about the nitrogen atom adjacent to an asymmetric centre.

Mass Spectra.—The main mass spectral bands of the new compounds are recorded in Table 3.

The mass spectra are in agreement with the proposed structures and in general the base peaks in the spectra are found at m/e 69(CF₃⁺); the exceptions are the olefins *cis*- and *trans*-(CF₃)₂N·CHiCHBr, which show base peaks at m/e 259 and 257 (M^+), and the compounds (CF₃)₂N·CH₂·CF₃ and (CF₃)₂N·CH₂·CHBr·CF₃, which both show a base peak at m/e 166 [(CF₃)₂N·CH₂·1]. The compound (CF₃)₂N·CHI·CHI·CH₂·CF₃ shows a very strong peak at m/e 239 (96%) due to loss of iodine from the parent.

All the compounds which contain a $(CF_3)_2N\cdot CH \leq \text{group}$, with one exception, show a peak at m/e 96 $(CF_3\cdot N\cdot CH^+)$; the exception, $(CF_3)_2N\cdot CH_2\cdot CBr\cdot CF_2$, differs from the other compounds in that it contains an allylic methylene group.

Various rearrangement peaks were also observed, *e.g.* (i) the compound $(CF_3)_2N$ ·CHBr·CHBr·CF₃ and all the bromo-olefins showed peaks at m/e 131 and 129 due to CF_2Br^+ , (ii) the compound $(CF_3)_2N$ ·CH₂·CBr:CF₂ showed peaks at m/e 176 and 174 $(C_3H_2BrF_3^+)$, and (iii) the acetylene $(CF_3)_2N$ ·C:C·N $(CF_3)_2$ showed a peak at m/e 264 due to loss of CF_2N from the parent and various other peaks due to breakdowns from this rearranged ion.

Infrared Spectra.—The spectra of the new compounds are shown in Table 4.

All previously reported compounds which contain a $(CF_3)_2N$ group have a strong band in their spectra between 9.9 and 10.5 μ assigned to the C-N stretch in the $(CF_3)_2N$ group. The new compounds reported also contain N-alkyl, N-vinyl, N-ethynyl, or N-propynyl groups, and other medium or strong bands found in the 9.5—10.4 μ region are assigned ¹⁶ to these C-N stretching modes. The C-H out-of-plane deformation modes for the olefins cannot be assigned with any certainty, since they occur in the same region as the C-N-C bending mode. The bands at 2.97 and 4.58 μ for the acetylene (I), due to C-H and CiC stretch respectively, are close to those reported ⁹ for the acetylene CF_3 ·CiCH (3.01 and 4.66 μ), and the band at 4.33 μ (CiC stretch) for the disubstituted acetylenes (4.42—4.57 μ).

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¹⁶ L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' 2nd edn., Methuen, London, 1958.