

Polyfluoroalkyl Derivatives of Nitrogen. Part 44.¹ The Reactions of *N*-Bromobis(trifluoromethyl)amine with Open-chain 1,3-Dienes and Cyclohexene under Ionic Conditions

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The reactions of *N*-bromobis(trifluoromethyl)amine with buta-1,3-diene, 2-methylbuta-1,3-diene, and 2,3-dimethylbuta-1,3-diene give relatively high yields of mixtures of the 1,2- and 1,4-adducts $(\text{CF}_3)_2\text{NCR}^1(\text{CH}_2\text{Br})\text{-CR}^2=\text{CH}_2$ and $\text{CH}_2\text{BrCR}^1=\text{CR}^2\text{CH}_2\text{N}(\text{CF}_3)_2$ in the ratios 75 : 25 ($\text{R}^1 = \text{R}^2 = \text{H}$), 47 : 53 ($\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$), and 11 : 89 ($\text{R}^1 = \text{R}^2 = \text{Me}$); the buta-1,3-diene reaction carried out in diethyl ether and methylene chloride gives the adducts in the ratio 16 : 84 and 59 : 41, respectively. With 2-methylbuta-1,3-diene the adducts $(\text{CF}_3)_2\text{NCH}(\text{CH}_2\text{Br})\text{CMe}=\text{CH}_2$ and $\text{CH}_2\text{BrCH}=\text{CMeCH}_2\text{N}(\text{CF}_3)_2$ are also formed (8%) in the ratio 44 : 56. The buta-1,3-diene 1,2- and 1,4-adducts dehydrobrominate readily (KOH) to afford 2- and 1-bis(trifluoromethyl)aminobuta-1,3-diene, respectively. The 1,2-adduct is stable at 220 °C, but the 1,4-adduct at this temperature slowly forms a mixture of rearranged products; on prolonged heating the major product is 3-bromobis(trifluoromethyl)but-1-enylamine. Addition of the *N*-bromoamine to cyclohexene at low temperature in the dark gives the *trans*-diequatorial adduct (86%) which is resistant to dehydrobromination under a variety of conditions.

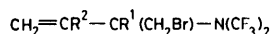
THE additions of *N*-bromobis(trifluoromethyl)amine, $(\text{CF}_3)_2\text{NBr}$ (1), to a variety of alkenes,^{1,2} alkynes,³ and allenes⁴ have been investigated under conditions favouring ionic (low temperature, liquid phase in the dark) or free-radical (room temperature, vapour phase, u.v. or daylight) reaction paths; electrophilic attack by amine $\overset{\delta-}{\text{N}}-\overset{\delta+}{\text{Br}}$ (1) polarised as $(\text{CF}_3)_2\text{N}^{\delta-}-\text{Br}^{\delta+}$, and radical attack by $(\text{CF}_3)_2\text{N}^\bullet$ have been postulated, respectively. The additions of the *N*-bromoamine (1) to buta-1,3-diene, 2-methylbuta-1,3-diene, 2,3-dimethylbuta-1,2-diene, and cyclohexene have now been studied.

RESULTS AND DISCUSSION

The results obtained from the reactions of amine (1) with the 1,3-dienes (1:1 molar ratio) are shown in Table 1.

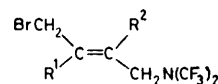
The 1,2-adducts (2) and (5) were readily distinguished from the corresponding 1,4-adducts (3), (6), and (8) by the following features in their n.m.r. and mass spectra. (a) The number of vinyl protons present (¹H n.m.r.). (b) The ¹⁹F n.m.r. chemical shifts for the $(\text{CF}_3)_2\text{N}$ groups; at *ca.* -20 p.p.m. for all the 1,4-adducts, but at increasingly lower field as the groups R^1 and R^2 in the

1,2- and 1,4-adducts corresponded to the allylic ions $[\text{M}-\text{CH}_2\text{Br}]^+$ and $[\text{M}-\text{Br}]^+$, respectively; the 1,4-adducts also showed a strong peak in their spectra at



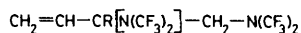
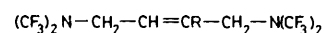
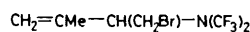
(2)

- a: $\text{R}^1 = \text{R}^2 = \text{H}$
b: $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$
c: $\text{R}^1 = \text{R}^2 = \text{Me}$

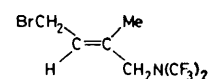


(3)

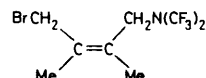
- a: $\text{R}^1 = \text{R}^2 = \text{H}$
b: $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$
c: $\text{R}^1 = \text{R}^2 = \text{Me}$

(4a) $\text{R} = \text{H}$; (7a) $\text{R} = \text{Me}$ (4b) $\text{R} = \text{H}$; (7b) $\text{R} = \text{Me}$ 

(5)



(6)



(8)

m/e 166 [51—66%, $(\text{CF}_3)_2\text{NCH}_2^+$], but in the spectra of the 1,2-adducts the peak was of lower intensity (12—29%).

In the ¹H n.m.r. spectrum of the 1,4-adduct from

TABLE 1
Reactions of *N*-bromobis(trifluoromethyl)amine with 1,3-dienes

Diene	Temperature (°C)	Time/h	Solvent	Products (yield %)*
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	-78	1.5	None	(2a) 48; (3a) 16; (4a) or (4b) 1.5; unknown 1.5
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	-78	1.0	CH_2Cl_2	(2a) 45; (3a) 32
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	-78	1.0	Et_2O	(2a) 14; (3a) 74
$\text{CH}_2=\text{CMe}-\text{CH}=\text{CH}_2$	-78	1.5	None	(2b) 36; (3b) 41.5; (5) 3.5; (6) 4.5; (7a) or (7b) 1.5; $\text{C}_6\text{H}_7\text{Br}$ 1
$\text{CH}_2=\text{CMe}-\text{CMe}=\text{CH}_2$	-78 then -45	1.0 0.5	None	(2c) 10; (3c) 71; (8) 5

* *NN*-Bis(trifluoromethyl)amine, perfluoro-2-azapropene, and polymeric residues were also obtained.

1,2-adducts $\text{BrCH}_2\text{CR}^1\text{R}^2\text{N}(\text{CF}_3)_2$ increased in bulk, *i.e.* $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}=\text{CH}_2$ (2a), -22.0; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CMe}:\text{CH}_2$ (5) -23.5; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{CH}:\text{CH}_2$ (2b), -29.9; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{CMe}:\text{CH}_2$ (2c), -30.4 p.p.m. (c) The base peaks in the mass spectra of the

buta-1,3-diene the vinylic proton coupling (15 Hz) observed indicates that the compound is the *anti*-isomer (3a). The configurations of the other 1,4-adducts obtained could not be determined from the spectral evidence available. However, on steric grounds

the isoprene-1,4-adducts and the major 1,4-adduct from 2,3-dimethylbuta-1,3-diene are tentatively assigned the *anti*-configurations (3b), (6), and (3c), respectively, and the minor 1,4-adduct from 2,3-dimethylbuta-1,3-diene is assigned the *syn*-configuration (8).

It has been observed⁵ that the reactions of the *N*-halogenobis(trifluoromethyl)amines $(CF_3)_2NX$ ($X = I, Br, \text{ or } Cl$) with cyclohexa-1,3-diene at $-78^\circ C$ in diethyl ether give the corresponding 1,2- and 1,4-adducts in the ratios 100:0 ($X = I$), 40:60 ($X = Br$), and 22:78



($X = Cl$); the 1,2-adducts were the *anti*-isomers exclusively, while the 1,4-adducts were mixtures of the *syn*- and *anti*-isomers. The amount of 1,2-addition thus decreases as the expected stability of the postulated bridged halonium ion decreases ($X = I > X = Br > X = Cl$), and therefore in the bridged iodonium ion there is little charge delocalisation, *i.e.* it tends towards structure (9), whereas the bridged bromonium and chloronium ions have considerable carbonium ion character, *i.e.* structure (10, $X = Cl$ or Br). The products then arise *via* exclusive *anti*-attack at the 2-position of ion (9) and *anti*-attack at the 2-position and *syn*- and *anti*-attack at the 4-position of ion (10) as shown (Scheme 1).

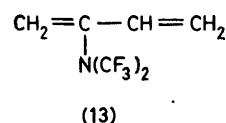
The variation in the 1,2- to 1,4-adduct ratios formed in the absence of solvent, *i.e.* 75:25 ($R^1 = R^2 = H$), 47:53 ($R^1 = Me, R^2 = H$), and 11:89 ($R^1 = R^2 = Me$), then indicates greater charge delocalisation in the bridged ion as the groups R^1 and R^2 become more bulky, thus favouring 1,4-addition.

In contrast to the addition of (1) to cyclohexa-1,3-diene, the 1,4-adducts formed from buta-1,3-diene and

known proportion of the *s-cis* form of the diene increasing in the order $CH_2=CH-CH=CH_2 < CH_2=CMe-CH=CH_2 < CH_2=CMe-CMe=CH_2$.

One feature of the reactions, especially with buta-1,3-diene, was the formation of polymeric material. In an attempt to reduce this the reactions of the *N*-bromoamine (1) with buta-1,3-diene in methylene chloride and diethyl ether at $-78^\circ C$ in the dark were investigated. Higher yields of 1:1 adducts (77 and 88%, respectively) were obtained and the adduct ratio (2a): (3a) changed from 75:25 (neat reactants) to 59:41 (CH_2Cl_2) and 16:84 (Et_2O), in agreement with a report that solvent polarity is the main factor affecting the extent of bridging in intermediates formed from bromonium ion attack on olefins.⁶

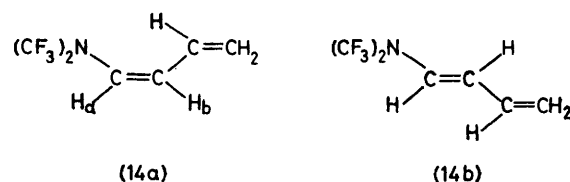
Coupled g.l.c.-mass spectrometric investigations of the minor products from the buta-1,3-diene and 2-methylbuta-1,3-diene reactions showed the presence of



bisaminodiene adducts [(4) and (7)] but it was not possible to differentiate between the alternative structures (4a or b) and (7a or b).

Dehydrobromination of the 1,2-adduct (2a) with powdered potassium hydroxide at elevated temperature occurred readily and gave 2-bis(trifluoromethyl)aminobuta-1,3-diene (13) (100%) which has been prepared previously⁷ by another route.

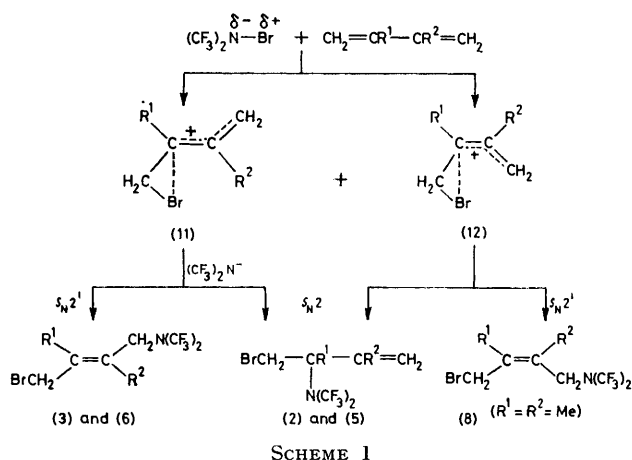
The corresponding 1,4-adduct (3a) dehydrobrominated under similar conditions, and gave a mixture (84%) of *cis*- and *trans*-1-bis(trifluoromethyl)aminobuta-1,3-diene (14a and b) in the ratio 60:40.



The major product was identified as the *cis*-isomer (14a) by (i) the magnitude of the n.m.r. coupling constant J_{ab} (7.9 Hz) and (ii) the ^{19}F chemical shift for the $(CF_3)_2N$ group (-16.5 p.p.m.) at higher field than in the minor isomer (-17.4 p.p.m.); *cf.* $(CF_3)_2NCH=CHMe$, ^{19}F δ *cis*-isomer -18.1 , *trans*-isomer -18.7 .⁸

A preliminary investigation of the thermal stabilities of adducts (2a) and (3a) was undertaken. The 1,2-adduct (2a) was stable at $220^\circ C$ (gas phase, 5 h), but the *trans*-1,4-adduct (3a) when heated gave a complex mixture of products. The conditions used for the thermolysis of the adduct (3a) and the products obtained are shown in Table 2.

The products were identified on the basis of their g.l.c. retention times, certain features in their mass

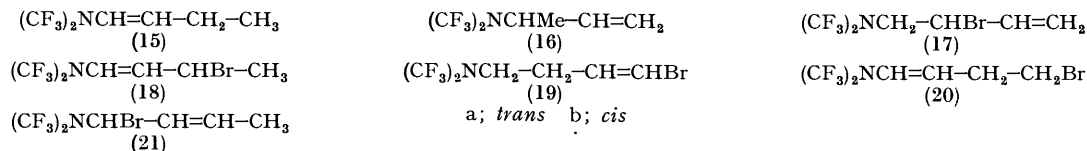


SCHEME 1

2-methylbuta-1,3-diene were exclusively the *anti*-isomers, *i.e.* formed *via* the sterically-favoured intermediate (11), but with 2,3-dimethylbuta-1,3-diene a small amount of the *syn*-1,4-adduct (8), formed *via* the intermediate (12), was detected. This is consistent with the

spectra, and the ^1H and ^{19}F n.m.r. spectra of the product mixture from Experiment 2; compounds (20) and (21) were only tentatively identified.

The mass spectrum of compound (15) and/or (16)



showed peaks at m/e 207 (20%, M^+), 192 (100%, [$M - \text{Me}$] $^+$), and 166 [39%, $(\text{CF}_3)_2\text{NCH}_2^+$], indicative of a methyl group bonded to an allylic carbon and the absence of a $(\text{CF}_3)_2\text{NCH}_2$ group; compounds containing

TABLE 2

Thermolysis of *trans*-4-bromobis(trifluoromethyl)but-2-enylamine

	Experiment 1	Experiment 2	Experiment 3
Temperature ($^\circ\text{C}$)	220	220	200
Time	5 h	7 d	3 h
Phase	Gas	Gas	Gas + liquid
Products (%) ^a	100	100 ^b	71 ^{b,c}
(14)	1	6	Trace
(15) and/or (16)	Trace	3	1.5
(4a) and/or (4b)			3
(2a)	5	5	6
(17)	12	4	8
(18)	1	39	Trace
Unknown	Trace	Trace	Trace
$[(\text{CF}_3)_2\text{NC}_4\text{H}_6\text{Br}]$			
(19a)	2	11	8
(19b)	1	5	3.5
(20)		4	
(21)	15	Trace	8
(3a) unchanged	62	22	33

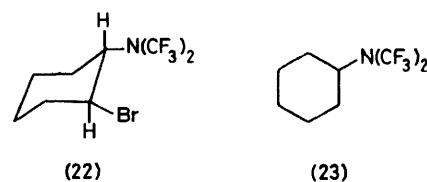
^a Based on g.l.c. peak areas; products given in order of g.l.c. retention time. ^b A number of minor unidentified products (<1%) also produced. ^c Polymeric material and SiF_4 also formed.

a $(\text{CF}_3)_2\text{NCH}_2$ group show a strong peak at m/e 166 (>50%). The relevant mass spectral features of compounds (17)–(21) [all $(\text{CF}_3)_2\text{NC}_4\text{H}_6\text{Br}$] and the unknown isomer are shown in Table 3.

bromine isomer (21), indicating that compound (18) is more thermodynamically stable than compound (21); and (iv) the only evidence for intermolecular $(\text{CF}_3)_2\text{N}$ transfer was obtained from the liquid + gas phase

reaction, *i.e.* formation of the bis(amino)compound (4a or b). The reason for the apparent thermal stability of adduct (2a) as compared to adduct (3a) is considered to be the absence of an allylic bromine atom in the former compound.

Reaction of the amine (1) with cyclohexene at -78°C gave the diequatorial 1:1 adduct isomer (22) (86%) resulting from *anti*-addition to the olefin; in the ^1H



n.m.r. spectrum of the product both the methine protons exhibited a triplet (J 10 Hz, two equal axial-axial couplings) of doublets (J 4 Hz, axial-equatorial coupling), which is consistent only with isomer (22). The adduct was resistant to dehydrobromination by hydroxide or *t*-butoxide at elevated temperature (94–100% recovered) or by flow pyrolysis at $<550^\circ\text{C}$; at 600°C complete decomposition occurred to give a complex mixture of products consisting mainly of perfluoro-2-azapropene. Reduction, however, took place with lithium aluminium hydride to afford bis(trifluoromethyl)-cyclohexylamine (23) (*ca.* 50%).

TABLE 3

m/e	Main mass spectral bands of the compounds $(\text{CF}_3)_2\text{NC}_4\text{H}_6\text{Br}$								
	(2a)	(3a)	(17)	(18)	(19a)	(19b)	(20)	(21)	Unknown
287, 285 (M^+)	Trace	2	0.5	3	3.5	0.5	Trace	Trace	
286, 284 ($[M - \text{H}]^+$)			Trace	13			7	Trace	2
285, 283 ($[M - 2\text{H}]^+$)				22	1	9			16
206 ($[M - \text{Br}]^+$)	6	100	68	53	15	16	73	100	48
205 ($[M - \text{HBr}]^+$)			7	51			14	45	1
192 ($[M - \text{CH}_2\text{Br}]^+$)	100	1	2	1	7	1	100	16	23
166 ($[(\text{CF}_3)_2\text{NCH}_2]^+$)	17	51	100	22	100	100	41	52	58
135, 133 ($\text{C}_4\text{H}_6\text{Br}^+$)	22	44	20	17	11	12	25	42	7

It is proposed that the identified products are formed as shown in Scheme 2. Rearrangement of adduct (3a) to (2a) is postulated *via* a thermally allowed intramolecular allylic $(\text{CF}_3)_2\text{N}$ shift ($2p + 2\sigma + 2\pi$).

The major features of the thermolyses are (i) the faster reaction which takes place when a liquid phase is present; (ii) the almost constant yields of the rearranged adduct (2a); (iii) the high yield of compound (18) in the prolonged thermolysis with only a low yield of the allylic

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. Products were separated either by repeated fractional distillation *in vacuo* or by preparative-scale g.l.c. [Perkin-Elmer F21 or Pye 104 machines using columns packed with Silicone SE30 oil (*ca.* 20%) on Celite]. The identities of products were established by elemental analysis, *i.e.* spectroscopy (Perkin-Elmer 257 spectro-

photometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 56.46 MHz for ^{19}F and 60.0 MHz for ^1H , or Varian HA100 spectrometer operating at 94.1 MHz for ^{19}F and 100.0 MHz for ^1H ; external trifluoroacetic acid and internal tetramethylsilane as the respective references), and mass spectrometry (A.E.I. MS 902 spectrometer).

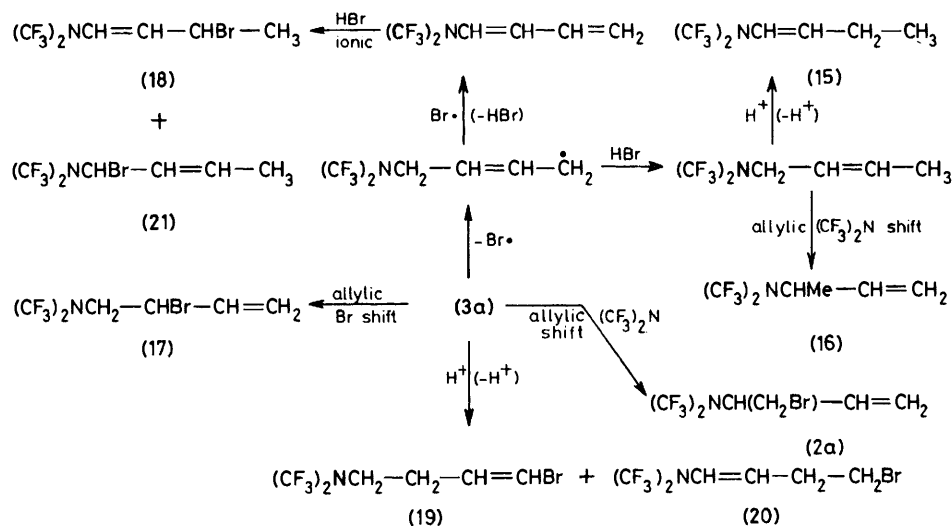
N-Bromobis(trifluoromethyl)amine was prepared from mercury(II) bis(trifluoromethyl)amide^{9,10} and the dienes and cyclohexene were commercial samples which were purified carefully before use.

N.m.r. and mass-spectral data for all the compounds described are deposited as Supplementary Publication No. SUP 22632 (15 pp.).*

Reactions of N-Bromobis(trifluoromethyl)amine.—(a) *With buta-1,3-diene in the absence of solvent.* The diene (0.70 g,

Further reactions carried out similarly at -45 and -10 °C gave lower yields (60 and 45%, respectively) of mixtures of the 1 : 1 adducts in similar ratios to that obtained at -78 °C, while reactions carried out at -78 °C in which the reactants were sealed *in vacuo* at -196 °C in Pyrex ampoules and then kept at -78 °C in the dark (0.5–1.0 h) gave low yields (20–30%) of 1 : 1 adducts and considerable amounts of polymeric material and a mixture of *NN*-bis(trifluoromethyl)amine and perfluoro-2-azapropene.

(b) *With buta-1,3-diene in methylene chloride.* The diene (0.83 g, 15.35 mmol) was slowly condensed *in vacuo* into a stirred solution of the *N*-bromoamine (3.56 g, 15.35 mmol) in methylene chloride (36.0 g, 0.424 mol) contained in a blackened flask (*ca.* 100 cm³) cooled to -78 °C (0.5 h) and the stirring was continued (0.5 h). The products were (i) *NN*-bis(trifluoromethyl)amine (0.22 g, 1.41 mmol); (ii) un-



SCHEME 2

13.0 mmol) was slowly condensed (*ca.* 1 h) *in vacuo* into a blackened Pyrex ampoule (*ca.* 50 cm³) cooled to -78 °C and containing the *N*-bromoamine (3.06 g, 13.0 mmol), and the ampoule and contents were maintained at -78 °C in the dark (0.5 h). The products were (i) a mixture (0.27 g, 2.0 mmol) of *NN*-bis(trifluoromethyl)amine and perfluoro-2-azapropene (*i.r.*); (ii) a 1 : 1 adduct fraction (2.51 g, 8.70 mmol, 67%); and (iii) a polymeric residue (0.95 g) which was not examined further. Separation of the two major components from the adduct fraction, which consisted of four components in the ratio 2 : 72 : 24 : 2, was achieved by g.l.c. (4 m column at 100 °C) and these were identified as 1-bromo-*NN*-bis(trifluoromethyl)prop-2-enylamine (2a) (1.80 g, 6.27 mmol, 48%) (Found: C, 25.4; H, 2.2; N, 4.8. $\text{C}_6\text{H}_6\text{BrF}_6\text{N}$ requires C, 25.1; H, 2.1; N, 4.9%), b.p. 120 °C; and 4-bromo-*NN*-bis(trifluoromethyl)but-2-enylamine (3a) (0.60 g, 2.09 mmol, 16%) (Found: C, 25.3; H, 2.2; N, 5.1%; M^+ , 286. $\text{C}_6\text{H}_6\text{BrF}_6\text{N}$ requires C, 25.1; H, 2.1; N, 4.9%; M , 286), b.p. 144 °C. The minor product of shortest retention time was identified by coupled g.l.c. (as above)—mass spectrometry as either 3,4-bis[bis(trifluoromethyl)amino]but-1-ene (4a) or less likely 1,4-bis[bis(trifluoromethyl)amino]but-2-ene (4b) (0.06 g, 0.17 mmol, 1.5%); but the minor product of longest retention time (*ca.* 0.05 g, *ca.* 0.17 mmol, *ca.* 1.5%) was not identified.

* For details see Notice to Authors No. 7, *J.C.S. Perkin I*, 1979, Index issue.

changed methylene chloride (36.0 g, 0.424 mol, 100% recovered); (iii) a 1 : 1 adduct fraction (3.38 g, 11.8 mmol, 77%) which was shown by g.l.c. and n.m.r. spectroscopy (4 m column at 100 °C) to consist of the adducts (2a) (2.00 g, 6.9 mmol, 45%) and (3a) (1.38 g, 4.9 mmol, 32%) in the ratio 59 : 41; and (iv) a polymeric residue (0.61 g) which was not examined further.

(c) *With buta-1,3-diene in diethyl ether.* A solution of the *N*-bromoamine (1.80 g, 7.75 mmol) in diethyl ether (13.63 g, 0.184 mol), treated with buta-1,3-diene (0.42 g, 7.75 mmol) at -78 °C as in the previous experiment (1 h), gave (i) *NN*-bis(trifluoromethyl)amine (0.04 g, 0.26 mmol); (ii) unchanged diethyl ether (13.66 g) contaminated with a trace of 1 : 1 adducts; (iii) a mixture of 1 : 1 adducts (1.96 g, 6.83 mmol, 88%), which was shown by g.l.c. (as before) and n.m.r. spectroscopy to consist of (2a) (0.32 g, 1.09 mmol, 14%) and (3a) (1.64 g, 5.74 mmol, 74%) in the ratio 16 : 84; and (iv) a polymeric residue (*ca.* 0.1 g) which was not examined further.

(d) *With 2-methylbuta-1,3-diene.* The diene (1.22 g, 18.0 mmol) was slowly condensed (*ca.* 1 h) *in vacuo* into a blackened Pyrex ampoule (*ca.* 50 cm³) cooled to -78 °C and containing the *N*-bromoamine (4.19 g, 18.0 mmol) and the ampoule and contents were kept at -78 °C in the dark (0.5 h). The products were (i) *NN*-bis(trifluoromethyl)amine (0.19 g, 1.25 mmol, 7%); (ii) a 1 : 1 adduct fraction (4.76 g, 15.86 mmol, 88%); and (iii) a polymeric residue

(ca. 0.4 g) which remained in the tube and was not examined further. Examination of the 1:1 adduct fraction by g.l.c. (4 m column at 100 °C) showed the presence of six components [(A)—(F)] in the ratio 2:1:4:41:5:47 and the four major components [(C)—(F)] were separated by g.l.c. (as above). Component (C) could not be obtained pure [admixed with component (D)], but it was identified as 1-bromomethyl-2-methyl-*NN*-bis(trifluoromethyl)prop-2-enylamine (5) (0.19 g, 0.63 mmol, 3.5%) by ¹⁹F n.m.r. spectroscopy [−23.5 (s) p.p.m.] and coupled g.l.c. (as above)—mass spectrometry; component (D) was identified as 1-bromomethyl-1-methyl-*NN*-bis(trifluoromethyl)prop-2-enylamine (2b) (1.95 g, 6.50 mmol, 36%) (Found: C, 28.2; H, 2.9; N, 4.7. C₇H₈BrF₆N requires C, 27.9; H, 2.65; N, 4.6%); component (E) was identified as 4-bromo-2-methyl-*NN*-bis(trifluoromethyl)but-2-enylamine (6) (0.24 g, 0.79 mmol, 4.5%); component (F) was identified as 4-bromo-3-methyl-*NN*-bis(trifluoromethyl)but-2-enylamine (3b) (2.24 g, 7.46 mmol, 41.5%) (Found: C, 28.1; H, 2.8; N, 4.7%; M⁺, 300). Components (A) and (B) were identified by g.l.c.—mass spectrometry as either 2-methyl-1,4-bis[bis(trifluoromethyl)amino]but-2-ene (7b) or 3-methyl-3,4-bis[bis(trifluoromethyl)amino]but-1-ene (7a) (0.12 g, 0.32 mmol, 1.5%); and a bromomethylbuta-1,3-diene (0.02 g, 0.16 mmol, 1%).

(e) *With 2,3-dimethylbuta-1,3-diene.* The *N*-bromoamine (1.45 g, 6.25 mmol), contained *in vacuo* in a blackened Pyrex ampoule (ca. 50 cm³) at −78 °C, was slowly treated (0.5 h) with portions of the diene (0.514 g, 6.25 mmol) and the ampoule and contents were kept at −78 °C (0.5 h) and then at −45 °C (0.5 h) to give (i) a mixture (0.07 g, 0.50 mmol, 8%) of *NN*-bis(trifluoromethyl)amine and perfluoro-2-azapropene (i.r.); (ii) a 1:1 adduct fraction (1.69 g, 5.38 mmol, 86%) (Found: C, 30.7; H, 3.3; N, 4.4. Calc. for C₈H₁₀BrF₆N: C, 30.5; H, 3.1; N, 4.5%); and (iii) a residue (ca. 0.2 g) which was not examined further. The 1:1 adduct fraction was separated by g.l.c. (4 m column at 110 °C) into its three components (ratio 12:6:82) identified as 1-bromomethyl-1,2-dimethyl-*NN*-bis(trifluoromethyl)prop-2-enylamine (2c) (0.20 g, 0.65 mmol, 10%); *cis*-4-bromo-2,3-dimethyl-*NN*-bis(trifluoromethyl)but-2-enylamine (8) (0.10 g, 0.32 mmol, 5%); and *trans*-4-bromo-2,3-dimethyl-*NN*-bis(trifluoromethyl)but-2-enylamine (3c) (1.39 g, 4.41 mmol, 71%) (Found: C, 30.5; H, 3.3; N, 4.6%).

(f) *With cyclohexene.* A mixture of the olefin (1.64 g, 20.0 mmol) and the *N*-bromoamine (4.64 g, 20.0 mmol), sealed in a Pyrex ampoule (ca. 50 cm³) and kept *in vacuo* at −78 °C in the dark (96 h), gave (i) *NN*-bis(trifluoromethyl)amine (0.41 g, 2.71 mmol, 13%); (ii) unchanged cyclohexene (0.08 g, 1.0 mmol, 5% recovered); (iii) *trans*-4-bromo-*NN*-bis(trifluoromethyl)cyclohexylamine (22) (5.37 g, 17.1 mmol, 86% on amine, 90% on olefin) (Found: C, 30.8; H, 3.3; N, 4.4; F, 36.0%; M⁺, 314. C₈H₁₀BrF₆N requires C, 30.55; H, 3.2; N, 4.5; F, 36.3%; M, 314); and (iv) a dark residue (ca. 0.4 g) which was not examined further.

*Dehydrobromination of 1-Bromomethyl-*NN*-bis(trifluoromethyl)prop-2-enylamine.*—The amine (1.43 g, 5.0 mmol), heated *in vacuo* with an excess of powdered potassium hydroxide (ca. 10 g) at 60 °C (2 h), gave unchanged amine (0.07 g, 0.25 mmol, 5% recovered) and 2-[*NN*-bis(trifluoromethyl)amino]buta-1,3-diene (8) (0.98 g, 4.75 mmol, 100%) (Found: C, 35.3; H, 2.6; N, 6.7%; M⁺, 205. Calc. for C₆H₅F₆N: C, 35.1; H, 2.4; N, 6.8%; M, 205); i.r. λ_{max}. 6.08w and 6.25m (conjugated C=C str) μm.

*Dehydrobromination of 4-Bromo-*NN*-bis(trifluoromethyl)but-2-enylamine.*—The 1,4-adduct (0.43 g, 1.5 mmol) condensed *in vacuo* onto an excess of powdered potassium hydroxide (11.41 g) and the mixture heated until the hydroxide became molten gave unchanged adduct (0.06 g, 0.21 mmol, 14% recovered) and 1-[*NN*-bis(trifluoromethyl)amino]buta-1,3-diene (0.22 g, 1.08 mmol, 84%) (Found: C, 35.1; H, 2.6%; M⁺, 205. C₆H₅F₆N requires C, 35.1; H, 2.4%; M, 205); i.r., λ_{max}. 6.05m and 6.27w (conjugated C=C str), 10.20s [C–N str in (CF₃)₂N], and 14.0s (CF₃ def) μm. The diene was shown by n.m.r. spectroscopy to be a mixture of the *cis*- and *trans*-isomers in the ratio 60:40 (the chemical shifts of the protons in the minor *trans*-isomer could not be determined because of overlapping of bands in *cis*-isomer).

*Thermolysis of 1-Bromomethyl-*NN*-bis(trifluoromethyl)prop-2-enylamine.*—The 1,2-adduct (0.15 g, 0.54 mmol) heated in a Pyrex ampoule (ca. 18 cm³) at 220 °C (5.5 h) gave a liquid product (0.15 g, 100%) which was shown by g.l.c. (2 m SE30 at 75 °C) to be predominantly (>95%) unchanged 1,2-adduct.

*Thermolysis of trans-4-Bromo-*NN*-bis(trifluoromethyl)but-2-enylamine.*—(a) *Experiment 1.* The *trans*-1,4-adduct (0.14 g, 0.49 mmol) heated in a Pyrex ampoule (ca. 18 cm³) at 220 °C (5 h) gave a liquid product (0.14 g, 100%) which was shown by g.l.c. (2 m SE30 at 75 °C) to be a mixture of ten components [(A)—(H), (K), and (L)] in the ratio 1:trace:12:5:1:trace:2:1:15:62; the mixture was subjected to g.l.c. (as above)—mass spectrometry and the mass spectra of the components were recorded. Component (L) was identified as unchanged *trans*-1,4-adduct (ca. 62% recovered) and component (D) was identified as the 1,2-adduct (2a) (ca. 5%). All the components except (A) and (B) were shown to have the same molecular formula as the reactant 1,4-adduct (C₈H₈BrF₆N; M, 287 and 285) and they were identified as follows: (i) 1-[*NN*-bis(trifluoromethyl)amino]buta-1,3-diene (14) possibly containing some of the 2-substituted isomer (8) [component (A), ca. 1%]; (ii) either *NN*-bis(trifluoromethyl)but-1-enylamine (15) or *NN*-bis(trifluoromethyl)-1-methylprop-2-enylamine (16) [component (B), trace]; (iii) 2-bromo-*NN*-bis(trifluoromethyl)but-3-enylamine (17) [component (C), ca. 12%]; (iv) 3-bromo-*NN*-bis(trifluoromethyl)but-1-enylamine (18) [component (E), ca. 1%]; (v) an unknown compound (C₈H₈BrF₆N) [component (F), trace]; (vi) *trans*-4-bromo-*NN*-bis(trifluoromethyl)but-3-enylamine (19a) [component (G), ca. 2%]; (vii) *cis*-4-bromo-*NN*-bis(trifluoromethyl)but-3-enylamine (19b) [component (H), ca. 1%]; and (viii) 1-bromo-*NN*-bis(trifluoromethyl)but-2-enylamine (21) [component (K), ca. 15%].

(b) *Experiment 2.* The *trans*-1,4-adduct (0.12 g, 0.42 mmol), heated in a Pyrex ampoule (ca. 18 cm³) *in vacuo* at 220 °C (7 d), gave a liquid product (0.12 g, 100%) which was shown by g.l.c. (2 m SE30 at 75 °C) and g.l.c. (as above)—mass spectrometry to be a mixture of components (A)—(H), (K), and (L) as obtained in the previous experiment and a new component (J) in the ratio 6:3:5:4:39:trace:11:5:4:trace:22, together with eight minor components (total <1%). Component (J) had the molecular formula C₆H₅BrF₆N and was possibly 4-bromo-*NN*-bis(trifluoromethyl)but-1-enylamine (20) (ca. 4%). The ¹H n.m.r. spectrum of the material had signals at δ 0.2 [=CHBr assigned to (19)], 1.2—1.9 (=CH- and =CH₂), 2.7 [CHBr assigned to (18)], 3.4—3.5 (CH₂Br, and CH₂N), 3.9—4.2 (=C–CH₂-), 4.4—5.2 (CH₂ and CH₃), and 5.55 [d, CHBrMe, J_{Me,H} 7 Hz assigned to (18)], high field from external 4-

$\text{ClC}_6\text{H}_4\text{Cl}$, and the ^{19}F spectrum showed 2 major signals at -18.2 and -18.8 p.p.m. (ratio 14:8), assigned to compounds (18) and (3a) [components (E) and (L)], respectively, and minor bands at -17.0 , -17.7 , -19.5 , -22.8 , and -23.2 p.p.m.

Experiment 3. The *trans*-1,4-adduct (0.21 g, 0.73 mmol), heated *in vacuo* in an n.m.r. tube at 200°C (3 h) (liquid and gas phases present), gave (i) silicon tetrafluoride (ca. 0.02 g); (ii) liquid product (0.15 g, 71%); and (iii) polymeric material (0.04 g) which coated the walls of the tube. The liquid product was shown by g.l.c. (2 m SE30 at 75°C) and g.l.c. (as above)—mass spectrometry to be a mixture of components (A)—(H), (K), and (L) as in experiment 1 in the ratio trace:2:9:11:trace:trace:11:5:11:46, a new component (B') (4 parts), and various minor unidentified components (<1%). Component (B') (ca. 3%) did not contain bromine and was tentatively identified as a bis-[bis(trifluoromethyl)amino]butene, probably the 3,4-disubstituted-but-1-ene (4a).

Reactions of trans-2-Bromo-NN-bis(trifluoromethyl)cyclohexylamine.—(a) *Attempted dehydrobromination.* Reactions of the amine with an excess of powdered potassium hydroxide *in vacuo* at temperatures in the range 60 — 120°C (2—12 h) and with potassium *t*-butoxide in *t*-butanol under reflux gave only unchanged reactant amine (94—100%).

(b) *Pyrolysis.* Passage of the amine (1.26 g, 4.0 mmol) *in vacuo* through a silica tube (50 cm, 1.5 cm internal diameter) at 600°C (0.5 h) gave a volatile fraction (0.48 g, 3.6 mmol) which was shown by i.r. spectroscopy to consist mainly of perfluoro-2-azapropene together with smaller

amounts of silicon tetrafluoride, trifluoromethyl isocyanate, trifluoromethane, and *NN*-bis(trifluoromethyl)amine. Pyrolysis at temperatures $<550^\circ\text{C}$ gave near-quantitative recoveries of reactant amine.

(c) *Reduction.* A mixture of the amine (0.63 g, 2.0 mmol) and lithium aluminium hydride (0.19 g, 5.0 mmol) in diethyl ether (20 cm^3) was heated under reflux (4 h). The excess of hydride was destroyed with water, the ether layer was separated, and the aqueous layer was extracted with ether (2 \times 10 cm^3). The combined extracts were dried (MgSO_4) and the ether removed *in vacuo* to give impure *NN*-bis(trifluoromethyl)cyclohexylamine (23) (ca. 0.25 g, ca. 1.04 mmol, ca. 52%).

[9/054 Received, 11th January, 1979]

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