

## Polyfluoroalkyl Derivatives of Nitrogen. Part XXXIX.<sup>1</sup> Preparation of *NN*-Bistrifluoromethylamino-substituted Allenes<sup>2</sup>

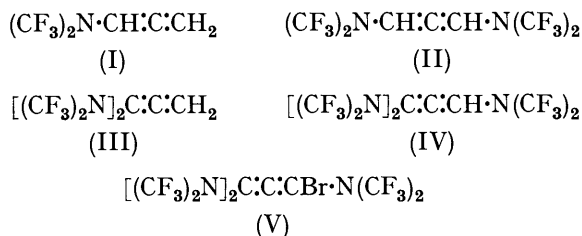
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*N*-Bromobistrifluoromethylamine reacts with an excess of allene in the vapour phase in light to give the 1:1 adducts 2-bromo-*NN*-bistrifluoromethylprop-2-enylamine and 2-(bistrifluoromethylamino)-3-bromopropene in the ratio 90:10; the 2:1 adduct 1,3-di-(*NN*-bistrifluoromethylamino)-2,2-dibromopropane is obtained from a 2:1 molar mixture of the *N*-bromo-amine and allene. The major 1:1 adduct and the 2:1 adduct are dehydrobrominated in high yield to give the allenes *NN*-bistrifluoromethylpropadienylamine and 1,3-di(bistrifluoromethylamino)propadiene, respectively. In the liquid phase in the dark the *N*-bromo-amine reacts with the monosubstituted allene to yield a mixture of 3,3-di(bistrifluoromethylamino)-2-bromopropene and *cis*- and *trans*-1,3-di(bistrifluoromethylamino)-2-bromopropene; the former adduct gives 1,1-di(bistrifluoromethylamino)propadiene on dehydrobromination. 1,3,3-Tri(bistrifluoromethylamino)propadiene is formed by dehydrobromination of the *N*-bromo-amine adduct with the 1,3-disubstituted allene; it reacts with the *N*-bromo-amine to afford *NN*-bistrifluoromethylamine and 1,1,3-tri(bistrifluoromethylamino)-3-bromopropadiene.

OLEFINS<sup>1,3</sup> and acetylenes<sup>4,5</sup> which contain a bistrifluoromethylamino-group are most conveniently synthesised by the dehydrohalogenation of suitable 1:1 adducts obtained by the reaction of *N*-bromobistrifluoromethylamine with various unsaturated compounds. Two substituted buta-1,3-dienes have also been prepared.<sup>6</sup>

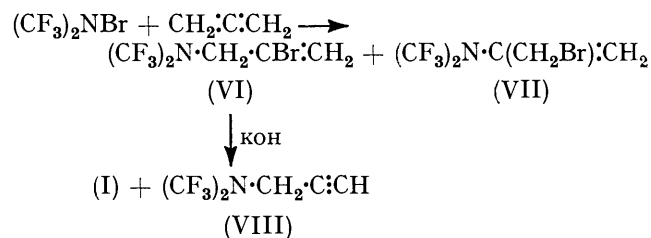
*NN*-Bistrifluoromethylpropadienylamine (I) has been reported previously as formed (i) by dehydrohalogenation<sup>1</sup> of the 1:1 adduct, (CF<sub>3</sub>)<sub>2</sub>N·CH<sub>2</sub>·CHBr·CH<sub>2</sub>Cl, of the *N*-bromo-amine with vinyl chloride (*ca.* 5% yield) and (ii) by dehydrobromination<sup>5</sup> of a mixture of *cis*- and *trans*-2-bromo-*NN*-bistrifluoromethylprop-1-enylamine (62% yield).

In the present work the allene (I) has been prepared by an improved route and the allenes (II)—(V) have also been synthesised.

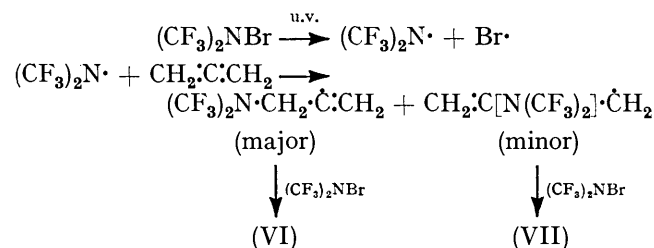


*NN*-Bistrifluoromethylpropadienylamine (I).—A mixture of the *N*-bromo-amine and an excess of allene in the vapour phase in daylight, gave a mixture of the 1:1 adducts 2-bromo-*NN*-bistrifluoromethylprop-2-enylamine (VI) (85%) and 2-(bistrifluoromethylamino)-3-bromopropene (VII) (10%) in the ratio 90:10. Treatment of the olefin (VI) with dry potassium hydroxide

*in vacuo* gave a mixture of the allene (I) (93%) and *NN*-bistrifluoromethylprop-2-ynylamine (VIII) (5%).



The reactions of the *N*-bromo-amine with olefins under photochemical or thermal conditions are considered<sup>7</sup> to proceed *via* free-radical mechanisms, involving initial attack on the olefin by the bistrifluoromethylamino-radical. Thus in the reaction with allene predominant radical attack takes place on the terminal CH<sub>2</sub> groups leading to the formation of adduct (VI) as the major product.



Similar results have been reported<sup>8</sup> for the majority of radical additions to allene and radical localisation energies calculated for allene suggest that initial attack should take place predominantly on the terminal sites.<sup>9</sup> However, with certain radical additions, *e.g.* with benzenethiol<sup>10</sup> and hydrogen bromide,<sup>11</sup> appreciable amounts of products, 20–30% and *ca.* 50%, respectively, from initial radical attack on the central

<sup>1</sup> Part XXXVIII, D. H. Coy, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, preceding paper.

<sup>2</sup> Preliminary communication, D. H. Coy, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *Chem. Comm.*, 1970, 456; Presented in part at the 6th International Fluorine Symposium, Durham, 1971.

<sup>3</sup> E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 796.

<sup>4</sup> J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 1096.

<sup>5</sup> J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1969, 1955.

<sup>6</sup> F. S. Fawcett to E. I. Du Pont de Nemours and Co., U.S.P. 3,311,599/1967.

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

<sup>8</sup> D. R. Taylor, *Chem. Rev.*, 1967, **67**, 317.

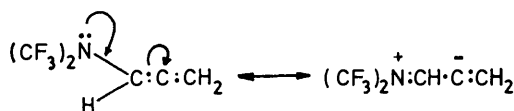
<sup>9</sup> B. Pullman, *J. Chem. Phys.*, 1958, **32**, 790.

<sup>10</sup> K. Griesbaum, A. A. Oswald, E. R. Quiram, and P. E. Butler, *J. Org. Chem.*, 1963, **28**, 1952; E. I. Heiba, *ibid.*, 1966, **31**, 776.

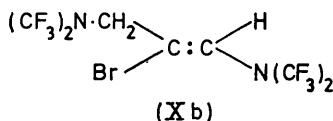
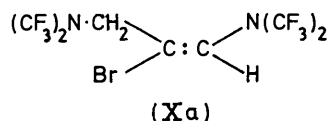
<sup>11</sup> P. I. Abell and R. S. Anderson, *Tetrahedron Letters*, 1964, 3727; K. Griesbaum, A. A. Oswald, and D. N. Hall, *J. Org. Chem.*, 1964, **29**, 2404.

carbon atom of allene are isolated. It has been suggested that in these additions terminal attack is reversible, but that central attack is followed by rapid achievement of allylic configuration and is then essentially non-reversible.<sup>10,11</sup> Radical attack on allene in general, therefore, may be governed by the degree of reversibility of attack at the terminal positions, which competes with the chain-transfer reaction. If the chain-transfer step is made more favourable by the use of an excess of the addend, then the degree of central attack should decrease provided that terminal attack is reversible. Thus in the present work only a trace of adduct (VII), formed by central attack, was isolated in a reaction for which a 2 : 1 molar ratio of *N*-bromo-amine to allene was used (see later). This suggests that terminal attack on allene by the  $(\text{CF}_3)_2\text{N}\cdot$  radical is to some extent reversible in the absence of an excess of the *N*-bromo-amine.

Dehydrobromination of adduct (VI) gave the allene (I) and the acetylene (VIII) in the ratio 95 : 5; it is interesting to compare this ratio with the allene : acetylene ratio (66 : 34) obtained in dehydroiodination of the olefin  $\text{CF}_3\cdot\text{CH}_2\cdot\text{CI}\cdot\text{CH}_2$ .<sup>12</sup> Since the inductive effects of the bistrifluoromethylamino- and trifluoromethyl groups are nearly equivalent,<sup>13</sup> any slight difference in the ease of removal of corresponding protons does not explain the widely differing product ratios. In the allene (I), however, increased stability, relative to the allene  $\text{CF}_3\cdot\text{CH}\cdot\text{C}\cdot\text{CH}_2$ , may be imparted by mesomeric interaction between the nitrogen lone pair and the adjacent  $\pi$ -electron system.



Evidence that mesomerism of this type occurs with all of the bistrifluoromethylamino-substituted allenes



prepared in the present work is found in their u.v. spectra (Table I). The predominant formation of the

TABLE I  
U.v. spectra

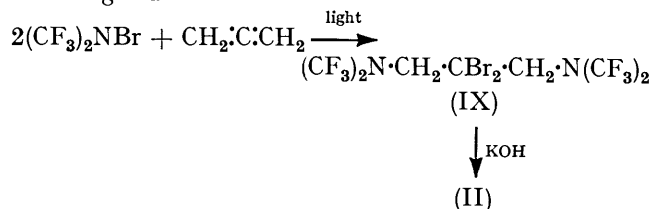
	$\lambda_{\text{max.}}$ / nm	$\epsilon_{\text{max.}}$	$\lambda_{\text{inf.}}$ /nm	$\epsilon_{\text{inf.}}$
$(\text{CF}_3)_2\text{N}\cdot\text{CH}\cdot\text{C}\cdot\text{CH}_2$	207	290	228—235	150—160
$[(\text{CF}_3)_2\text{N}]_2\text{C}\cdot\text{C}\cdot\text{CH}_2$	209	590	219—223	440—450
$(\text{CF}_3)_2\text{N}\cdot\text{CH}\cdot\text{C}\cdot\text{CH}\cdot\text{N}(\text{CF}_3)_2$	211	560	225—232	300—350
$[(\text{CF}_3)_2\text{N}]_2\text{C}\cdot\text{C}\cdot\text{CH}\cdot\text{N}(\text{CF}_3)_2$	213	2220	232—242	620—790
$[(\text{CF}_3)_2\text{N}]_2\text{C}\cdot\text{C}\cdot\text{CBr}\cdot\text{N}(\text{CF}_3)_2$	211	13,200	252—257	830—920

allene (I) in the present case may result from the

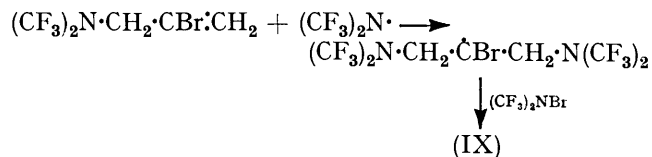
<sup>12</sup> R. N. Haszeldine, K. Leedham, and B. R. Steele, *J. Chem. Soc.*, 1954, 2040.

absence of mesomerism of the type shown by the alkyne (VIII) and the allene  $\text{CF}_3\cdot\text{CH}\cdot\text{C}\cdot\text{CH}_2$ .

1,3-Di(bistrifluoromethylamino)propadiene (II).—This compound was synthesised in high overall yield by the following route:



The reaction of a 2 : 1 molar mixture of the *N*-bromo-amine and allene in the vapour phase in daylight gave the 2 : 1 adduct 1,3-di(bistrifluoromethylamino)-2,2-dibromopropane (IX) (93%), together with a small amount (3%) of a mixture of the 1 : 1 adducts (VI) and (VII). It is considered that the 2 : 1 adduct (IX) is formed *via*  $(\text{CF}_3)_2\text{N}\cdot$  radical attack on the terminal  $\text{CH}_2$  group of the initially formed 1 : 1 adduct (VI), which would give the more stable intermediate tertiary radical.

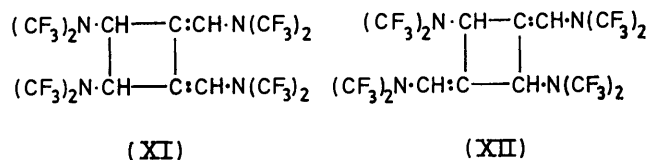


Products arising from radical attack on the isomeric 1 : 1 adduct (VII) or from radical attack on (VI) at the central carbon atom were not detected.

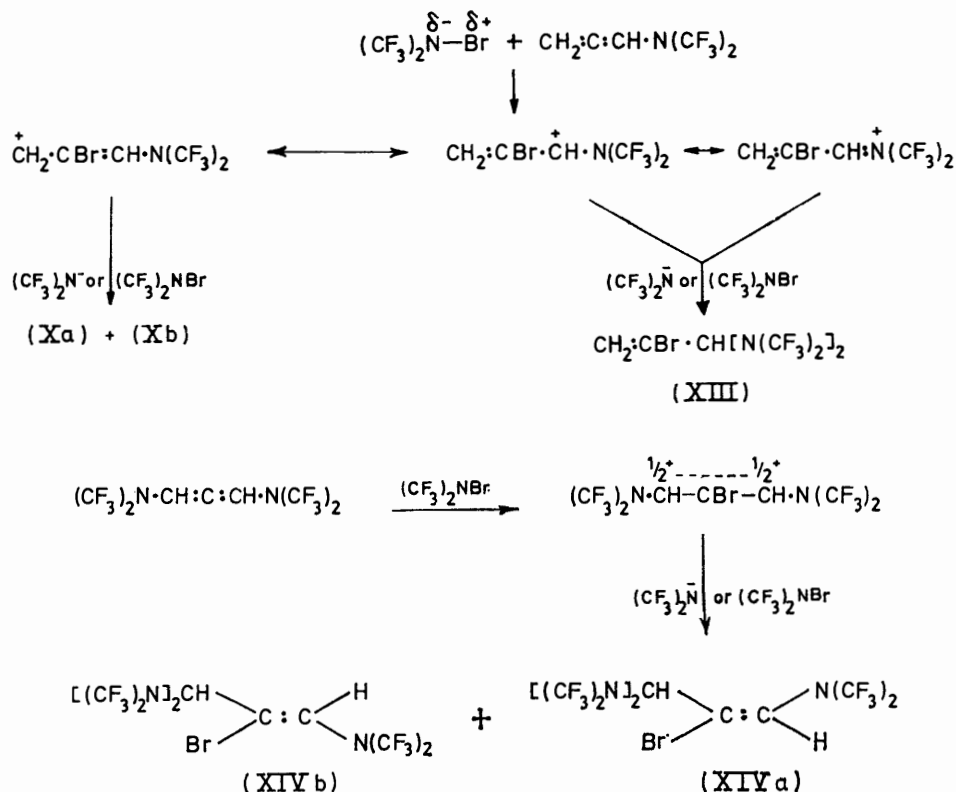
Complete dehydrobromination of the 2 : 1 adduct (IX) over potassium hydroxide gave the allene (II) (97%) as the only volatile product.

Dehydrobromination under milder conditions enabled the intermediate *cis*- (Xa) (20%) and *trans*- (Xb) (40%) olefin isomers of 1,3-di(bistrifluoromethylamino)-2-bromopropene to be isolated together with the allene (II) (36%).

When kept *in vacuo* at room temperature samples of the allene (II) partially solidified owing to the formation of a dimer believed to be 1,2-di(bistrifluoromethylamino)-3,4-di(bistrifluoromethylaminomethylene)cyclobutane (XI) or (less probably) the head-to-tail isomer (XII).



<sup>13</sup> F. S. Fawcett and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1965, 87, 4341.



At  $60^\circ$  rapid dimerisation of (II) took place (97% yield).

The  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. spectra of the dimer (Table 2) showed it to consist entirely of one isomer, but it is not possible on the present evidence to assign the structure with certainty.

*1,1-Di(bistrifluoromethylamino)propadiene* (III).—The reaction of the *N*-bromo-amine with the allene (I) in the liquid phase at  $-78^\circ$  in the dark gave *3,3*-di(bistrifluoromethylamino)-2-bromopropene (XIII) (71%) and a mixture (24%) of the *cis*- and *trans*-olefins (Xa) and (Xb), respectively, in the ratio 42 : 58.

Electrophilic attack on the allene (I) would be expected to take place on the central carbon atom since a resultant linear carbonium ion would be stabilised by the nitrogen lone pair and possibly by allylic resonance. It is also possible that cyclic bromonium ion intermediates are involved in the reaction.

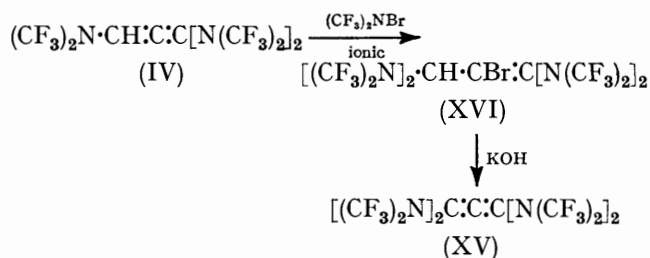
Dehydrobromination of the bromo-olefin (XIII) gave the allene (III) (96%) as the only volatile product.

*1,1,3-Tri(bistrifluoromethylamino)propadiene* (IV).—The addition under ionic conditions ( $-78^\circ$ , liquid phase, dark) of the *N*-bromo-amine to the 1,3-disubstituted allene (II) gave a mixture (98%) of the 1 : 1 adducts *cis*- and *trans*-1,3,3-tri(bistrifluoromethylamino)-2-bromopropene (XIVa and b), respectively, in the ratio 44 : 56.

Dehydrobromination of the olefins (XIVa) and (XIVb) separately gave the allene (IV) in 94 and 90% yields, respectively.

*1,1,3-Tri(bistrifluoromethylamino)-3-bromopropadiene*

(V).—The following route to the tetrasubstituted allene (XV) was investigated:



The liquid-phase reaction at  $-78^\circ$  of the *N*-bromo-amine with the allene (IV) did not give the expected 1 : 1 adduct (XVI), but instead the bromo-allene (V) (93%) and *NN*-bistrifluoromethylamine (98%) were formed. These products probably arise *via* initial electrophilic attack on the allene (IV) by the *N*-bromo-amine, or by a trace of bromine present in the amine, followed by proton loss from the resultant intermediate carbonium ion.

#### EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system in order to avoid contamination with air and moisture. *N*-Bromobistrifluoromethylamine reacts with mercury and was, therefore, manipulated in a special apparatus attached to the main system. All reaction vessels were thoroughly dried before use, but the products from the *N*-bromo-amine reactions frequently contained small quantities of the hydrolysis products, *NN*-bistrifluoromethylamine and perfluoro-2-aza-

propene. Products were separated either by repeated fractional distillation *in vacuo* or by preparative scale g.l.c. (Perkin-Elmer 116, 154B, or 451 Fraktometers) and identified by molecular weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer 21 instrument with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 spectrophotometer operating at 60.0 MHz for  $^1\text{H}$  and 56.46 MHz for  $^{19}\text{F}$ ), mass spectrometry (A.E.I. MS/2H instrument with a resolution of 1 in 700), and g.l.c. B.p.s of liquids were determined by the Siwoloboff method.

**Reaction of N-Bromobis(trifluoromethyl)amine with an Excess of Allene.**—The *N*-bromo-amine (2.69 g, 11.60 mmol) and allene (0.60 g, 15.00 mmol), in the vapour phase at room temperature in a Pyrex bulb (5 l) exposed to daylight (4 h), gave (i) unchanged allene (0.13 g, 3.25 mmol, 22% recovered) contaminated with a trace of perfluoro-2-azapropene, (ii) *NN*-bis(trifluoromethyl)amine (0.06 g, 0.37 mmol), and (iii) a higher-boiling fraction (3.20 g, 11.00 mmol, 95%) separated by g.l.c. (4 m silicone SE 30 oil at 60°) into 2-bromo-*NN*-bis(trifluoromethyl)prop-2-enylamine (VI) (2.88 g, 9.90 mmol, 85%) (Found: C, 22.1; H, 1.5; N, 5.5%; *M*, 274.  $\text{C}_5\text{H}_4\text{BrF}_6\text{N}$  requires C, 22.1; H, 1.5; N, 5.2%; *M*, 272), b.p. 93° at 758 mmHg, and 2-(*NN*-bis(trifluoromethyl)amino)-3-bromopropene (VII) (0.32 g, 1.10 mmol, 10%) (Found: C, 22.1; H, 1.5; N, 5.3%; *M*, 271), b.p. 102° at 758 mmHg.

**Reaction of a 2 : 1 Molar Excess of N-Bromobis(trifluoromethyl)amine with Allene.**—The *N*-bromo-amine (2.61 g, 11.20 mmol) and allene (0.22 g, 5.60 mmol), in the vapour phase at room temperature in a Pyrex bulb (5 l) exposed to daylight (5 h), gave a mixture (0.08 g, 0.30 mmol, 3%) of the 1 : 1 adducts 2-bromo-*NN*-bis(trifluoromethyl)prop-2-enylamine and 2-(*NN*-bis(trifluoromethyl)amino)-3-bromopropene, and 1,3-di(bis(trifluoromethyl)amino)-2,2-dibromopropane (IX) (2.62 g, 5.19 mmol, 93%) (Found: C, 16.8; H, 0.9; N, 5.7.  $\text{C}_7\text{H}_4\text{Br}_2\text{F}_{12}\text{N}_2$  requires C, 16.6; H, 0.8; N, 5.5%), b.p. 171—172° at 756 mmHg.

**Reaction of 2-Bromo-*NN*-bis(trifluoromethyl)prop-2-enylamine (VI) with Potassium Hydroxide.**—The bromo-olefin (2.77 g, 10.18 mmol), refluxed at 10 cmHg over a large excess of dry, powdered potassium hydroxide (4 h), gave (i) a low-boiling fraction (1.77 g, 9.26 mmol, 98%) separated by g.l.c. (8 m fluorosilicone FS 1 oil at 50°) into *NN*-bis(trifluoromethyl)propadienylamine (I) (1.68 g, 8.80 mmol, 93%) (Found: C, 31.3; H, 1.7; N, 7.3%; *M*, 194.  $\text{C}_5\text{H}_3\text{F}_6\text{N}$  requires C, 31.2; H, 1.6; N, 7.3%; *M*, 191), b.p. 51° at 770 mmHg,  $\lambda_{\text{max}}$  5.09  $\mu\text{m}$  (C:C str.), and *NN*-bis(trifluoromethyl)prop-2-enylamine (0.09 g, 0.46 mmol, 5%),  $\lambda_{\text{max}}$  2.98  $\mu\text{m}$  (C-H str.) and 4.56  $\mu\text{m}$  (C:C str.), and (ii) unchanged bromo-olefin (0.17 g, 0.63 mmol, 6% recovered).

**Reaction of 1,3-Di(bis(trifluoromethyl)amino)-2,2-dibromopropane (IX) with Potassium Hydroxide under Harsh Conditions.**—The dibromide (2.62 g, 5.19 mmol), refluxed under reduced pressure (3 cmHg) over a large excess of dry, powdered potassium hydroxide (3 h), gave 1,3-di(bis(trifluoromethyl)amino)propadiene (II) (1.72 g, 5.03 mmol, 97%) (Found: C, 25.0; H, 0.7; N, 7.8%; *M*, 342.  $\text{C}_7\text{H}_2\text{F}_{12}\text{N}_2$  requires C, 24.7; H, 0.6; N, 8.0%; *M*, 342), b.p. 106° at 758 mmHg,  $\lambda_{\text{max}}$  5.03  $\mu\text{m}$  (C:C str.).

**Reaction of 1,3-Di(bis(trifluoromethyl)amino)-2,2-dibromopropane (IX) with Potassium Hydroxide under Mild Conditions.**—The dibromide (3.00 g, 5.95 mmol), refluxed *in vacuo* over a large excess of dry, powdered potassium

hydroxide (1 h), gave unchanged dibromide (0.31 g, 0.61 mmol, 10% recovered) and a mixture (1.99 g, 5.08 mmol, 96%) which was separated by g.l.c. (8 m fluorosilicone FS 1 oil at 150°) into 1,3-di(bis(trifluoromethyl)amino)propadiene (0.67 g, 1.96 mmol, 36%), *trans*-1,3-di(bis(trifluoromethyl)amino)-2-bromopropene (Xa) (0.88 g, 2.08 mmol, 40%) (Found: C, 19.9; H, 0.9; N, 6.7.  $\text{C}_7\text{H}_3\text{BrF}_{12}\text{N}_2$  requires C, 19.9; H, 0.7; N, 6.6%), b.p. 130° at 750 mmHg, and *cis*-1,3-di(bis(trifluoromethyl)amino)-2-bromopropene (Xb) (0.44 g, 1.04 mmol, 20%) (Found: C, 19.9; H, 0.9; N, 6.7%), b.p. 133° at 750 mmHg.

**Reaction of 1,3-Di(bis(trifluoromethyl)amino)propadiene (II) on Heating.**—The diene (0.86 g, 2.51 mmol) on heating at 60° (72 h) in a Pyrex ampoule (*ca.* 10 ml) gave unchanged diene (0.25 g, 0.72 mmol, 28% recovered) and the *dimer* (0.60 g, 0.85 mmol, 97%) (Found: C, 24.8; H, 0.8; N, 7.9.  $\text{C}_{14}\text{H}_4\text{F}_{24}\text{N}_4$  requires C, 24.7; H, 0.6; N, 8.0%), m.p. 58—59°.

**Reaction of N-Bromobis(trifluoromethyl)amine with *NN*-Bis(trifluoromethyl)propadienylamine.**—The *N*-bromo-amine (2.25 g, 9.70 mmol) and the diene (2.11 g, 11.04 mmol), sealed in a Pyrex ampoule (*ca.* 20 ml) and kept at -78° in the dark (3 h), gave unchanged diene (0.25 g, 1.31 mmol, 12% recovered) and a mixture (3.90 g, 9.22 mmol, 95%) which was separated by g.l.c. (8 m fluorosilicone FS 1 oil at 150°) into 3,3-di(bis(trifluoromethyl)amino)-2-bromopropene (XIII) (2.77 g, 6.54 mmol, 71%) (Found: C, 20.1; H, 1.0; N, 6.4.  $\text{C}_7\text{H}_3\text{BrF}_{12}\text{N}_2$  requires C, 19.9; H, 0.7; N, 6.6%), b.p. 128° at 756 mmHg, *trans*-1,3-di(bis(trifluoromethyl)amino)-2-bromopropene (0.63 g, 1.49 mmol, 14%), and *cis*-1,3-di(bis(trifluoromethyl)amino)-2-bromopropene (0.50 g, 1.19 mmol, 10%).

**Reaction of 3,3-Di(bis(trifluoromethyl)amino)-2-bromopropene (XIII) with Potassium Hydroxide.**—The bromo-olefin (1.38 g, 3.26 mmol), refluxed at 2 cmHg over a large excess of dry, powdered potassium hydroxide (3 h), gave 1,1-di(bis(trifluoromethyl)amino)propadiene (III) (1.07 g, 3.12 mmol, 96%) (Found: C, 24.8; H, 0.7; N, 8.1%; *M*, 342.  $\text{C}_7\text{H}_2\text{F}_{12}\text{N}_2$  requires C, 24.7; H, 0.6; N, 8.0%; *M*, 342), b.p. 96° at 760 mmHg.

**Reaction of N-Bromobis(trifluoromethyl)amine with 1,3-Di(bis(trifluoromethyl)amino)propadiene (II).**—The *N*-bromo-amine (1.64 g, 7.06 mmol) and the diene (1.21 g, 3.53 mmol) were sealed in a Pyrex ampoule (*ca.* 20 ml) and kept at -78° in the dark (3 h). Excess of *N*-bromo-amine was removed by shaking *in vacuo* with mercury. The volatile product (2.00 g, 3.48 mmol, 98%) was separated by g.l.c. (4 m Kel-F oil at 110°) into *cis*-1,3,3-tri(bis(trifluoromethyl)amino)-2-bromopropene (XIVa) (0.90 g, 1.57 mmol, 44%) (Found: C, 18.9; H, 0.5; N, 7.2.  $\text{C}_9\text{H}_2\text{BrF}_{18}\text{N}_3$  requires C, 18.8; H, 0.4; N, 7.3%), b.p. 156° at 757 mmHg, and *trans*-1,3,3-tri(bis(trifluoromethyl)amino)-2-bromopropene (XIVb) (1.10 g, 1.91 mmol, 54%) (Found: C, 18.9; H, 0.6; N, 7.1%), b.p. 162—163° at 757 mmHg.

**Reaction of *cis*-1,3,3-Tri(bis(trifluoromethyl)amino)-2-bromopropene (XIVa) with Potassium Hydroxide.**—The bromo-olefin (0.50 g, 0.87 mmol), refluxed at *ca.* 1 cmHg over a large excess of dry, powdered potassium hydroxide (3 h), gave 1,1,3-tri(bis(trifluoromethyl)amino)propadiene (IV) (0.38 g, 0.77 mmol, 94%) (Found: C, 22.0; H, 0.3; N, 8.2.  $\text{C}_9\text{HF}_{18}\text{N}_3$  requires C, 21.9; H, 0.7; N, 8.5%), b.p. 132° at 769 mmHg,  $\lambda_{\text{max}}$  5.05  $\mu\text{m}$  (C:C str.).

**Reaction of *trans*-1,3,3-Tri(bis(trifluoromethyl)amino)-2-bromopropene with Potassium Hydroxide.**—The bromo-olefin (0.62 g, 1.08 mmol), refluxed at *ca.* 1 cmHg over dry,

powdered potassium hydroxide (3 h), gave 1,1,3-tri(bistrifluoromethylamino)propadiene (0.58 g, 0.97 mmol, 90%).

*Reaction of N-Bromobistrifluoromethylamine with 1,1,3-Tri(bistrifluoromethylamino)propadiene.*—The *N*-bromoamine (0.66 g, 2.84 mmol) and the diene (0.70 g, 1.44 mmol) were sealed in a Pyrex ampoule (*ca.* 10 ml) and kept at

than one *cis* to a bromine atom. Since no vicinal proton coupling was detected for either isomer of the olefin  $(CF_3)_2N \cdot CH_2 \cdot CBr \cdot CH \cdot N(CF_3)_2$ , the *cis*- and *trans*-configurations were assigned on this basis. A vicinal proton coupling was found for one isomer only of the olefin  $[(CF_3)_2N]_2CH \cdot CBr \cdot CH \cdot N(CF_3)_2$ , and this was given the

TABLE 2  
N.m.r. spectral data

	$^{19}F$			Chem. shift (p.p.m.)	$^1H$			Chem. shift ( $\tau$ )	Coupling constants ( $J/Hz$ )
	Group	Type	Intensity		Group	Type	Intensity		
$(CF_3)_2N \cdot \overset{a}{CH} \cdot \overset{b}{C} : \overset{c}{CH_2}$	a	s(br)		-18.4	b	tsept	1	4.64	ab, 1.5
$(CF_3)_2N \cdot \overset{a}{CH_2} \cdot \overset{b}{C} : \overset{c}{CH} \cdot N(CF_3)_2$	a	s		-20.2	c	d	2	4.73	bc, 6.6
$[(CF_3)_2N]_2 \overset{a}{C} : \overset{b}{C} : CH_2$	a	s		-19.4	b	s		4.50	
$[(CF_3)_2N]_2 \overset{a}{C} : \overset{b}{C} : \overset{c}{CH} \cdot N(CF_3)_2$	a	s	2	-19.5	b	s		3.21	
$[(CF_3)_2N]_2 \overset{a}{C} : \overset{b}{C} : \overset{c}{CH} \cdot N(CF_3)_2$	c	s	1	-17.8					
$[(CF_3)_2N]_2 \overset{a}{C} : \overset{b}{C} : CBr \cdot N(CF_3)_2$	a	s	2	-20.2					
$[(CF_3)_2N]_2 \overset{a}{C} : \overset{b}{C} : \overset{c}{CH} \cdot N(CF_3)_2$	b	s	1	-20.2					
$(CF_3)_2N \cdot \overset{a}{CH_2} \cdot \overset{b}{C} : \overset{c}{CH}$	a	t		-17.5	b	dsept	2	6.00	ab, 1.2
$(CF_3)_2N \cdot \overset{a}{CH} \cdot \overset{b}{C} : \overset{c}{CH} \cdot N(CF_3)_2$	c	t	1	7.80	c	t	1	7.80	bc, 2.4
$(CF_3)_2N \cdot \overset{a}{CH} - \overset{b}{C} : \overset{c}{CH} \cdot N(CF_3)_2$	a	s	1	-19.7	b	s	1	5.15	
$(CF_3)_2N \cdot \overset{a}{CH} - \overset{b}{C} : \overset{c}{CH} \cdot N(CF_3)_2$	d	s	1	-23.9	c	s	1	3.97	
$[(CF_3)_2N \cdot \overset{a}{CH_2}]_2 CBr_2$	a	t		-22.5	b	sept		5.81	ab, 0.6
$(CF_3)_2N \cdot \overset{a}{H_2}C \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_d \\ H_e \end{matrix}$	a	t		-20.1	b	complex	2	5.98	ab, 1.2
					c	dt	1	4.25	bc, 1.9
					d	dt	1	4.05	bd, 1.8
									cd, 2.8
$(CF_3)_2N \cdot \overset{a}{C} : \overset{b}{C} \begin{matrix} H_c \\ H_d \end{matrix}$	a	s		-22.9	b	s	2	5.68	cd, 0.6
$BrH_2C \cdot \overset{a}{C} : \overset{b}{C} \begin{matrix} H_c \\ H_d \end{matrix}$					c	d	1	3.80	
					d	d	1	3.59	
$(CF_3)_2N \cdot \overset{a}{H_2}C \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_c \\ H_d \end{matrix}$	a	t	1	-19.0	b	s(br)	2	5.54	ab, 1.6
$Br \cdot \overset{a}{H_2}C \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_c \\ H_d \end{matrix}$	d	d	1	-19.3	c	sept	1	3.52	cd, 1.1
$(CF_3)_2N \cdot \overset{a}{H_2}C \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_c \\ H_d \end{matrix}$	a	s	1	-18.6	b	s	2	5.75	
$Br \cdot \overset{a}{H_2}C \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_c \\ H_d \end{matrix}$	d	s	1	-19.6	c	s	1	3.68	
$[(CF_3)_2N]_2 \overset{a}{HC} \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_d \\ H_e \end{matrix}$	a	s		-22.9	b	dd	1	3.79	bc, 3.5
$Br \cdot \overset{a}{HC} \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_d \\ H_e \end{matrix}$	c	dd	1	4.12	c	dd	1	4.25	bd, 2.0
	d	dd	1	4.25	d	dd	1	4.25	cd, 3.6
$[(CF_3)_2N]_2 \overset{a}{HC} \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_d \\ H_e \end{matrix}$	a	s	2	-23.2	b	d	1	3.26	bc, 2.4
$Br \cdot \overset{a}{HC} \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_d \\ H_e \end{matrix}$	d	s	1	-19.6	c	d	1	4.04	
$[(CF_3)_2N]_2 \overset{a}{HC} \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_d \\ H_e \end{matrix}$	a	s	2	-24.4	b	s	1	3.43	
$Br \cdot \overset{a}{HC} \cdot \overset{b}{C} : \overset{c}{C} \begin{matrix} H_d \\ H_e \end{matrix}$	d	s	1	-19.0	c	s	1	3.51	

-78° in the dark (24 h). Excess of *N*-bromoamine was removed by shaking *in vacuo* with mercury. The volatile products were *NN*-bistrifluoromethylamine (0.21 g, 1.42 mmol, 99%) and 1,1,3-tri(bistrifluoromethylamino)-3-bromopropadiene (V) (0.74 g, 1.30 mmol, 93%) (Found: C, 19.0; H, 0.3; N, 7.2.  $C_6BrF_{18}N_3$  requires C, 18.9; H, 0.0; N, 7.3%), b.p. 146° at 760 mmHg,  $\lambda_{max}$  5.03  $\mu$ m (C:C str.).

*N.m.r. Spectra.*—The data in Table 2 were recorded with trifluoroacetic acid as external reference for  $^{19}F$  and tetramethylsilane as internal reference for  $^1H$ .

It has been found previously,<sup>4</sup> and also in the spectra of certain olefins prepared in this Department, that a proton *trans* to a bromine atom absorbs at lower field

*cis*-configuration in which the coupling of the protons *trans* to each other would be expected to be greater.<sup>14</sup>

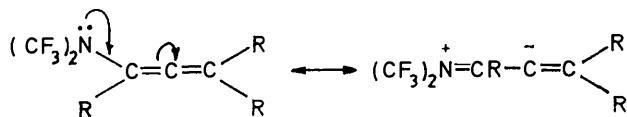
The allene  $(CF_3)_2N \cdot CH_2 \cdot C : CH_2$  exhibits a  $CH-CH_2$  coupling constant (6.6 Hz) which is in agreement with the exceptionally high values (*ca.* 6.7 Hz) reported<sup>8</sup> for allenes in general.

*U.v. Spectra.*—The positions of the maxima in the spectra (Table 1), at longer wavelengths than those reported for allene<sup>15</sup> (171 nm) and its simple homologues (*e.g.*

<sup>14</sup> J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectra,' vol. 2, Pergamon, Oxford, 1966.

<sup>15</sup> L. H. Sutcliffe and A. D. Walsh, *J. Chem. Soc.*, 1952, 899.

EtCH:C:CH<sub>2</sub>,<sup>16</sup> 170 nm), suggest that mesomerism takes place of the type illustrated. This was postulated earlier to



account for the preferential formation of the bistrifluoromethylamino-substituted allenes in certain dehydrobromination reactions. Similar  $n-\pi^*$  interactions between halogen atoms and the C:C system have been reported to explain the relatively long-wavelength maxima of the absorption in the u.v. spectra of tetrafluoroallene<sup>17</sup> (208—210 nm) and  $\alpha$ -halogenoallenes<sup>18</sup> (200—207 nm).

The following substituted allenes are listed in order of increasing  $\lambda_{\max}$  value:  $(\text{CF}_3)_2\text{N}\cdot\text{CH}:\text{C}:\text{CH}_2 < [(\text{CF}_3)_2\text{N}]_2\text{C}:\text{C}:\text{CH}_2 < (\text{CF}_3)_2\text{N}\cdot\text{CH}:\text{C}:\text{CH}\cdot\text{N}(\text{CF}_3)_2 < [(\text{CF}_3)_2\text{N}]_2\text{C}:\text{C}:\text{CBr}\cdot$

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

<sup>16</sup> L. C. Jones and L. W. Taylor, *Analyt. Chem.*, 1955, **27**, 228.

$\text{N}(\text{CF}_3)_2 < [(\text{CF}_3)_2\text{N}]_2\text{C}:\text{C}:\text{CH}\cdot\text{N}(\text{CF}_3)_2$ . The trend indicates that the degree of electron donation into the allenic electron system increases with the number of  $(\text{CF}_3)_2\text{N}$  groups present. The fact that the allene  $[(\text{CF}_3)_2\text{N}]_2\text{C}:\text{C}:\text{CH}_2$  absorbs at lower wavelength than its isomer  $(\text{CF}_3)_2\text{N}\cdot\text{CH}:\text{C}:\text{CH}\cdot\text{N}(\text{CF}_3)_2$  indicates that steric interaction between geminal  $(\text{CF}_3)_2\text{N}$  groups may reduce the degree of orbital interaction between the nitrogen atoms and the C:C system. Similarly, the allene  $[(\text{CF}_3)_2\text{N}]_2\text{C}:\text{C}:\text{CBr}\cdot\text{N}(\text{CF}_3)_2$  absorbs at shorter wavelength than the allene  $[(\text{CF}_3)_2\text{N}]_2\text{C}:\text{C}:\text{CH}\cdot\text{N}(\text{CF}_3)_2$ , which contains the same number of  $(\text{CF}_3)_2\text{N}$  groups but no bulky bromine atom.

Mass and i.r. spectral data are listed in Supplementary Publication No. SUP 20647 (6 pp.).†

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[2/1743 Received, 25th July, 1972]

<sup>17</sup> R. E. Banks, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc.*, 1965, 978.

<sup>18</sup> S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, *J. Chem. Soc. (C)*, 1966, 1223.