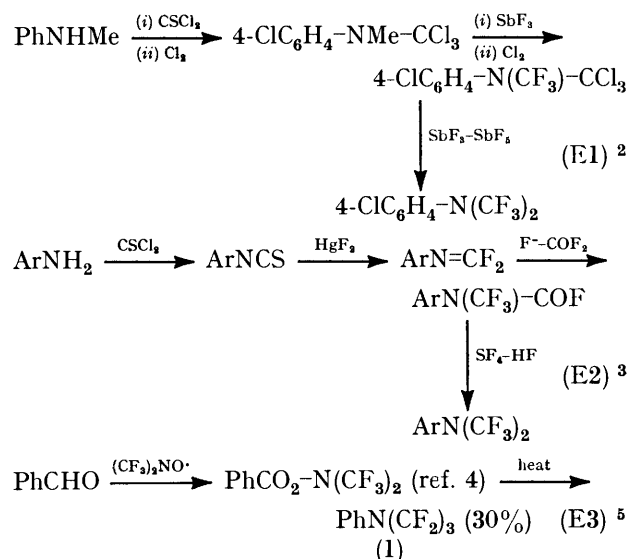


Polyfluoroalkyl Derivatives of Nitrogen. Part 48.¹ The Addition of *N*-Halogenoamines (CF₃)₂NX to Cyclohexa-1,3- and -1,4-dienes; a New Synthesis of *NN*-Bistrifluoromethylaniline

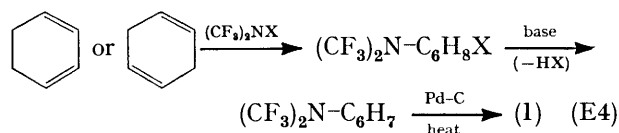
By Terence W. Hart, Robert N. Haszeldine,* and Anthony E. Tipping,* Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Treatment of cyclohexa-1,3-diene with the *N*-halogenoamines (CF₃)₂NX (X = Cl or Br) at -78 °C gives a mixture of the 1 : 1 adducts, *trans*-(CF₃)₂N-CH-CHX-[CH₂]₂-CH=CH and *cis*- and *trans*-(CF₃)₂N-CH-CH=CH-CHX-CH₂-CH₂; in contrast (CF₃)₂NI affords the former adduct exclusively. All three amines react with cyclohexa-1,4-diene under analogous conditions to yield the 1 : 1 adduct *trans*-(CF₃)₂N-CH-CH₂-CH=CH-CH₂-CHX only. Dehydrohalogenation of the 1,3-diene adducts (X = Cl or Br) with various bases (KOH powder, PrⁱONa, Bu^tOK) affords a mixture of 1- and 2-*NN*-bistrifluoromethylamino)cyclohexa-1,3-diene. The latter diene forms a Diels-Alder adduct with trifluoronitrosomethane and the diene mixture dehydrogenates readily over a Pd-C catalyst at 180–190 °C to give *NN*-bistrifluoromethylaniline exclusively in high yield.

THREE routes to *NN*-bistrifluoromethylaniline (1) and its derivatives have been reported [equations (E1)–(E3)] but these are either not readily reproducible or give low overall yields.



In the present work a new route [equation (E4)] has been investigated, since attempted repeated pyrolysis of the ester PhCO₂-N(CF₃)₂ [equation (E3)] under the conditions reported⁵ failed to give (1).



RESULTS AND DISCUSSION

The results obtained from the reactions of the *N*-halogenobistrifluoromethylamines (CF₃)₂NX (X = Cl, Br, or I) with cyclohexa-1,3- and -1,4-diene at -78 °C are shown in Table 1.

The adducts (2)–(5) were identified by consideration of their n.m.r., i.r., and mass spectra, g.l.c. retention times, and refractive indices.

The ¹H n.m.r. spectra of the adducts assigned structures (3) and (4) showed the presence of the (CF₃)₂N-CH_c-CH_b=CH_a-CH_dX grouping by the observed couplings, *J*_{b,c} and *J*_{a,d}. For two of the adducts the two couplings were of comparable magnitude, indicating that the methine protons H_c and H_d were in similar environments, while for the other two adducts the couplings were significantly different. Since the (CF₃)₂N group, because of its bulk, is expected to occupy a

TABLE 1
Reaction of the *N*-halogenoamines with the cyclohexadienes

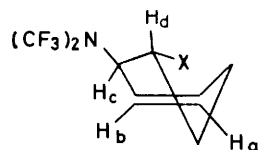
(CF ₃) ₂ NX	Diene	Products (%) ^a					
		(CF ₃) ₂ NH	Benzene	(2)	(3)	(4)	(5)
X = Cl	1,3	38	21	16	10	34	
X = Br	1,3	13		30	21	26	
X = I ^b	1,3	trace		72			
X = Cl	1,4	36	17				59
X = Br	1,4	18					74
X = I	1,4	18					72

^a Higher-boiling viscous material also formed. ^b In diethyl ether as solvent; solvent absent in other reactions.

pseudo-equatorial position and lock the ring in the preferred half-chair conformation, the methine proton H_c will occupy a pseudo-axial position. On this basis, in the adducts which show comparable couplings the methine proton H_d also occupies a pseudo-axial position, i.e. the adducts are the *trans*-isomers (3a) and (3b), while in the other adducts the methine proton H_d occupies a pseudo-equatorial position and the adducts are the *cis*-isomers (4a) and (4b). The remaining cyclohexa-1,3-diene products must then be either the *trans*-(2) or *cis*-(6) 1,2-adducts, but since coupling between the methine protons (*J*_{c,d}) could not be evaluated from the complex ¹H n.m.r. absorptions, assignments could not be made although the *trans*-adducts (2) would be

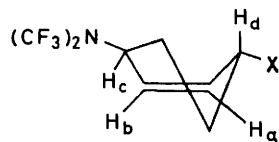
favoured on steric grounds. In contrast, however, the spectra of the 1,4-diene adducts each showed methine coupling, $J_{e,a}$ ca. 11.5 Hz, of the magnitude expected for *trans*-coupling between pseudo-axial protons and hence these adducts are the *trans*-isomers (5).

The i.r. spectra of the adducts (2)—(5) were quite distinctive from each other and were independent of the



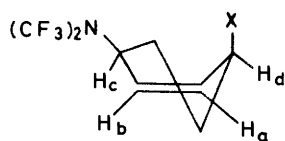
(2)

a; X = Cl
b; X = Br
c; X = I



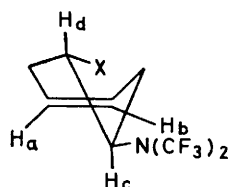
(3)

a; X = Cl
b; X = Br



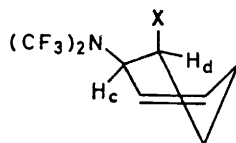
(4)

a; X = Cl
b; X = Br



(5)

a; X = Cl
b; X = Br
c; X = I



(6)

nature of the halogen X except for differences in the frequencies of the C-halogen stretching mode. As expected, absorption due to the C=C stretch was more intense for adducts (2) than for the more symmetrical adducts (3) and (4).

The mass spectra of adducts (2)—(4) were very similar with differences only in the intensities of the ion peaks. The spectra of the adducts (5) were also similar except that they showed a peak at m/e 54 ($C_4H_6^+$) and an absence of peaks at m/e 205 ($M^+ - C_2H_3X$) and 192 ($M^+ - C_3H_4X$). All the spectra, except those of the bromo-compounds (3b) and (4b), exhibited parent-ion peaks and base peaks were observed at m/e 232 ($M^+ - X$) [for (3b), (4b), and (5c)], 205 [for (2a) and (2b)], 79 ($C_6H_7^+$) [for (2c) and (5b)], 78 ($C_6H_6^+$) [for (3a) and (4a)], and 54 [for (5a)].

An isomer having the more axial conformation will in general have a higher boiling point, refractive index, and density than an isomer with a fully equatorial conformation.⁶ Therefore it would be expected that the refractive indices and boiling points of the adducts would increase in the order (5) < (2) < (3) < (4) < (6). The

observed refractive indices (n_D^{20}) [(5a) 1.394 0, (2a) 1.394 7, (3a) 1.401 3, and (4a) 1.402 3; (5b) 1.412 2, (2b) 1.413 8, (3b) 1.420 7, and (4b) 1.422 4; (5c) 1.445 5 and (2c) 1.445 7] indicate that the correct structural assignments have been made.

The boiling points of the adducts containing allylic halogen could not be determined accurately due to thermal rearrangement and decomposition. However, the retention times on a g.l.c. SE 30 column at a given temperature are normally in the order of increasing boiling point as exemplified by the retention order of the bromine-cyclohexa-1,3-diene adducts, *i.e.* *trans*-1,2- < *trans*-1,4- < *cis*-1,4- < *cis*-1,2.⁷ The observed order in the present work (5) < (2) < (3) < (4) is thus further evidence for the assigned structures.

Thermal studies on adducts (2)—(4) between 80 and 150 °C revealed that only one adduct did not decompose or rearrange. This was isomer (2), in which the halogen is non-allylic, and shows that the $(CF_3)_2N$ group is thermally stable in an allylic position.

The isomer ratios obtained for the reactions of the *N*-chloro- and *N*-bromo-amines with cyclohexa-1,3-diene were found to vary considerably with temperature and with the nature of the solvent. A detailed discussion of the mechanism of addition is deferred, however, until a later paper in which additions of the amines $(CF_3)_2NX$ (X = Cl, Br, and I) to other cyclic 1,3-dienes are also reported.

The adducts are considered to be formed as shown in Scheme 1.

The lower yields of adducts obtained from the *N*-chloroamine reactions were accompanied by appreciable

TABLE 2

Base	Adduct ratio			Product ratio			Yield (%)
	(2b) :	(3b) :	(4b)	(7) :	(8) :	(9) :	
Powdered KOH	40	30	30	43		57	67
Pr ^t ONa	40	30	30	37	63		35
Pr ⁱ ONa	100			87	13		46
Bu ^t OK	40	30	30	40	60		62
EtOK	40	30	30			50 50	83*
	(2a) : (3a) : (4a)						
Powdered KOH	30	20	50	25	75		36

* Based on compounds (3b) + (4b); isomer (2b) (69% recovered).

amounts of bistrifluoromethylamine and benzene in a 2 : 1 ratio. These by-products are considered to arise as shown in Scheme 2.

Further reaction of the chlorine produced with the diene gave a mixture of dichlorocyclohexenes which were detected by g.l.c.-mass spectrometry.

The results obtained from treatment of the adducts (2)—(4) with various bases are shown in Table 2.

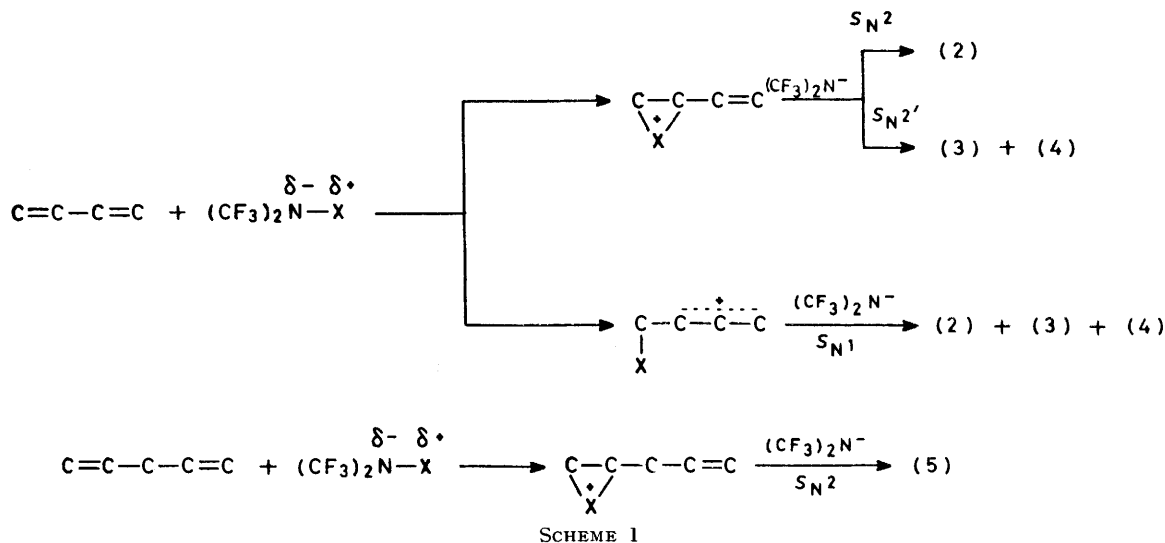
The ¹H n.m.r. spectra of the dienes each showed the presence of three vinylic protons and two methylene groups thus precluding structure (11), but assignment of structures (7) and (8) to the dienes could not be made on

the basis of i.r., u.v., n.m.r., or mass-spectral evidence; the u.v. spectra of both dienes showed distinct bathochromic and hypsochromic effects relative to that of cyclohexa-1,3-diene.

Attempted reaction of each of the dienes with maleic anhydride and chloranil gave no Diels–Alder adducts,

Other 1,3-dienes, *e.g.* buta-1,3-diene,⁸ have been reported to give Diels–Alder adducts with trifluoronitrosomethane rather than the alternative oxazetidines (1,2-adducts).

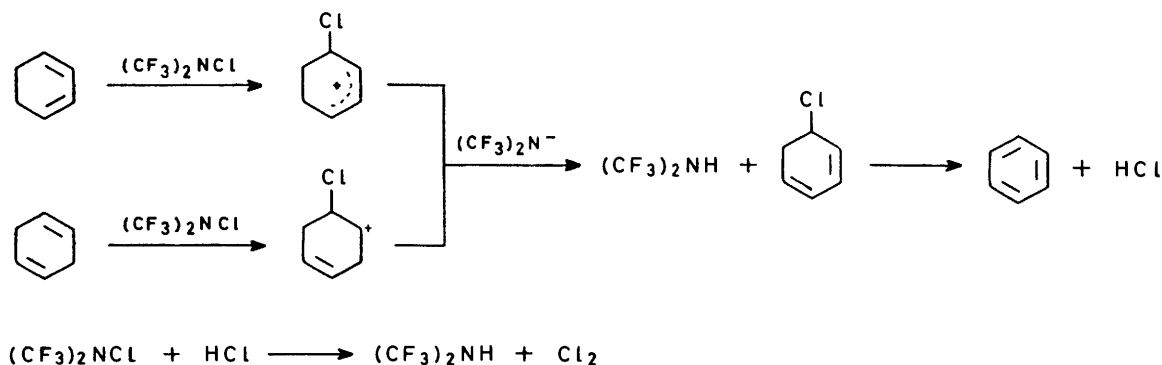
The reaction of sodium isopropoxide with adduct (2b) gave the diene (7) as the major product while reaction of



but an adduct was formed between one of the dienes and trifluoronitrosomethane, which was assigned structure (12) on the basis of the following evidence.

The ¹H n.m.r. spectrum showed absorptions at δ 6.37 (1 H, d, H_a, J_{a,b} 6 Hz), 4.36 (1 H, s, H_c), 4.08 (1 H, dd, H_b, J_{b,a} 6 and J_{b,d} 2 Hz), 2.00 (2 H, complex, H_d + H_{d'}), and 1.34 (2 H, complex, H_e). Both Diels–Alder adducts formed from diene (8) contain two vinylic protons and

mixtures of the adducts (2b), (3b), and (4b) (ratio 2b : 3b + 4b = 40 : 60) with the bases KOH, PrⁱONa, or Bu^tOK gave dienes (7) and (8) in the ratio *ca.* 40 : 60. Similarly, treatment of a mixture of adducts (2a), (3a), and (4a) (ratio 2a : 3a + 4a = 30 : 70) with powdered KOH gave dienes (7) and (8) in the ratio 25 : 75. These results indicate that diene (7) is formed mainly from adduct (2) while diene (8) is formed mainly from adducts

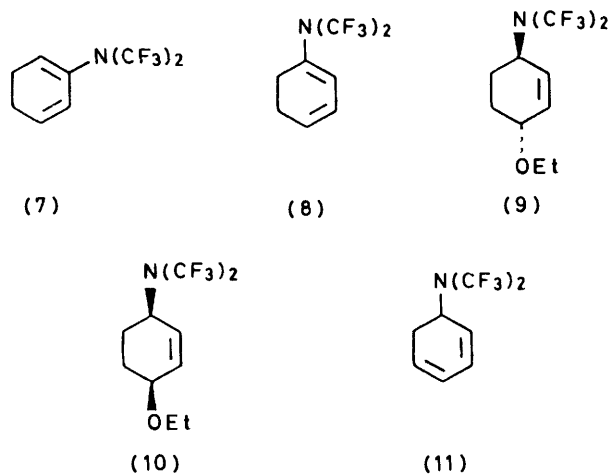


are thus ruled out. The observation that the higher-field methine proton H_b (adjacent to N) couples to the vinylic proton H_a while the lower-field methine proton H_c (adjacent to O) shows no coupling indicates that the adduct has structure (12) and not the alternative structure (13). The adduct is thus formed from diene (7) and it is probable that the bulky (CF₃)₂N group on C-1 in diene (8) sterically prevents Diels–Alder adduct formation with this diene.

(3) and (4) although some base-catalysed isomerisation takes place. In these adducts abstraction involves the most acidic proton, *i.e.* that in the allylic (CF₃)₂N–CH< grouping, and it is considered possible that the eliminations proceed *via* E1cb mechanisms in which the intermediate carbanions can ring-flip if necessary so that the halogen is in a preferred pseudo-axial position for elimination (Scheme 3).

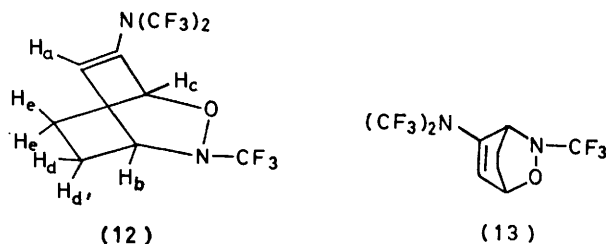
Reaction of a mixture of adducts (2b), (3b), and (4b)

with potassium ethoxide, a better nucleophile than solid KOH, Pr^iONa , or Bu^tOK , gave adduct (2b) (69% recovered) and a mixture (83%) of the ethers (9) and (10) in a 1:1 ratio resulting from nucleophilic substitution; dienes (7) and (8) were not detected. Thus ethoxide-ion displacement of bromide ion from adduct (2b) is un-

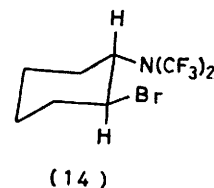


favourable, presumably because the halogen is rigidly held in a pseudo-equatorial position and steric interactions hinder approach of the nucleophile. With isomers (3b) and (4b) the halogen is in pseudo-equatorial and pseudo-axial positions, respectively, and $\text{S}_{\text{N}}2$ attack can occur because steric interactions are con-

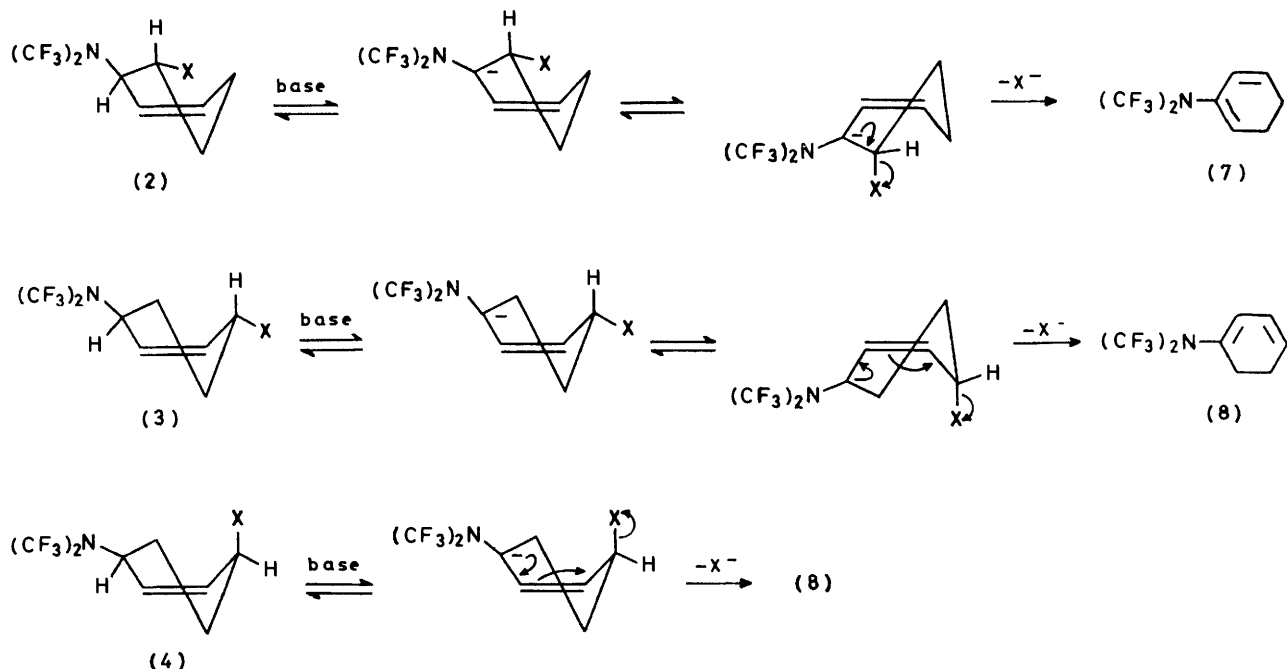
Attempted hydrohalogenation of adduct (5b) with powdered KOH, Pr^iONa , or Bu^tOK at temperatures up to 160 °C were unsuccessful. The stability of this



adduct to dehydrobromination is probably due to the acidic $(\text{CF}_3)_2\text{NCH}<$ hydrogen being non-allylic and hence less susceptible to abstraction by base. A comparable stability towards dehydrobromination by base was shown by the corresponding *trans*-cyclohexane derivative (14).⁹ The results obtained from an in-



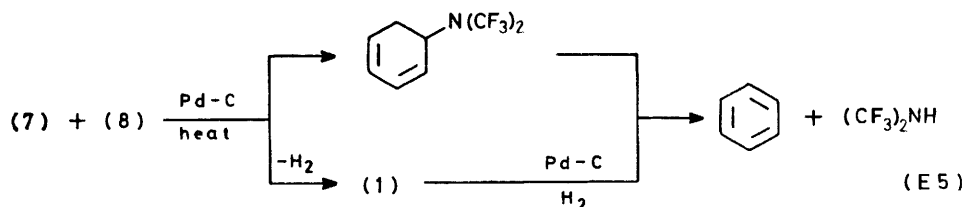
vestigation of the dehydrogenation of a mixture of dienes (7) and (8) over a palladium-charcoal catalyst are given in Table 3.



SCHEME 3

siderably less, and ring flexibility greater, than in isomer (2b). It is also possible that substitution occurs *via* an $\text{S}_{\text{N}}1$ mechanism since the halogen atom in both isomers is allylic.

The large amounts of benzene formed at the higher temperatures possibly arise either *via* a diene rearrangement or by palladium-catalysed hydrogenolysis of the C-N bond in (1) as shown in equation (E5).



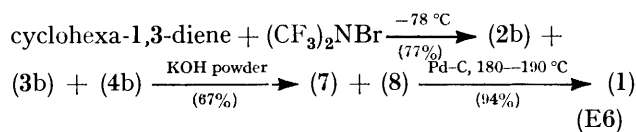
A new three-stage route to the aniline (1) has thus been satisfactorily established from the amine $(\text{CF}_3)_2\text{N}$ -

TABLE 3

Dehydrogenation of *NN*-bistrifluoromethylamino-substituted cyclohexadienes

Temperature	Ratio of products		Total yield (%)
	Benzene	(1)	
280	100	0	85
260	64	36	90
220	47	53	89
200	27	73	92
190	0	100	94
180	0	100	92

NBr and cyclohexa-1,3-diene with an overall yield of 48% as shown in equation (E6).



EXPERIMENTAL

Reactants and products were manipulated, where possible, in a vacuum system to avoid contamination with air or moisture.

Products were separated by distillation at atmospheric or reduced pressure, by fractional condensation *in vacuo*, or by g.l.c. [Pye model 104 machine with flame ionisation detector; columns packed with Celite impregnated with silicone oil (SE30) and polyethyleneglycol adipate (PEGA) (10% by weight)] and were identified by molecular-weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer 257 or 621 spectrophotometers with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 or R20 instruments operating at 60.0 MHz for ^1H and 56.46 MHz for ^{19}F (δ_{F} given in p.p.m.), or a Varian HA100 instrument operating at 100.0 MHz for ^1H and 94.1 MHz for ^{19}F using internal benzene or tetramethylsilane and external trifluoroacetic acid as the respective references), mass spectrometry (A.E.I. MS902 machine), and u.v. spectroscopy (where appropriate; Unicam SP700 and Hilger and Watts Ultrascan instruments using ethanol and *n*-hexane as solvents).

The *N*-halogenoamines $(\text{CF}_3)_2\text{NX}$ were prepared by literature methods ($\text{X} = \text{Cl}$; $^{10} \text{X} = \text{Br}$; $^{10,11} \text{X} = \text{I}$; 12,13); cyclohexa-1,3-diene was prepared by allylic bromination of cyclohexene (*N*-bromosuccinimide) followed by dehydrobromination in quinoline under reflux; cyclohexa-1,4-diene was a commercial sample.

Reaction of the N-Halogenoamines with Cyclohexa-1,3-diene.—(a) *N-Chlorobistrifluoromethylamine.* A mixture of the *N*-chloroamine (3.20 g, 17.3 mmol) and cyclohexa-1,3-

diene (1.60 g, 20.0 mmol), sealed in a Pyrex ampoule (*ca.* 15 cm³) and kept at -78°C *in vacuo* in the dark (72 h), gave (i) bistrifluoromethylamine (0.98 g, 6.5 mmol, 38%) (Found: *M*, 153. Calc. for $\text{C}_2\text{HF}_6\text{N}$: *M*, 153); (ii) benzene (0.32 g, 4.1 mmol, 21%); and (iii) higher-boiling material (3.24 g) which was distilled under reduced pressure to yield a 1 : 1 adduct fraction (2.80 g, 10.4 mmol, 60%), b.p. 75°C at 34 mmHg, and a viscous residue (0.44 g) which was not examined further. The adduct fraction was separated by g.l.c. (4 m PEGA at 90°C) into its three components (ratio 27 : 17 : 57) identified as: *trans*-6-chloro-*NN*-bistrifluoromethylcyclohex-2-enylamine (2a) (0.72 g, 2.7 mmol, 16%) (Found: C, 36.0; H, 3.0; Cl, 13.7%; M^+ , 269/267, $\text{C}_6\text{H}_5\text{ClF}_6\text{N}$ requires C, 36.0; H, 3.0; Cl, 13.3%; *M*, 267.5); ν_{max} 1 645w cm⁻¹ (C=C str.); δ_{F} -23.2 : *trans*-4-chloro-*NN*-bistrifluoromethylcyclohex-2-enylamine (3a) (0.50 g, 1.8 mmol, 10%) (Found: C, 36.4; H, 3.2%; M^+ , 269/267); ν_{max} 1 640w cm⁻¹ (C=C str.); δ_{F} -22.7 : and *cis*-4-chloro-*NN*-bistrifluoromethylcyclohex-2-enylamine (4a) (1.60 g, 5.9 mmol, 34%) (Found: C, 36.3; H, 3.2%; M^+ , 269/267); ν_{max} 1 680w cm⁻¹ (C=C str.); δ_{F} -22.7 .

(b) *N-Bromobistrifluoromethylamine.* A mixture of the amine (3.50 g, 15.1 mmol) and the diene (1.28 g, 16.0 mmol), sealed in a Pyrex ampoule (*ca.* 15 cm³) *in vacuo* and kept in the dark at -78°C (72 h), gave bistrifluoromethylamine (0.30 g, 2.0 mmol, 13%; *M*, 152) and a higher-boiling material (4.4 g), which was distilled under reduced pressure (*ca.* 50 mmHg) to yield a 1 : 1 adduct fraction (3.64 g, 11.7 mmol, 78%) and a viscous residue (0.74 g) which was not examined further. The adduct fraction was separated by g.l.c. (10m SE30 at 125°C) into its three components (ratio 39 : 27 : 34) which were identified as: *trans*-6-bromo-*NN*-bistrifluoromethylcyclohex-2-enylamine (2b) (1.42 g, 4.5 mmol, 30%) (Found: C, 31.1; H, 2.7; Br, 25.6; F, 36.7; N, 4.4%; M^+ , 313/311. $\text{C}_6\text{H}_5\text{BrF}_6\text{N}$ requires C, 30.8; H, 2.6; Br, 25.6; F, 36.4; N, 4.5%; *M*, 312); ν_{max} 1 652w cm⁻¹ (C=C str.); δ_{F} -23.5 : *trans*-4-bromo-*NN*-bistrifluoromethylcyclohex-2-enylamine (3b) (0.98 g, 3.1 mmol, 21%) (Found: C, 31.1; H, 2.8; Br, 26.0; N, 4.2%); ν_{max} 1 640w cm⁻¹ (C=C str.); δ_{F} -23.1 : and *cis*-4-bromo-*NN*-bistrifluoromethylcyclohex-2-enylamine (4b) (1.24 g, 4.0 mmol, 26%) (Found: C, 30.8; H, 2.7; Br, 26.1; N, 4.4%), δ_{F} -23.0 .

(c) *N-Iodobistrifluoromethylamine.* A mixture of the amine (1.63 g, 5.8 mmol) and the diene (0.50 g, 6.2 mmol) in diethyl ether (0.95 g), sealed in a Pyrex ampoule (*ca.* 15 cm³) *in vacuo* and kept at -78°C in the dark (72 h), gave: (i) a low-boiling fraction (1.0 g) which was shown by i.r. spectroscopy to be mainly unchanged diethyl ether contaminated with small amounts of perfluoro-2-azapropene and bistrifluoromethylamine and; (ii) a higher-boiling material (2.0 g) which was distilled at reduced pressure (*ca.* 0.1 mmHg) to afford *trans*-6-iodo-*NN*-bistrifluoromethylcyclohex-2-enylamine (2c) (1.50 g, 4.2 mmol, 72%) (Found: C, 27.2; H, 2.4; F, 31.4; I, 35.1; N, 3.5%; M^+ , 359. $\text{C}_8\text{H}_5\text{F}_6\text{IN}$

requires C, 26.8; H, 2.2; F, 31.7; I, 35.3; N, 3.9%; M , 359; ν_{\max} , 1 650 cm^{-1} (C=C str.); δ_{F} -23.6; and a viscous residue (0.5 g) which was not examined further.

Reaction of the N-Halogenoamines with Cyclohexa-1,4-diene.—(a) *N-Chlorobis(trifluoromethyl)amine*. A mixture of the amine (7.76 g, 41.2 mmol) and the diene (3.60 g, 45.0 mmol), sealed in a Pyrex ampoule (ca. 45 cm^3) *in vacuo* and kept in the dark at -78°C (65 h), gave: (i) bis(trifluoromethyl)amine (2.27 g, 14.8 mmol, 36%); (ii) benzene (0.60 g, 7.7 mmol, 17%); and (iii) higher-boiling material (8.4 g) which was distilled at reduced pressure to yield *trans-6-chloro-NN-bis(trifluoromethyl)cyclohex-3-enylamine* (5a) (6.5 g, 24.3 mmol, 59%) (Found: C, 35.7; H, 3.3%; M^+ , 269/267. $\text{C}_8\text{H}_8\text{ClF}_6\text{N}$ requires C, 36.0; H, 3.0%; M , 267.5), b.p. 90°C at 60 mmHg; ν_{\max} , 1 650 cm^{-1} (C=C str.); δ_{F} -23.0; and a viscous residue (1.9 g) which was not examined further.

(b) *N-Bromobis(trifluoromethyl)amine*. A mixture of the amine (9.35 g, 40.0 mmol) and the diene (3.40 g, 42.5 mmol), sealed in a Pyrex tube (ca. 100 cm^3) *in vacuo* and kept in the dark at -78°C (72 h), gave bis(trifluoromethyl)amine (1.10 g, 7.2 mmol, 18%; M , 150) and a higher-boiling material (11.6 g) which was distilled at reduced pressure to afford *trans-6-bromo-NN-bis(trifluoromethyl)cyclohex-3-enylamine* (5b) (9.19 g, 29.5 mmol, 74%) (Found: C, 31.0; H, 2.8; N, 4.5%; M^+ , 313/311. $\text{C}_8\text{H}_8\text{BrF}_6\text{N}$ requires C, 30.8; H, 2.6; N, 4.5%; M , 312), b.p. 106°C at 90 mmHg; ν_{\max} , 1 665 cm^{-1} (C=C str.); δ_{F} -23.3; and a viscous residue (2.4 g) which was not examined further.

(c) *N-Iodobis(trifluoromethyl)amine*. A mixture of the amine (0.90 g, 3.2 mmol), sealed in a Pyrex tube (ca. 15 cm^3) *in vacuo* and kept in the dark at -78°C (20 h), gave a low-boiling mixture (0.09 g, 0.58 mmol, 18%; M , 148) of perfluoro-2-azapropene, bis(trifluoromethyl)amine, and a higher-boiling material (1.1 g) which was distilled at reduced pressure (ca. 0.1 mmHg) to afford *trans-6-iodo-NN-bis(trifluoromethyl)cyclohex-3-enylamine* (5c) (0.82 g, 2.3 mmol, 72%) (Found: C, 26.7; H, 2.3%; M^+ , 359. $\text{C}_8\text{H}_8\text{F}_6\text{I}\text{N}$ requires C, 26.8; H, 2.2%; M , 359); ν_{\max} , 1 666 cm^{-1} (C=C str.); δ_{F} -23.3; and a viscous residue (0.28 g) which was not examined further.

Reactions of the N-Bromoamine-Cyclohexa-1,3-diene Adducts.—(a) *With potassium ethoxide*. A mixture of the adducts (2b), (3b), and (4b) (1.80 g, 5.8 mmol) (ratio 4 : 3 : 3) and potassium hydroxide (0.69 g, 15.0 mmol) in ethanol (1.80 g, 40.0 mmol) was heated under reflux (2 h). The ethanol was removed *in vacuo* and the higher-boiling material was distilled under reduced pressure to yield a fraction (1.4 g), b.p. $70\text{--}75^\circ\text{C}$ at 34 mmHg, which was separated by g.l.c. (10 m SE30 at 120°C) into its components identified as: (i) *4-ethoxy-NN-bis(trifluoromethyl)cyclohex-2-enylamine* (0.80 g, 2.9 mmol, 83%) (Found: C, 43.4; H, 4.8%; M^+ , 277. $\text{C}_{10}\text{H}_{13}\text{F}_6\text{NO}$ requires C, 43.4; H, 4.9%; M , 277); ν_{\max} , 1 640 cm^{-1} (C=C str.), which was shown by n.m.r. spectroscopy to be a mixture of the *cis*-(9) and *trans*-(10) isomers in the ratio 1 : 1; δ_{H} 5.58 (2 H, dd, CH=CH), 4.10 (1 H, complex, CH-O), 3.70 (1 H, complex, CH-N), 3.30 (2 H, q, OCH_2), 2.0 (4 H, complex, 2 CH_2), and 1.0 (3 H, t, Me); δ_{F} -23.2 (*cis*) and -22.9 (*trans*); and (ii) unchanged reactant (2b) (0.5 g, 1.6 mmol, 69% recovered).

(b) *With potassium hydroxide*. A mixture (1.40 g, 4.5 mmol) of the adducts (2b), (3b), and (4b) (ratio 4 : 3 : 3) and powdered potassium hydroxide (2.8 g, 50.0 mmol) was heated at 170°C (30 min) and the product was dried (MgSO_4) and distilled to afford a fraction (0.70 g, 3.0 mmol,

67%), b.p. 121°C , which was separated by g.l.c. (10 m SE30 at 80°C) into its two components (ratio 43 : 57) which were identified as: *NN-bis(trifluoromethyl)cyclohex-1,5-dienylamine* (7) (0.30 g, 1.3 mmol, 29%) (Found: C, 41.2; H, 3.3; N, 5.7%; M^+ , 231. $\text{C}_8\text{H}_7\text{F}_6\text{N}$ requires C, 41.6; H, 3.0; N, 6.1%; M , 231), ν_{\max} , 1 596 m and 1 660 cm^{-1} (C=C str. in 1,3-diene); λ_{\max} (hexane) 260 nm (ϵ_{\max} , 2 370); δ_{H} 5.75 (1 H, complex, CH=C-N), 5.50 (2 H, complex, CH=CH), and 1.95 (4 H, complex, 2 CH_2); δ_{F} -20.5; and *NN-bis(trifluoromethyl)cyclohex-1,3-dienylamine* (8) (0.40 g, 1.7 mmol, 38%) (Found: C, 41.3; H, 3.2%; M^+ , 231); ν_{\max} , 1 596 m and 1 654 cm^{-1} (C=C str. in 1,3-diene); λ_{\max} (hexane) 257 nm (ϵ_{\max} , 2 960); δ_{H} 85.6 (3 H, complex, 3 CH=) and 1.9 (4 H, complex, 2 CH_2); δ_{F} -20.8.

(c) *With sodium isopropoxide*. A mixture (5.40 g, 17.2 mmol) of the adducts (2b), (3b), and (4b) (ratio 4 : 3 : 3) and sodium isopropoxide (5.5 g, 67.0 mmol) in diglyme (10 g) was heated at 160°C under nitrogen (2 h). The product was washed with water, dried (MgSO_4), and distilled to give a fraction (1.4 g), b.p. $118\text{--}121^\circ\text{C}$, which was shown by g.l.c. (10 m SE30 at 80°C) to consist of the 1,5-dienylamine (7) (0.50 g, 2.2 mmol, 13%) and the 1,3-dienylamine (8) (0.85 g, 3.7 mmol, 22%) in the ratio 37 : 63.

(d) *With potassium *t*-butoxide*. A mixture (3.12 g, 10.0 mmol) of the adducts (2b), (3b), and (4b) (ratio 4 : 3 : 3) was treated with solid potassium *t*-butoxide (3.36 g, 30.0 mmol) at room temperature. An exothermic reaction took place and the product was condensed into a trap *in vacuo*, washed (H_2O), dried (MgSO_4), and then distilled to afford a mixture of the 1,5-dienylamine (7) (0.57 g, 2.5 mmol, 25%) and the 1,3-dienylamine (8) (0.86 g, 3.7 mmol, 37%), in the ratio 40 : 60 as shown by g.l.c. (2 m SE30 at 30°C).

Reaction of trans-6-Bromo-NN-bis(trifluoromethyl)cyclohex-2-enylamine with Sodium Isopropoxide.—The adduct (2b) (1.76 g, 5.6 mmol) was heated at 160°C (1 h) with sodium isopropoxide (1.8 g, 22.0 mmol) in diglyme (5 g) and after work-up and distillation of the product a fraction, b.p. 121°C , was obtained which was identified as a mixture of the 1,5-dienylamine (7) (0.50 g, 2.16 mmol, 38%), and the 1,3-dienylamine (8) (0.10 g, 0.44 mmol, 8%) in the ratio 83 : 17 by g.l.c. (2 m SE30 at 30°C).

Reaction of the N-Chloroamine-Cyclohexa-1,3-diene Adducts with Potassium Hydroxide.—A mixture (2.2 g, 8.2 mmol) of the adducts (2a), (3a), and (4a) (ratio 3 : 2 : 5) and powdered potassium hydroxide (5.6 g, 0.10 mol) was heated at 150°C (1 h). The product was collected, washed (H_2O), dried (MgSO_4), and distilled to give benzene (0.20 g, 2.6 mmol, 33%) and a mixture, b.p. $118\text{--}120^\circ\text{C}$, of the 1,5-dienylamine (7) (0.17 g, 0.76 mmol, 9%) and the 1,3-dienylamine (8) (0.53 g, 2.25 mmol, 27%) in the ratio 25 : 75 as shown by g.l.c. (2 m SE30 at 30°C).

Reaction of NN-Bis(trifluoromethyl)cyclohexa-1,5-dienylamine with Trifluoronitrosomethane.—A mixture of the diene (7) (0.20 g, 0.9 mmol) and trifluoronitrosomethane (0.10 g, 1.0 mmol), sealed *in vacuo* in a Pyrex ampoule (ca. 15 cm^3) at -196°C and allowed to warm slowly to room temperature (0.5 h), gave, after purification by g.l.c. (2 m SE30 at 100°C), *3-trifluoromethyl-6-NN-bis(trifluoromethyl)amino-2-oxa-3-azabicyclo[2.2.2]oct-5-ene* (12) (0.20 g, 0.6 mmol, 67%) (Found: C, 33.0; H, 2.0; N, 8.6%; M^+ , 330. $\text{C}_9\text{H}_7\text{F}_9\text{N}_2\text{O}$ requires C, 32.7; H, 2.1; N, 8.5%; M , 330); ν_{\max} , 1 640 cm^{-1} (C=C str.); δ_{F} -20.7 [6 F, q, $(\text{CF}_3)_2\text{N}$] and -7.8 (3 F, septet, CF_3).

A reaction carried out under identical conditions with the 1,3-dienylamine (8) gave only unchanged reactants.

TABLE 4
¹H N.m.r. spectral data

Adduct	Chemical shifts (δ)					Coupling constants (Hz)					
	H _a	H _b	H _c	H _d	CH ₂	J _{a,b}	J _{a,c}	J _{a,d}	J _{b,c}	J _{b,d}	J _{c,d}
(2a)	5.4	5.7	4.0	4.0	2.0	10.0					
(2b)	5.6	5.9	4.3	4.3	2.1	10.0					
(2c)	5.7	6.1	4.5	4.5	2.3	10.0					
(3a)	5.7	5.6	4.1	4.4	2.0	9.8	-1.7	2.9	3.0	-1.8	
(3b)	6.0	5.7	4.3	4.6	2.1	10.5	-1.8	3.2	3.1	-1.6	
(4a)	5.7	5.6	4.1	4.4	2.0	10.8	-2.1	4.3	2.0	-1.4	
(4b)	5.9	5.7	4.3	4.6	2.2	10.0	-2.4	5.3	2.5	-1.6	
(5a)	5.4	5.4	3.6	4.1	2.4						11.4
(5b)	5.5	5.5	3.7	4.3	1.7						11.5
(5c)	5.9	5.5	3.8	4.5	2.6						11.5

and 3.0

Dehydrogenation of a Mixture of the 1,3-Dienylamine and 1,5-Dienylamine with Palladium-Charcoal.—A mixture (1.20 g, 5.2 mmol) of the dienes (7) and (8) (ratio 4 : 6) was passed through a silica tube (90 cm, 1.5 cm i.d.) heated to 190 °C and containing (5%) palladium-charcoal (10 g). The product was distilled to give *NN*-bistrifluoromethyl-aniline (1.10 g, 4.8 mmol, 92%) (Found: C, 42.0; H, 2.4%; *M*⁺, 229. Calc. for C₈H₅F₆N: C, 41.9; H, 2.2%; *M*, 229), b.p. 116–118 °C.

Further reactions were carried out at various temperatures and the results obtained are shown in Table 3.

Compounds (3) and (4) showed very similar ¹H n.m.r. spectra with complex ABMN₂X₂Y₂ symmetry, characteristic of 3,6-disubstituted cyclohexenes. A second-order analysis was possible, however, because the methine absorptions (H_c and H_d) are well separated from the other absorptions and the magnitudes of J_{c,d} are small compared to the chemical shift separations of H_c and H_d. Thus, since the vinylic and methylene protons do not show appreciable coupling to each other, the methine and vinylic proton signals can be treated as an ABRX system the solution of which is well described.^{14,15} Double-resonance experiments involving irradiation of the methylene protons gave results in good agreement with the second-order analysis. The negative values obtained for the ⁴J_{HH} allylic couplings are consistent with values reported for comparable systems.¹⁵

The ¹H n.m.r. spectra of the adducts (2)—(5) are given in Table 4.

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