Unsaturated nitrogen compounds containing fluorine. Part 10 [1]. Reaction of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene with halide ion and oxygen- and sulphur-centred nucleophiles and of its 2,5-di-iodo analogue with reducing agents and certain nucleophiles [2]

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Abstract

The azines $CF_3CR{=}NN{=}CRCF_3$(R = F, I, PhO, 2,4-$Cl_2C_6H_3O$, PhS and EtO) are formed by treatment of the title dichloroazine **1** with an excess of the appropriate nucleophile, while reaction with phosphorus (V) sulphide at 180 °C gives 2,5-bis(trifluoromethyl)-1,3,4-thiadiazole in quantitative yield. In the reaction with NaOEt, the compound $CF_3C(OEt){=}NN{=}C(ONa)CF_3$ is also produced from the NaOH impurity present. Di-iodoazine **3b** undergoes ready reaction with aniline (1:2 molar ratio) and potassium diethyl phenylmalonate (1:1 molar ratio) to afford the monosubstituted compounds $PhN{=}C(CF_3)NHN{=}ClCF_3$ and $(EtO_2C)_2CPhC(CF_3){=}NN{=}ClCF_3$, respectively. Azine **1** is not reduced by the reagents NaH, $LiAlH_4$ and $NaBH_4$, but di-iodoazine **3b** is reduced by tri-n-butyltin hydride at *c.* 90 °C to give mainly the compounds $CF_3CH{=}NN{=}CHCF_3$, $CF_3CH{=}NN{=}ClCF_3$, $CFCH_2NHN{=}ClCF_3$ and possibly $CF_3CH{=}NNHCH_2CF_3$; with hydrogen iodide at 200 °C, the major products are the hydroazines $CF_3CH{=}NN{=}CHCF_3$ and $CF_3CH{=}NN{=}ClCF_3$ and 2,4,6-tris(trifluoromethyl)-1,3,5-triazene.

Introduction

In the previous paper in this series [1], the synthesis of the dichloroazine **1** from trifluoroacetic acid and hydrazine was described and its reactions with a variety of primary and secondary amines given. The reactions of azine **1** with triethylamine in light [3] and with phenyl-lithium [4] have also been reported.

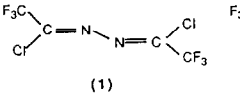
We now report an extension of this work to the reactions of **1** with halide ion and various oxygen- and sulphur-centred nucleophiles. Certain of these results have been described in a preliminary communication [2].

Results and discussion

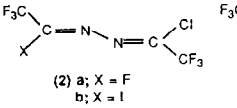
The passage of dichloroazine **1** at low pressure (1–2 mmHg) through a tube packed with dried potassium fluoride at 220–240 °C gave a mixture of mono- and di-substituted products, i.e. chloroheptafluoroazine (**2a**) (21%) and the perfluoroazine **3a** (60%), which were separated by distillation. In contrast to dichloroazine **1**, the perfluoroazine **3a** is hydrolysed readily by water (presumably to the hydrazide $CF_3CONHNHCOCF_3$) showing an increased electron deficiency at the imino carbons (as expected) on replacement of chlorine by fluorine.

Di-iodoazine **3b** (94%) was prepared by treatment of azine **1** with sodium iodide (1:2:5 molar ratio) in acetone at room temperature, while use of a 1:1 molar ratio of reactants afforded a mixture of the monosubstituted compound chloroiodoazine **2b** (18%) and **3b** (41%).

The azines **2a**, **2b**, **3a** and **3b** were each formed as single isomers and on steric grounds are considered to have the (*ZZ*)-configuration. In support of this assignment, aminochloroazine **4** has been shown to have the (*ZZ*)-configuration by an X-ray crystallographic study [5].



(1)



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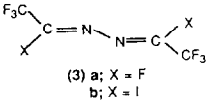
b; X = I



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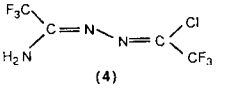

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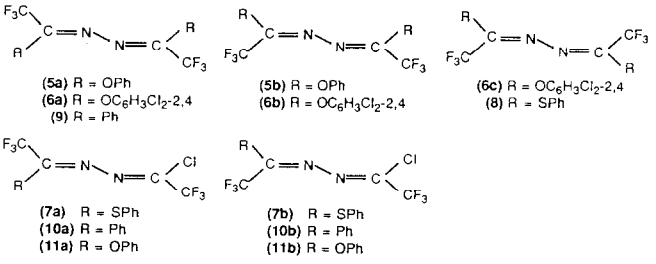
Treatment of azine **1** with the phenols PhOH and 2,4-$Cl_2C_6H_3OH$ in the presence of triethylamine (1:2:2 molar ratio) in diethyl ether at room temperature gave the corresponding disubstituted products, the bis(aryloxy)azines **5** (61%) and **6** (54%). However, a mixture of azine **1**, thiophenol and triethylamine (1:2:2 molar ratio) in $CHCl_3$ as the solvent, heated under reflux, afforded a mixture of mono- and di-substituted products, i.e. the chlorothiophenoxy azine **7** (38%) and bis(thiophenoxy)azine **8** (29%). The triethylamine was employed to generate the phenoxide and thiophenoxide ions and to remove the eliminated chloride ion as the insoluble amine hydrochloride. Since the reactant ratio used was that required theoretically to afford the di-substituted azines, it is clear that with thiophenol (a weaker acid than either of the phenols employed) removal of the SH proton was slow, even under reflux in $CHCl_3$, and all of the initial product, monosubstituted azine **7**, was not converted to the disubstituted azine **8**.

The disubstituted azine **8** was formed as a single isomer (^{19}F NMR spectroscopy), but the azines **5**, **6** and **7** were formed as mixtures of isomers (ratios 64:36, 52:42:6 and 55:45, respectively).

The diphenylazine **9** (from **1** + PhLi) has the (*EE*)-configuration as determined by an X-ray crystallographic study [4, 6], and on steric grounds the major and minor isomers (ratio 95:5) of the chlorophenylazine **10** were assigned the (*EZ*)- and (*ZZ*)-configurations, **10a** and **10b**, respectively [4]. The major and minor isomers (ratio 82:18) of the chlorophenoxyazine **11**, prepared in 73% yield by reaction of azine **1** with lithium phenoxide in diethyl ether, were assigned analogously as having the (*ZZ*)- and (*EZ*)-configurations, **11a** and **11b**, respectively [4]. From these assignments, and from the assignments made to the mono- and di-substituted products from the reaction of azine **1** with primary and secondary amines [1], it was concluded that CF_3 groups *syn* to the nitrogen lone pair in such compounds have higher-field ^{19}F NMR chemical shifts than CF_3 groups *anti* to the nitrogen lone pair. The isomers of the bis(aryloxy) azines **5** and **6** have been assigned on this basis and these assignments and the relevant ^{19}F NMR chemical shifts are shown in Table 1.

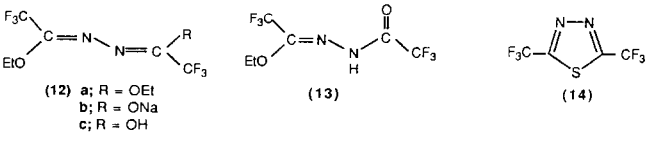
Since the SPh group is bulkier than the OPh group, it would be expected that the thiophenoxy azines **7** and **8** would each contain a higher proportion of the isomer in which the $CF_3C(SPh)=N$ group has the (*E*)-configuration than would the corresponding phenoxy-azines **11** and **5**. It is therefore probable that the single isomer of bis(thiophenoxy)azine **8** formed has the (*EE*)-configuration. Surprisingly, the chemical shifts of the CF_3 groups in the $CF_3C(SPh)=N$ groupings of the two isomers of the mono(thiophenoxy)azine **7** were coincident and so it was not possible to assign configurations to the isomers with certainty. However, if the assignment of azine **8** is correct, it is considered likely that the major isomer of azine **7** has the (*EZ*)-configuration **7b** (Table 1).



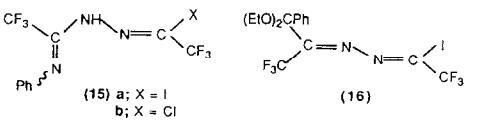
The reaction of azine **1** with excess sodium ethoxide in ethanol gave the bis(ethoxy)azine **12a** (25%) as a single isomer (^{19}F NMR spectroscopy) assigned the (*ZZ*)-configuration, and the sodium enolate **12b** (25%) which was converted quantitatively to amide **13** on treatment with dilute aqueous hydrochloric acid. Evidence for the presence of the hydroxyazine tautomer **12c** of amide **13** was not obtained (IR and NMR spectroscopy).

The enolate **12b** was an unexpected product and presumably arose via a reaction involving hydroxide ion present as impurity in the sodium ethoxide.

A successful preparation of the 1,3,4-thiadiazole **14** (100%) was achieved by heating a mixture of azine **1** with phosphorus(V) sulphide at 180 °C *in vacuo* in a sealed tube.



Di-iodoazine **3b** was also found to be susceptible to nucleophilic attack, and reaction with aniline (1:2 molar ratio) in diethyl ether and with potassium diethyl phenylmalonate (1:1 molar ratio) in THF gave the imidoyl compound **15a** (77%) as a mixture of the (*EZ*)- and (*ZZ*)-isomers in the ratio 50:50 and a single isomer of the monosubstituted azine **16** (88%), respectively. On steric grounds, azine **16** is considered to be the (*EZ*)-isomer with the bulky phenylmalonate group occupying the *anti* position. It has been reported previously that reaction of aniline with azine **1** affords a mixture of the (*EZ*)- and (*ZZ*)-isomers of the imidoyl compound **15b** in the ratio 54:46 [1].



In a preliminary investigation of the reduction of azines **1** and **3b**, it was found that azine **1** was not

TABLE 1. ^{19}F NMR chemical shifts (ppm to low field of TFA) and assignments

R	$CF_3CR=NN=CClCF_3$				R	$CF_3CR=NN=CRCF_3$			
	A	B				A	B		
	δ_A (ppm)	δ_B (ppm)	Isomer (%)	Assignment		δ_A (ppm)	δ_B (ppm)	Isomer (%)	Assignment
SPh	12.1	5.5	45	(*ZZ*?) **7a**	SPh	14.3	14.3	100	(*EE*) **8**
	12.1	5.6	55	(*EZ*?) **7b**					
Ph	10.6	8.1	95	(*EZ*) **10a**	Ph	11.5	11.5	100	(*EE*) **9**
	16.5	8.5	5	(*ZZ*) **10b**					
OPh	7.0	8.0	82	(*ZZ*) **11a**	OPh	7.0	7.0	64	(*ZZ*) **5a**
	10.9	8.0	18	(*EZ*) **11b**		10.9	6.7	36	(*EZ*) **5b**
					$OC_6H_3Cl_2$	7.0	7.0	52	(*ZZ*) **6a**
						12.2	7.0	42	(*EZ*) **6b**
						11.9	11.9	6	(*EE*) **6c**

reduced by the nucleophilic reagents sodium hydride (1:1 molar ratio in diglyme at 20 °C), sodium borohydride (2:1 molar ratio in diglyme at 20 °C) and lithium aluminium hydride (2:1 molar ratio in diglyme at 60 °C). However, a mixture of azine **3b** and tri-n-butyltin hydride (1:1.1 molar ratio) heated *in vacuo* in a sealed tube at 80–100 °C (14 d) gave a volatile material (49% by weight by reactant azine) and a higher-boiling residue which was shown (^{19}F NMR spectroscopy) to contain some unchanged azine **3b**. The volatile material was separated by fractional condensation into a minor (−78 °C fraction) and a major (−23 °C fraction) and the IR, ^1H NMR and ^{19}F NMR and mass spectra of the two fractions were recorded together with the mass spectra of the individual components (coupled GLC/mass spectrometry).

The two major components (A and D) of the −78 °C fraction were identified as (*EE*)-trifluoroacetaldazine (**17**) [^1H NMR δ: 7.92 (q, $CF_3CH=N$, $J=c.$ 3.5 Hz) ppm. ^{19}F NMR δ: +6.65 (d, $J=c.$ 3.5 Hz) ppm. Mass spectrum *mz*: 192 (M^+) and fragmentation peaks for $(M-F)^+$; $(M-CF_3)^+$; CF_3CH^+; and CF_3^+ (base peak)] and the monohydroazine **18** [^1H NMR δ: 7.60 (q, $CF_3CH=N$, $J=c.$ 3.5 Hz) ppm. ^{19}F NMR δ: +8.25 (s, 3F, $CF_3Cl=N$); and +7.0 (d, 3F, $CF_3CH=N$, $J=c.$ 3.5 Hz) ppm. Mass spectrum m/z: 318 (M^+) and fragmentation peaks for $(M-F)^+$; $(M-I)^+$; CF_3CHN^+; and CF_3^+ (base peak)]. The azine **17** has been made previously by the thermal decomposition of the diazoalkane CF_3CHN_2 [7] and the ^{19}F NMR data reported [δ +4.95 (d, $J=3.8$ Hz) ppm] are in reasonable agreement with those obtained in the present work. A minor component present in the fraction was tentatively identified as the hydrazone **19** [^1H NMR δ: 4.3 (d, CF_3CH_2N, $J=c.$ 5 Hz) ppm. ^{19}F NMR δ: +6.3 (t, 3F, CF_3CH_2, $J=c.$ 5 Hz); and +6.0 (d, 3F, $CF_3CH=N$, $J=c.$ 3.5 Hz)].

The remaining ^{19}F NMR absorptions at +11.2, +10.5 and +7.25 ppm were all assigned to the $CF_3CH=N$ grouping (d, $J=c.$ 3.5 Hz). The two lower-field absorptions are probably due to the grouping in the (*Z*)-configuration, with the higher field absorption due to the grouping in the sterically-favoured (*E*)-configuration {CF_3 groups *anti* to nitrogen lone pair in general absorb to lower field than CF_3 groups *syn* to the nitrogen lone pair in azines [1, 4]}. It is therefore possible that the absorptions are due to the (*EZ*)- and (*ZZ*)-isomers of trifluoroacetaldazine **17**.

The −23 °C fraction contained three major (A, D, E) and two minor (B, C) components. A and D were the hydroazines **17** and **18**, respectively, and component E was identified as the iodohydrazone **20** [^1H NMR δ: 6.73 (broad, 1H, NH); and 4.18 (q, 2H, CF_3CH_2, $J=c.$ 5 Hz) ppm. ^{19}F NMR δ: +10.9 (s, 3F, $CF_3Cl=N$); and +4.6 (t, 3F, CF_3CH_2N, $J=c.$ 5 Hz) ppm. Mass spectrum *m/z*: 222 (CF_3ClN^+); and 83 (base peak, $CF_3CH_2^+$)]. The minor components B and C were tentatively identified as hydrazone **21** [Mass spectrum *m/z*:320 (M^+) and fragmentation peaks for CF_3CHIN^+, $CF_3CHN_2^+$, CF_3CHN^+ and CF_3^+ (base peak)] and a compound of molecular formula $C_6H_4F_9N_3$, possibly $CF_3CH_2NHN=C(CF_3)-N=CHCF_3$ [mass spectrum *m/z*: 289 (M^+) and fragmentation peaks for $C_4H_2F_5N_2^+$, $CF_3CH_2N_2^+$, $CF_3CHN_2^+$, $CF_3CH_2^+$, CF_2CHN^+ and CF_3^+ (base peak)].

$CF_3CH=NN=CHCF_3$ (17) $CF_3CH=NN=ClCF_3$ (18) $CF_3CH_2NHN=CHCF_3$ (19)

$CF_3CH_2NHN=ClCF_3$ (20) $CF_3CHINHN=CHCF_3$ (21)

The hydroazines **17** and **18** could have been formed by a free-radical chain mechanism, as proposed for the

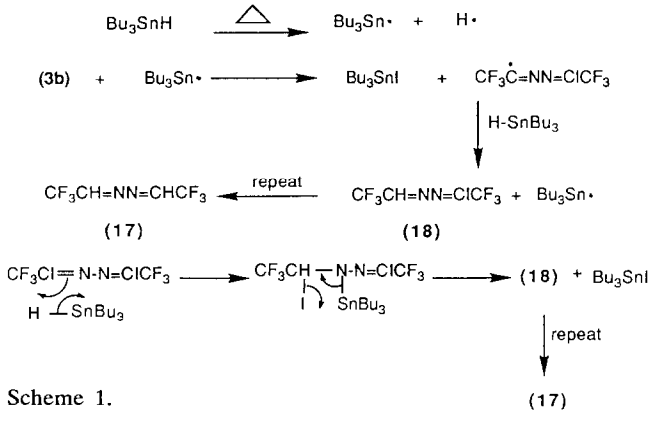
reduction of alkyl [8, 9] and vinyl [10] halides, or via an addition–elimination mechanism, as postulated for the reduction of fluorovinyl compounds [11, 12] as shown in Scheme 1.

Further reduction of azines **17** and **18** then took place to some extent to give hydrazones **19–21**. The reduction of aldehydes and ketones to the corresponding alcohols by tin hydrides takes place by a two-step mechanism, the second step of which represents a general polar reaction between organotin hydrides and organotin compounds containing electronegative atoms bonded to tin, e.g. RO–, R_2N– [1, 13]; the hydrazones **19–21** are considered to be formed in a similar manner (Scheme 2).

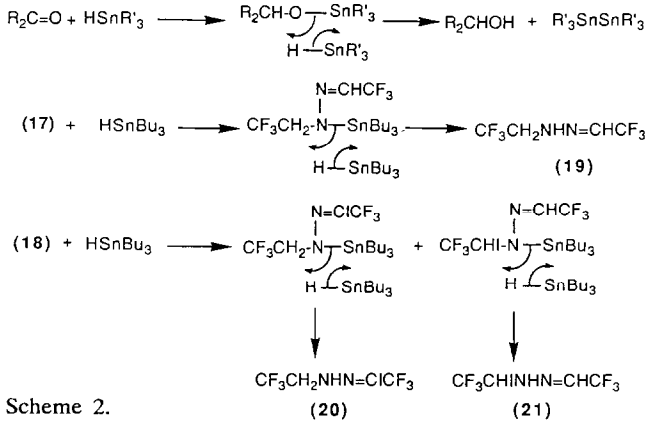
Alternatively, hydrazone **19** could have been produced by further reduction of hydrazones **20** and **21**.

From the results obtained the approximate yields of the products were **17** (*c.* 10%), **18** (*c.* 35%), **19** (*c.* 2%), **20** (*c.* 15%), and **21** (*c.* 1%).

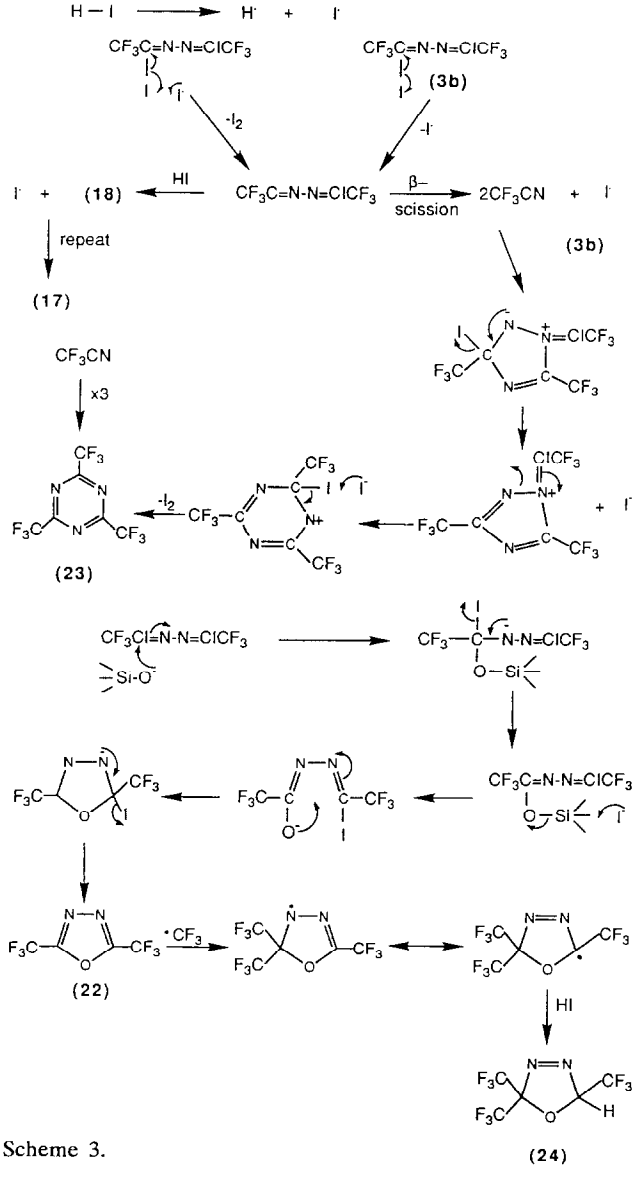
Hydrogen iodide is an effective reagent for the reduction of alkyl iodides to alkanes under thermal conditions and has been used for the reduction of polyfluoroalkyl iodides, see, for example ref. 14; a free-radical or a four-centre mechanism could be operative. The reaction of azine **3b** with hydrogen iodide (1:1 molar ratio) at 200 °C *in vacuo* (24 h) gave volatile material (17% by weight of reactant azine) which was examined (as described for the products from the Bu_3SnH reaction) and found to contain the hydroazines **17** and **18**, and three other major components identified as the oxadiazole **22** [^{19}F NMR δ: +11.3 ppm, lit. value [15], δ +9.6 ppm. Mass spectrum *m/z*: 206 (M^+) and peaks for $(M-F)^+$; $(M-CF_3)^+$; $CF_3CN_2^+$, CF_3CO^+; and CF_3^+ (base peak)], the 1,3,5-triazene **23** [^{19}F NMR δ: +4.5 (s) ppm. Mass spectrum *m/z*: 285 (M^+) and peaks for $(M-F)^+$; $M-CF_3CN)^+$; and CF_3^+ (base peak)] and a compound of molecular formula $C_5HF_9N_2O$, possibly the oxadiazole **24** {mass spectrum *m/z*: 276 (M^+) and peaks for $(M-F)^+$; $[(M-CF_3)^+$, base peak)]; $(M-C_3F_6)^+$; $CF_3CHN_2^+$; and CF_3^+}. The approximate yields of the products were **17** (*c.* 1%), **18** (*c.* 7%), **22** (*c.* 8%), **23** (*c.* 14%) and **24** (*c.* 1.5%) and they are considered to be formed as shown in Scheme 3.



Scheme 1.



Scheme 2.



Scheme 3.

The triazene **23** could have been formed by trimerisation of the nitrile CF_3CN arising from the intermediate radical **25** by β-scission, but it is perhaps more likely that it is produced via 1,3-dipolar cycloaddition of azine **3b** to the nitrile; azine **1** has been found to undergo 1,3-dipolar cycloaddition to a variety of alkenes and dienes [16]. The formation of oxadiazole **22** (and hence **24**) requires oxygen, the most likely source of which is $Si-O^-$ or Si–OH groups present on the walls of the Pyrex reaction vessel. The CF_3 radicals necessary for the formation of oxadiazole **24** must arise from decomposition of azine **3b** (or an intermediate derived from **3b**) at 200 °C.

The other bands observed in the NMR spectra [^{1}H NMR δ: 5.43 (broad, 1H, NH); and 3.85 (q, 2H, CF_3CH_2, J=6.5 Hz) ppm. ^{19}F NMR δ: +10.5 (t, CF_3CH_2, J= 6.5 Hz)] indicated the presence of a compound containing the CF_3CH_2NH grouping (possibly $CF_3CH_2NHNHCH_2CF_3$), but no mass-spectral evidence was obtained for such a compound.

From the results obtained, it is clear that the tin hydride is more effective than hydrogen iodide for reduction of azine **3b**.

Experimental

The organic reagents used were commercial samples, the purities of which were checked before use, and the halides KF and NaI were dried thoroughly. Azine **1** was prepared (60%) by reaction of trifluoroacetic acid (TFA) with hydrazine and treatment of the resulting 1,2-bis(trifluoroacetyl) hydrazine with *N,N*-dimethylaniline hydrochloride and phosphoryl chloride [1].

The reaction products were separated or purified as indicated in the text and were examined by IR spectroscopy (Perkin-Elmer 197 or 257 instruments), ^{1}H NMR [Perkin-Elmer R32 (90 MHz) or R34 (220 MHz) spectrometers; reference internal Me_4Si] and ^{19}F NMR spectroscopy [Perkin-Elmer R32 (84.6 MHz) instrument; reference external TFA] and mass spectrometry (A.E.I. MS 902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded using neat liquids or solutions [in $CDCl_3$ or $(CD_3)_2CO$] as given in the text and chemical shifts to low field of reference are designated positive. GLC and coupled GLC/mass spectrometry were carried out on a Pye 104 instrument using columns (2.5 m, silicone SE30 oil (30%) on Celite) at 70 °C.

Boiling points were determined by distillation or by Siwoloboff's method and melting points are uncorrected.

Reactions of the dichloroazine 1

(a) With potassium fluoride

Dichloroazine **1** (24.43 g, 93.5 mmol) was passed (for 1 h) at low pressure (1–2 mmHg) through a silica tube (2×50 cm) packed with dried potassium fluoride (160 g) and heated to 220–240 °C with the product collected in a cooled trap (−196 °C) connected to the vacuum system. The material (22.08 g) which collected in the cold trap was found to contain some unreacted azine **1** (IR, C=N str. at 1640 cm^{-1}) and so it was repassed through the tube (repacked with fresh KF) to give the product (17.46 g). Distillation of this material through a Vigreux column (25 cm^3) afforded 1,1,1,2,5,6,6,6-octafluoro-3,4-diazahexa-2,4-diene (**3a**) (nc) (12.78 g, 56.1 mmol, 60%) (Analysis: Found: C, 21.0; F, 66.4; N, 12.6%; mol. wt., 228. $C_4F_8N_2$ requires: C, 21.1; F, 66.6; N, 12.3%; mol wt., 228), b.p. 39–45 °C. ^{19}F NMR (neat) δ: +12.3 (br., IF, CF); and +2.9 (d, 3F, CF_3, J=5 Hz) ppm. IR (ν_{max}) (cm^{-1}): 1720 (s) (C=N str.); 1240–1120 (s) (C–F str.); and 740 (s) (CF_3 def.). Mass spectrum *m/z*: 228 (28.8%, M^+); 209 [15.7, $(M-F)^+$]; 159 [10.0, $(M-CF_3)^+$]; 100 (11.1, $C_2F_4^+$); 69 (100.0, CF_3^+); 50 (9.2, CF_2^+); and 31 (9.1, CF^+).

The pot residue was identified as 2-chloro-1,1,1,5,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**2a**) (nc) (4.68 g, 19.2 mmol, 21%) (Analysis: Found: C, 19.7; F, 54.6; N, 11.4%; mol. wt., 244/246. $C_4ClF_7N_2$ requires: C, 19.6; F, 54.4; N, 11.5%; mol. wt., 244.5), b.p. 63–65 °C. ^{19}F NMR (neat) δ: +11.9 (br., IF, CF); +6.6 (s, 3F, CF_3CCl); and +3.2 (d, 3F, CF_3, J=5 Hz) ppm. IR (ν_{max}) (cm^{-1}): 1707 and 1629 (m) (C=N str.); 1240–1150 (s) (C–F str.); and 755 (m) (CF_3 def.). Mass spectrum *m/z*: 244/246 (100.0%, M^+); 225/227 [32.7, $(M-F)^+$]; 209 [75.2, $(M-Cl)^+$]; 175/177 [84.6, $(M-CF_3)^+$]; 125/127 (9.6, $C_2ClF_2N_2^+$); 116/118 (7.7, $C_2ClF_3^+$); 85/87 (19.5, $CClF_2^+$); 76 (5.9, $C_2F_2N^+$); 69 (98.3, CF_3^+); and 50 (7.3, CF_2^+).

(b) With sodium iodide (molar ratio 2.5:1)

Sodium iodide (25.4 g, 0.169 mol) was added to a stirred solution of dichloroazine **1** (17.0 g, 65.1 mmol) in acetone (60 cm^3) and stirring was continued (65 h). The precipitate of sodium chloride (7.39 g, 0.126 mol, 97%) was filtered off and the solvent was removed under reduced pressure from the filtrate. The residue was treated with diethyl ether (25 cm^3), filtered, washed with water (25 cm^3), then with aqueous sodium metabisulphite (*c.* 20% w/w, 25 cm^3) and again with water (25 cm^3). The ethereal layer was dried ($MgSO_4$) and the ether removed under reduced pressure to give a pale yellow oil identified as 2,5-di-iodo-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**3b**) (nc) (27.21 g, 61.3 mmol, 94%) (Analysis: Found: C, 11.1; F, 25.4; I, 57.1; N, 6.6%; mol. wt., 444. $C_4F_6I_2N_2$ requires: C, 10.8; F, 25.7; I, 57.2; N, 6.3%; mol. wt., 444), b.p. 165–167 °C/751 mmHg. ^{19}F NMR (neat) δ: +10.6 (s, CF_3) ppm. IR (ν_{max}) (cm^{-1}): 1620 (s) (C=N str.); 1270–1168 (s) (C–F str.); and 745 (s) (CF_3 def.). Mass spectrum *m/z*: 444 (4.7%, M^+); 317 [100.0, $(M-I)^+$];

254 (10.8, I_2^+); 222 (13.3, $C_2F_3IN^+$); 127 (75.4, I^+); and 69 (78.5, CF_3^+).

(c) With sodium iodide (molar ratio 1:1)

A solution of sodium iodide (0.66 g, 4.41 mmol) in acetone (20 cm^3) was added to a stirred solution of dichloroazine **1** (1.15 g, 4.41 mmol) in acetone (10 cm^3) and stirring was continued (22 h). The precipitate of sodium chloride (0.24 g) was filtered off and the solvent was removed from the filtrate under reduced pressure. Diethyl ether (20 cm^3) was added to the residue which was then filtered and the solvent removed under reduced pressure from the filtrate to afford a yellow oil (1.08 g) which was shown (^{19}F NMR and mass spectrometry) to consist of a mixture (7:3 molar ratio) of the di-iodoazine **3b** (0.81 g, 1.82 mmol, 41%) and 2-chloro-1,1,1,6,6,6-hexafluoro-5-iodo-3,4-diazahexa-2,4-diene (**2b**) (0.27 g, 0.78 mmol, 18%). ^{19}F NMR (neat) δ: +9.9 (s, 3F, CF_3Cl); and +7.9 (s, 3F, CF_3CCl) ppm. Mass spectrum *m/z*: 225/227 [31.2%, $(M-I)^+$].

(d) With the phenoxide ion

A solution of triethylamine (0.93 g, 9.2 mmol) in diethyl ether (10 cm^3) was added to a stirred mixture of dichloroazine **1** (1.20 g, 4.6 mmol) and phenol (0.86 g, 9.2 mmol) in diethyl ether (50 cm^3) and stirring was continued (6 h). The white precipitate of triethylamine hydrochloride (0.81 g, 5.9 mmol, 64%) was filtered off, the filtrate dried ($MgSO_4$) and the solvent removed under reduced pressure to give a white solid (1.73 g) which on recrystallisation from aqueous ethanol afforded 2,5-bis(phenoxy)-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**5**) (nc) (1.05 g, 2.8 mmol, 61%) (Analysis: Found: C, 51.0; H, 2.6; F, 30.2; N, 7.4%; mol. wt., 376. $C_{16}H_{10}F_6N_2O_2$ requires: C, 51.1; H, 2.7; F, 30.3; N, 7.4%; mol. wt., 376), m.p. 69–70 °C. ^1H NMR ($CDCl_3$) δ: 7.5–6.5 (mult., C_6H_5) ppm. ^{19}F NMR δ: +10.9 (s, CF_3); +7.0 (s, CF_3); and +6.7 (s, CF_3) ppm in the ratio 2:7:2. IR (ν_{max}) (cm^{-1}): 1670 (s) (C=N str.); 1223–1160 (s) (C–F str.); 1120 (s) (C–O str.); and 753 (s) (CF_3 def.). Mass spectrum *m/z*: 376 (2.5%, M^+); 307 [31.3, $(M-CF_3)^+$]; 283 [100.0, $(M-C_6H_5O)^+$]; 188 (47.4, $C_8H_5F_3NO^+$); 172 (32.6, $C_8H_5F_3N^+$); 168 (46.4, $C_8H_4F_2NO^+$); 94 (41.5, $C_6H_6O^+$); 93 (68.9, $C_6H_5O^+$); 77 (99.3, $C_6H_5^+$); 69 (24.9, CF_3^+); 65 (71.5, $C_5H_5^+$); and 44 (20.5, $C_2H_4O^+$).

(e) With the 2,4-dichlorophenoxide ion

A solution of 2,4-dichlorophenol (1.64 g, 10.04 mmol) and triethylamine (1.01 g, 10.04 mmol) in diethyl ether (50 cm^3) was added slowly during 20 min to a stirred solution of dichloroazine **1** (1.31 g, 5.02 mmol) in diethyl ether (25 cm^3) and stirring was continued (3 h). The white precipitate of triethylamine hydrochloride (1.05 g, 7.6 mmol, 76%) was filtered off and the filtrate was stored overnight during which time a further amount of triethylamine hydrochloride (0.15 g, 1.1 mmol, 11%) was precipitated. After filtration, the solvent was removed from the filtrate to give a cream solid (2.64 g) which could not be recrystallised successfully from ethanol, aqueous ethanol or chloroform/light petroleum. However, purification was achieved by trituration with cold (0 °C) ethanol (*c.* 20 cm^3) which gave a white solid (m.p. 94 °C), and the residue, after removal of the ethanol from the filtrate, on trituration with ethyl acetate (*c.* 20 cm^3) afforded a further amount of solid with the same melting point. The solids were combined and identified as 2,5-bis(2,4-dichlorophenoxy)-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**6**) (nc) (1.40 g, 2.7 mmol, 54%) (Analysis: Found: C, 37.5; H, 1.0; Cl, 27.3; F, 22.1; N, 5.2%; mol. wt., 512/514/516/518/520. $C_{16}H_6Cl_4F_6N_2O_2$ requires: C, 37.4; H, 1.2; Cl, 27.6; F, 22.2; N, 5.5%; mol. wt., 514), m.p. 94 °C. ^1H NMR ($CDCl_3$ δ: 7.65–7.45 (mult., C_6H_5) ppm. ^{19}F NMR δ: +12.2 (s, CF_3); +11.9 (s, CF_3); and +7.0 (s, CF_3) ppm in the ratio 7:2:24. IR (ν_{max}) (cm^{-1}): 1678 (s) (C=N str.); 1245–1175 (s) (C–F str.); 1125 and 1105 (s) (C–O str.); and 753 (m) (CF_3 def.). Mass spectrum *m/z*: 512/514/516 (1.0%, M^+); 351/353/355 (71.2, $C_{10}H_3Cl_2F_6N_2O^+$); 256/258/260 (68.8, $C_8H_3Cl_2F_3NO^+$); 226/228/230 (47.9, $C_8H_6Cl_2F_2O^+$); 187/189/191 (21.1, $C_7H_3NCl_2NO^+$); 161/163/165 (76.0, $C_6H_3Cl_2O^+$); 145/147/149 (27.2, $C_6H_3Cl_2^+$); 133/135/137 (100.0, $C_5H_3Cl_2^+$); 109 (17.2, $C_2F_3N_2^+$); and 69 (31.8, CF_3^+).

(f) With sodium ethoxide in ethanol

Sodium metal (1.3 g, 56.6 mmol) was added in small pieces to ethanol (50 cm^3) and a solution of dichloroazine **1** (6.50 g, 24.9 mmol) in dry ethanol (25 cm^3) then added and the mixture stirred at room temperature (69 h). A ^{19}F NMR examination indicated the absence of reactant dichloroazine **1**. The white precipitate of sodium chloride (2.94 g, 50.3 mmol, 89%) was filtered off and the volatile material removed from the filtrate by distillation at atmospheric pressure to give a white solid identified as sodium [2-ethoxy-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene-5-oxide] (**12b**) (nc) (1.73 g, 6.3 mmol, 25%) (Analysis: Found: C, 26.0; H, 1.7; F, 41.2; N, 9.9; Na, 8.8%. $C_6H_5F_6N_2O_2Na$ requires: C, 26.3; H, 1.8; F, 41.6; N, 10.3; Na, 8.4%), m.p. 153–154 °C. ^1H NMR [$(CD_3)_2CO$] δ: 4.85 (q, 2H, CH_2–O, J=7.3 Hz); and 1.27 (t, 3H, CH_3, J=7.3 Hz) ppm. ^{19}F NMR δ: +2.7 (s, 3F, CF_3); and +1.9 (s, 3F, CF_3) ppm. IR (ν_{max}) cm^{-1}): 1660–1620 (s) (C=N str.); 1220–1180 (s) (C–F str.); 1105 (s) (C–O str.); and 705 (s) (CF_3 def.). Mass spectrum *m/z*: 297 [100.0%, $(M+Na)^+$]; 274 (0.4, M^+); 224 (12.4, $C_5H_5F_4N_2O_2Na^+$); 154 (26.1, $C_4H_5F_3N_2O^+$); 69 (25.3, CF_3^+); and 29 (14.5, $C_2H_5^+$).

The volatile material was redistilled at atmospheric pressure through a column (25 cm^3) packed with glass helices. After the bulk of the ethanol had been removed, (up to 79 °C), the residue was transferred to a micro-distillation unit and the liquid which remained after all the solvent had been removed identified as 2,5-bis-(ethoxy)-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**12a**) (nc) (2.4 g, 8.6 mmol, 35%) of >90% purity (^1H and ^{19}F NMR) from the spectral data obtained. ^1H NMR δ: 3.83 (q, 2H, CH_2–O, J=7 Hz); and 0.86 (t, 3H, CH_3, J=7 Hz) ppm. ^{19}F NMR δ: +9.8 (s, CF_3) ppm. IR (ν_{max}) (cm^{-1}):1645 (s) (C=N str.); 1280–1140 (s) (C–F str.); 1120 (s) (C–O str.); and 740 (s) (CF_3def.). Mass spectrum *m/z*: 280 (2.0%, M^+); 211 [9.6, $(M-CF_3)^+$]; 155 (45.9, $C_4H_6F_3N_2O^+$); 140 (9.7, $C_4H_5F_3NO^+$); 114 (16.0, $C_3H_5F_3O^+$); 69 (53.3, CF_3^+); 45 (30.6, $C_2H_5O^+$); and 29 (100.0, $C_2H_5^+$).

When a stirred solution of enolate **12b** (0.19 g, 0.69 mmol) in water (10 cm^3) was treated with dilute hydrochloric acid (2 M, 0.5 cm^3) a white precipitate formed immediately. This was separated by filtration, dried (vacuum desiccator) and identified as 2-ethoxy-1,1,1,6,6,6-hexafluoro-3,4-diazahex-2-ene-5-one (**13**) (nc) (0.174 g, 0.69 mmol, 100%) (Analysis: Found: C, 28.5; H, 2.6; N, 11.0%. $C_6H_6F_6N_2O_2$ requires: C, 28.6; H, 2.4; N, 11.1%), m.p. 71–72 °C. ^1H NMR ($CDCl_3$ δ: 9.42 (br., 1H, NH); 4.47 (q, 2H, OCH_2, J=7 Hz); and 1.45 (t, 3H, CH_3, J=7 Hz) ppm. ^{19}F NMR δ: +11.7 (s, 3F, CF_3C=N); and +3.4 (s, 3F, CF_3C=O) ppm. IR (ν_{max}) (cm^{-1}): 3200 and 3050 (m) (N–H str.); 1720 (s) (C=O str.); 1660 (s) (C=N str.); and 1280–1120 (s) (C–F str.).

(g) With thiophenoxide

A solution of dichloroazine 1 (3.0 g, 11.4 mmol) in chloroform (25 cm^3) was added to a solution of thiophenol (2.5 g, 22.7 mmol) and triethylamine (2.3 g, 22.8 mmol) in chloroform (25 cm^3) and the mixture heated under reflux (6h). The solvent was removed under reduced pressure and the residue treated with diethyl ether (25 cm^3). The resulting solid was filtered off and identified as triethylamine hydrochloride (2.2 g, 16.0 mmol, 70%) and the filtrate was washed with dilute sulphuric acid (2 M, 30 cm^3). The ether layer was separated, washed with water (2×10 cm^3), dried ($MgSO_4$) and the solvent then removed under reduced pressure to give a clear amber oil (3.12 g). The oil was separated by DCFC [light petroleum/dichloromethane (1:2 v/v)] into its two components identified as follows.

(i) 2-Chloro-1,1,1,6,6,6-hexafluoro-5-thiophenoxy-3,4-diazahexa-2,4-diene (**7**) (nc) (1.46 g, 4.33 mmol, 38%) (Analysis: Found: C, 36.1; H, 1.6; F, 33.9; N, 8.3%; mol. wt., 334/336. $C_{10}H_5ClF_6N_2S$ requires: C, 35.9; H, 1.4; F, 34.1; N, 8.4%; mol. wt., 334.5). ^1H NMR ($CDCl_3$ δ: 7.3–7.1 (mult., C_6H_5) ppm. ^{19}F NMR δ: 12.1 (s, CF_3); +5.6 (s, CF_3CCl); and +5.5 (s, CF_3CCl) ppm in the ratio 11:6:5. IR (ν_{max}) (cm^{-1}): 1630 (m) (C=N str.); 1185–1145 (s) (CF_3 str.); and 758 (s) (CF_3 def.). Mass spectrum *m/z*: 334/336 (2.3%, M^+); 299 [100.0, $(M-Cl)^+$]; 225/227 [12.3, $(M-C_6H_5S)^+$]; 182 (20.6, $C_4F_4N_2S^+$); 121 (16.3, $C_7H_5S^+$); 110 (21.3, $C_6H_6S^+$); 109 (100.0, $C_6H_5S^+$); 108 (15.9, $C_6H_4S^+$); 77 (43.6, $C_6H_5^+$); 69 (33.6, CF_3^+); 65 (31.2, $C_5H_5^+$); and 51 (21.6, $C_4H_3^+$).

(ii) 2,5-Bis(thiophenoxy)-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**8**) (nc) (1.35 g, 3.31 mmol, 29%) (Analysis: Found: C, 47.4; H, 2.2; F, 28.0; N, 6.9; S, 15.6%; mol. wt., 408. $C_{16}H_{10}F_6N_2S_2$ requires: C, 47.1; H, 2.5; F, 27.9; N, 6.9; S, 15.7%; mol. wt., 408), m.p. 59.5–60 °C. ^1H NMR ($CDCl_3$) δ: 7.53–7.30 (mult., C_6H_5) ppm. ^{19}F NMR δ: +14.3 (s, CF_3) ppm. IR (ν_{max}) (cm^{-1}): 1620 (s) (C=N str.); 1190–1151 (s) (C–F str.); and 768 (s) (CF_3 def.) Mass spectrum *m/z*: 408 (0.6%, M^+); 301 (36.1, $C_{10}H_7F_6N_2S^+$); 300 (62.5, $C_{10}H_6F_6N_2S^+$); 299 [100.0, $(M-C_6H_5S)^+$]; 184 (37.3, $C_4F_4N_2S^+$); 121 (40.9, $C_7H_5S^+$); 110 (55.7, $C_6H_6S^+$); 109 (76.3, $C_6H_5S^+$); 108 (37.1, $C_6H_4S^+$); 78 (20.9, $C_6H_6^+$); 77 (85.9, $C_6H_5^+$); 69 (58.5, CF_3^+); 65 (84.8, $C_5H_5^+$); and 51 (64.2, $C_4H_3^+$).

(h) With phosphorus(V) sulphide

A mixture of phosphorus(V) sulphide (1.32 g, 5.9 mmol) and dichloroazine **1** (0.14 g, 0.54 mmol) was heated *in vacuo* in a Pyrex tube (*c.* 70 cm^3) at 180 °C (10 d). The tube was opened *in vacuo* and the volatile material separated by fractional condensation to give (i) a −196 °C fraction (trace), which was identified as hydrogen chloride and (ii) a combined −23 °C and −48 °C fraction, which was identified as 2,5-bis(trifluoromethyl)-1,3,4-thiadiazole (**14**) (nc) (0.12 g, 0.54 mmol, 100%) (Analysis: Found: C, 21.7; F, 50.9; N, 12.9; S, 14.5%; mol. wt., 222. $C_4F_6N_2S$ requires: C, 21.6; F, 51.4; N, 12.6; S, 14.4%; mol. wt., 222); b.p. 105–106 °C. ^{19}F NMR δ: +6.2 (s, CF_3) ppm. IR (ν_{max}) (cm^{-1}): 1480 (s) (C=N str.); 1240–1180 (s) (C–F str.); and 760 (s) (CF_3 def.). Mass spectrum *m/z*: 222 (72.2%, M^+); 203 [21.8, $(M-F)^+$]; 127 (46.1, $C_2F_3NS^+$); 113 (38.9, $C_2F_3S^+$); 69 (100.0, CF_3^+); 63 (14.6, CFS^+); and 58 (17.6, CNS^+).

(i) With nucleophilic reducing agents

Mixtures of (i) dichloroazine **1** (2.0 g, 7.63 mmol), sodium hydride (0.184 g, 7.6 mmol) and diglyme (5 cm^3) and (ii) azine **1** (2.0 g, 7.63 mmol), sodium borohydride (0.14 g, 3.70 mmol) and diglyme (5 cm^3), sealed *in vacuo* in Rotaflo tubes (*c.* 50 cm^3) and shaken at room temperature (24 h) gave a volatile material identified as unchanged azine **1** (1.95 g, 7.40 mmol, 98% recovered) and (1.93 g, 7.36 mmol, 96.5% recovered), respectively.

A solution of azine **1** (5.0 g, 19.0 mmol) in diglyme (20 cm^3) was added to lithium aluminium hydride (0.36 g, 9.4 mmol) in a flask (*c.* 100 cm^3) connected via a condenser to the vacuum system. The flask contents were stirred and heated at 60 °C (4 h) and the volatile material then condensed in the vacuum system and identified as unchanged azine **1** (4.90 g, 18.7 mmol, 98% recovered).

*Reactions of 2,5-di-iodo-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**3b**)*

(a) With aniline

A solution of aniline (0.16 g, 1.76 mmol) in diethyl ether (10 cm^3) was added to a stirred solution of di-iodoazine **3b** (0.39 g, 0.88 mmol) in ether (10 cm^3) and the stirring continued (0.5 h). The precipitate of aniline hydroiodide was filtered off and the filtrate washed with dilute hydrochloric acid (2 M, 2×50 cm^3), dried ($MgSO_4$) and the solvent removed under reduced pressure to give a dark oil. This was further dried (vacuum desiccator) to give 5-iodo-1-phenyl-6,6,6-trifluoro-2-trifluoromethyl-1,3,4-triazahexa-1,4-diene (**15a**) (nc) (0.28 g, 0.68 mmol, 77%) (Analysis: Found: C, 29.7; H, 1.6; F, 27.7; I, 30.7; N, 10.3%; mol. wt., 409. $C_{10}H_6F_6IN_3$ requires: C, 29.4; H, 1.5; F, 27.9; I, 31.0; N, 10.3%; mol. wt., 409). ^1H NMR ($CDCl_3$) δ: 7.78 (s, 1H, NH); 7.64 (s, 1H, NH); and 7.5–6.9 (mult., 10H, C_6H_5) ppm. ^{19}F NMR δ: +12.6 (s, CF_3); +12.0 (s, CF_3); and +11.8 (s, CF_3) ppm in the ratio 2:1:1. IR (ν_{max}) (cm^{-1}): 3440 (s) (N–H str.); 1625 (s) (C=N str.); 1595 (s) (N–H bend); 1220–1120 (s) (C–F str.); and 755 and 740 (m) (CF_3 def.). Mass spectrum *m/z*: 409 (5.5%, M^+); 282 [100.0, $(M-I)^+$]; 262 (12.7, $C_{10}H_5F_5N_3^+$); 167 (18.2, CIN_2^+); 118 (17.8, $C_7H_6N_2^+$); 92 (21.7, $C_6H_5N^+$); 77 (27.4, $C_6H_5^+$); 69 (9.1, CF_3^+); 65 (27.5, $C_5H_5^+$); 51 (11.1, $C_4H_3^+$); and 39 (9.3, $C_3H_3^+$).

(b) With potassium diethyl phenylmalonate

A solution of diethyl phenylmalonate (2.00 g, 8.46 mmol) in dry THF (15 cm^3) was added dropwise to stirred potassium hydride (0.37 g, 9.32 mmol) under a nitrogen atmosphere and cooled to −20 °C. The stirring was continued (0.5 h) and the mixture then cooled to −50 °C and a solution of di-iodoazine **3b** (3.75 g, 8.46 mmol) in THF (20 cm^3) added dropwise. After stirring at this temperature (3 h), the material was warmed to room temperature and the precipitate of potassium iodide (1.09 g, 6.6 mmol, 78%) filtered off. The solvent was removed from the filtrate under reduced pressure to give a reddish oil (4.72 g), which was shown by TLC (chloroform) to contain one major and two minor components. Separation of the mixture by DCFC (same eluant) gave the following compounds.

(i) Unchanged di-diodoazine **3b** (0.70 g, 1.57 mmol, 19% recovered).

(ii) Diethyl (1,1,1,6,6,6-hexafluoro-2-iodo-3,4-diaza-hexa-2,4-dien-5-yl)phenylmalonate (**16**) (nc) (3.32 g, 6.0 mmol, 88%) (Analysis: Found: C, 36.9; H, 2.8; F, 20.5; N, 5.1%; mol. wt., 552. $C_{17}H_{15}F_6IN_2O_4$ requires: C, 36.9; H, 2.7; F, 20.6; N, 5.1%; mol. wt., 555) as a yellow oil. ^1H NMR ($CDCl_3$ δ: 7.45 (mult., 5H, C_6H_5); 4.43 (q, 4H, $2CH_2$–O, J=7 Hz); and 1.35 (t, 6H, $2CH_3$, J=7 Hz) ppm. ^{19}F NMR δ: +15.2 (s, 3F, CF_3); and +10.1 (s, 3F, CF_3Cl) ppm. IR (ν_{max}) (cm^{-1}): 1740 (s) (C=O str.); 1600 (s) C=N str.); and 1260–1140 (s) (C–F str.). Mass spectrum *m/z*: 557 (4.7%, M^+); 434 (46.5, $C_{12}H_5F_6IN_2O^+$); 307 (39.2, $C_{12}H_5F_6N_2O^+$); 184 (100.0, $C_9H_5F_3N^+$); 161 (25.0, $C_{10}H_9O_2^+$); 133 (16.0, $C_8H_5O_2^+$); 105 (36.3, $C_7H_5O^+$); 89 (23.4, $C_7H_5^+$); 77 (34.4, $C_6H_5^+$); 69 (31.7, CF_3^+); 58 (26.5, $C_2H_2O_2^+$); and 57 (28.5, $C_2HO_2^+$).

(iii) Unchanged diethyl phenylmalonate (0.40 g, 1.69 mmol, 20% recovered).

(c) With tri-n-butyltin hydride

A mixture of tri-n-butyltin hydride (6.12 g, 21.04 mmol) and di-iodoazine **3b** (8.50 g, 19.14 mmol), sealed *in vacuo* in a Pyrex tube (*c.* 200 cm^3) and heated at 80–100 °C for 14 d, gave a volatile material (4.18 g) which was subjected to fractional condensation *in vacuo* through traps cooled to 0, −23, −78 and −196 °C to give the following fractions.

(i) A −78 °C fraction (0.87 g). ^1H NMR (neat) δ: 7.92 (q, *c.* 9H, CF_3CH=, J=3.5 Hz); 7.60 (q, *c.* 1H, CF_3CH=, J=3.5 Hz); 7.39 (br., *c.* 0.2H, CF_3CH=); 7.24 (br., *c.* 0.1H, CF_3CH=); and 4.30 (q, *c.* 0.5H, CF_3CH_2, J=4.5 Hz) ppm. ^{19}F NMR δ: +11.2 (d, *c.* 1F, CF_3CH=, J=3.5 Hz); +10.5 (d, *c.* 1F, CF_3CH=, J=3.5 Hz); +8.3 (s, 2.5F, CF_3Cl); +7.3 (d, *c.* 1F, CF_3CH=, J=3.5 Hz; +7.0 (d, 2.5F, CF_3CH=, J=3.5 Hz); −6.7 (d, 7F, CF_3CH=, J=3.5 Hz); +6.3 (t, *c.* 1F, CF_3CH_2, J=4.5 Hz); and +6.0 (d, *c.* 1F, CF_3CH=, J=3.5 Hz) ppm. IR (ν_{max}) (cm^{-1}): 3290 (w) (N–H str.); 1620 (s) (C=N str.); 1270–1150 (s) (C–F str.); and 720 (s) (CF_3 def.). Mass spectrum *m/z*: 318 (1.2%, $C_4HF_6IN_2^+$); 222 (0.7, $C_2F_3IN^+$); 209 (4.2, $C_2HF_3I^+$); 192 (85.6, $C_4H_2F_6N_2^+$); 191 (5.7, $C_4HF_6N_2^+$); 190 (2.8, $C_4F_6N_2^+$); 173 (33.5, $C_4H_2F_5N_2^+$); 127 (4.8, I^+); 123 (12.7, $C_3H_2F_3N_2^+$); 111 (3.0, $C_2H_2F_3N_2^+$); 96 (8.5, $C_2HF_3N^+$); 83 (2.5, $C_2H_2F_3^+$); 82 (3.4, $C_2HF_3^+$); 77 (5.3, $C_2HF_2N^+$); 69 (100.0, CF_3^+); and 43 (15.9, C_2F^+).

(ii) A −23 °C fraction (3.31 g). ^1H NMR (neat) δ: 7.92 (q, 1H, CF_3CH=, J=3.5 Hz); 7.60 (q, 2.2H, CF_3CH=, J=3.5 Hz); 7.32 (q, 1.4 H, CF_3CH=, J=3.5 Hz); 6.73 (br., 1H, NH); and 4.18 (q, 2H, CF_3CH_2, J=4.5 Hz) ppm. ^{19}F NMR δ: +11.2 (s, 2F, CF_3Cl); +10.6 (s, 3F, CF_3Cl); +8.8 (s, 1F, CF_3Cl); +8.5 (s, 5.5F, CF_3Cl); +7.1 (d, 5.5F, CF_3CH=, J=3.5 Hz); +6.8 (q, 2.75F, CF_3CH=, J=3.5 Hz); and +4.6 (t, 3F, CF_3CH_2, J=4.5 Hz) ppm. IR (ν_{max}) (cm^{-1}): 3330

(w) (N–H str.); 1620 (s) (C=N str.); 1270 and 1150 (s) (C–F str.); and 740 (m) (CF_3 def.). Mass spectrum *m/z*: 320 (0.1%, $C_4H_3F_6IN_2^+$); 318 (0.3, $C_4HF_6IN_2^+$); 299 (5.5, $C_4HF_5IN_2^+$); 191 (32.4, $C_4HF_6N_2^+$); 154 (2.1, $CHIN^+$); 146 (9.2, IF^+); 96 (8.8, $C_2HF_3N^+$); 76 (1.8, $C_2F_2N^+$); 69 (100.0, CF_3^+); 53 (2.8, $C_2HN_2^+$); 50 (2.2, CF_2^+); 40 (3.7, CN_2^+); and 20 (9.6, HN_2^+).

A GLC (2.5 m SE30 at 70 °C) examination of the −78 °C fraction showed it contained two major components (A and D) which were identified by coupled GLC/mass spectrometry as follows: (i) 1,1,1,6,6,6,-Hexafluoro-3,4-diazahexa-2,4-diene (**17**). Mass spectrum *m/z*: 192 (4.0%, M^+); 173 [4.0, $(M-F)^+$]; 146 (3.0, IF^+); 123 [16.1, $(M-CF_3)^+$]; 96 (2.2, $M^+/2$); 82 (1.8, $C_2HF_3^+$); 77 (2.4, CHF_2N^+); 69 (100.0, CF_3^+); 50 (12.3, CF_2^+); and 31 (11.9, CF^+). (ii) 1,1,1,6,6,6-Hexafluoro-2-iodo-3,4-diazahexa-2,4-diene (**18**). Mass spectrum *m/z*: 318 (3.3%, M^+); 299 [2.4, $(M-F)^+$]; 208 (1.7, $C_2F_3I^+$); 191 [40.4, $(M-I)^+$]; 154 (1.0, $CHIN^+$); 146 (2.1, IF^+); 127 (36.7, I^+); 96 (8.9, $C_2HF_3N^+$); 76 (6.2, $C_2F_2N^+$); 69 (100.0, CF_3^+); 50 (11.9, CF_2^+); and 31 (10.3, CF^+).

A similar GLC/mass spectrometric examination of the five major (A–E) components of the −23 °C fraction was carried out; components A and D were identified as compounds **17** and **18**, respectively. Component B was tentatively identified as 1,1,1,6,6,6-hexafluoro-5-iodo-3,4-diazahex-2-ene (**21**). Mass spectrum *m/z*: 320 (3.2%, M^+); 299 [1.7, $(M-H_2F)^+$]; 223 (2.3, $C_2HF_3IN^+$); 191 (50.4, $C_4HF_6N_2^+$); 173 (0.9, $C_4H_2F_5N_2^+$); 139 (2.1, CI^+); 127 (18.0, I^+); 110 (1.7, $C_2HF_3N_2^+$); 96, (10.4, $C_2HF_3N^+$); 83 (5.2, CF_3N^+); 76 (5.8, $C_2F_2N^+$); 69 (100.0, CF_3^+); 50 (10.1, CF_2^+); and 29 (6.2, HN_2^+). Component C was identified as a compound of molecular formula $C_6H_4F_9N_3$. Mass spectrum *m/z*: 289 (19.7%, M^+); 173 (3.3, $C_4H_2F_5N_2^+$); 111 (7.7, $C_2H_2F_3N_2^+$); 91 (7.2, $C_2HF_2N_2^+$); 83 (64.8, $CF_3CH_2^+$); 77 (15.8, $C_2HF_2N^+$); 69 (100.0, CF_3^+); 51 (9.2, CHF_2^+); 40 (19.7, CN_2^+); and 31 (27.3, CF^+). Component E was identified as 1,1,1,6,6,6-hexafluoro-2-iodo-3,4-diazahex-2-ene (**20**). Mass spectrum *m/z*: 222 (6.3%, CF_3CIN^+); 203 (5.1, $C_2F_2IN^+$); 153 (29.6, $C_4HF_4N_2^+$ and/or CIN^+); 110 (1.8, $C_2HF_3N_2^+$); 96 (2.2, $C_2HF_3N^+$); 83 (100.0, $CF_3CH_2^+$); 69 (40.3, CF_3^+); 63 (1.7, $C_2HF_2^+$); 51 (2.0, CHF_2^+); and 31 (1.9, CF^+).

(d) With hydrogen iodide

A mixture of hydrogen iodide (1.78 g, 13.9 mmol) and di-iodoazine **3b** (6.20 g, 13.9 mmol), heated *in vacuo* in a Pyrex tube (*c.* 300 cm^3) at 200 °C (24 h), gave a volatile material (1.05 g) which was separated by fractional condensation *in vacuo* through traps cooled to 0, −23 and −78 °C into the following fractions.

(i) A −78 °C fraction (0.57 g). ^1H NMR (neat) δ: 7.90 (q, 1.5H, $CF_3CH=$, $J=3.5$ Hz); 7.55 (q, 1.7H, $CF_3CH=$, $J=3.5$ Hz); 7.44 (q, 1H, $CF_3CH=$, $J=3.5$ Hz); 5.43 (br., 3.4H, NH); and 3.85 (q, 6.4H, CF_3CH_2, $J=6.5$ Hz) ppm. ^{19}F NMR δ: +11.3 (s, 15.2F, CF_3); +10.5(t, 3.8F, CF_3CH_2, $J=6.5$ Hz); +9.0 (d, 1F, $CF_3CH=$, $J=3.5$ Hz); +8.1 (s, 1.4F, CF_3); +6.6 (d, 1.4F, $CF_3CH=$, $J=3.5$ Hz); +6.4 (d, 1.8F, $CF_3CH=$, $J=3.5$ Hz); and +4.5 (s, 13.6F, CF_3) ppm. IR (ν_{max}) (cm^{-1}): 3250 (w) (N–H str.); 1600 (m) (C=N str.); 1560 (m) (N–H bend); and 1250–1150 (s) (C–F str.).

(ii) A −23 °C fraction (0.48 g). ^1H NMR (neat) δ: +7.9 (q, 0.1H, $CF_3CH=$, $J=3.5$ Hz); +7.5 (q, 1.8H, $CF_3CH=$, $J=3.5$ Hz); and +4.2 (q, 1H, CF_3CH_2, $J=7.2$ Hz) ppm. ^{19}F NMR δ: +11.3 (s, 1.2F, CF_3); +8.5 (s, 1F, CF_3); +8.3 (s, 5F, CF_3); +7.3 (d, 5.3F, $CF_3CH=$, $J=3.5$ Hz); +6.5 (d, 0.25F, $CF_3CH=$, $J=3.5$ Hz); and +5.0 (s, 13.1F, CF_3) ppm. IR (ν_{max}) (cm^{-1}): 3300 (w) (N–H str.); 1600 (m) (C=N str.), 1550 (w) (C–H bend); and 1250–1150 (m) (C–F str.).

A GLC/mass spectrometric examination of the −78 °C fraction showed that it contained four major components (A–D), while the −23 °C fraction also contained four major components (B–E). Components A–D were identified as 2,5-bis(trifluoromethyl)-1,3,4-oxadiazole (**22**), dihydroazine **17**, 2,4,6-tris(trifluoromethyl)-1,3,5-triazene (**23**) and monohydroazine **18**, while component E was tentatively identified as 2,2,5-tris(trifluoromethyl)-2,5-dihydro-1,3,4-oxadiazole (**24**).

Compound **22**: Mass spectrum *m/z*: 206 (12.3%, $C_4F_6N_2O^+$, M^+); 187 [79.6, $(M-F)^+$]; 137 [19.7, $(M-CF_3)^+$]; 109 (18.2, $C_2F_3N_2^+$); 97 (31.4, $C_2F_3O^+$); 90 (3.0, $C_2F_2N_2^+$); 69 (100.0, CF_3^+), 50 (12.3, CF_2^+); and 28 (27.7, CO^+).

Compound **23**: Mass spectrum *m/z*: 285 (40.2%, $C_6F_9N_3^+$, M^+); 266 [28.3, $(M-F)^+$]; 190 [11.8, $(M-CF_3CN^+$]; 121 (34.9, $C_3F_3N_2^+$); 102 (10.3, $C_3F_2N_2^+$); 76 (24.9, $C_2F_2N^+$); 69 (100.0, CF_3^+); 50 (11.7, CF_2^+); and 31 (14.8, CF^+).

Compound **24**: Mass spectrum *m/z*: 276 (42.3%, $C_5HF_7N_2O^+$, M^+); 257 [40.0, $(M-F)^+$]; 207 [100.0, $(M-CF_3)^+$]; 110 (79.6, $C_2HF_3N_2^+$); 69 (40.2, CF_3^+); and 51 (5.0, CHF_2^+).

(e) With sodium hydride

A mixture of azine **3b** (2.0 g, 4.5 mmol) and sodium hydride (0.18 g, 4.5 mmol) in diglyme (5 cm^3) was sealed *in vacuo* in a Rotaflo tube (*c.* 50 cm^3), the tube heated and shaken at 50 °C (24 h). No volatile material was formed and after filtering the residue was shown (IR and ^1H and ^{19}F NMR spectroscopy) to consist of unchanged azine **3b** and diglyme.

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