

Unsaturated nitrogen compounds containing fluorine. Part 10 [1]. Reaction of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahepta-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 $\text{CF}_3\text{CR}=\text{NN}=\text{CRCF}_3$ ($\text{R}=\text{F}$, I , PhO , $2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O}$, 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 $\text{CF}_3\text{C}(\text{OEt})=\text{NN}=\text{C}(\text{ONa})\text{CF}_3$ 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 $\text{PhN}=\text{C}(\text{CF}_3)\text{NHN}=\text{ClCF}_3$ and $(\text{EtO}_2\text{C})_2\text{CPhC}(\text{CF}_3)=\text{NN}=\text{ClCF}_3$, 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 $\text{CF}_3\text{CH}=\text{NN}=\text{CHCF}_3$, $\text{CF}_3\text{CH}=\text{NN}=\text{ClCF}_3$, $\text{CFCH}_2\text{NHN}=\text{ClCF}_3$ and possibly $\text{CF}_3\text{CH}=\text{NNHCH}_2\text{CF}_3$; with hydrogen iodide at 200°C , the major products are the hydroazines $\text{CF}_3\text{CH}=\text{NN}=\text{CHCF}_3$ and $\text{CF}_3\text{CH}=\text{NN}=\text{ClCF}_3$ 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].

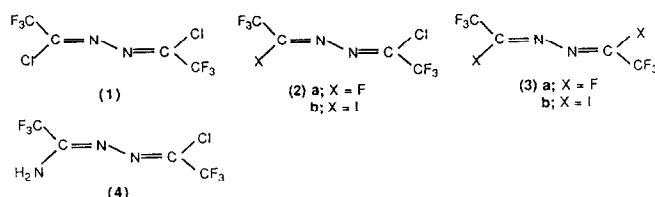
Results and discussion

The passage of dichloroazine **1** at low pressure (1–2 mmHg) through a tube packed with dried potassium fluoride at $220\text{--}240^\circ\text{C}$ 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 $\text{CF}_3\text{CONHNHCOCF}_3$) 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 chloriodoazine **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].



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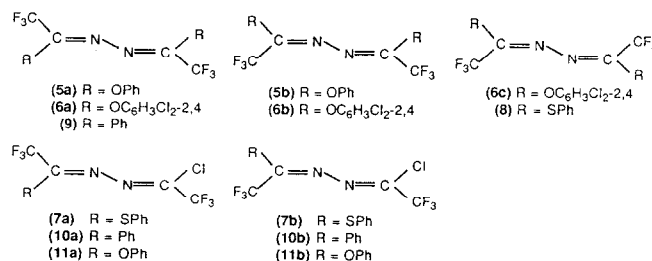
Treatment of azine **1** with the phenols PhOH and 2,4-Cl₂C₆H₃OH in the presence of triethylamine (1:2:2 molar ratio) in diethyl ether at room temperature gave the corresponding disubstituted products, the bis(aryloxy)azines **5** (61%) and **6** (54%). However, a mixture of azine **1**, thiophenol and triethylamine (1:2:2 molar ratio) in CHCl₃ 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 CHCl₃, 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 (¹⁹F 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 CF₃ groups *syn* to the nitrogen lone pair in such compounds have higher-field ¹⁹F NMR chemical shifts than CF₃ 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 ¹⁹F 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 CF₃C(SPh)=N group has the (*E*)-configuration than would the corresponding phenoxyazines **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 CF₃ groups in the CF₃C(SPh)=N groupings of the two isomers of the mono(thiophenoxy)azine **7** were coincident and so it was not possible to assign configurations

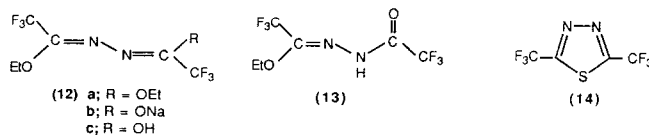
to the isomers with certainty. However, if the assignment of azine **8** is correct, it is considered likely that the major isomer of azine **7** has the (*EZ*)-configuration **7b** (Table 1).



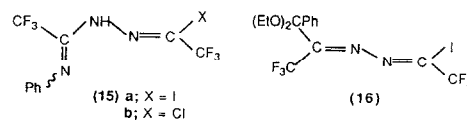
The reaction of azine **1** with excess sodium ethoxide in ethanol gave the bis(ethoxy)azine **12a** (25%) as a single isomer (¹⁹F NMR spectroscopy) assigned the (*ZZ*)-configuration, and the sodium enolate **12b** (25%) which was converted quantitatively to amide **13** on treatment with dilute aqueous 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

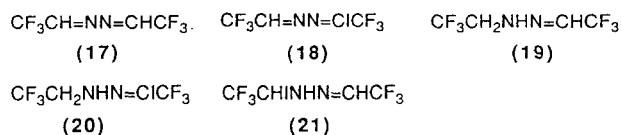
R	$\text{CF}_3\text{CR}=\text{NN}=\text{CClCF}_3$				R	$\text{CF}_3\text{CR}=\text{NN}=\text{CRCF}_3$			
	A	B				A	B		
	δ_{A} (ppm)	δ_{B} (ppm)	Isomer (%)	Assignment		δ_{A} (ppm)	δ_{B} (ppm)	Isomer (%)	Assignment
SPh	12.1	5.5	45	(ZZ?) 7a	SPh	14.3	14.3	100	(EE) 8
	12.1	5.6	55	(EZ?) 7b					
Ph	10.6	8.1	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
					$\text{OC}_6\text{H}_3\text{Cl}_2$	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, $\text{CF}_3\text{CH}=\text{N}$, $J=c$. 3.5 Hz) ppm. ^{19}F NMR δ : +6.65 (d, $J=c$. 3.5 Hz) ppm. Mass spectrum m/z : 192 (M^+) and fragmentation peaks for ($\text{M}-\text{F}$) $^+$; ($\text{M}-\text{CF}_3$) $^+$; CF_3CH^+ ; and CF_3^+ (base peak)] and the monohydroazine 18 [^1H NMR δ : 7.60 (q, $\text{CF}_3\text{CH}=\text{N}$, $J=c$. 3.5 Hz) ppm. ^{19}F NMR δ : +8.25 (s, 3F, $\text{CF}_3\text{Cl}=\text{N}$); and +7.0 (d, 3F, $\text{CF}_3\text{CH}=\text{N}$, $J=c$. 3.5 Hz) ppm. Mass spectrum m/z : 318 (M^+) and fragmentation peaks for ($\text{M}-\text{F}$) $^+$; ($\text{M}-\text{I}$) $^+$; 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, $\text{CF}_3\text{CH}_2\text{N}$, $J=c$. 5 Hz) ppm. ^{19}F NMR δ : +6.3 (t, 3F, CF_3CH_2 , $J=c$. 5 Hz); and +6.0 (d, 3F, $\text{CF}_3\text{CH}=\text{N}$, $J=c$. 3.5 Hz)].

The remaining ^{19}F NMR absorptions at +11.2, +10.5 and +7.25 ppm were all assigned to the $\text{CF}_3\text{CH}=\text{N}$ 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, $\text{CF}_3\text{Cl}=\text{N}$); and +4.6 (t, 3F, $\text{CF}_3\text{CH}_2\text{N}$, $J=c$. 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^+ , $\text{CF}_3\text{CHN}_2^+$, CF_3CHN^+ and CF_3^+ (base peak)] and a compound of molecular formula $\text{C}_6\text{H}_4\text{F}_9\text{N}_3$, possibly $\text{CF}_3\text{CH}_2\text{NHN}=\text{C}(\text{CF}_3)-\text{N}=\text{CHCF}_3$ [mass spectrum m/z : 289 (M^+) and fragmentation peaks for $\text{C}_4\text{H}_2\text{F}_5\text{N}_2^+$, $\text{CF}_3\text{CH}_2\text{N}_2^+$, $\text{CF}_3\text{CHN}_2^+$, CF_3CH_2^+ , CF_2CHN^+ and CF_3^+ (base peak)].



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

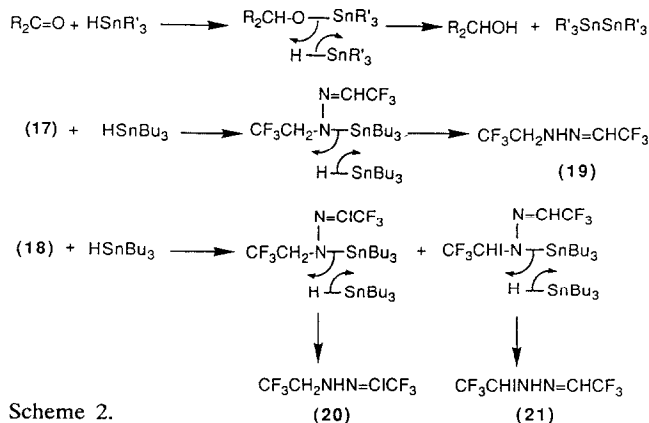
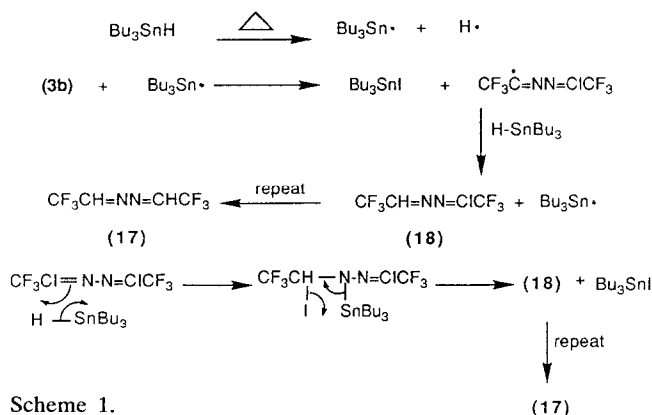
reduction of alkyl [8, 9] and vinyl [10] halides, or via an addition-elimination mechanism, as postulated for the reduction of fluorovinyl compounds [11, 12] as shown in Scheme 1.

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- , $\text{R}_2\text{N-}$ [1, 13]; the hydrazones **19–21** are considered to be formed in a similar manner (Scheme 2).

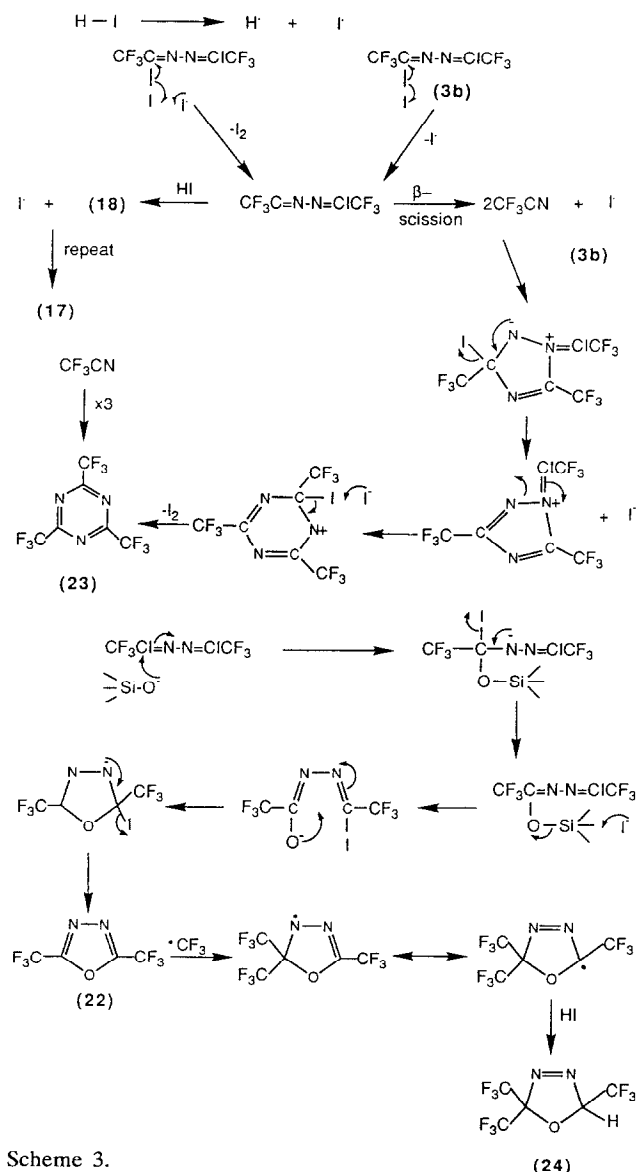
Alternatively, hydrazone **19** could have been produced by further reduction of hydrazones **20** and **21**.

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 poly-fluoroalkyl 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 hydrazines **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 $(\text{M}-\text{F})^+$; $(\text{M}-\text{CF}_3)^+$; 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 $(\text{M}-\text{F})^+$; $\text{M}-\text{CF}_3\text{CN}^+$; and CF_3^+ (base peak)] and a compound of molecular formula $\text{C}_5\text{HF}_9\text{N}_2\text{O}$, possibly the oxadiazole **24** {mass spectrum m/z : 276 (M^+) and peaks for $(\text{M}-\text{F})^+$; $[(\text{M}-\text{CF}_3)^+$, base peak]; $(\text{M}-\text{C}_3\text{F}_6)^+$; $\text{CF}_3\text{CHN}_2^+$; 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.



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 [^1H 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 $\text{CF}_3\text{CH}_2\text{NH}$ grouping (possibly $\text{CF}_3\text{CH}_2\text{NHNHCH}_2\text{CF}_3$), 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), ^1H 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 $(\text{CD}_3)_2\text{CO}$] 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, $\text{C}=\text{N}$ 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 cm³) afforded 1,1,1,2,5,6,6,6-octafluoro-3,4-diazahepta-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. $\text{C}_4\text{F}_8\text{N}_2$ 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., 1F, CF); and +2.9 (d, 3F, CF_3 , $J=5$ Hz) ppm. IR (ν_{max}) (cm^{-1}): 1720 (s) ($\text{C}=\text{N}$ str.); 1240–1120 (s) (C–F str.); and 740 (s) (CF_3 def.). Mass spectrum m/z : 228 (28.8%, M^+); 209 [15.7, ($\text{M}-\text{F}$)⁺]; 159 [10.0, ($\text{M}-\text{CF}_3$)⁺]; 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-diazahepta-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. $\text{C}_4\text{ClF}_7\text{N}_2$ 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., 1F, 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) ($\text{C}=\text{N}$ 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, ($\text{M}-\text{F}$)⁺]; 209 [75.2, ($\text{M}-\text{Cl}$)⁺]; 175/177 [84.6, ($\text{M}-\text{CF}_3$)⁺]; 125/127 (9.6, $\text{C}_2\text{ClF}_2\text{N}_2^+$); 116/118 (7.7, C_2ClF_3^+); 85/87 (19.5, CClF_2^+); 76 (5.9, $\text{C}_2\text{F}_2\text{N}^+$); 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 cm³) 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 cm³), filtered, washed with water (25 cm³), then with aqueous sodium metabisulphite (c. 20% w/w, 25 cm³) and again with water (25 cm³). 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-diazahepta-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. $\text{C}_4\text{F}_6\text{I}_2\text{N}_2$ 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) ($\text{C}=\text{N}$ str.); 1270–1168 (s) (C–F str.); and 745 (s) (CF_3 def.). Mass spectrum m/z : 444 (4.7%, M^+); 317 [100.0, ($\text{M}-\text{I}$)⁺];

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 cm³) was added to a stirred solution of dichloroazine **1** (1.15 g, 4.41 mmol) in acetone (10 cm³) 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 cm³) 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 (¹⁹F NMR and mass spectrometry) to consist of a mixture (7:3 molar ratio) of the diiodoazine **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%). ¹⁹F 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 cm³) 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 cm³) 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 (MgSO₄) 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. C₁₆H₁₀F₆N₂O₂ requires: C, 51.1; H, 2.7; F, 30.3; N, 7.4%; mol. wt., 376), m.p. 69–70 °C. ¹H NMR (CDCl₃) δ : 7.5–6.5 (mult., C₆H₅) ppm. ¹⁹F NMR δ : +10.9 (s, CF₃); +7.0 (s, CF₃); and +6.7 (s, CF₃) 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) (CF₃ def.). Mass spectrum m/z : 376 (2.5%, M⁺); 307 [31.3, (M–CF₃)⁺]; 283 [100.0, (M–C₆H₅O)⁺]; 188 (47.4, C₈H₅F₃NO⁺); 172 (32.6, C₈H₅F₃N⁺); 168 (46.4, C₈H₄F₂NO⁺); 94 (41.5, C₆H₆O⁺); 93 (68.9, C₆H₅O⁺); 77 (99.3, C₆H₅⁺); 69 (24.9, CF₃⁺); 65 (71.5, C₅H₅⁺); and 44 (20.5, C₂H₄O⁺).

(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 cm³) was added slowly during 20 min to a stirred solution of dichloroazine **1** (1.31 g, 5.02 mmol) in diethyl ether (25 cm³) 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 cm³) 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 cm³) 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. C₁₆H₆Cl₄F₆N₂O₂ 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 (CDCl₃) δ : 7.65–7.45 (mult., C₆H₅) ppm. ¹⁹F NMR δ : +12.2 (s, CF₃); +11.9 (s, CF₃); and +7.0 (s, CF₃) 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) (CF₃ def.). Mass spectrum m/z : 512/514/516 (1.0%, M⁺); 351/353/355 (71.2, C₁₀H₃Cl₂F₆N₂O⁺); 256/258/260 (68.8, C₈H₃Cl₂F₃NO⁺); 226/228/230 (47.9, C₈H₆Cl₂F₂O⁺); 187/189/191 (21.1, C₇H₃NCl₂NO⁺); 161/163/165 (76.0, C₆H₃Cl₂O⁺); 145/147/149 (27.2, C₆H₃Cl₂⁺); 133/135/137 (100.0, C₅H₃Cl₂⁺); 109 (17.2, C₂F₃N₂⁺); and 69 (31.8, CF₃⁺).

(f) *With sodium ethoxide in ethanol*

Sodium metal (1.3 g, 56.6 mmol) was added in small pieces to ethanol (50 cm³) and a solution of dichloroazine **1** (6.50 g, 24.9 mmol) in dry ethanol (25 cm³) then added and the mixture stirred at room temperature (69 h). A ¹⁹F 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%. C₆H₅F₆N₂O₂Na requires: C, 26.3; H, 1.8; F, 41.6; N, 10.3; Na, 8.4%), m.p. 153–154 °C. ¹H NMR [(CD₃)₂CO] δ : 4.85 (q, 2H, CH₂–O, J =7.3 Hz); and 1.27 (t, 3H, CH₃, J =7.3 Hz) ppm. ¹⁹F NMR δ : +2.7 (s, 3F, CF₃); and +1.9 (s, 3F, CF₃) 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) (CF₃ def.). Mass spectrum m/z : 297 [100.0%, (M+Na)⁺]; 274 (0.4, M⁺); 224 (12.4, C₅H₅F₄N₂O₂Na⁺); 154 (26.1, C₄H₅F₃N₂O⁺); 69 (25.3, CF₃⁺); and 29 (14.5, C₂H₅⁺).

The volatile material was redistilled at atmospheric pressure through a column (25 cm³) 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 ¹⁹F NMR) from the spectral data obtained. ¹H NMR δ : 3.83 (q, 2H, CH₂-O, $J=7$ Hz); and 0.86 (t, 3H, CH₃, $J=7$ Hz) ppm. ¹⁹F NMR δ : +9.8 (s, CF₃) ppm. IR ($\nu_{\max}$) (cm⁻¹): 1645 (s) (C=N str.); 1280–1140 (s) (C-F str.); 1120 (s) (C-O str.); and 740 (s) (CF₃ def.). Mass spectrum m/z : 280 (2.0%, M⁺); 211 [9.6, (M-CF₃)⁺]; 155 (45.9, C₄H₆F₃N₂O⁺); 140 (9.7, C₄H₅F₃NO⁺); 114 (16.0, C₃H₅F₃O⁺); 69 (53.3, CF₃⁺); 45 (30.6, C₂H₅O⁺); and 29 (100.0, C₂H₅⁺).

When a stirred solution of enolate **12b** (0.19 g, 0.69 mmol) in water (10 cm³) was treated with dilute hydrochloric acid (2 M, 0.5 cm³) 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%. C₆H₆F₆N₂O₂ requires: C, 28.6; H, 2.4; N, 11.1%), m.p. 71–72 °C. ¹H NMR (CDCl₃) δ : 9.42 (br., 1H, NH); 4.47 (q, 2H, OCH₂, $J=7$ Hz); and 1.45 (t, 3H, CH₃, $J=7$ Hz) ppm. ¹⁹F NMR δ : +11.7 (s, 3F, CF₃C=N); and +3.4 (s, 3F, CF₃C=O) ppm. IR ($\nu_{\max}$) (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 cm³) was added to a solution of thiophenol (2.5 g, 22.7 mmol) and triethylamine (2.3 g, 22.8 mmol) in chloroform (25 cm³) and the mixture heated under reflux (6h). The solvent was removed under reduced pressure and the residue treated with diethyl ether (25 cm³). 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 cm³). The ether layer was separated, washed with water (2×10 cm³), dried (Mg SO₄) 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. C₁₀H₅ClF₆N₂S requires: C, 35.9; H, 1.4; F, 34.1; N, 8.4%; mol. wt., 334.5). ¹H NMR (CDCl₃) δ : 7.3–7.1 (mult., C₆H₅) ppm. ¹⁹F NMR δ : 12.1 (s, CF₃);

+5.6 (s, CF₃CCl); and +5.5 (s, CF₃CCl) ppm in the ratio 11:6:5. IR ($\nu_{\max}$) (cm⁻¹): 1630 (m) (C=N str.); 1185–1145 (s) (CF₃ str.); and 758 (s) (CF₃ def.). Mass spectrum m/z : 334/336 (2.3%, M⁺); 299 [100.0, (M-Cl)⁺]; 225/227 [12.3, (M-C₆H₅S)⁺]; 182 (20.6, C₄F₄N₂S⁺); 121 (16.3, C₇H₅S⁺); 110 (21.3, C₆H₆S⁺); 109 (100.0, C₆H₅S⁺); 108 (15.9, C₆H₄S⁺); 77 (43.6, C₆H₅⁺); 69 (33.6, CF₃⁺); 65 (31.2, C₅H₅⁺); and 51 (21.6, C₄H₃⁺).

(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. C₁₆H₁₀F₆N₂S₂ 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 (CDCl₃) δ : 7.53–7.30 (mult., C₆H₅) ppm. ¹⁹F NMR δ : +14.3 (s, CF₃) ppm. IR ($\nu_{\max}$) (cm⁻¹): 1620 (s) (C=N str.); 1190–1151 (s) (C-F str.); and 768 (s) (CF₃ def.) Mass spectrum m/z : 408 (0.6%, M⁺); 301 (36.1, C₁₀H₇F₆N₂S⁺); 300 (62.5, C₁₀H₆F₆N₂S⁺); 299 [100.0, (M-C₆H₅S)⁺]; 184 (37.3, C₄F₄N₂S⁺); 121 (40.9, C₇H₅S⁺); 110 (55.7, C₆H₆S⁺); 109 (76.3, C₆H₅S⁺); 108 (37.1, C₆H₄S⁺); 78 (20.9, C₆H₆⁺); 77 (85.9, C₆H₅⁺); 69 (58.5, CF₃⁺); 65 (84.8, C₅H₅⁺); and 51 (64.2, C₄H₃⁺).

(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 cm³) 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. C₄F₆N₂S requires: C, 21.6; F, 51.4; N, 12.6; S, 14.4%; mol. wt., 222); b.p. 105–106 °C. ¹⁹F NMR δ : +6.2 (s, CF₃) ppm. IR ($\nu_{\max}$) (cm⁻¹): 1480 (s) (C=N str.); 1240–1180 (s) (C-F str.); and 760 (s) (CF₃ def.). Mass spectrum m/z : 222 (72.2%, M⁺); 203 [21.8, (M-F)⁺]; 127 (46.1, C₂F₃NS⁺); 113 (38.9, C₂F₃S⁺); 69 (100.0, CF₃⁺); 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 cm³) and (ii) azine **1** (2.0 g, 7.63 mmol), sodium borohydride (0.14 g, 3.70 mmol) and diglyme (5 cm³), sealed *in vacuo* in Rotaflo tubes (c. 50 cm³) 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 cm³) was added to lithium aluminium hydride (0.36 g, 9.4 mmol) in a flask (c. 100 cm³) 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 cm³) was added to a stirred solution of diiodoazine **3b** (0.39 g, 0.88 mmol) in ether (10 cm³) 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 cm³), dried (MgSO₄) 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. C₁₀H₆F₆IN₃ requires: C, 29.4; H, 1.5; F, 27.9; I, 31.0; N, 10.3%; mol. wt., 409). ¹H NMR (CDCl₃) δ: 7.78 (s, 1H, NH); 7.64 (s, 1H, NH); and 7.5–6.9 (mult., 10H, C₆H₅) ppm. ¹⁹F NMR δ: +12.6 (s, CF₃); +12.0 (s, CF₃); and +11.8 (s, CF₃) 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) (CF₃ def.). Mass spectrum *m/z*: 409 (5.5%, M⁺); 282 [100.0, (M–I)⁺]; 262 (12.7, C₁₀H₅F₅N₃⁺); 167 (18.2, CIN₂⁺); 118 (17.8, C₇H₆N₂⁺); 92 (21.7, C₆H₅N⁺); 77 (27.4, C₆H₅⁺); 69 (9.1, CF₃⁺); 65 (27.5, C₅H₅⁺); 51 (11.1, C₄H₃⁺); and 39 (9.3, C₃H₃⁺).

(b) With potassium diethyl phenylmalonate

A solution of diethyl phenylmalonate (2.00 g, 8.46 mmol) in dry THF (15 cm³) 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 diiodoazine **3b** (3.75 g, 8.46 mmol) in THF (20 cm³) 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-iodoazine **3b** (0.70 g, 1.57 mmol, 19% recovered).

(ii) Diethyl (1,1,1,6,6,6-hexafluoro-2-iodo-3,4-diazahexa-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. C₁₇H₁₅F₆IN₂O₄ requires: C, 36.9; H, 2.7; F, 20.6; N, 5.1%; mol. wt., 555) as a yellow oil. ¹H NMR (CDCl₃) δ: 7.45 (mult., 5H, C₆H₅); 4.43 (q, 4H, 2CH₂–O, *J* = 7 Hz); and 1.35 (t, 6H, 2CH₃, *J* = 7 Hz) ppm. ¹⁹F NMR δ: +15.2 (s, 3F, CF₃); and +10.1 (s, 3F, CF₃Cl) 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, C₁₂H₅F₆IN₂O⁺); 307 (39.2, C₁₂H₅F₆N₂O⁺); 184 (100.0, C₉H₅F₃N⁺); 161 (25.0, C₁₀H₉O₂⁺); 133 (16.0, C₈H₅O₂⁺); 105 (36.3, C₇H₅O⁺); 89 (23.4, C₇H₅⁺); 77 (34.4, C₆H₅⁺); 69 (31.7, CF₃⁺); 58 (26.5, C₂H₂O₂⁺); and 57 (28.5, C₂HO₂⁺).

(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 diiodoazine **3b** (8.50 g, 19.14 mmol), sealed *in vacuo* in a Pyrex tube (c. 200 cm³) 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, CF₃CH=, *J* = 3.5 Hz); 7.60 (q, c. 1H, CF₃CH=, *J* = 3.5 Hz); 7.39 (br., c. 0.2H, CF₃CH=); 7.24 (br., c. 0.1H, CF₃CH=); and 4.30 (q, c. 0.5H, CF₃CH₂, *J* = 4.5 Hz) ppm. ¹⁹F NMR δ: +11.2 (d, c. 1F, CF₃CH=, *J* = 3.5 Hz); +10.5 (d, c. 1F, CF₃CH=, *J* = 3.5 Hz); +8.3 (s, 2.5F, CF₃Cl); +7.3 (d, c. 1F, CF₃CH=, *J* = 3.5 Hz); +7.0 (d, 2.5F, CF₃CH=, *J* = 3.5 Hz); –6.7 (d, 7F, CF₃CH=, *J* = 3.5 Hz); +6.3 (t, c. 1F, CF₃CH₂, *J* = 4.5 Hz); and +6.0 (d, c. 1F, CF₃CH=, *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) (CF₃ def.). Mass spectrum *m/z*: 318 (1.2%, C₄HF₆IN₂⁺); 222 (0.7, C₂F₃IN⁺); 209 (4.2, C₂HF₃I⁺); 192 (85.6, C₄H₂F₆N₂⁺); 191 (5.7, C₄HF₆N₂⁺); 190 (2.8, C₄F₆N₂⁺); 173 (33.5, C₄H₂F₅N₂⁺); 127 (4.8, I⁺); 123 (12.7, C₃H₂F₃N₂⁺); 111 (3.0, C₂H₂F₃N₂⁺); 96 (8.5, C₂HF₃N⁺); 83 (2.5, C₂H₂F₃⁺); 82 (3.4, C₂HF₃⁺); 77 (5.3, C₂HF₂N⁺); 69 (100.0, CF₃⁺); and 43 (15.9, C₂F⁺).

(ii) A –23 °C fraction (3.31 g). ¹H NMR (neat) δ: 7.92 (q, 1H, CF₃CH=, *J* = 3.5 Hz); 7.60 (q, 2.2H, CF₃CH=, *J* = 3.5 Hz); 7.32 (q, 1.4 H, CF₃CH=, *J* = 3.5 Hz); 6.73 (br., 1H, NH); and 4.18 (q, 2H, CF₃CH₂, *J* = 4.5 Hz) ppm. ¹⁹F NMR δ: +11.2 (s, 2F, CF₃Cl); +10.6 (s, 3F, CF₃Cl); +8.8 (s, 1F, CF₃Cl); +8.5 (s, 5.5F, CF₃Cl); +7.1 (d, 5.5F, CF₃CH=, *J* = 3.5 Hz); +6.8 (q, 2.75F, CF₃CH=, *J* = 3.5 Hz); and +4.6 (t, 3F, CF₃CH₂, *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) (CF₃ def.). Mass spectrum *m/z*: 320 (0.1%, C₄H₃F₆IN₂⁺); 318 (0.3, C₄HF₆IN₂⁺); 299 (5.5, C₄HF₅IN₂⁺); 191 (32.4, C₄HF₆N₂⁺); 154 (2.1, CHIN⁺); 146 (9.2, IF⁺); 96 (8.8, C₂HF₃N⁺); 76 (1.8, C₂F₂N⁺); 69 (100.0, CF₃⁺); 53 (2.8, C₂HN₂⁺); 50 (2.2, CF₂⁺); 40 (3.7, CN₂⁺); and 20 (9.6, HN₂⁺).

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–CF₃)⁺]; 96 (2.2, M⁺/2); 82 (1.8, C₂HF₃⁺); 77 (2.4, CHF₂N⁺); 69 (100.0, CF₃⁺); 50 (12.3, CF₂⁺); 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, C₂F₃I⁺); 191 [40.4, (M–I)⁺]; 154 (1.0, CHIN⁺); 146 (2.1, IF⁺); 127 (36.7, I⁺); 96 (8.9, C₂HF₃N⁺); 76 (6.2, C₂F₂N⁺); 69 (100.0, CF₃⁺); 50 (11.9, CF₂⁺); 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–H₂F)⁺]; 223 (2.3, C₂HF₃IN⁺); 191 (50.4, C₄HF₆N₂⁺); 173 (0.9, C₄H₂F₅N₂⁺); 139 (2.1, CI⁺); 127 (18.0, I⁺); 110 (1.7, C₂HF₃N₂⁺); 96 (10.4, C₂HF₃N⁺); 83 (5.2, CF₃N⁺); 76 (5.8, C₂F₂N⁺); 69 (100.0, CF₃⁺); 50 (10.1, CF₂⁺); and 29 (6.2, HN₂⁺). Component C was identified as a compound of molecular formula C₆H₄F₉N₃. Mass spectrum *m/z*: 289 (19.7%, M⁺); 173 (3.3, C₄H₂F₅N₂⁺); 111 (7.7, C₂H₂F₃N₂⁺); 91 (7.2, C₂HF₂N₂⁺); 83 (64.8, CF₃CH₂⁺); 77 (15.8, C₂HF₂N⁺); 69 (100.0, CF₃⁺); 51 (9.2, CHF₂⁺); 40 (19.7, CN₂⁺); 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%, CF₃CIN⁺); 203 (5.1, C₂F₂IN⁺); 153 (29.6, C₄HF₄N₂⁺ and/or CIN⁺); 110 (1.8, C₂HF₃N₂⁺); 96 (2.2, C₂HF₃N⁺); 83 (100.0, CF₃CH₂⁺); 69 (40.3, CF₃⁺); 63 (1.7, C₂HF₂⁺); 51 (2.0, CHF₂⁺); 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 cm³) 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, CF₃CH=, *J*=3.5 Hz); 7.55 (q, 1.7H, CF₃CH=, *J*=3.5 Hz); 7.44 (q, 1H, CF₃CH=, *J*=3.5 Hz); 5.43 (br., 3.4H, NH); and 3.85 (q, 6.4H, CF₃CH₂, *J*=6.5 Hz) ppm. ¹⁹F NMR δ: +11.3 (s, 15.2F, CF₃); +10.5 (t, 3.8F, CF₃CH₂, *J*=6.5 Hz); +9.0 (d, 1F, CF₃CH=, *J*=3.5 Hz); +8.1 (s, 1.4F, CF₃); +6.6 (d, 1.4F, CF₃CH=, *J*=3.5 Hz); +6.4 (d, 1.8F, CF₃CH=, *J*=3.5 Hz); and +4.5 (s, 13.6F, CF₃) 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, CF₃CH=, *J*=3.5 Hz); +7.5 (q, 1.8H, CF₃CH=, *J*=3.5 Hz); and +4.2 (q, 1H, CF₃CH₂, *J*=7.2 Hz) ppm. ¹⁹F NMR δ: +11.3 (s, 1.2F, CF₃); +8.5 (s, 1F, CF₃); +8.3 (s, 5F, CF₃); +7.3 (d, 5.3F, CF₃CH=, *J*=3.5 Hz); +6.5 (d, 0.25F, CF₃CH=, *J*=3.5 Hz); and +5.0 (s, 13.1F, CF₃) 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%, C₄F₆N₂O⁺, M⁺); 187 [79.6, (M–F)⁺]; 137 [19.7, (M–CF₃)⁺]; 109 (18.2, C₂F₃N₂⁺); 97 (31.4, C₂F₃O⁺); 90 (3.0, C₂F₂N₂⁺); 69 (100.0, CF₃⁺), 50 (12.3, CF₂⁺); and 28 (27.7, CO⁺).

Compound **23**: Mass spectrum *m/z*: 285 (40.2%, C₆F₉N₃⁺, M⁺); 266 [28.3, (M–F)⁺]; 190 [11.8, (M–CF₃CN⁺); 121 (34.9, C₃F₃N₂⁺); 102 (10.3, C₃F₂N₂⁺); 76 (24.9, C₂F₂N⁺); 69 (100.0, CF₃⁺); 50 (11.7, CF₂⁺); and 31 (14.8, CF⁺).

Compound **24**: Mass spectrum *m/z*: 276 (42.3%, C₅HF₇N₂O⁺, M⁺); 257 [40.0, (M–F)⁺]; 207 [100.0, (M–CF₃)⁺]; 110 (79.6, C₂HF₃N₂⁺); 69 (40.2, CF₃⁺); and 51 (5.0, CHF₂⁺).

(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 cm³) was sealed *in vacuo* in a Rotaflo tube (c. 50 cm³), 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 ¹⁹F NMR spectroscopy) to consist of unchanged azine **3b** and diglyme.

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