Unsaturated nitrogen compounds containing fluorine. Part 9 [1]. The preparation of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene and its reaction with amines*

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Abstract

2,5-Dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**1**) has been prepared in good yield (60%) by the reaction of 1,2-bis(trifluoroacetyl)hydrazine with a mixture of *N,N*-dimethylaniline hydrochloride and phosphoryl chloride. Nucleophilic displacement of chlorine from azine **1** occurs readily on reaction with primary amines RNH_2 (R = Pr^i, Bu^s, Ph, 4-FC_6H_4, 2,6-$Cl_2C_5H_2NCH_2$-4) and with secondary amines (morpholine and Et_2NH); in general, mono- or di-substitution can be achieved by varying the azine/amine ratio (1:2 or 1:4). The products are the azines $CF_3(NRR')=NN=CClCF_3$ (**7**) (R = H, R' = Pr^i; R = R' = Et) and $CF_3C(NRR')=NN=C(NRR')CF_3$ (**8**) (R = H, R' = Pr^i, Bu^s and 2,6-Cl_2pyCH_2-4; R–R' = Et; R–R' = $CH_2CH_2OCH_2CH_2$) and the imidoyl tautomers $PhN=C(CF_3)NHN=CClCF_3$ (**9a**) and $ArN=C(CF_3)NHNHC(CF_3)=NAr$ (**10**) (Ar = Ph and 4-FC_6H_4). On heating at temperatures up to 120 °C, the compounds **10a** (Ar = Ph), **10b** (Ar = 4-FC_6H_4) and **9a** undergo cyclisation (with elimination of $ArNH_2$ or HCl) to afford the corresponding 4-aryl-4*H*-1,2,4-triazoles (**22**); the azine **8a** (R = Pr^i) does not cyclise under these conditions. The azine **7a** (R = H, R' = Pr^i) on hydrolysis (NaOH/EtOH then H_3O^+) gives the trifluoroacetylhydrazine $Pr^iN=C(CF_3)NHNHCOCF_3$ (**20**) in excellent yield (92%).

Introduction

Nucleophilic displacement of chlorine from dichloroazines of the type RCCl=N–N=CClR occurs readily and provides routes to other azines [3] and nitrogen heterocycles [4], and in a continuation of our work on fluorinated azines it was decided to prepare the dichloroazine **1** and investigate its chemistry.

It has been reported [5] that the dichloroazine **1** can be prepared by oxidative cyclisation of trifluoroacetamidine **2** according to the method of

*Reported, in part, as a preliminary communication; see ref. 2.

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Graham [6] followed by thermolytic decomposition of the resulting chlorodiazirine **3**.

$$HN{=}C(CF_3)NH_2 \xrightarrow[DMSO/H_2O]{ClO^-/Cl^-} \overline{CF_3CCl{-}N{=}N} \xrightarrow{\Delta} CF_3CCl{=}N{-}N{=}CClCF_3$$

(2) **(3)** **(1)**

Unfortunately, attempts to make the diazirine **3** from the amidine **2** were unsuccessful [7] and so an alternative method of preparation of azine **1** was sought.

1,2-Diaroylhydrazines yield dichloroazines on treatment with phosphorus(V) chloride, e.g. see ref. 8:

$$PhCONHNHCOPh \xrightarrow[\Delta]{PCl_5} PhCCl{=}N{-}N{=}CClPh$$

and so the preparation and subsequent chlorination of 1,2-bis(trifluoroacetyl)hydrazine (**4**) as a route to azine **1** was investigated.

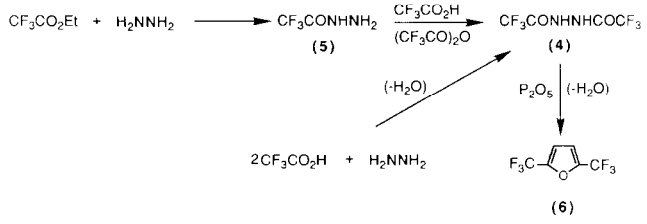
Results and discussion

The bishydrazine **4** can be made by reaction of ethyl trifluoroacetate with hydrazine to give the monohydrazide **5**, followed by treatment with trifluoroacetic acid and trifluoroacetic anhydride [9] (Scheme 1). However, it has also been reported that treatment of hydrazine hydrate in benzene with 2 equiv. trifluoroacetic acid under reflux with azeotropic removal of the water gave an unidentified white solid, which was dehydrated by phosphorus(V) oxide to 2,5-bis(trifluoromethyl)-1,3,4-oxadiazole (**6**) [10].

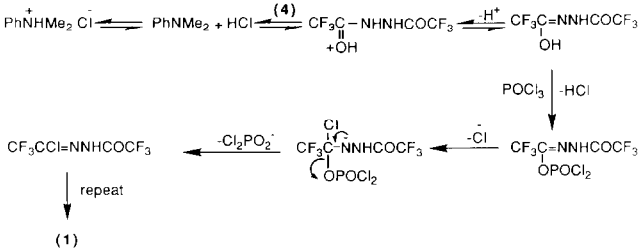
It seemed probable that the white solid was compound **4** and this was confirmed by repeating the reaction to give analytically pure bishydrazide **4** (78%) on filtration.

Initial experiments on the chlorination of **4** (PCl_5, 120 °C; PCl_5/PCl_3/quinoline, 100 °C; $PCl_5/POCl_3/PhNMe_2$, 100 °C) gave trifluoroacetyl chloride, oxydiazole **6** (8–33%) and higher-boiling mixtures of azine **1** {IR spectra of mixtures compared with that reported for **1** [5]}, phosphorus(III) chloride and phosphoryl chloride; with the chlorinating agents $SOCl_2$/PhMe, reflux; $SbCl_5/PhNMe_2$, 100 °C, reaction did not occur.

However, a mixture of **4** and *N*,*N*-dimethylaniline hydrochloride (molar ratio 1:2.1) together with an excess of phosphoryl chloride, heated under



Scheme 1.



Scheme 2.

reflux (3.5 h), gave two layers which were hydrolysed separately with ice/water and the resulting organic material distilled to afford pure azine **1** (60%), b.p. 89–90.5 °C. A reaction using a mixture of **4** and *N*,*N*-dimethylaniline (1:3 molar ratio) together with an excess of phosphoryl chloride, heated under reflux (11 h), gave azine **1** (33%); the hydrochloride, $PhNHMe_2^+ Cl^-$, was shown (IR spectroscopy) to be formed in this reaction when the amine and phosphoryl chloride were mixed. When the *N*,*N*-dimethylaniline hydrochloride was replaced by triethylamine hydrochloride, only a low yield (7%) of azine **1** was obtained.

It is considered that azine **1** is formed via enolisation of hydrazide **4** (Scheme 2). Triethylamine hydrochloride, being a weaker acid than *N*,*N*-dimethylaniline hydrochloride, was less efficient at protonating **4** and this resulted in a lower yield of azine **1**.

The dichloroazine **1** underwent facile reaction with a variety of primary amines, and also with secondary amines, at or below room temperature using neat reactants or a solvent (Et_2O), to afford either mono- or di-substitution products depending on the reactant ratio employed (except with Et_2NH in the absence of solvent which gave a mixture) as shown in Table 1.

The monosubstitution products formed from the primary amines and from diethylamine were mixtures of two isomers (ratio *c.* 1:1), while the disubstitution products arising from the primary amines were present as single isomers (^{19}F NMR spectroscopy). In contrast, the disubstitution products from the reactions of both secondary amines consisted of three isomers of which one was major (75–80% of mixture).

While the products from the secondary amine reactions can only be the azines **7** and **8**, the monosubstitution products arising from the primary amines can be azines **7** or their imidoyl tautomers **9**, and the corresponding disubstitution products can be azines **8**, bisimidoylhydrazines **10** or the monoimidoyl compounds **11**. The structural assignments which have been made are based on the following evidence and the relevant ^{19}F NMR chemical shifts are listed in Table 2.

The product of the reaction of ammonia with dichloroazine **1** (2:1 molar ratio) has been identified (X-ray) as the aminoazine **7c** in the (*ZZ*)-configuration (CF_3 *syn* to nitrogen lone pair) [11]. This azine on treatment with aniline gave the monoimidoyl compound **11a** [phenyl (*E*); $CF_3C(NH_2)=N$ (*Z*)] as

TABLE 1

Reactions of dichloroazine **1** with amines

Amine	Molar ratio amine/**1**	Temp. (°C)	Solvent	Products[a]	Yield (%)
Pr^iNH_2	2:1	0	Et_2O	**7a**	86
Pr^iNH_2	4:1	0	Et_2O	**8a**	95
Bu^sNH_2	4:1	0	–	**8b**	82
$PhNH_2$	2:1	0	Et_2O	**9a**	89
$PhNH_2$	4:1	0	Et_2O	**10a**	93
4-$FC_6H_4NH_2$	4:1	20	Et_2O	**10b**	80
2,6-$Cl_2pyCH_2NH_2$-4	4:1	20	Et_2O	**8c**	59[b]
$CH_2CH_2O(CH_2)_2NH$	4:1	20	Et_2O	**8d**	96
Et_2NH	2:1	0	–	**7b**	39[c]
				8e	32
Et_2NH	2:1	0	Et_2O	**7b**	75[d]

[a] $CF_3CR{=}NN{=}CClCF_3$ (**7**) **a**; R = Pr^iNH; **b**; R = Et_2N; **c**; R = H_2N; **d**; R = Ph; **e**; R = PhO

$CF_3CR{=}NN{=}CRCF_3$ (**8**) **a**; R = Pr^iNH; **b**; R = Bu^sNH; **c**; R = 2,6-Cl_2pyCH_2NH-4; **d**; R = $CH_2CH_2O(CH_2)_2N$; **e**; R = Et_2N; **f**; R = Ph

$RN{=}C(CF_3)NHN{=}CClCF_3$ (**9**) **a**; R = Ph

$RN{=}C(CF_3)NHNHC(CF_3){=}NR$ (**10**) **a**; R = Ph; **b**; R = 4-FC_6H_4

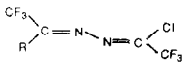
$RN{=}C(CF_3)NHN{=}CR'CF_3$ (**11**) **a**; R = Ph, R' = NH_2

[b] After recrystallisation.

[c] Azine **1** (18%) recovered.

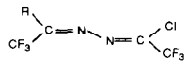
[d] Ref. 1.

shown by an X-ray study [11]. Thus, conjugation involving an aromatic ring is more important than azine conjugation.



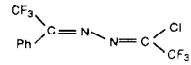
(ZZ)

(7a) R = ^{i}PrNH
(7b) R = Et_2N
(7c) R = H_2N
(7e) R = PhO



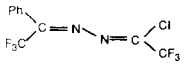
(EZ)

(7a) R = ^{i}PrNH
(7b) R = Et_2N
(7e) R = PhO



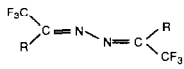
(EZ)

(7d)



(ZZ)

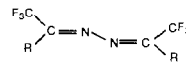
(7d)



(ZZ)

(8a) R = ^{i}PrNH
(8b) R = ^{s}BuNH
(8c) R = 2,6-Cl_2 Py CH_2NH-4

(8d) R = $CH_2CH_2O(CH_2)_2N$
(8e) R = Et_2N



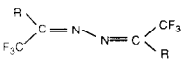
(ZE)

(8d) R = $CH_2CH_2O(CH_2)_2N$
(8e) R = Et_2N

TABLE 2

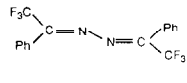
^{19}F NMR chemical shifts (ppm to low field of TFA) and assignments

Compound	$CF_3CR=NN=CClCF_3$ δ	δ	Isomer (%)	Assignment	Compound	$CF_3CR=NN=CRCF_3$ δ	δ	Isomer (%)	Assignment
7a	8.5	7.7	50	(*ZZ*)	**8a**	10.5	10.5	100	(*ZZ*)
	10.4	8.5	50	(*EZ*)	**8b**	10.9	10.9	100	(*ZZ*)
7b	12.4	7.9	53	(*ZZ*)	**8c**	10.6	10.6	100	(*ZZ*)
	18.0	8.3	47	(*EZ*)	**8d**	13.9	13.9	80	(*ZZ*)
7d	10.6	8.1	95	(*EZ*)		13.9	17.1	14	(*ZE*)
	16.5	8.5	5	(*ZZ*)		17.4	17.4	6	(*EE*)
7e	7.0	8.0	82	(*ZZ*)	**8e**	12.9	12.9	75	(*ZZ*)
	10.9	8.0	18	(*EZ*)		12.7	16.8	17	(*ZE*)
					8f	11.5	11.5	100	(*EE*)
	$RN=C(CF_3)NHN=CClCF_3$					$RN=C(CF_3)NHNHC(CF_3)=NR$			
9a	10.7	7.8	54	(*EZ*)	**10a**	13.8	13.8	100	(*EE*)
	11.6	8.3	46	(*ZZ*)	**10b**	13.5	13.5	100	(*EE*)



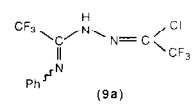
(EE)

(8d) R = $CH_2CH_2O(CH_2)_2N$
(8e) R = Et_2N

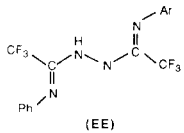


(EE)

(8f)

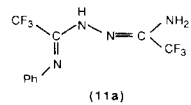


(9a)



(EE)

(10a) Ar = Ph
(10b) Ar = 4-FC_6H_4



(11a)

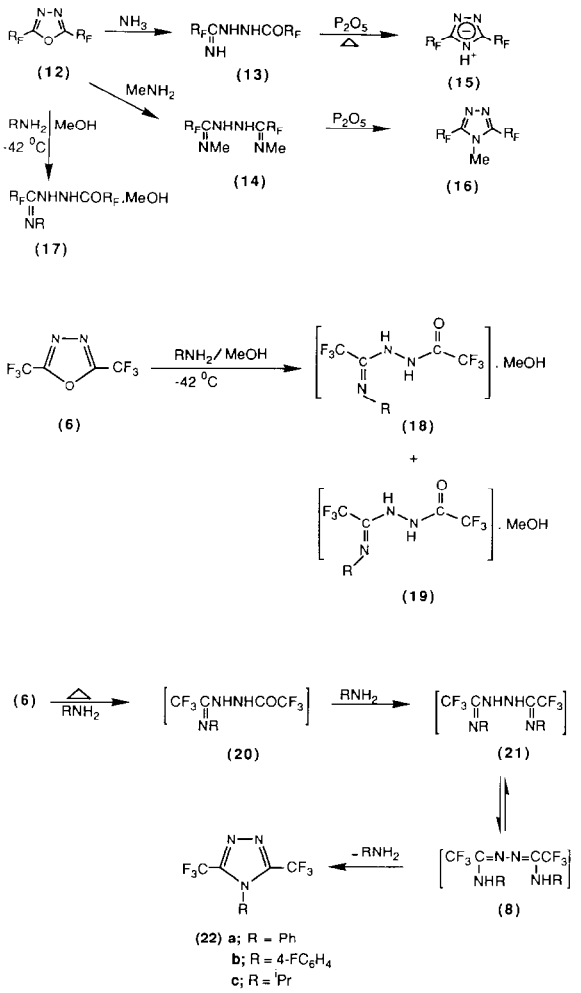
It is therefore concluded that the monosubstitution compound formed from aniline is a mixture of the *syn*(*Z*)- and *anti*(*E*)-isomers of the imidoyl compound **9a** and that the disubstitution products formed from aniline and 4-fluoroaniline are the (*EE*)-bisimidoylhydrazines **10a** and **10b**, respectively.

The mono- and di-substitution products formed from reaction of dichloroazine **1** with methylamine and the glycine esters $H_2NCH_2CO_2R$ (R = Me and Et) [12] all show coupling in their ^1H NMR spectra involving the N—H proton and the methyl or methylene hydrogens, thus confirming the presence of the $NHCH_2R'$ (R' = H or CO_2R) group, i.e. the products are the azines **7** and **8**. Hence, the compounds formed from the primary amines in the present work are considered to be the azines **7a** and **8a–8c**.

The diphenylazine **8f** [13] has been identified (X-ray) as the (*EE*)-isomer [14] and the monophenylazine **7d** and the monophenoxyazine **7e** were formed as mixtures of the two isomers in the ratio 95:5 and 82:18, respectively [13]. On steric grounds, it was concluded that the $CF_3CCl{=}N$ grouping in the dichloroazine **1** and in the monochloroazines **7d** and **7e** had the (*Z*-configuration [13], as has more recently been confirmed for azine **7c** [11]. Thus, the major isomers of azines **7d** and **7e** were assigned the (*EZ*)- and (*ZZ*)-configurations, respectively, and the minor isomers the corresponding (*ZZ*)- and (*EZ*)-configurations; these assignments are consistent with CF_3 groups *syn* to a nitrogen lone pair having higher field ^{19}F NMR chemical shifts than CF_3 groups *anti* to a nitrogen lone pair [13]. The (*E*)- and (*Z*-configurations for the present compounds have been assigned analogously (Table 2).

It was reported in 1962 that 2,5-bis(perfluoroalkyl)-1,3,4-oxadiazoles **12** ($R_F = CF_3$, CF_2CF_3, $CF_2CF_2CF_3$) on reaction with ammonia gave the corresponding 1-(perfluoroacylimidoyl)-2-(perfluoroacyl)hydrazines **13** [15]. In contrast, the reaction with methylamine afforded products presumed to be the symmetrical 1,2-bis-(*N*-methyl perfluoroacimidoyl)hydrazines **14**. Treatment of hydrazines **13** and **14** with phosphorus(V) oxide at elevated temperature gave the 1,2,4-triazoles **15** and **16**, respectively [15] (Scheme 3).

In 1989 it was found that treatment of the oxadiazoles **12** with primary alkylamines in methanol at −42 °C gave hydrogen-bonded methanol complexes



Scheme 3.

of monoadducts **17** [16]. An X-ray study of the product from the treatment of oxadiazole **6** with methylamine showed that it was the methanol complex of *syn*(*Z*)-1-(*N*-methyltrifluoroacetimidoyl)-2-(trifluoroacetyl)hydrazine **18** (R = Me). The corresponding complexes from the reaction with ethylamine and s-butylamine were mixtures of the (*Z*)-**18** and (*E*)-**19** (R = Et and Bu^s) isomers in the ratio 80:20 and 20:80, respectively [16].

These monoadduct-methanol complexes could be converted to the corresponding 4-alkyl-2,5-bis(trifluoromethyl)-4*H*-1,2,4-triazoles **22** by heating under reflux in methanol. It was also found that acceptable yields of the triazoles **22** could be obtained directly from oxadiazole **6** by heating with the appropriate aryl- or alkyl-amine in the absence of solvent [16] (Scheme 3).

The compounds considered [15, 16] to be the bisimidoylhydrazines **14** and **21** (R = alkyl) are now known to be the tautomeric azines **8**.

In the present work, the monochloroazine **7a** was hydrolyzed with sodium hydroxide in ethanol followed by an acidic work-up to give a product presumed to be the imidoylhydrazine **20** ($R = Pr^i$) (92%) as a mixture of the (*Z*)- and (*E*)-isomers in the ratio 30:70. This is close to the ratio 20:80 reported [16] for the (*Z*)-**18** and (*E*)-**19** isomers of the imidoylhydrazine **20** ($R = Bu^s$), isolated as its methanol adduct via the treatment of oxadiazole **6** with s-butylamine in methanol at low temperature.

The 4-aryl-2,5-bis(trifluoromethyl)-4*H*-1,2,4-triazoles **22a** (76%) and **22b** (96%) were prepared from the bisimidoylhydrazines **10a** and **10b** by heating under reflux in petroleum ether (b.p. 100–120 °C) and ethanol, respectively. Attempted preparation of triazole **22c** ($R = Pr^i$) by heating azine **8a** under reflux in petroleum ether (b.p. 100–120 °C) was unsuccessful and it is possible that a higher temperature is required.

It was also found that the triazole **22a** could be prepared (37%) by heating the monoimidoyl compound **9a** under reflux in petroleum ether (b.p. 100–120 °C).

Triazoles **22** can thus be prepared by reaction of oxadiazole **6** or dichloroazine **1** with primary amines, and both reactions involve common intermediates.

Experimental

The amines employed and trifluoroactetic acid were commercial samples which were distilled, where necessary, and their purities checked before use.

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], ^{19}F NMR spectroscopy [Perkin-Elmer R32 (84.6 MHz) instruments; reference external CF_3CO_2H] 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 [$CDCl_3$, CCl_4 or $(CD_3)_2CO$] as indicated in the text and chemical shifts to low field of the reference are designated positive.

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

Preparation of 1,2-bis(trifluoroacetyl)hydrazine (4)

Hydrazine hydrate (25 cm^3, 0.50 mol) was added to a stirred solution of trifluoroactetic acid (38 cm^3, 0.50 mol) in benzene (300 cm^3) and the mixture was heated under reflux (2 h). A Dean and Stark trap was fitted, reflux was continued (3.5 h) and then a further quantity of trifluoroacetic acid (38 cm^3, 0.50 mol) was added. Reflux was continued in the absence of the Dean and Stark trap (2 h) and then with the trap refitted (20 h). The

resulting white solid was collected by filtration, dried (vacuum desiccator) and identified as 1,2-bis(trifluoroacetyl)hydrazine (**4**) (87.5 g, 0.39 mol, 78%). Analysis: Found: C, 21.4; H, 0.8; F, 50.8; N, 12.5%; mol.wt., 224. $C_4H_2F_6H_2O_2$ requires: C, 21.4; H, 0.9; F, 50.9; N, 12.5%; mol.wt., 224. M.p. 174–175 °C; lit. [9] m.p. 175–176 °C. ^{19}F NMR $(CD_3)_2CO$ δ: 2.3 (s, CF_3CO) ppm.

Preparation of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (1)

A mixture of *N,N*-dimethylaniline hydrochloride (153.46 g, 0.974 mol), 1,2-bis(trifluoroacetyl)hydrazine (**4**) (103.0 g, 0.460 mol) and phosphoryl chloride (150 cm^3) was stirred for 10 min under nitrogen in a flask fitted with a condenser leading to a cold trap (−78 °C). The mixture was heated under reflux (3.5 h) and then allowed to cool and stored overnight. The flask contents and the small amount of material which had condensed in the cold trap were combined and the two layers which had formed were separated. The lower layer was added to ice water (*c.* 750 cm^3) and the mixture vigorously stirred (0.5 h) in a flask fitted with a condenser. Separation of the lower organic layer gave the main batch of crude product (60.4 g). The original dark upper layer was treated similarly with ice water (*c.* 75.0 cm^3) and the organic layer subjected to preliminary purification by trap-to-trap distillation at low pressure (*c.* 0.2 mmHg) to afford a second batch of crude product (14.65 g). Distillation of the combined product (75.05 g) through a vacuum-jacketed Vigreux column gave 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**1**) (72.43 g, 0.278 mol, 60%). Analysis: Found: C, 18.2; F, 43.7; N, 10.8%; mol.wt., 260/262/264. $C_4Cl_2F_6N_2$ requires: C, 18.4; F, 43.7; N, 10.8%; mol. wt., 260/262/264. $C_4Cl_2F_6N_2$ requires: C, 18.4; F, 43.7; N, 10.7%; mol.wt., 261. B.p. 89–90.5 °C at 758 mmHg. ^{19}F NMR (neat) δ: 6.3 (s, CF_3) ppm. IR ν_{max} (cm^{-1}): 1640 (s, C=N str.); 1280 and 1220 (s, C−F str.); and 748 (s, CF_3 def.). Mass spectrum (*m/z*): 260/262/264 (96.2%, M^+); 225/227 [78.0, $(M-Cl)^+$]; 191/193/195 [76.0, $(M-CF_3)^+$]; 116/118 (29.6, $C_2ClF_3^+$); 85/87 (35.8, $CClF_2^+$); 76 (28.9, $C_2F_2N^+$); 69 (100.0, CF_3^+); 61/63 (16.3, $CClN^+$); 50 (24.5, CF_2^+); 47/49 (15.1, CCl^+); and 31 (26.4, CF^+).

In a second experiment in the absence of the amine hydrochloride, a mixture of *N,N*-dimethylaniline (54.45 g, 0.45 mol), hydrazine **4** (51.30 g, 0.23 mol) and phosphoryl chloride (150 cm^3) was heated under reflux (11 h) and the volatile material then removed by distillation until the still-head temperature reached 103 °C. The distillate was added dropwise to ice water (500 cm^3), stirred (0.5 h) and the lower layer separated and distilled to give azine **1** (19.6 g, 75.1 mmol, 33%).

Reactions of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (1)

(a) With diethylamine

A mixture of dichloroazine **1** (0.85 g, 3.27 mmol) and freshly distilled diethylamine (0.48 g, 6.6 mmol) was stirred (0.5 h) and the volatile material

removed *in vacuo* to a cold trap (−78 °C) and identified as unchanged dichloroazine **1** (0.16 g, 0.61 mmol, 18% recovered). The remaining material was filtered to remove diethylamine hydrochloride and the filtrate treated with water (2 cm^3) to give a yellow oil which was extracted with ether (2×5 cm^3), dried ($MgSO_4$) and the solvent removed *in vacuo* to afford a non-volatile yellow oil (0.69 g). The two components of the oil were separated by preparative-scale GLC (5 m OV17 at 140 °C) to give two fluorescent yellow oils which were identified as follows.

(i) 2-Chloro-5-diethylamino-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-2,4-diene (**7b**) (nc) (0.31 g, 1.04 mmol, 39%). Analysis: Found: C, 32.6; H, 3.3; Cl, 11.5; F, 38.0; N, 14.2%; mol.wt., 297/299. $C_8H_{10}ClF_6N_3$ requires: C, 32.3; H, 3.4; Cl, 11.9; F, 38.3; N, 14.1%; mol.wt., 297.5. ^{1}H NMR (neat) δ: 3.22 (q, 2H, CH_2—N, J=7 Hz); and 0.78 (t, 3H, CH_3, J=7 Hz) ppm. ^{19}F NMR δ: 18.0 (s, CF_3); 12.4 (s, CF_3); 8.3 (s, CF_3CCl); and 7.9 (s, CF_3CCl) ppm, in the ratio 47:53:47:53. IR ν_{max} (cm^{-1}): 1630–1540 (s, C=N str.); 1295 and 1240 (s, C—F str.); and 750 (s, CF_3 def.). Mass spectrum (*m/z*): 297/299 (16.2%, M^+); 262 [20.8, $(M-Cl)^+$]; 225/227 [15.4, $(M-Et_2N)^+$; 167 [31.0, $M-CF_3Cl=N)]^+$; 166 (28.2, $C_6H_9F_3N_2^+$); 165 (36.7, $C_6H_8F_3N_2^+$); 124 (59.4, $C_4H_5F_3N^+$); 96 (21.7, $C_5H_8N_2^+$); 71 (47.8, $C_4H_9N^+$); 69 (65.0, CF_3^+); 56 (85.7, $C_3H_6N^+$); 42 (32.2, $C_2H_4N^+$); and 29 (100.0, $C_2H_5^+$).

(ii) 2,5-Bis(diethylamino)-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**8a**) (nc) (0.28 g, 0.84 mmol, 32%). Analysis: Found: C, 43.0; H, 6.2; F, 33.7; N, 16.7%; mol.wt., 334. $C_{12}H_{20}F_6N_4$ requires: C, 43.1; H, 6.0; F, 34.1; N, 16.8%; mol.wt., 334. ^{1}H NMR (neat) δ: 3.15 (q, 2H, CH_2—N, J=7 Hz); and 0.88 (t, 3H, CH_3, J=7 Hz) ppm. ^{19}F NMR δ: 16.8 (s, CF_3); 12.9 (s, CF_3); and 12.7 (s, CF_3) ppm, in the ratio 6:27:3. IR ν_{max} (cm^{-1}): 1600 (s, C=N str.); 1292 and 1221 (s, C—F str.); and 745 (m, CF_3 def.). Mass spectrum (*m/z*): 334 (33.7%, M^+); 262 [9.6, $(M-Et_2N)^+$]; 169 (37.5, $C_6H_{12}F_3N_2^+$]; 167 (17.3, $C_6H_{10}F_3N_2^+$); 165 (27.6, $C_6H_8F_3N_2^+$); 139 (19.6, $C_4H_6F_3N_2^+$); 124 (30.9, $C_4H_5F_3N^+$); 72 (73.4, $C_4H_{10}N^+$); 71 (75.5, $C_4H_9N^+$); 69 (10.7, CF_3^+); 56 (100.0, $C_3H_6N^+$); 44 (35.2, $C_2H_6N^+$); and 29 (89.6, $C_2H_5^+$).

(b) With s-butylamine

s-Butylamine (0.60 g, 8.18 mmol) was added during 5 min to dichloroazine **1** (0.55 g, 2.12 mmol) at 0 °C. The reactants were stirred during the addition and then for a further 5 min, after which time the volatile material was removed *in vacuo* and collected in a cold trap (−78 °C) and identified as unchanged amine (0.15 g, 2.0 mmol, 24% recovered). Aqueous sodium hydroxide (0.5 M, 3 cm^3) was added to the residue, which was then extracted with ether (3×5 cm^3), dried ($MgSO_4$) and the solvent removed under reduced pressure to give a white solid (0.68 g). Sublimation of the solid (47 °C at *c.* 1 mmHg) gave 2,5-bis(s-butylamino),1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**8b**) (nc) (0.58 g, 1.70 mmol, 82%). Analysis: Found: C, 43.3; H, 6.1; F, 33.9; N, 17.1%; mol.wt., 334. $C_{12}H_{20}F_6N_4$ requires: C, 43.1; H, 6.0; F, 34.1; N, 16.8%; mol.wt., 334. M.p. 42 °C. ^{1}H NMR ($CDCl_3$) δ: 5.72 (br.,

1H, NH); 3.64 (sextet, 1H, >CH−N, J=7 Hz); 1.52 (pentet, 2H, CH_2, J=7 Hz); 1.17 (d, 3H, CH_3CH, J=7 Hz) and 0.92 (t, 3H, CH_3CH_2, J=7 Hz) ppm. ^{19}F NMR δ: 10.9 (s, CF_3) ppm. IR ν_{max} (cm^{-1}): 3340 (m, N−H str.); 1625 (s, C=N str.); 1258 and 1170 (s, C−F str.); and 762 (m, CF_3 def.). Mass spectrum (*m/z*): 334 (3.0%, M^+); 167 (8.8, $M/2^+$); 165 (10.4, $C_6H_8F_3N_2^+$); 97 (21.3, $C_5H_9N_2^+$); 95 (13.4, $C_5H_7N_2^+$); 71 (24.3, $C_4H_8N^+$); 69 (28.9, CF_3^+); 57 (44.5, $C_3H_6N^+$ and $C_4H_9^+$); 55 (28.4, $C_3H_4N^+$ and $C_4H_7^+$); 41 (26.8, $C_2H_3N^+$); and 40 (100.0, $C_2H_2N^+$).

(c) With isopropylamine (molar ratio 1:2)

A solution of isopropylamine (1.50 g, 25.3 mmol) in diethyl ether (20 cm^3) was added dropwise (20 min) to a stirred solution of dichloroazine **1** (3.30 g, 12.6 mmol) in diethyl ether (20 cm^3) at 0 °C and the mixture warmed to room temperature and stirring continued (16 h). The precipitated isopropylamine hydrochloride was filtered off and the filtrate was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a yellow oil identified as 2-chloro-1,1,1,6,6,6-hexafluoro-5-(isopropylamino)-3,4-diazahexa-2,4-diene (**7a**) (nc) (3.05 g, 10.8 mmol, 86%). Analysis: Found: C, 29.9; H, 2.8; Cl, 12.4; F, 40.1; N, 14.8%; mol.wt., 283/285. $C_7H_8ClF_6N$ requires: C, 29.6; H, 2.8; Cl, 12.5; F, 40.2; N, 14.8%; mol.wt., 283.5. B.p. 180 °C at 751 mmHg. ^{1}H NMR ($CDCl_3$) δ: 5.26 (br., 1H, NH); 3.90 (septet, 1H, >CH−N, J=6.6 Hz); and 1.02 and 0.98 [2d, 6H, $(CH_3)_2C$, J=6.6 Hz] ppm. ^{19}F NMR δ: 10.4 (s, 3F, CF_3); 8.5 (s, 3F, CF_3); 8.1 (s, 3F, CF_3CCl); and 7.7 (s, 3F, CF_3CCl) ppm. IR ν_{max} (cm^{-1}) 3470 (s, N−H str.); 1635 (s, C=N str.); 1580 (s, N−H bend); 1240–1140 (s, C−F str.); and 755 (s, CF_3 def.). Mass spectrum (*m/z*): 283/285 (24.1%, M^+); 248 [27.6, $(M-Cl)^+$]; 206 (27.9, $C_4H_2F_6N_3^+$); 186 (11.4, $C_4HF_5N_3^+$); 172/174 (12.2, $C_3H_2ClF_3N_3^+$); 151 (100.0, $C_5H_6F_3N_2^+$); 112 (15.3, $C_4H_7F_3^+$); 96 (12.0, $C_2HF_3N^+$); 69 (64.8, CF_3^+); 43 (99.2, $C_3H_7^+$); 42 (44.8, $C_3H_6^+$); and 41 (37.0, $C_3H_5^+$).

(d) With isopropylamine (molar ratio 1:4)

A solution of isopropylamine (3.00 g, 50.2 mmol) in diethyl ether (30 cm^3) was added dropwise (0.5 h) to a stirred solution of dichloroazine **1** (3.30 g, 12.5 mmol) in diethyl ether (20 cm^3) at 0 °C and stirring continued (1 h). The precipitate of isopropylamine hydrochloride (2.12 g, 22.2 mmol, 44%) was filtered off and the filtrate was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a pale-yellow solid identified as 2,5-bis(isopropylamino)-1,1,1,6,6,6,-hexafluoro-3,4-diazahexa-2,4-diene (**8a**) (nc) (3.61 g, 11.8 mmol, 95%). Analysis: Found: C, 39.1; H, 5.0; F, 37.2; N, 18.2%; mol.wt., 306. $C_{10}H_{16}F_6N_4$ requires: C, 39.2; H, 5.2; F, 37.3; N, 18.3%; mol.wt., 306. M.p. 57–58 °C. ^{1}H NMR ($CDCl_3$) δ: 5.80 (br., 1H, NH); 3.90 (sept., 1H, >CH−N, J=6.6 Hz); and 1.23 [d, 6H, $(CH_3)_2C$, J=6.6 Hz] ppm. ^{19}F NMR δ: 10.5 (s, CF_3) ppm. IR ν_{max} (cm^{-1}): 3340 (m, N−H str.); 1630 (s, C=N str.); 1220−1140 (s, C−F str.); and 765 (m, CF_3 def.). Mass spectrum (*m/z*): 306 (39.0%, M^+); 155 (35.4, $C_5H_{10}F_3N_2^+$); 153 (67.2, M/

2^+); 151 (100.0, $C_5H_6F_3N_2^+$); 113 (52.7, $C_4H_8F_3^+$); 69 (18.0, CF_3^+); 58 (35.2, $C_3H_8N^+$); 43 (83.8, $C_3H_7^+$); 42 (32.7, $C_3H_6^+$); and 41 (38.0, $C_3H_5^+$).

(e) With morpholine

A solution of morpholine (1.20 g, 13.6 mmol) in diethyl ether (30 cm^3) was added to a stirred solution of dichloroazine **1** (0.89 g, 3.4 mmol) in diethyl ether (20 cm^3) and stirring continued (16 h). The deliquescent precipitate of morpholine hydrochloride was filtered off and the solvent was removed from the filtrate under reduced pressure. The residue was recrystallized from ethanol to give a white solid identified as 2,5-bis(morpholino)-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**8d**) (nc) (1.15 g, 3.2 mmol, 96%). Analysis: Found: C, 39.9; H, 4.4; F, 31.5; N, 15.8%; mol.wt., 362. $C_{12}H_{16}F_3N_4O_2$ requires: C, 39.8; H, 4.4; F, 31.5; N, 15,5%; mol.wt., 362. M.p. 78–79 °C. ^{1}H NMR ($CDCl_3$) δ: 3.8–3.4 (complex, CH_2-O and CH_2-N) ppm. ^{19}F NMR δ: 17.4 (s, CF_3); 17.1 (s, CF_3); and 13.9 (s, CF_3) ppm, in the ratio 6:7:87. IR ν_{max} (cm^{-1}): 1605 (s, C=N str.); and 1250–1135 (s, C–F str.). Mass spectrum (*m/z*): 362 (59.3%, M^+); 276 [19.1, $(M-C_4H_8NO)^+$]; 183 (38.7, $C_6H_{10}F_3N_2O^+$); 181 (33.0, $M/2^+$); 109 (19.8, $C_3H_2F_3N^+$); 87 (26.2, $C_4H_9NO^+$); 86 (92.0, $C_4H_8NO^+$); 85 (100.0, $C_4H_7NO^+$); 69 (23.2, CF_3^+); 56 (34.4, $C_3H_6N^+$); 55 (94.4, $C_3H_5N^+$); and 42 (20.7, $C_2H_4N^+$).

(f) With aniline (molar ratio 1:2)

Freshly distilled aniline (2.10 g, 22.9 mmol) in diethyl ether (20 cm^3) was added dropwise (0.5 h) to a stirred solution of dichloroazine **1** (3.00 g, 11.5 mmol) in diethyl ether (20 cm^3) at 0 °C and stirring continued (1 h). The precipitate of aniline hydrochloride (1.50 g, 11.5 mmol, 50%) was filtered off, the filtrate dried ($MgSO_4$) and solvent removed under reduced pressure to give an amber oil identified as 5-chloro-1-phenyl-6,6,6-trifluoro-2-trifluoromethyl-1,3,4-triazahexa-1,4-diene (**9a**) (nc) (3.26 g, 10.27 mmol, 89%). Analysis found: C, 37.7; H, 1.8; Cl, 11.2; F, 36.1; N, 12.9%; mol.wt., 317/319. $C_{10}H_6ClF_6N_3$ requires: C, 37.8; H, 1.9; Cl, 11.2; F, 35.9; N, 13.2%; mol.wt., 317.5. ^{1}H NMR (neat) δ: 7.76 (s, 0.45H, NH); 7.72 (s, 0.55H, NH); and 7.5–7.1 (mult., 5H, C_6H_5) ppm. ^{19}F NMR δ: 11.6 (s, CF_3); 10.7 (s, CF_3); 8.3 (s, CF_3CCl); and 7.8 (s, CF_3CCl) ppm, in the ratio 6:7:6:7. IR ν_{max} (cm^{-1}): 3450 and 3340 (m, N–H str.); 1632 (s, C=N str.); 1585 (s, N–H bend); 1205–1150 (s, C–F str.); and 750 (s, CF_3 def.). Mass spectrum (*m/z*): 317/319 (97.1%, M^+); 282 [100.0, $(M-Cl)^+$]; 187 [11.8, $(M-C_2ClF_3N)^+$]; 172 (20.9, $C_8H_5F_3N^+$); 118 (31.7, $C_7H_6N_2^+$); 77 (96.4, $C_6H_5^+$); 69 (25.9, CF_3^+); 65 (38.2, $C_5H_5^+$); 51 (25.1, $C_4H_3^+$); and 39 (15.3, $C_3H_3^+$).

(g) With aniline (molar ratio 1:4)

A solution of dichloroazine **1** (4.69 g, 18.0 mmol) in diethyl ether (50 cm^3) was added slowly (0.5 h) to a stirred solution of aniline (6.69 g, 72.0 mmol) in diethyl ether (100 cm^3) at 0 °C and stirring continued (3 h). The mixture was then stored overnight (16 h). The precipitate of aniline hydrochloride (4.35 g, 33.6 mmol, 47%) was filtered off and the solvent removed

from the filtrate under reduced pressure to give a white solid identified as 1,2-bis(*N*-phenyltrifluoroacetimidoyl)hydrazine (**10a**) (nc) (6.26 g, 16.74 mmol, 93%). Analysis: Found: C, 51.4; H, 3.3; F, 30.3; N, 14,7%; mol.wt., 374. $C_{16}H_{12}F_6N_4$ requires: C, 51.3; H, 3.2; F, 30.5; N, 15.0%. mol.wt., 374. M.p. 152 °C. ^{1}H NMR ($CDCl_3$) δ: 7.83 (s, 1H, NH); and 7.3–7.1 (mult., 5H, C_6H_5) ppm. ^{19}F NMR δ: 13.8 (s, CF_3) ppm. IR ν_{max} (cm^{-1}): 3250 (m, N–H str.); 1620 (s, C=N str.); 1590 (s, N–H bend); 1238–1132 (s, C–F str.); and 745 (m, CF_3 def.). Mass spectrum (*m/z*): 374 (2.4%, M^+); 282 [54.6, $(M-C_6H_5NH)^+$]; 281 [27.8 $(M-C_6H_5NH_2)^+$]; 172 (18.7, $C_8H_5F_3N^+$); 93 (100.0, $C_6H_7N^+$); 77 (85.1, $C_6H_5^+$); and 65 (21.1, $C_5H_5^+$).

Storage of compound **10a** in solution ($CDCl_3$) for any length of time resulted in the gradual formation of 4-phenyl-3,5-bis(trifluoromethyl)-4*H*-1,2,4-triazole (**22a**), whilst attempted recrystallization from aqueous ethanol resulted in complete cyclisation to triazole **22a**.

(h) With 4-fluoroaniline (A.O.A. Eltoum)

A solution of dichloroazine **1** (4.00 g, 15.3 mmol) in diethyl ether (50 cm^3) was added slowly (0.5 h) to a stirred solution of 4-fluoroaniline (6.60 g, 59.5 mmol) in diethyl ether (100 cm^3) and stirring continued (2 h). The precipitate of 4-fluoroaniline hydrochloride (3.69 g, 25.0 mmol, 84%) was filtered off and the solvent removed from the filtrate under reduced pressure to give a white solid identified as 1,2-bis(*N*-4-fluorophenyltrifluoroacetimidoyl)hydrazine (**10b**) (nc) (4.99 g, 12.29 mmol, 80%). Analysis: Found: C, 47,0; H, 2.5; N, 13.9%; mol.wt., 410. $C_{16}H_{10}F_8N_4$ requires: C, 46.8; H, 2.45; N, 13.7%; mol.wt., 410. M.p. 158 °C. ^{1}H NMR ($CDCl_3$) δ: 7.75 (br., 1H, NH); and 7.1 (mult., 5H, C_6H_5) ppm. ^{19}F NMR δ: 13.5 (s, 3F, CF_3); and −36.2 (mult., 1F, ArF) ppm. IR ν_{max} (cm^{-1}): 3320 (m, N–H str.); 1640 (s, C=N str.); 1570 (m, N–H bend); 1160 (s, C–F str.); and 760 (m, CF_3 def.). Mass spectrum (*m/z*); 410 (2.2%, M^+); 300 [31.3, $(M-FC_6H_4NH)^+$]; 299 [100.0, $(M-FC_6H_4NH_2)^+$]; 190 (21.7, $C_4F_6N_2^+$); 184 (38.0, $C_8H_3F_3N_2^+$); 135 (20.6, $C_7H_4FN_2^+$); 111 (90.1, $C_6H_6FN^+$); 109 (49.6, $C_6H_4FN^+$); 95 (47.5, $C_6H_4F^+$); 83 (27.9, CF_3N^+); and 69 (18.0, CF_3).

(i) With 4-aminomethyl-2,6-dichloropyridine

A solution of dichloroazine **1** (1.55 g, 5.95 mmol) in diethyl ether (10 cm^3) was added slowly during 15 min to a stirred solution of the amine (3.90 g, 22.0 mmol) in diethyl ether (60 cm^3) and stirring continued (16 h). The precipitate of 4-aminomethyl-2,6-dichloropyridine hydrochloride (1.72 g, 8.06 mmol, 37%) was filtered off, the filtrate dried ($MgSO_4$) and the solvent removed under reduced pressure to give a sandy-yellow solid (2.82 g). This was recrystallized first from light petroleum/chloroform (1:1 v/v) and then from aqueous ethanol to afford a white solid identified as 2,5-bis(4-aminomethyl-2,6-dichloropyridyl)-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**8c**) (nc) (1.90 g, 3.51 mmol, 59%). Analysis: Found: C, 35.3; H, 1.8; Cl, 25.9; N, 15.4%; mol.wt., 540/542/544. $C_{16}H_{10}Cl_4F_6N_4$ requires: C, 35.4; H, 1.9; Cl, 26.2; N, 15.5%; mol.wt., 542.2. M.p. 147–148 °C. ^{1}H NMR ($CDCl_3$)

δ: 7.18 (s, 2H, ring =CH); 6.40 (t, 1H, NH, J=7 Hz); and 4.59 (d, 2H, CH_2–N, J=7 Hz) ppm. ^{19}F NMR δ: 10.6 (s, CF_3) ppm. IR ν_{max} (cm^{-1}): 3260 and 3240 (m, N–H str.); 1638 (s, C=N str.); 1584 (s, N–H bend); 1172 and 1165 (s, C–F str.); and 755 (m, CF_3 def.). Mass spectrum (*m/z*): 540/542/544 (6.4%, M^+); 364/366/368 (26.2, $C_{10}H_4Cl_2F_6N_4^+$); 272/274/276 (37.3, $C_8H_7Cl_2F_3N_3^+$); 271/273/275 (65.3, $C_8H_6Cl_2F_3N_3^+$); 270/272/274 (84.2, $C_8H_5Cl_2F_3N_3^+$); 175/177/179 (49.6, $C_6H_5Cl_2N_2^+$); 174/176/178 (34.5, $C_6H_4Cl_2N_2^+$); 160/162/164 (100.0, $C_6H_4Cl_2N^+$); 125/127 (19.2, $C_6H_4ClN^+$); 124/126 (22.7, $C_6H_3ClN^+$); 96 (23.1, $C_2HF_3N^+$); 69 (44.7, CF_3^+); 40 (47.9, $C_2H_2N^+$); and 29 (36.8, CH_3N^+).

Thermal cyclisations

*(a) 1,2-Bis(N-phenyltrifluoroacetimidoyl)hydrazine (**10a**)*

Compound **10a** (0.41 g, 1.2 mmol) was heated under reflux (20 h) in petroleum ether (b.p. 100–120 °C, 50 cm^3), the solution filtered and the solvent removed under reduced pressure to give a waxy solid (0.31 g). Vacuum sublimation (40 °C, *c.* 1 mmHg) of this gave a white solid identified as 3,5-bis(trifluoromethyl)-4-phenyl-4*H*-1,2,4-triazole (**22a**) (0.26 g, 0.92 mmol, 76%). Analysis: Found: C, 43.0; H, 1.5; F, 40.5; N, 14.7%; mol.wt., 281. $C_{10}H_5F_6N_3$ requires: C, 42.7; H, 1.8; F, 40.5; N, 14.9%; mol.wt., 281. M.p. 79–80 °C; lit. [16] m.p. 79–82 °C. ^{1}H NMR (CCl_4) δ: 7.75–7.35 (mult., C_6H_5) ppm. ^{19}F NMR δ: 17.0 (s, CF_3) ppm. IR ν_{max} (cm^{-1}): 1600 (m, C=N str.); 1180–1160 (s, C–F str.); and 785 (m, CF_3 def.). Mass spectrum (*m/z*); 281 (100.0%, M^+); 262 [9.2, $(M-F)^+$]; 172 (15.3, $C_8H_5F_3N^+$); 117 (10.5, $C_7H_5N_2^+$); 91 (16.9, $C_6H_5N^+$); 77 (58.8, $C_6H_5^+$); and 51 (20.4, $C_4H_3^+$).

*(b) 1,2-Bis(N-4-fluorophenyltrifluoroacetimidoyl)hydrazine (**10b**) (A.O.A. Eltoum)*

A solution of compound **10b** (0.50 g, 1.22 mmol) in aqueous ethanol (10 cm^3) was heated under reflux (4 h) and the solvent removed *in vacuo* to give a white solid identified as 3,5-bis(trifluoromethyl)-4-(4-fluorophenyl)-4*H*-1,2,4-triazole (**22b**) (0.35 g, 1.17 mmol, 96%). Analysis: Found: C, 39.9; H, 1.3; F, 44.2; N, 14.1%; mol.wt., 299. $C_{10}H_4F_7N_3$ requires: C, 40.1; H, 1.3; F, 44.5; N, 14.0%; mol.wt., 299. M.p. 101–102 °C; lit. [16] m.p. 101–103 °C. ^{1}H NMR ($CDCl_3$) δ; 7.3 (mult., C_6H_4) ppm. ^{19}F NMR δ: 17.5 (s, 6F, $2CF_3$); and −28.8 (mult., 1F, ArF) ppm. IR ν_{max} (cm^{-1}): 1610 (s, C=N str.); 1210 and 1160 (s, C–F str.); and 720 (m, CF_3 def.). Mass spectrum (*m/z*): 299 (100.0%, M^+); 280 [10.8, $(M-F)^+$]; 184 (32.6, $C_8H_3F_3N_2^+$); 117 (21.7, $C_7H_3F_4N^+$); 135 (11.8, $C_7H_4FN_2^+$); 109 (32.3, $C_6H_4FN^+$); 95 (23.6, $C_6H_4F^+$); and 69 (17.0, CF_3^+).

*(c) 5-Chloro-1-phenyl-6,6,6-trifluoro-2-trifluoromethyl-1,3,4-triazahexa-1,4-diene (**9a**)*

A solution of compound **9a** (3.26 g, 10.27 mmol) in petroleum ether (b.p. 100–120 °C, 40 cm^3) was heated under reflux (24 h) and the grey-white precipitate of the hydrochloride of compound **9a** (0.31 g, 0.90 mmol,

9%) filtered off. The solvent was removed under reduced pressure from the filtrate and the resulting solid (1.46 g) recrystallized from light petroleum to afford triazole **22a** (1.07 g, 3.81 mmol, 37%).

*(d) 2,5-Bis(isopropylamino)-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (**8a**)*

A solution of azine **8a** (0.87 g, 2.84 mmol) in petroleum ether (b.p. 100–120 °C, 50 cm^3) was heated under reflux (23 h), but reaction did not take place and the azine was recovered unchanged. Similarly, reaction did not occur when azine **8a** (0.51 g, 1.67 mmol) was heated under reflux (72 h) in dry ethanol (15 cm^3).

*Hydrolysis of 2-chloro-1,1,1,6,6,6-hexafluoro-5-(isopropylamino)-3,4-diazahexa-2,4-diene (**7a**)*

A stirred solution of monochloroazine **7a** (0.42 g, 1.48 mmol) in ethanol (5 cm^3) was treated with a solution of sodium hydroxide (0.43 g, 10.75 mmol) in ethanol (15 cm^3) and stirring continued (0.5 h). The precipitate (0.13 g) of sodium chloride and sodium hydroxide was filtered off and the solvent removed from the filtrate under reduced pressure to give a residue which was dissolved in water (20 cm^3) and then treated with dilute hydrochloric acid (2 M, 3.3 cm^3). A white precipitate formed immediately and this was collected by filtration, dried at the pump and identified as 1-(*N*-isopropyltrifluoroacetimidoyl)-2-(trifluoroacetyl)hydrazine (**20**) (0.36 g, 1.36 mmol, 92%). Analysis: Found: C, 32.0; H, 3.5; N, 16.1%; mol.wt., 265. $C_7H_9F_6N_3O$ requires: C, 31.7; H, 3.4; N, 15.8%; mol.wt., 265. M.p. 160 °C. ^1H NMR [$(CD_3)_2CO$] δ: 4.0 (sept., 1H, $\rangle CH-N$, $J = 6.7$ Hz); and 1.2 [d, 6H, $(CH_3)_2C$, $J = 6.7$ Hz] ppm. ^{19}F NMR δ: 10.0 (s, CF_3); 9.8 (s, CF_3); 2.8 (s, CF_3CO); and 2.5 (s, CF_3CO) ppm, in the ratio 7:3:7:3. IR ν_{max} (cm^{-1}): 3280–3220 (s, N–H str.); 3060 (m, N–H str.); 1700 (m, C=O str.); 1630 (s, C=N str.); 1590 (s, N–H bend); and 1220–1160 (s, C–F str.). Mass spectrum (*m/z*): 266 [100.0%, $(M+H)^+$]; 265 (14.7, M^+); 154 (46.9, $C_5H_9F_3N_2^+$); 153 (51.2, $C_5H_8F_3N_2^+$); 69 (25.5, CF_3^+); 43 (88.6, $C_3H_7^+$); 42 (29.8, $C_3H_6^+$); and 41 (31.6, $C_3H_5^+$).

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