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PRELIMINARY NOTE

The Preparation and Some Reactions of 2,5-Dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene

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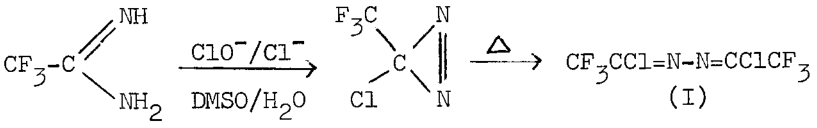
SUMMARY

The title azine(I) can be conveniently prepared by treatment of 1,2-bistrifluoroacetylhydrazine with NN-dimethylaniline hydrochloride in phosphoryl chloride at ca. 100 °C. It undergoes facile displacement of one or both chlorine atoms on treatment with a variety of nitrogen-, oxygen- and sulphur-centred nucleophiles as well as with iodide and fluoride ions. The bisanilino-substituted azine(Vd) is thermally unstable and cyclises with elimination of aniline to the triazole (Vla), while the perfluoroazine (Vj) undergoes cycloaddition with acetylene.

The dichloroazine (I) has been prepared previously by oxidative cyclisation of trifluoroacetamidine followed by thermolysis of the resulting chlorodiazirine [1], i.e.



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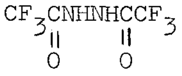
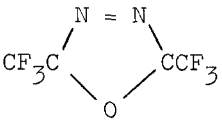
In our hands the cyclisation stage failed and so an alternative route was sought. This involved the preparation of 1,2-bistrifluoroacetylhydrazine (II) from trifluoroacetic acid and hydrazine [2] followed by chlorination. The initial chlorinating agents investigated either did not react with the hydrazide (II)($SOCl_2$/PhMe, reflux;$SbCl_5$/$PhNMe_2$, 100 °C) or gave the dehydration product, the oxadiazole (III)[2](8-33%), together with the dichloroazine (I) in low yield ($<$ 10%) (PCl_5/$POCl_3$/quinoline, 100 °C; PCl_5/$POCl_3$/$PhNMe_2$, 100 °C; PCl_5, 120 °C); trifluoroacetyl chloride and trichlorophosphine were also formed in these latter reactions.

However, treatment of the hydrazide (II) with NN - dimethylaniline hydrochloride (molar ratio 1:2) in phosphoryl chloride under reflux gave hydrogen chloride and trifluoroacetyl chloride (ca. 30%) as volatile products together with higher-boiling material to which was added cold dilute hydrochloric acid at 0 °C to destroy phosphoryl chloride. The lower of the resulting two layers was separated and distilled to afford pure dichloroazine (I)(48%), b.p. 73 °C.



$$CF_3\underset{\underset{O}{\|}}{C}NHNH\underset{\underset{O}{\|}}{C}CF_3$$

(II)



(III)

The results obtained from the reaction of the azine (I) with a variety of nucleophiles are summarised in the Table.

The dichloroazine (I) also undergoes ready reaction with i) KCN in CH_3CN or EtOH, ii) KSCN in CH_3CN and iii) H_2NCSNH_2 in Et_2O or EtOH but the products have not yet been characterised.

$CF_3CCl=N-N=CRCF_3$

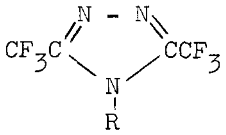
(IV)

a, $R=Et_2N$

b, $R=Pr^iNH$

c, $R=PhNH$.

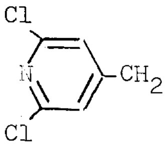
d, $R=F$

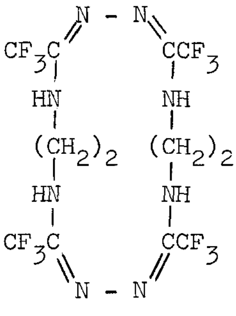


(VI)

a, $R=Ph$

b, R=





(VII)

$CF_3CR=N-N=CRCF_3$

(V)

a, $R=Et_2N$

b, $R=Pr^iNH$

c, $R=Bu^{sec}NH$

d, $R=PhNH$

e, $R=\overline{CH_2CH_2O(CH_2)_2N}$

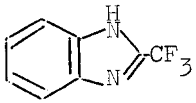
f, $R=PhO$

g, $2,4-Cl_2C_6H_3O$

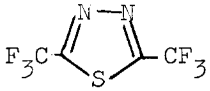
h, $R=PhS$

i, $R=I$

j, $R=F$



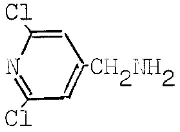
(VIII)



(IX)

TABLE

The reactions of the dichloroazine (I) with nucleophiles

Nucleophile	Molar ratio Nucleophile:Azine	Temp. (°C)	Time	Solvent	Products	% Yield
Et_2NH	2:1	0	10 min	-	(lVa) (Va)	39 32
Pr^iNH_2	2:1	0	16 h	Et_2O	(lVb)	86
Pr^iNH_2	4:1	0	1 h	Et_2O	(Vb)	95
$Bu^{sec}NH_2$	4:1	0	10 min	-	(Vc)	82
$PhNH_2$	2:1	0	1 h	Et_2O	(lVc)	89
$PhNH_2$	4:1	0	1 h	Et_2O	(Vd) (Vla)	58 15
	4:1	20	3 h	Et_2O	(Vlb)	59
$\overline{CH_2CH_2O(CH_2)_2NH}$	4:1	20	12 h	Et_2O	(Ve)	96
$H_2N(CH_2)_2NH_2$	2:1	0	30 min	Et_2O	(Vll)	52

$\underline{o}$-$C_6H_4(NH_2)_2$	1:1	10	3 h	Et_2O*	(Vlll)	97
PhO^-Na^+	2:1	20	12 h	Et_2O*	(Vf)	61
2,4-$Cl_2C_6H_3O^-Na^+$	2:1	20	3 h	Et_2O*	(Vg)	54
PhS^-Na^+	2:1	60	3 h	$CHCl_3$	(Vh)	77
P_2S_5†	10:1	180	10 days	-	(lX)	100
NaI	3:1	20	12 h	Me_2CO	(Vi)	74
KF ‡	-	240	-	-	(lVd) (Vj)	14 56

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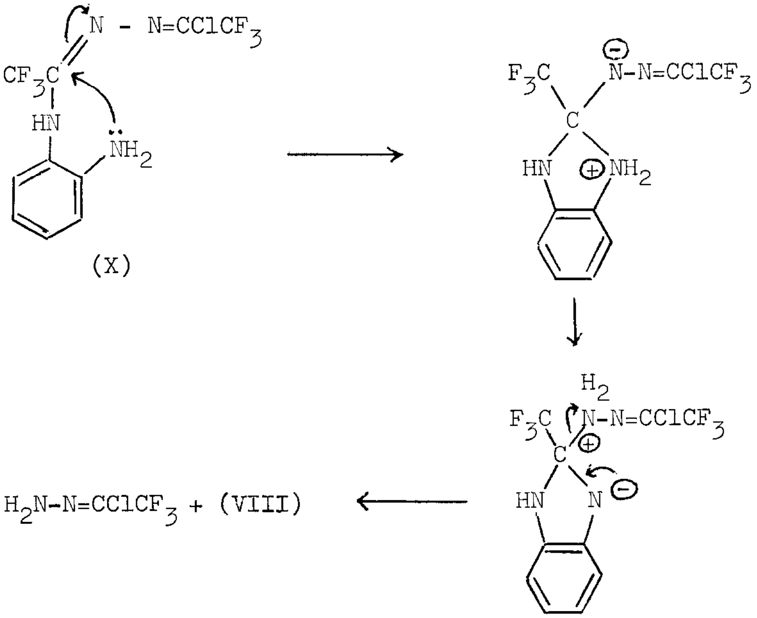
* Triethylamine (equimolar amount relative to nucleophile) also present.

† Sealed tube *in vacuo*.

‡ Azine passed slowly at 1-2 mm *in vacuo* through a Pyrex tube packed with a large excess of anhydrous potassium fluoride.

The compounds (VI)-(VIII) were unexpected products and the structure (VII) was proved by X-ray diffraction [3]. It was shown that the triazole (Vla) could be formed by heating at 100 °C either the mixed azine (lVc) (33% yield) or, more surprisingly, the symmetrical azine (Vd) (76% yield.)

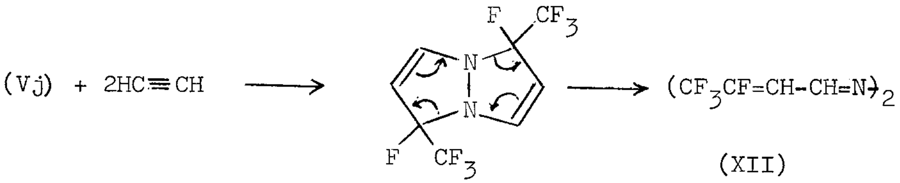
The formation of 2-trifluoromethylbenzimidazole (VIII)[4] indicates that nucleophilic attack by the free amino group in the azine intermediate (X) is less favoured on the carbon bearing chlorine than on the amino-substituted carbon, *i.e*.



The reaction of the di-iodoazine (Vi) with aniline (1:2 molar ratio) was observed to be slower than that involving azine (I) and gave the monosubstituted compound $CF_3CI{=}NN{=}C(CF_3)NHPh$ (94%).

In contrast to the dichloroazine (I), which is inert to water at room temperature over a period of several days, the perfluoroazine (Vj) is rapidly hydrolysed to the hydrazide (II).

A preliminary investigation of the reaction of the perfluoroazine (Vj) with acetylene has been carried out at 80 °C in a sealed tube. Although the products have not been completely characterised it appears that the criss-cross adduct (XI) is formed initially and then undergoes ring opening to some extent to give compound (XII); analagous reaction has been found with the criss-cross adduct formed from hexafluoroacetone azine and acetylene [5].



(XI)

(XII)

The structure of the products were established spectroscopically[i.r., n.m.r. (^{1}H and ^{19}F) and mass] and all possessed correct elemental compositions.

We thank the S.E.R.C. for a grant (to N.J.O'R.).

1 M.W. Graystone and D.M. Lemal, J. Am. Chem. Soc., 98 (1976) 1287.

2 W.J. Chambers and D.D. Coffman, J. Org. Chem., 26 (1961) 4410.

3 B. Beagley, N.J. O'Reilly, R. Pritchard and A.E. Tipping, unpublished results.

4 2 - Trifluoromethylbenzimidazole was first prepared by reaction of trifluoroacetic acid with o-phenylenediamine; W.T. Smith Jun. and E.C. Steinle Jun., J. Amer. Chem. Soc. 75 (1953) 1292.

5 T.P. Forshaw and A.E. Tipping, J. Chem. Soc.(C),(1971)2404; K. Burger, H. Schickaneder and W. Thenn, Tetrahedron Letters, (1975) 1125.