Journal of Fluorine Chemistry, *38* (1988) 217–241

Received: June 8, 1987; accepted: November 24, 1987

FLUOROCARBON DERIVATIVES OF NITROGEN. PART 14. STUDIES ON SOME $(CF_3)_2NO$-SUBSTITUTED FLUOROAROMATICS; THERMAL REARRANGEMENT OF 4-[BIS(TRIFLUOROMETHYL)AMINO-OXY]TETRAFLUOROPYRIDINE

RONALD E.BANKS*, M.SAMI FALOU, ROY FIELDS, NURENI O.OLAWORE and ANTHONY E. TIPPING*

Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD (U.K.)

SUMMARY

The sodium salt $(CF_3)_2NO^-Na^+$ (I) [from $(CF_3)_2NOH$ + NaH in Et_2O], is an alternative bis(trifluoromethyl)amino-oxylating agent to the adduct $(CF_3)_2NOH.CsF$ (III). With pentafluoropyridine it affords $4\text{-}X.C_5F_4N$ (II) + $2,4\text{-}X_2.C_5F_3N$ (IV), [X = $(CF_3)_2NO$]. It has been used to obtain a number of new bis(trifluoromethyl)amino-oxy-compounds; i.e. the following conversions have been effected: perfluoro-(4-isopropylpyridine) → $2\text{-}X.C_5F_3N.CF(CF_3)_2\text{-}4$ (V) + $2,6\text{-}X_2.C_5F_2N.CF(CF_3)_2\text{-}4$ (VI); 3-chlorotetrafluoropyridine → $4\text{-}X.C_5F_3N.Cl\text{-}3$ (VII) and $2\text{-}X.C_5F_3N.Cl\text{-}5$ (VIII) (not separated) + $2,4\text{-}X_2.C_5F_2N.Cl\text{-}5$ (IX), 3,5-dichlorotrifluoropyridine → 2- (XI) and $4\text{-}X.C_5F_2N.Cl_2\text{-}3,5$ (X) (not separated) + $2,4\text{-}X_2.C_5FN.Cl_2\text{-}3,5$ (XII); and perfluorotoluene → $4\text{-}X.C_6F_4.CF_3\text{-}1$ (XIII). Hexafluorobenzene resisted attack by $(CF_3)_2NONa$ under the conditions used with these aromatic substrates (ca 20 °C). Static pyrolysis (125 °C) of 4-[bis(trifluoromethyl)amino-oxy]tetrafluoropyridine (II) gave a mixture of 6-[bis(trifluoromethyl)amino]tetrafluoro-4-azacyclohexa-2, 4-dienone (XV) and 4-[bis(trifluoromethyl)amino]tetrafluoro-4--azacyclohexa-2,5-dienone (XVI). The ^{13}C chemical shifts, assigned by analysis of ^{19}F-coupled and ^{19}F broad-band decoupled ^{13}C n.m.r. spectra,

*To whom enquiries should be addressed.

0022-1139/88/$3.50

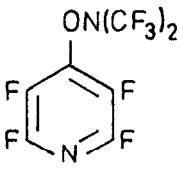
are in accord with a +M effect similar to that of fluorine for a $(CF_3)_2NO$- substituent in the 2-and 4- positions of a polyfluoropyridine, and a slightly smaller -I effect; the steric effect of $(CF_3)_2NO$ on the shifts is less than that of chlorine. In contrast, a ring carbon carrying a $(CF_3)_2CF$- substituent is markedly shielded compared with one carrying fluorine, presumably by a steric effect.

INTRODUCTION

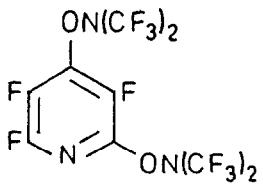
Only three previous reports mention the synthesis of aromatic bis-(trifluoromethyl)amino-oxy derivatives via S_NAr reactions between halogeno-benzenes or -pyridines and sodium bis(trifluoromethyl)amino-oxide, $(CF_3)_2NO^-Na^+$ (I) [1-3], and only two of the conversions involved fluorine as the nucleofugal entity, namely 2-fluoropyridine ⟶ 2-$(CF_3)_2NO.C_5H_4N$ [2] and pentafluoropyridine ⟶ 4-$(CF_3)_2NO.C_5F_4N$ (II) [3]. The need to synthesise the product of the latter conversion for pyrolysis studies provided an opportunity to extend the reaction to other polyfluoroaromatic substrates. Our interest in the thermal decomposition of 4-[bis(trifluoromethyl)amino-oxy]tetrafluoropyridine (II) stemmed from the observation [2] that at 130 °C 2-[bis(trifluoromethyl)amino-oxy]-3-nitropyridine rearranges to 6-[bis(trifluoromethyl)amino]-2-nitro-6-azacyclohexa-2,4-dienone.

RESULTS AND DISCUSSION

Synthesis of $(CF_3)_2NO$-Substituted Compounds



(II)



(IV)

4-[Bis(trifluoromethyl)amino-oxy]tetrafluoropyridine (II) has been prepared previously in 28 or 84% yield, respectively, by treating pentafluoropyridine with the salt $(CF_3)_2NO^-Na^+$ (I) [from $(CF_3)_2NOH$ + NaOH] [3] or with the adduct (III) NN-bistrifluoromethylhydroxylamine forms with anhydrous caesium fluoride [4]. Full details of only the latter work have been published [4]; indeed, knowledge of the synthesis of the pyridine derivative (II) via the sodium salt (I) is restricted to a 'one-shot' reaction carried out as part of a general survey of nucleophilic routes to a variety of $(CF_3)_2NO$-derivatives, as distinct from radical routes involving bistrifluoromethyl nitroxide. Reinvestigation of the action of each nucleophilic reagent on pentafluoropyridine has now shown quite clearly that the sodium salt (I) is far more effective in displacing nuclear fluorine from pentafluoropyridine than is the $(CF_3)_2NOH$-CsF adduct (III) (see Table 1). Note that when a 50% excess of $(CF_3)_2NO^-Na^+$ was employed (experiment 6), considerable disubstitution of the fluoroaromatic substrate was achieved; clearly it ought to be possible to obtain an excellent yield of 2,4-bis[bis(trifluoromethyl)amino-oxy]trifluoropyridine (IV) by using an appropriate reactant ratio.

In addition to giving higher conversion yields at lower temperatures when attacking pentafluoropyridine than does the $(CF_3)_2NOH$-CsF adduct, the sodium salt $(CF_3)_2NO^-Na^+$ is no more troublesome to prepare than the adduct: one simply condenses the highly toxic hydroxylamine (b.p. 32.5 °C) into an evacuated, cooled (-196 °C) Pyrex Rotaflo tube containing sodium hydride and anhydrous diethyl ether; hydrogen released as the tube is warmed to room temperature is pumped away.

Further examples of the use of this technique to effect displacement of nuclear fluorine from highly-activated fluoroaromatics, namely perfluoro-(4-isopropylpyridine), 3-chlorotetrafluoro- and 3,5-dichlorotrifluoro-pyridine, and octafluorotoluene, are displayed in Table 2.Of the new compounds [(V)-(XIV)] thus produced, (V), (VI), (IX), (XII) and (XIII) were isolated in a pure state; products (VII) and (VIII), like (X) and (XI), could not be separated chromatographically (GLC). Structural assignments rest on the results of n.m.r. analyses: ^{19}F spectral data are presented in Table 3, together with those of relevant model compounds; ^{13}C measurements will be discussed later.

TABLE 1

Reaction of pentafluoropyridine with $(CF_3)_2NOH$-CsF(III) and $(CF_3)_2NO^-Na^+$(I)

Expt.	Mol.ratio C_5F_5N: $(CF_3)_2NOH$ used for (III)* or (I)	Conditions Temp. (°C)	Conditions Time (h)	Solvent	C_5F_5N recovered (%)	Products	(%)
1	1:1.0	50	24	None	43	(II)	84
2	1:2.3	44	240	None	43	(II)	99
3	1:1.02	50	96	None	36	(II)	100
4	1:1.0	ca. 20	96	THF		(II)	28+
5	1:1.0	ca. 20	72	Et_2O	24	(II)	99
6	1:1.5	ca. 20	192	Et_2O	6.5	(II)	78
						(IV)	22

*Adduct composition ca.$[(CF_3)_2NOH]_2CsF$

+Isolated yield.

The orientations of the S_NAr reactions observed in this study do not conflict with expectations based on the outcome of numerous reactions of the same type [12,13], theories for which have long formed part of the methodology of fluoroaromatic synthesis [14]. Thus initial attack by $(CF_3)_2NO^-$ occurred preferentially at the 4-position in pentafluoropyridine [⟶(II)] and in octafluorotoluene [⟶(XIII)]; subsequent attack on the primary products by the excess of $(CF_3)_2NO^-Na^+$ resulted in substitution of fluorine adjacent to ring nitrogen [⟶(IV)] or the trifluoromethyl group [⟶(XIV)], as theory predicts.

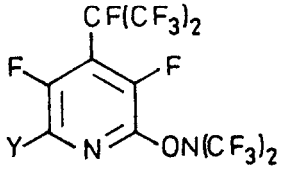
2-Substitution in perfluoro-(4-isopropylpyridine) [⟶(V)] also conformed with expectation. Assuming no intervention of a kinetic vs. thermodynamic control phenomenon analogous to that found with attack of perfluoroisopropyl anion on perfluoro-(2,4-di-isopropylpyridine)[15], formation of the minor product (VI) in the reaction involving perfluoro-(4-isopropylpyridine) indicates that inductive (-I) stabilization of the para-quinonoid canonical form of the σ-complex presumed to be involved in 5-substitution in (VI) is reduced by a $+I_{-\pi}$ effect (see Scheme 1). Clearly steric effects would also

TABLE 2

Reaction of $(CF_3)_2NONa$(I) with polyfluoropyridines and with octafluorotoluene

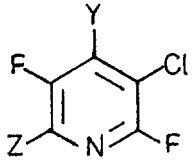
Pyridine or Arene	Molar ratio of Pyridine or Arene: (I)	Time* (h)	Recovered Pyridine or Arene (%)	Products	(%)
$4\text{-}(CF_3)_2CF.C_5F_4N$	1:1:2	72	12	(V)	96
				(VI)	3
$3\text{-}Cl.C_5F_4N$	1:1.1	72	23	(VII)	27
				(VIII)	40
				(IX)	29
$3,5\text{-}Cl_2.C_5F_3N$	1:1.1	96	58	(X)	23
				(XI)	64
				(XII)	2
$CF_3.C_6F_5$	1:1.1	96	38	(XIII)	98
				(XIV)	1.5

* All reactions were carried out at room temperature in Et_2O.



(V) Y = F

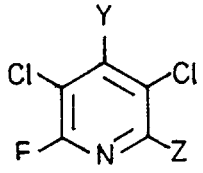
(VI) Y = $ON(CF_3)_2$



(VII) Y = $ON(CF_3)_2$, Z=F

(VIII) Y = F, Z = $ON(CF_3)_2$

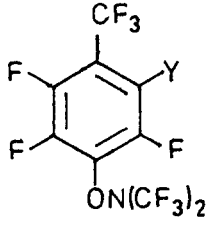
(IX) Y = Z = $ON(CF_3)_2$



(X) Y = $ON(CF_3)_2$, Z = F

(XI) Y = F, Z = $ON(CF_3)_2$

(XII) Y = Z = $ON(CF_3)_2$



(XIII) Y = F

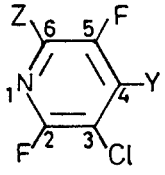
(XIV) Y = $ON(CF_3)_2$

TABLE 3

^{19}F NMR Chemical Shifts

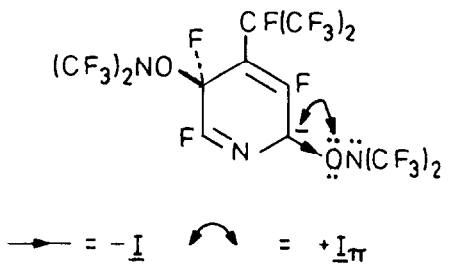
Compound	δ_F(p.p.m.)					Ref.
	2-F	3-F	4-F	5-F	6-F	
C_5F_5N	-11.8	-86.0	-57.5	-86.0	-11.8	[5]
(II)	-12.5	-80.6		-80.6	-12.5	[4]
4-MeO.C_5F_4N	-14.3	-80.1		-80.1	-14.3	[6]
(IV)		-75.9		-78.8	-10.6	
2,4-$(MeO)_2$.C_5F_3N		-83.7		-90.7	-16.9	[7]
4-$(CF_3)_2CF$.C_5F_4N	-11.8	-59.8		-59.8	-11.8	[8]
(V)		-56.3		-59.7	-11.3	
4-$(CF_3)_2CF$.C_5F_3N.OMe-2		-58.4		-70.8	-15.2	[9]
(VI)		-55.6		-55.6		
4-$(CF_3)_2CF$.C_5F_2N.$(OMe)_2$-2,6		-70.4		-70.4		[8]
3-Cl.C_5F_4N	+4.4		-39.9	-88.4	-9.4	[7]
(VII)	+4.2			-80.7	-10.0	
3-Cl.C_5F_3N.NH_2-4	+0.1			-88.8	-17.5	[10]
(VIII)	+4.7*		-39.8	-85.9*		
(IX)	+5.2*			-79.8*		
3,5-Cl_2.C_5F_3N	+8.2		-16.2		+8.2	[10]
(X)	+9.9				+9.9	
3,5-Cl_2.C_5F_2N.OMe-4	+6.8				+6.8	[10]
(XI)			-18.7		+8.1	
3,5-Cl_2.C_5F_2N.NHAr-2[+]			-22.9		+8.9	[11]
(XII)					+10.7	
C_6F_5,CF_3	-64.3	-85.2	-76.7	-85.2	-64.3	
(XIII)	-63.6	-75.9		-75.9	-63.6	
4-NH_2.C_6F_4.CF_3	-70.5	-89.0		-89.0	-70.5	[11]
(XIV)		-67.5		-86.1	-64.1	

*The compounds (VIII) and (IX) are numbered to enable a direct comparison to be made with 3,5-Cl_2.C_5F_3N



[+]Ar = 2,4,6-Me_3.C_6H_2

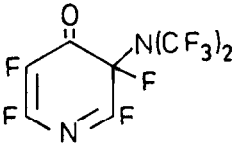
encourage attack at the 6-position [⟶(VI)]. With hindsight, it would have proved useful to undertake a detailed study of the reaction between compound (V) and $(CF_3)_2NO^-Na^+$; and to have determined quantitatively the effect of a $(CF_3)_2NO$ group on the acidity of an adjacent C-H bond.



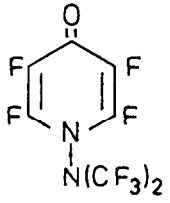
Scheme 1

Steric effects can be invoked to explain the observed orientation (Table 2) of nucleophilic substitution in 3-chlorotetrafluoropyridine and 3,5-dichlorotrifluoropyridine [cf.13]. As expected, the former substrate reacted faster than the latter with $(CF_3)_2NO^-Na^+$, and polysubstitution occurred to a greater extent; thus it was not possible in the single experiment carried out to determine an accurate ratio for 4- vs. 6-substitution since the bis[bistrifluoromethylamino-oxy]-compound (IX) could have arisen either via monosubstituted compound (VII) or (VIII).

Pyrolysis Studies



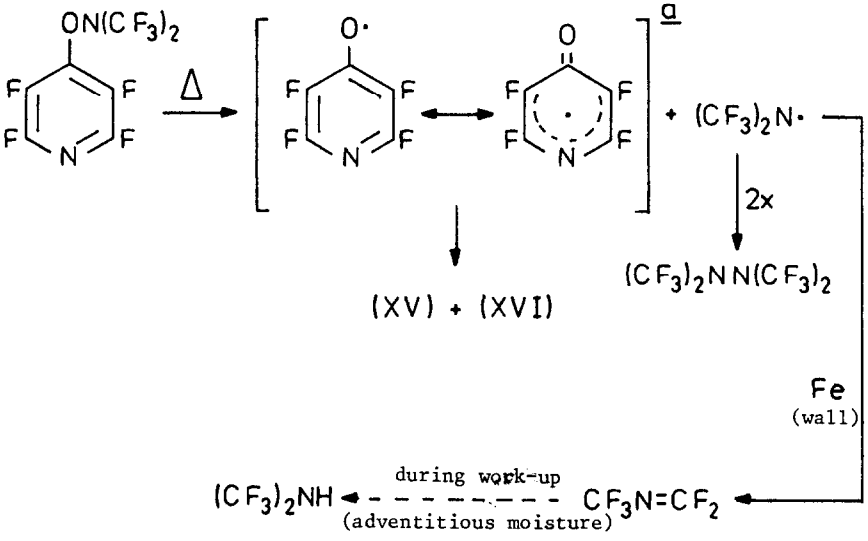
(XV)



(XVI)

Following a series of pilot runs to ascertain the 'best' conditions (these included flow pyrolyses) [16], 4-[bis(trifluoromethyl)amino-oxy]-tetrafluoropyridine (II) was heated under anaerobic conditions in a stain-

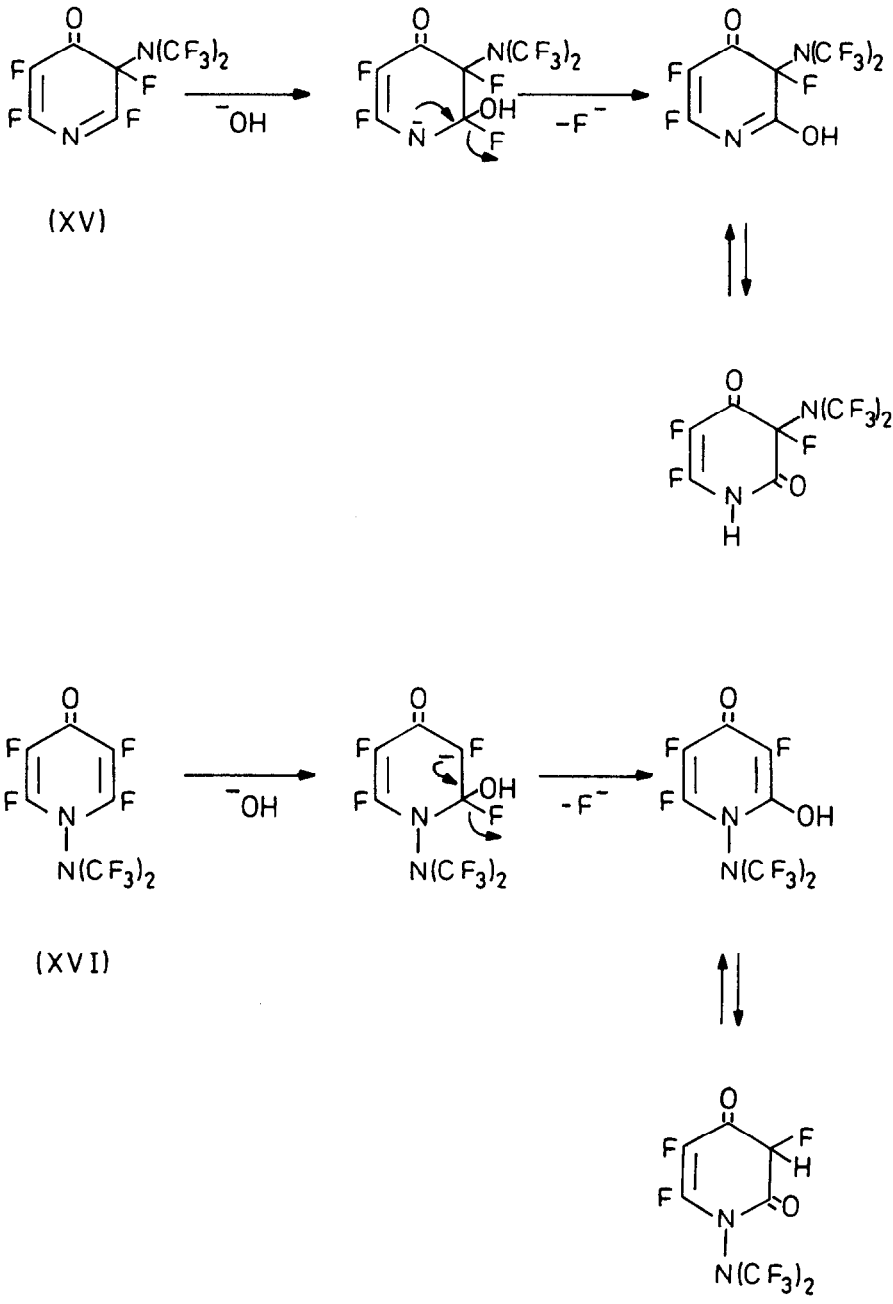
less steel vessel at 125 °C for 96 hours. Almost quantitative (94%) conversion occurred to a mixture of bis(trifluoromethyl)amine, tetrakis-(trifluoromethyl)hydrazine (trace), 6-[bis(trifluoromethyl)amino]tetrafluoro-4- azacyclohexa-2,4-dienone (XV), 4-[bis(trifluoromethyl)amino]-tetrafluoro-4-azacyclohexa-2,5-dienone (XVI),and two minor unidentified compounds. The two major products (XV) and (XVI) (72% yield; ratio 2:3), which are considered to be formed as shown in Scheme 2, could not be separated chromatographically,so their identification rests on ^{19}F n.m.r. analysis. In an effort to destroy preferentially the imidoyl fluoride (XV), an ethereal solution of the mixture was treated with aqueous sodium hydroxide. Both isomers were attacked but only (XV) was completely destroyed, so sufficient of compound (XVI) for ^{19}F n.m.r. analysis was subsequently recovered. Plausible mechanisms for the initial stages of the reactions are written in Scheme 3; presumably these steps are followed by ring-opening events which lead to complete breakdown.



a

According to mass spectrometric analyses [peaks observed at m/z 332 ($C_{10}F_8N_2O_2^{+\cdot}$) and 636 ($C_{14}F_{20}N_4O_2^{+\cdot}$)], the two minor unidentified higher-boiling products may have been a dimer of the tetrafluoro-4-pyridinyloxy radical and that dimer + two $(CF_3)_2N$ radicals, respectively.

Scheme 2



(XV)

(XVI)

Scheme 3

^{13}C NMR Spectra

(a) Assignments

The ^{13}C NMR spectra, obtained both at 20 MHz with broad-band ^{19}F decoupling and at 75 MHz as fully coupled spectra, are summarised in Tables 4 and 5.

TABLE 4

^{13}C NMR chemical shifts[a]

Compound	δ_C (p.p.m.) C-2	C-3	C-4	C-5	C-6	Others
C_5F_5N[b]	144.8	134.3	150.3	134.3	144.8	
(II)	144.2	134.2	145.4	134.2	144.2	120.4(CF_3)$_2$NO
(IV)	143.4	134.4	144.9	134.3	144.9	120.3 2-(CF_3)$_2$NO
						120.5 4-(CF_3)$_2$NO
4-(CF_3)$_2$CF.C_5F_4N (XVII)	144.8	140.4	119.3	140.4	144.8	119.8 ($\underline{C}F_3$)$_2$CF
						92.0 (CF_3)$_2\underline{C}F$
(V)	144.2	140.3	118.8	140.3	145.4	120.3 (CF_3)$_2$NO
						119.8 ($\underline{C}F_3$)$_2$CF
						92.1 (CF_3)$_2\underline{C}F$
3-Cl.C_5F_4N[b]	152.3	105.2	157.7	134.4	148.2	
(VII)	151.4	104.7	152.6	134.6	148.8	120.5 (CF_3)$_2$NO
(VIII)	151.8	103.6	156.1	133.4	147.1	120.3 (CF_3)$_2$NO
(IX)	151.9	104.5	152.0	134.5	148.0	120.3 6-(CF_3)$_2$NO
						120.5 4-(CF_3)$_2$NO

[a] Positive values to low field (high frequency) of TMS.

[b] From Ref.[17].

TABLE 5

^{13}C - ^{19}F coupling constants[a]

(a) Ring carbons and fluorines

Coupling		Compound						
		(II)	(IV)	(XVII)	(V)	(VII)	(VIII)	(IX)
^1J	C-2F	244.8	-	248.4	-	243.3	243.0	242.9
	C-3F	(264)[b,c]	267.4	271.5	271.0	-	-	-
	C-4F	-	-	-	-	-	265.6	-
	C-5F	(264)[b,c]	266.7	271.5	271.0	266.4	264.9	268.0
	C-6F	244.8	243.7	248.4	247.0	246.3	-	-
^2J	C-2 F-3	15.0	12.1	17.6	14.7	-	-	-
	C-3 F-2	-[c]	-	32.1	-	38.3	39.1	38.9
	C-3 F-4	-	-	-	-	-	17.7	-
	C-4 F-3	9.3	8.7	11.1	10.9	-	-	-
	C-4 F-5	9.3	8.7	11.1	10.9	4.9	11.6	5.8
	C-5 F-4	-	-	-	-	-	14.7	-
	C-5 F-6	-[c]	31.9	32.1	-	30.5	-	-
	C-6 F-5	15.0	14.6	17.6	17.8	15.7	14.8	14.2

^3J: (II) C-2 F-6, 15.0; C-4 F-2(6), 4.5: (IV) C-2 F-6,12.1;C-3 F-5,2.6 C-4 F-6 4.8; C-5 F-3,2.3: (XVII) C-2 F-6, 13.2:(V) C-2 F-6,10.7: (VII) C-2 F-6 14.7; C-3 F-5,3.0; C-4 F-2,4.9; C-4 F-6,4.9; C-6 F-2, 15.7: (VIII) C-2 F-4,4.9; C-3 F-5, 2.5; C-4 F-2,5.5; C-6 F-2, 9.7; C-6 F-4,5.3:(IX) C-3 F-5,2.7; C-4 F-2,4.4; C-6 F-2, 12.4 Hz

^4J: (II) C-2 F-5,3.6: (IV) C-2 F-5,3.9; C-3 F-6,6.9; C-6 F-3, 3.8:(XVII) C-2 F-5,4.1: (V) C-2 F-5, 3.7; C-6 F-3, 3.8: (VII) C-2 F-5,3.4; C-3 F-6,7.2; C-5 F-2, 7.6: (VIII) C-2 F-5, 3.7; C-5 F-2,7.3: (IX) C-2 F-5,3.6; C-5 F-2,7.2 Hz.

(continued)

TABLE 5 (cont.)

(b) Other couplings

Coupling	Compound						
	(II)	(IV)	(XVII)	(V)	(VII)	(VIII)	(IX)
$^1J(CF_3)$	273.7	271.0[d]	287.8[f]	287.1[h]	274.1	271.6	268[j]
		272.6[e]		271.0[d]			274[e]
$^1J(CF)$			212.2[g]	212.7[i]			

[a] In Hz. Data-point resolution ± 0.3Hz. [b] Major doublet splitting. [c] Bands show higher order complexity. [d] 2-ON$(CF_3)_2$. [e] 4-ON$(CF_3)_2$. [f] ^2J CF_3CF, 27.2, [g] ^2J $CFCF_3$, 36.6 [h] $^2JCF_3CF$, 27.0. [i] $^2JCFCF_3$, 36.5. [j] 6-ON$(CF_3)_2$.

The assignment of the fluoroalkyl group resonances was straightforward, as these showed the expected quartet for the $(CF_3)_2NO$- groups and quartet of doublets, accompanied by a weaker doublet of septets at lower frequency, for the $(CF_3)_2CF$- groups.

The quaternary ring carbons were assigned initially on the basis of their low intensities. In (V) and in perfluoro-(4-isopropylpyridine) (XVII), C-4 was a 22.4 Hz doublet, due to coupling to the alkyl CF, of ca.11Hz triplets, due to coupling to the adjacent ring fluorines. The largest coupling in the signals due to C-2 or C-6 substituted by $(CF_3)_2NO$ was close to 15Hz, but with the substituent in the 4-position, the largest coupling was less than 10Hz, allowing assignment of these carbons even where the shifts are very close as in (IV).

Assignment of the high frequency band in the spectrum of (XVII) to C-2/C-6 is in accord with the assignments given by Chambers et al. [17] for pentafluoro- and 4-chlorotetrafluoro-pyridine, and was confirmed by selective irradiation at the F-2/F-6 frequency, which collapsed the band at δ_C = 144.8 to a doublet (8.2Hz), and at the F-3/F-5 frequency, which collapsed the band

at δ_C = 140.4. The C-3/C-5 resonance also shows a large (> 30Hz) doublet splitting from the adjacent fluorine on C-2/C-6; as has previously been noted for the monofluoropyridines [18] and for chlorofluoropyridines [17], this coupling is considerably larger than any of the other two-bond couplings from fluorine to ring carbons.

The remaining assignments are derived from the observed spin-spin couplings from fluorine to carbon and from the chemical shifts of (II), (IV),(V), and (XVII), combined with the substituent chemical shift values reported [17] for replacement of the 3-fluorine in pentafluoropyridine by chlorine.

(b) Substituent chemical shifts (SCS)

SCS values for replacement of fluorine in pentafluoropyridine by the $-ON(CF_3)_2$ group in the 2-(6-) and 4-positions, and by $-CF(CF_3)_2$ in the 4-position are given in Table 6.

TABLE 6

^{13}C substituent chemical shifts

Substituent and Position	SCS at position: (p.p.m.)				
	C-2	C-3	C-4	C-5	C-6
3-Cl[a]	+7.0	-30	+7.0	0	+3.5
4-$ON(CF_3)_2$	-0.6	-0.1	-5.0	-0.1	-0.6
2-$ON(CF_3)_2$	-0.6	+0.2	-0.5	+0.1	+0.7
4-$CF(CF_3)_2$	0	+6.1	-31.0	+6.1	0

[a]From Ref.[17].

Replacement of fluorine at C-2 or C-6 by a $(CF_3)_2NO-$ group has very little effect on the shifts either of the substituted carbon itself, or of any of the remaining ring carbons. The replacement of fluorine at C-4 causes a modest shielding of the ipso carbon, but has very little effect on the other ring carbons.

Inductive withdrawal of electron density by $(CF_3)_2NO$ is thus shown to be somewhat less effective than by F, but mesomeric release is much the same. In contrast, the $(CF_3)_2CF$- group strongly shields the ipso carbon compared with fluorine at C-4. Since inductive withdrawal by the $(CF_3)_2CF$- group is very similar to that of fluorine [19], some other influence, presumably steric, must be involved here. The adjacent ring carbons are moderately deshielded by the 4-$CF(CF_3)_2$ group compared with a 4-fluorine, as expected, since mesomeric release by the fluoroalkyl group is not possible.

The SCS values for 2- and 4- $ON(CF_3)_2$ groups remain the same whether C-3 carries fluorine or chlorine substituents. The steric effect of the $(CF_3)_2NO$- group is thus less than that of chlorine (i.e. the bulky CF_3 groups are sufficiently far from the ring not to interfere with an adjacent substituent), since two adjacent chlorines require the use of a 'correction term' with SCS [17].

The approximately linear relationship between δ_C and δ_F for C-2(6) and for C-3(5) and C-4 noted for perfluoropyridine and for fluorochloropyridines [17] is less successful in the present series of compounds. The fit for C-2(6) is good only where the substituents are all meta to the position under consideration [(II),(IV),(V) and (XVII)], but shows more deviation with chlorine ortho or para [(VII),(VIII),(IX),(XI)]. For C-3(5) and C-4 the scatter is much more pronounced for all the compounds studied here than for the chlorofluoropyridines.

(c) Coupling constants

The ^1JCF values for the ring carbons (Table 5) are smaller in magnitude for C-2 and C-6 (242.9 - 248.6 Hz) than for C-3 and C-5 (264.9 - 271.5 Hz), and ^2JCF is much larger for C-3 F-2 (or C-5 F-6) than for the other carbons, in accord with Lichter and Wasylishen's observations for 2- and 3- fluoropyridine [18]. The value for JC-3 F 2 is larger when C-3 carries a chlorine (38.3 - 39.1 Hz) than when it carries a fluorine (30.5 - 32.1 Hz), also in accord with observations on fluorochloropyridines [17]. ^2JC-4 F-3(5) also varies with the substituents at C-4. In (VIII), with fluorine at C-4, the value is 11.6 Hz, slightly larger than in compounds with $(CF_3)_2CF$- at C-4 (10.9, 11.1 Hz), and with $(CF_3)_2NO$- at C-4, the values are smaller still (4.9

- 9.3 Hz). These contrast with the values of 16 to 19 Hz noted for compounds with Cl at C-4 [17].

As noted previously [18] for 2-fluoropyridine, three-bond coupling via nitrogen (^3JC-6 F-2 or ^3JC-2 F-6) is relatively large, and this is especially so when the carbon itself carries a fluorine (13.2 - 15.7 Hz); as with ^2JC-4 F-3(5), a $(CF_3)_2NO$- group apparently leads to weaker coupling (9.7 - 12.4 Hz). Four-bond couplings (3.4-7.6 Hz) were observed in almost every case possible, but did not show a discernible pattern.

In compounds where the position of substitution was known unambiguously, ^1JCF for the $(CF_3)_2NO$ group as the 2-substituent was slightly smaller in magnitude (271-272 Hz) than for the 4-substituent (273-274 Hz), and so in (IV) and (IX) the signal with the smaller coupling has been assigned to the 2-substituent.

EXPERIMENTAL

Starting Materials

Pentafluoropyridine, 3-chlorotetrafluoropyridine, 3,5-dichlorotrifluoropyridine, octafluorotoluene and hexafluorobenzene were commercial samples whose purity was checked before use. Perfluoro-(4-isopropylpyridine) was prepared (91%) by the reaction of pentafluoropyridine with the carbanion $(CF_3)_2\bar{C}F\ Cs^+$ (formed in situ from hexafluoropropene and anhydrous caesium fluoride) in sulpholane [8,10] and the hydroxylamine $(CF_3)_2NOH$ (39%) was prepared by the standard route from trifluoroacetic anhydride via trifluoronitrosomethane followed by reaction with gaseous ammonia [20].

General Techniques

Reactions were carried out in vacuo either in sealed Rotaflo tubes (ca. 270 cm^3 unless stated otherwise), which were shaken at the appropriate temperature, or in rocked stainless steel autoclaves (ca. 50 cm^3) at elevated temperature.

Volatile reaction products were separated initially by fractional condensation in vacuo, and the fractions are designated in the text by the temperature of the traps in which they condensed. Such fractions were examined by i.r. spectroscopy (Perkin-Elmer 197 Or 357 instruments), and where necessary by g.l.c. [Pye 104 instrument using columns (1.5m, 4mm i.d.) packed with Silicone SE30 oil or Kel-F 10 oil (10% $^{w}/w$) on Chromosorb W or OV-17 (3% $^{w}/w$) on Chromosorb WHP], g.l.c. - i.r. spectroscopy, g.l.c. - mass spectrometry [G.E.C. - A.E.I. MS 902 Spectrometer (electron beam energy 70 eV)] and/or n.m.r. [Perkin-Elmer R32 spectrometer (^{19}F at 84.6 and ^{1}H at 90 MHz) using external CF_3CO_2H and Me_4Si as the respective references; chemical shifts to low field of reference are positive].

Individual components of liquid mixtures were separated by preparative-scale g.l.c. [Perkin-Elmer F21 instrument using columns (3-5 m packed with Silicone SE30 oil (10% $^{w}/w$ on chromosorb W)] and were examined by some or all of the following spectral techniques: i.r., n.m.r. (^{1}H, ^{13}C and ^{19}F) and mass. Solid mixtures were examined by t.l.c. and the individual components were separated by dry-column 'flash' chromatography (5cm × 5cm i.d.) using silica gel (mesh 230).

^{13}C N.m.r. spectra were recorded on a Bruker WP80 spectrometer operating at 20.1 MHz with D_2O as the deuterium lock signal.

Reactions of the NN-Bis(trifluoromethyl)hydroxylamine-Caesium Fluoride Adduct (III)

(a) With pentafluoropyridine

A mixture of pentafluoropyridine (2.14g, 12.66 mmol) and the preformed $(CF_3)_2NOH$-CsF adduct (III) [prepared from $(CF_3)_2NOH$ (2.34g, 13.85 mmol) and CsF (1.02g, 6.71 mmol)] heated in a tube at 67 °C (3d), gave (i) unchanged hydroxylamine (0.55g, 3.25 mmol, 23% recovered) (-78 °C fraction), (ii) unchanged pentafluoropyridine (0.63g, 3.73 mmol, 30% recovered) (-48 °C fraction), (iii) a mixture (1.52g) which was shown [i.r. and g.l.c. (1.5m Kel-F10 at 60 °C)] to consist of unchanged pentafluoropyridine (0.11g, 0.65 mmol, 5% recovered) and 4-[bis(trifluoromethyl)amino-oxy]tetrafluoropyridine (II) (1.41g, 4.43 mmol, 53.5%) (-23 °C fraction), and (iv) compound (II) (1.22g, 3.84 mmol,46.5%) as shown by a comparison of its i.r., ^{19}F n.m.r., and mass spectra with those reported [4] (0 °C fraction).

A second reaction using pentafluoropyridine (1.28g, 7.57 mmol) and the adduct (III) [prepared from $(CF_3)_2NOH$ (2.80g, 17.57 mmol) and CsF (1.07g, 7.04 mmol)] heated at 44 °C (10d), gave (i) unchanged $(CF_3)_2NOH$ (1.49g, 8.82 mmol, 53% recovered), (ii) unchanged pentafluoropyridine (0.55g, 3.25 mmol, 43% recovered), and (iii) compound (II) (1.36g, 4.28 mmol, 99%).

A third reaction using pentafluoropyridine (1.89g, 11.18 mmol) and the adduct (III) [prepared from $(CF_3)_2NOH$ (1.92g, 11.36 mmol) and CsF (0.89g, 5.86 mmol)] heated in a tube (ca. 100 cm^3) at 50 °C (4d), gave (i) unchanged $(CF_3)_2NOH$ (0.32g, 1.89 mmol, 17% recovered), (ii) unchanged pentafluoropyridine (0.68g, 4.03 mmol, 36% recovered), and (iii) compound (II) (2.27g, 7.14 mmol, 100%).

(b) With octafluorotoluene

A mixture of octafluorotoluene (1.58g, 6.69 mmol) and the adduct (III) [prepared from $(CF_3)_2NOH$ (1.18g, 6.98 mmol) and CsF (0.52g, 6.85 mmol)] heated in a tube (ca. 100 cm^3) at 44 °C (6d) gave (i) unchanged $(CF_3)_2NOH$ (0.23g, 1.36 mmol, 19.5% recovered) (-78 °C fraction) and (ii) a mixture (1.72g), which was shown [g.l.c. (2m SE30 at 80 °C) - i.r. and ^{19}F n.m.r.] to consist of unchanged $(CF_3)_2NOH$ (0.40g, 2.34 mmol, 34% recovered), unchanged octafluorotoluene (1.30g, 5.51 mmol, 82.5% recovered) and 4-[bis(trifluoromethyl)amino-oxy]heptafluorotoluene (XIII) (0.32g, 0.83 mmol, 99%) (combined -48 and -23 °C fraction).

Reactions of Sodium Bis(trifluoromethyl)amino-oxyl (I)

(a) With pentafluoropyridine (1:1 molar ratio)

A mixture of pentafluoropyridine (7.21g, 42.66 mmol) and the sodium salt (I) [prepared from $(CF_3)_2NOH$ (7.31g, 43.25 mmol) and NaH (1.02g, 42.50 mmol)] in anhydrous diethyl ether (10 cm^3) maintained at ca 20 °C in a tube, gave (i) a mixture (5.76g) of diethyl ether and unchanged $(CF_3)_2NOH$ (combined -196 and -78 °C fraction), (ii) a mixture (1.18g), which was shown [g.l.c. (1.5m SE30 at 70 °C)] to consist of diethyl ether (0.41g) and unchanged pentafluoropyridine (0.77g, 4.56 mmol, 11% recovered) (-48 °C fraction),

(iii) a mixture (2.54g), which was shown [g.l.c. (1.5m SE30 at 70 °C) - i.r.] to consist of unchanged pentafluoropyridine (0.97g, 5.74 mmol, 13% recovered) and 4-[bis(trifluoromethyl)amino-oxy]tetrafluoropyridine (II) (1.57g, 4.94 mmol, 15%) (-23 °C fraction), and (iv) compound (II) (8.68g, 27.30 mmol, 84%) identified by ^{19}F n.m.r. spectroscopy (0 °C fraction).

(b) With pentafluoropyridine (1.5:1 molar ratio)

A mixture of pentafluoropyridine (4.87g, 28.82 mmol) and the salt (I) [prepared from $(CF_3)_2NOH$ (7.49g, 44.32 mmol) and NaH (1.01g,42.08 mmol)] in ether (8 cm^3) maintained at ca. 20 °C in a tube (8d), gave (i) (combined -196 and 78 °C fractions) a mixture (5.19g) of diethyl ether and unchanged $(CF_3)_2NOH$, (ii) (-48 °C fraction) a mixture of diethyl ether (1.0g) and unchanged pentafluoropyridine (0.25g, 1.48 mmol, 5% recovered) [i.r. and g.l.c. (1.5m SE30 at 70 °C)] and (iii) (combined -23 and 0 °C fractions) a mixture (10.49g) of diethyl ether (1.01g)and unchanged pentafluoropyridine (0.07g, 0.41 mmol, 1% recovered) together with two higher-boiling compounds (A and B) [g.l.c. (1.5m SE30 at 70 °C)] which were separated by preparative g.l.c. (3m SE30 at 80 °C); compound A was identified as 4-[bis(trifluoromethyl)amino-oxy]tetrafluoropyridine (II) (6.70g, 21.07 mmol, 78%) (Found:C, 26.6; F,60.1; N,8.8%; $\underline{M}^{+\cdot}$, 318.Calc. for $C_7F_{10}N_2O$: C, 26.4 ; F, 59.7 ; N, 8.8%;M, 318), b.p. 130 °C (Siwoloboff) {lit.[4], b.p.131 °C (Siwoloboff)} by a comparison of its i.r., ^{19}F n.m.r. and mass spectra with those found previously, and compound B was identified as 2,4-bis[bis(trifluoromethyl)-amino-oxy]trifluoropyridine (IV) (2.71g, 5.80 mmol, 20%) (Found: C,23.4;F,61.5; N, 9.1%, $\underline{M}^{+\cdot}$, 467.$C_9F_{15}N_3O_2$ requires C,23.1; F, 61.0; N, 9.0%;M, 467), b.p. 180 °C with decomposition (Siwoloboff); $\nu_{max.}$ 1635s and 1475s (ring in-plane def.), 1320s, 1260s and 1200s (C-F str.), 970s (C-N str.) and 710s (CF_3 def.) cm^{-1}; δ_F (neat liquid) + 8.4 [s, 6F, 2-$(CF_3)_2NO$], + 8.0 [t, 6F, 4-$(CF_3)_2NO$, $\underline{J}_{3F\text{-}CF_3} \simeq \underline{J}_{5F\text{-}CF_3}$ 3.8 Hz], -10.6 (dd, 1F, 6-F, $\underline{J}_{3F\text{-}6F}$ 27.1 Hz, $\underline{J}_{5F\text{-}6F}$ 20.3 Hz), -75.9 (dsepd, 1F, 3-F, $\underline{J}_{6F\text{-}3F}$ 27.1 Hz, $\underline{J}_{4CF_3\text{ -}3F}$ 3.8 Hz, $\underline{J}_{5F\text{-}3F}$ ca. 2 Hz), and -78.8 (dsepd, 1F, 5-F, $\underline{J}_{6F\text{-}5F}$ 20.3 Hz, $\underline{J}_{4CF_3\text{-}5F}$ 3.8 Hz. $\underline{J}_{3F\text{-}5F}$ ca. 2 Hz) p.p.m; m/z 467 (48.3%, $\underline{M}^{+\cdot}$), 315 {22.9%, $[\underline{M}\text{-}(CF_3)_2N]^+$}, 287 {19.1%, $[\underline{M}\text{-}(CF_3)_2NCO]^+$}, 135 (100%, $C_4F_3NO^+$), 90 (16.9%. $C_3F_2O^+$) and 69 (50.8%, CF_3^+).

(c) With perfluoro-(4-isopropylpyridine)

Perfluoro-(4-isopropylpyridine) (4.78g, 14.98 mmol) was syringed into a tube containing the sodium salt (I) [prepared from $(CF_3)_2NOH$ (3.09g, 18.28 mmol) and NaH (0.47g, 19.58 mmol)] and diethyl ether (10 cm^3) and the tube maintained at ca. 20 °C (3d); this gave (i) (combined -196 and -78°C fractions) a mixture (6.15g) of diethyl ether and unchanged $(CF_3)_2NOH$, (ii) (combined -48 and -23 °C fractions) a mixture of diethyl ether (1.34g) and unchanged perfluoro-(4-isopropylpyridine) (0.36g, 1.13 mmol, 7.5% recovered) [i.r. and g.l.c. (1.5m SE30 at 85 °C)], and (iii) (-10 °C fraction) a mixture (6.52g) of diethyl ether (0.13g), unchanged perfluoro-(4-isopropylpyridine) (0.20g, 0.63 mmol, 4% recovered) and two higher-boiling components (C and D) in the ratio 2:3:91:4 [g.l.c. (1.5m SE30 at 85 °C)]. Components C and D were separated by preparative-scale g.l.c. (3m SE30 at 85 °C); component C was identified as perfluoro-[2-(dimethylamino-oxy)-4-isopropylpyridine] (V) (5.93g, 12.67 mmol, 96%) (Found: C, 25.3; F, 65.4; N, 6.3%, $\underline{M}^+$, 468. $C_{10}F_{16}N_2O$ requires C, 25.6; F, 65.0; N, 6.0%; $\underline{M}$, 468), b.p. 170 °C with decomposition (Siwoloboff), $\nu_{max.}$ 1638m and 1470s (ring in plane def.), 1310s, 1290s, 1268s, 1240s and 1220s (C-F str.), 988s and 964s (C-N str.), 972s [C-N str. in $(CF_3)_2NO$], and 758s, 745s and 712s (CF_3 def.) cm^{-1}, δ_F (neat liquid) + 8.4 [s, 6F, 2-$(CF_3)_2NO$], +1.1 [td, 6F,4-$(\underline{CF}_3)_2CF$, $\underline{J}_{3F-CF_3}$ $\underline{J}_{5F-CF_3}$ 13.1 Hz, $\underline{J}_{F-CF_3}$(vic) 5.6 Hz],-11.3 (mult, 1F, 6-F), -56.3 (mult, 1F, 3-F), -59.7 (mult, 1F, 5-F), and 102.6 [tmult, 1F, $\underline{CF}(CF_3)_2$, $\underline{J}_{3F-CF} \simeq \underline{J}_{5F-CF}$ 46 Hz] p.p.m.;$\underline{m/z}$ 468 (1.0%, $\underline{M}^+$), 316 {5.7% [$\underline{M}$ - $(CF_3)_2N]^+$}, 219 (6.4%, $C_6F_7N^+$), 216 (9.3%, $C_6F_6NO^+$), 197 (26.0%, $C_6F_5NO^+$), 114 (10.9%, $C_2F_4N^+$) and 69 (100%, CF_3^+), and component D, a low-melting solid, was identified as perfluoro - [2, 6 - bis (dimethylamino-oxy) -4- isopropylpyridine] (VI) (0.26g, 0.42 mmol, 3%), $\nu_{max.}$ 1620m and 1440s (ring in-plane def.), 1290s, 1250s, 1230s, and 1200s (C-F str.), 980s and 960s (C-N str.) and 730w, 710w and 700s (CF_3 def.) cm^{-1}, δ_F (30% solution in Et_2O) + 9.3 [s, 12F, 2- and 6-$(CF_3)_2NO$], +2.0 [td, 3F, $(\underline{CF}_3)_2CF$, $\underline{J}_{3F-CF_3} = J_{5F-CF_3}$ 12.2Hz, $\underline{J}_{F-CF_3}$(vic) 5.6 Hz], -55.6 (mult, 2F, 3-F and 5-F), and -102.7 [tmult, 1F, $C\underline{F}(CF_3)_2$ $\underline{J}_{3F-CF} = \underline{J}_{5F-CF}$ 41.4 Hz] p.p.m.

(d) With 3 - chlorotetrafluoropyridine

3 - Chlorotetrafluoropyridine (5.43g, 29.27 mmol) was syringed into a tube containing the sodium salt [prepared from $(CF_3)_2NOH$ (5.75g, 34.02

mmol) and NaH (0.79g, 32.92 mmol)] and diethyl ether ($7cm^3$) and the tube maintained at ca. 20 °C (3d). The volatile products were (i) (combined -196, -78 and -48 °C fractions) a mixture (6.49g) of diethyl ether and a small amount of unchanged $(CF_3)_2NOH$ and (ii) (combined - 23 and -10 °C fractions) higher-boiling material (7.47g).

The residue in the tube was extracted with diethyl ether ($10cm^3$) and the ether was evaporated to give a liquid (2.31g) which was combined with the -23 and -10 °C fractions (total 9.88g). This material was shown by g.l.c. (2m SE30 at 70 °C) to consist of diethyl ether (0.36g), unchanged 3-chlorotetrafluoropyridine (1.27g, 6.85 mmol, 23% recovered) and two higher-boiling components (E and F) present in the ratio 3.5:12.5:52:32. Components E and F were separated by preparative-scale g.l.c. (4m SE30 at 85 °C); component E was identified as a mixture (5.02g, 15.01 mmol, 67%) (Found: C,24.5; F,52.9; Cl, 10.4%; $\underline{M}^+$, 334. Calc. for $C_7F_9N_2OCl$: C,25.1; F,51.1; Cl, 10.6%; M, 334.5), b.p. 150 °C with decomposition (Siwoloboff) of 4-[bis(trifluoromethyl)amino-oxy]-3-chlorotrifluoropyridine (VII) (2.16g, 6.44 mmol, 28%) and 2-[bis(trifluoromethyl)amino-oxy]-5-chlorotrifluoropyridine (VIII) (2.86g, 8.56 mmol, 38%) $\nu_{max.}$ 1620s, 1605s, 1490s, and 1470s (ring in-plane def.), 1320s, 1260s, 1240s, and 1210s (C-F str.), 970s (C-N str.) and 710s (CF_3 def.) cm^{-1}, δ_F (neat liquid) for minor compound (VIII) + 8.5 [d, 4.5F, 4-$(CF_3)_2NO$, J_{5F-CF_3} 6.5 Hz], + 4.2 (dd, 0.75F, 2-F, J_{5F-2F} 27.3 Hz, J_{6F-2F} 14.1 Hz),(-10.0 dd, 0.75F, 6-F, J_{5F-6F} 19.2 Hz, J_{2F-6F} 14.1 Hz) and-80.7 (mult, 0.75F, 5-F) p.p.m. and for major compound (IX) + 8.7 [s, 6F, 2-$(CF_3)_2NO$], + 4.7 (dd, 1F, 6-F, J_{3F-6F} 25.4 Hz, J_{4F-6F} 11.3 Hz), -39.8 (dd, 1F, 4-F, J_{3F-4F} 16.9 Hz, J_{6F-4F} 11.3 Hz) and -85.9 (dd, 1F, 3-F, J_{6F-3F} 25.4 Hz, J_{4F-3F} 16.9 Hz) p.p.m., m/z 334/336 (10.5%, $\underline{M}^+$), 182/184 {15.7%, $[\underline{M}-(CF_3)_2N]^+$},154/156 {29.4%$[\underline{M}-(CF_3)_2NCO]^+$} and 69 (100%,$CF_3^+$), and component F was identified as 2,4-bis[bis(trifluoromethyl)amino-oxy]-5-chlorodifluoropyridine (IX) (3.13g, 6.48 mmol, 29%) (Found:C,22.8; N,9.1; Cl, 7.3%; $\underline{M}^+$, 483. $C_9F_{14}N_3O_2Cl$ requires C,22.3; N,8.7; Cl, 7.3%; M, 483.5), $\nu_{max.}$ 1610s and 1472s (ring in-plane def.), 1310s, 1250s, and 1200s (C-F str.), 972s (C-N str.) and 710s (CF_3 def.) cm^{-1}, δ_F (neat liquid) + 8.7 [s, 6F, 2-$(CF_3)_2NO$], + 8.2 [d, 6F, 4-$(CF_3)_2NO$, J_{3F-CF_3} 6.6 Hz], + 5.2 (d, 1F, 6-F, J_{3F-6F} 26.7 Hz), and -79.8 (dsep, 1F, 3-F, J_{6F-3F} 26.7 Hz, J_{CF_3-3F} 6.6 Hz) p.p.m., m/z 483/485 (24%, $\underline{M}^+$), 331/333 {18.0%$[\underline{M}-(CF_3)_2N]^+$}, 153 (28.4%, $C_4F_2NO^{37}Cl^+$), 151 (86.1%, $C_4F_2NO^{35}Cl^+$), 116 (26%, $C_4F_2NO^+$), 69 (100%, CF_3^+) and 31 (32.5%, CF^+).

(e) With 3,5-dichlorotrifluoropyridine

The dichloro-compound (4.67g, 23.12 mmol) was syringed into a tube containing the sodium salt [prepared from $(CF_3)_2NOH$ (4.49g, 26.57 mmol) and NaH (0.61g, 25.42 mmol)] in anhydrous diethyl ether (10 cm^3) and the tube maintained at ca. 20 °C(4d). The volatile products were (i) (combined -196 and -78 °C fractions) a mixture (1.84g) of diethyl ether and a small amount of unchanged $(CF_3)_2NOH$, (ii) (combined -48 and -23 °C fractions) a mixture (7.58g) which was shown [g.l.c. (2m SE30 at 80 °C)] to consist of diethyl ether (5.61g), unchanged 3,5-dichlorotrifluoropyridine (1.52g, 7.52 mmol, 32.5% recovered) and a component (G) (0.45g), and (iii) (-10 °C fraction) a liquid (3.17g).

The solid residue in the tube was extracted with diethyl ether (10 cm^3) and the ether was evaporated to afford a liquid (0.74g) which was combined with the -10 °C fraction; g.l.c. examination (2m SE30 at 80 °C) of this combined material (3.91g) showed that it consisted of diethyl ether (0.04g), unchanged 3,5-dichlorotrifluoropyridine (1.21g, 5.99 mmol, 26% recovered) and two higher-boiling components G and H) present in the ratio 1:31:64:4. Components G and H were separated by preparative-scale g.l.c. (3m SE30 at 90 °C); component G was identified as a mixture (2.95g, 8.40 mmol, 87%) (Found:C, 23.6; F, 43.8, N, 8.3%; $M^{+\cdot}$, 350. Calc. for $C_7F_8N_2OCl_2$: C,23.9; F, 43.3; N, 8.0%; M, 351) of 2-[bis(trifluoromethyl)amino-oxy]-3, 5-dichlorodifluoropyridine (XI) (2.20g, 6.23 mmol, 65%), and 4-[bis(trifluoromethyl)amino-oxy]-3,5-dichlorodifluoropyridine (X) (0.76g, 2.17 mmol, 22%) in the ratio 2.8:1.0, $\nu_{max.}$ 1610s, 1590s, 1450s, and 1430s (ring in plane def.), 1310s, 1260s, 1242s, and 1205s (C-F str.), 974 (C-N str.), and 710 (CF_3 def.) cm^{-1}, δ_F (neat liquid) for major component (XI) + 9.2 [s,6F, 2-$(CF_3)_2NO$], + 8.1 (d, 1F, 6-F, J_{4F-6F} 15.1 Hz) and -18.7 (d, 1F, 4-F, J_{6F-4F} 15.1 Hz) p.p.m. and for minor component (X) + 9.9 (s, 0.72F, 2- and 6-F) and + 9.2 [s,2.2F, 4-$(CF_3)_2NO$] p.p.m., m/z 350/352/354 (47.8%, $M^{+\cdot}$), 281/283/285 [43.5%, $(M-CF_3)^+$], and 170/172/174 {11.1%, $[M-(CF_3)_2NCO]^+$} together with peaks due to the formation of the hydrazine $(CF_3)_2NN(CF_3)_2$ in the mass spectrometer at m/z 304 (11.2%, $M^{+\cdot}$), 285 [28.4% $(M-F)^+$}, 216 [27.4%, $(M-CF_4)^+$], 197 (100%, $C_3F_7N_2^+$), and 69 (98.8%, CF_3^+) and component H was identified as 2,4-bis[bis(trifluoromethyl)amino-oxy]-3,5-dichloro-

fluoropyridine (XII) (0.16g, 0.32 mmol, 3%), δ_F (neat liquid) + 10.7 (s,1F, 6-F), + 10.1 [s,6F, 2-$(CF_3)_2NO$] and +9.3 [s, 6F, 4-$(CF_3)_2NO$] p.p.m., m/z 464/466 [2.7%, $(\underline{M}\text{-}Cl)^+$], 347/349 {1.5% $[\underline{M}\text{-}(CF_3)_2N]^+$}, 272/274 (3.3%, $C_5F_6N_2Cl_2^+$), 200/202 (1.8%, $C_4F_2N_2OCl_2^+$), and 69 (100%, CF_3^+) together with strong peaks due to formation of the hydrazine $(CF_3)_2NN(CF_3)_2$ in the mass spectrometer.

(f) With octafluorotoluene

A mixture of octafluorotoluene (3.38g, 14.32 mmol) and the sodium salt [prepared from $(CF_3)_2NOH$ (3.70g, 21.89 mmol) and NaH (0.46g, 19.17 mmol)] in anhydrous diethyl ether (8 cm^3) maintained in a tube at ca. 20 °C (4d), gave (i) (combined -196 and -78 °C fractions) a mixture (4.97g) of diethyl ether and unchanged $(CF_3)_2NOH$, (ii) (combined -48 and - 23 °C fractions) a liquid (2.92g) which was shown [g.l.c. (2m SE30 at 80 °C)] to consist of diethyl ether (1.75g), unchanged octafluorotoluene (0.82g, 3.47 mmol, 24% recovered) and a higher-boiling component (J) (0.35g) in the ratio 60:28:12, and (iii) (-10 °C fraction) a liquid (3.78g) which was shown [g.l.c.(1.5m SE30 at 80 °C)] to consist of diethyl ether (0.23g), unchanged octafluorotoluene (0.45g, 1.91 mmol, 13% recovered) and two higher-boiling components (J) (3.02g) and (K) (0.08g). Component J was separated by g.l.c. (3m SE30 at 90 °C) and was identified as 4-[bis(trifluoromethyl)amino-oxy]heptafluorotoluene (XIII) (3.37g, 8.75 mmol, 98%) (Found:C,27.8; F,64.3; N, 3.5%; $\underline{M}^+$, 385. $C_9F_{13}NO$ requires C,28.0; F,64.2; N,3.6%; M, 385), b.p. 140 °C with decomposition (Siwoloboff), $\nu_{max.}$ 1640m and 1500s (ring C=C str.), 1340s, 1318s, 1300s, 1260s, 1240s, 1230s, and 1210s (C-F str.), 960vs (C-N str.) and 710s (CF_3 def.) cm^{-1}, δ_F (neat liquid) + 19.8 (t, 3F, CF_3, $J_{2F,6F\text{-}CF_3}$ 22.6 Hz), + 8.4 [t, 6F, 4-$(CF_3)_2NO$, $J_{3F,5F\text{-}CF_3}$ 5.6 Hz), -63.6 (mult, 2F, 2- and 6-F), and -75.9 (mult, 2F, 3- and 5-F) p.p.m., m/z 385 (4.2%, $\underline{M}^+$), 285 (4.2%, $C_7F_9NO^+$), 216 (6.8%, $C_6F_6NO^+$), 197 (18.2%, $C_6F_5NO^+$), 114 (5.7%, $C_2F_4N^+$), 85 (9.6%, CF_3O^+), and 69 (100%, CF_3^+). Attempted separation of component K by g.l.c. (as above) did not give a pure sample, but it was tentatively identified as 2,4-bis[bis(trifluoromethyl)amino-oxy]hexafluorotoluene (XIV) (0.08g, 0.15 mmol, 1.5%) by a consideration of the ^{19}F n.m.r. and mass spectra of a mixture of compound (XIII) and component K (ca. 90:10), δ_F (neat liquid) + 19.6 (CF_3 in both compounds), + 9.9 [s,6F 2-$(CF_3)_2NO$],+8.4 [4-$(CF_3)_2NO$ in both compounds],-64.1 [mult,6-F in (XIV) and 2-

and 6-F in (XIII)], -67.5 (mult, 1F, 3-F), and - 86.1 (mult, 1F, 5-F) p.p.m., m/e 515 [30.1%, $(M-F)^+$], 366 {1.0%, $[M-(CF_3)_2NO]^+$}, 214 {2.2%, $[M-(CF_3)_2NON(CF_3)_2]^+$}, 186 {$[M-(CF_3)_2NCOON(CF_3)_2]^+$}, and 69 (78.2%, CF_3^+).

(g) With hexafluorobenzene

A mixture of hexafluorobenzene (5.65g, 30.38 mmol) and the sodium salt [prepared from $(CF_3)_2NOH$ (5.10g, 30.18 mmol) and NaH (0.68g, 28.33 mmol)] in anhydrous diethyl ether (ca. $10cm^3$), kept in a tube at ca. 20 °C (3d), gave (i) (-196 °C fraction) a mixture (9.08g) of diethyl ether and unchanged $(CF_3)_2NOH$, and (ii) (-78 °C fraction) a mixture (6.99g) shown by g.l.c. (1.5m SE30 at 70 °C) to consist of diethyl ether (0.63g), a diethyl ether-hydroxylamine complex (1.05g) and unchanged hexafluorobenzene (5.31g, 28.70 mmol, 94.5% recovered). The solid residue in the tube was extracted with ether (ca. $5cm^3$) and the ether was evaporated to afford a crystalline diethyl ether - hydroxylamine complex (0.54g) as shown by i.r. and ^{19}F n.m.r. spectroscopy.

A second reaction carried out at ca. 20 °C (60d) gave comparable results.

Pyrolysis of 4-[Bis(trifluoromethyl)amino-oxy]tetrafluoropyridine (II)

The pyridine derivative (4.67g, 14.68 mmol) was syringed under nitrogen into an evacuated autoclave [predried under dynamic vacuum using a gentle Bunsen flame (1h)] and the autoclave heated at 125 °C (4d). The volatile reaction products (0.21g, 1.23 mmol; M, 170.1) were shown (i.r. and ^{19}F n.m.r.) to consist of NN-bis(trifluoromethyl)amine (0.16g, 1.07g, 8%) and tetrakis(trifluoromethyl)hydrazine (0.05g, 0.16 mmol, 1%). The liquid remaining in the autoclave was washed out with diethyl ether (3 x 30 cm^3) and the ether removed by evaporation to give a yellow oil which was shown [g.l.c.(2m SE30 at 150 °C)] to consist of diethyl ether (0.08g), unreacted starting material (II) (0.28g, 0.88 mmol, 6% recovered) and three higher-boiling components (L) (0.44g), (M) (3.17g) and (N) (0.04g) present in the ratio 2:7:11:79:1.

Component M was separated by preparative-scale g.l.c. (5 m SE30 at 160 °C) and was identified as a mixture (3.17g, 9.97 mmol, 72%) (Found : C, 26.3; F, 59.7; N, 9.0%; $\underline{M}^+$, 318. Calc. for $C_7F_{10}N_2O$: C, 26.4; F, 59.7; N, 8.8%; $\underline{M}$, 318) of 6-[bis(trifluoromethyl)amino]tetrafluoro-4-azacyclohexa-2, 4-dienone (XV) (1.27g, 3.99 mmol, 29%) and 4-[bis(trifluoromethyl)amino]-tetrafluoro-4-azacyclohexa-2,5-dienone (XVI) (1.90g, 5.97 mmol, 43%), $\nu_{max.}$ 1795s (C=O str.), 1738s (C=N str.), 1615s (CF=CF str.), 1480s, 1330s, 1270s, 1240s and 1200s (C-F str.), 980s (C-N str.), and 720s and 710s (CF_3 def.) cm^{-1}, δ_F (neat liquid) for the major product (XVI) +26.2[t, 6F, N-N$(CF_3)_2$, $\underline{J}_{3F,5F-CF_3}$ 10.4Hz] -11.4(mult, 2F, 3-and 5-F) and -74.9(mult, 2F, 2-and 6-F) p.p.m. and for the minor product (XV) +38.7(mult, 0.67F, 5-F), +24.4[mult, 4F, C-N$(CF_3)_2$], -2.7(mult, 0.67F, 3-F), -53.4(mult, 0.67F, 2-F or 6-F), and -57.8(mult, 0.67F, 6-F or 2-F) p.p.m. Attempts to separate the isomers by g.l.c. on a variety of columns and by t.l.c. employing a variety of solvents were unsuccessful as were attempts to obtain samples of components L and N.

Treatment of a mixture (ca. 1.0g) of the isomers (XV) and (XVI) in diethyl ether with aqueous sodium hydroxide (3M, $3cm^3$) resulted in an exothermic reaction and formation of a precipitate (probably sodium fluoride). The precipitate was removed, the aqueous filtrate extracted with diethyl ether ($3x5cm^3$), the extracts dried ($MgSO_4$) and the ether removed by evaporation to afford a much reduced yield (0.3g) of a yellow oil which was identified by ^{19}F n.m.r. spectroscopy as the major isomer (XVI).

ACKNOWLEDGEMENT

We wish to thank the Lebanese National Scientific Research Council for a grant (to M.S.F.).

REFERENCES

1 R.E. Banks, A.K. Brown, R.N. Haszeldine, A. Kenny and A.E. Tipping, J. Fluorine Chem., 17 (1981) 85.

2 C.M. Irvin and A.E. Tipping, J. Fluorine Chem., 17 (1981) 591.

3 R.E. Banks, R.N. Haszeldine and D.L Hyde, Chem. Comm., (1967) 413.

4 R.E. Banks and D.R. Choudhury, J. Chem. Soc., Perkin Trans. I, (1981) 1443.

5 J. Lee and K.G. Orrell, J. Chem. Soc., (1965) 582.

6 R.D. Chambers, J. Hutchinson and W.K.R. Musgrave, J. Chem. Soc., (1964) 3736.

7 J.W. Emsley and L. Phillips, J. Chem. Soc. (B), (1969) 434.

8 C.J. Drayton, Ph.D. Thesis,University of Manchester, (1970).

9 M. Mamaghani, Ph.D. Thesis,University of Manchester, (1980).

10 R.D. Chambers, J. Hutchinson and W.K.R. Musgrave, J. Chem. Soc., (1964) 5634.

11 I.M. Madany, Ph.D. Thesis,University of Manchester (1984).

12 L.S. Kobrina, Fluorine Chem. Rev., 7 (1974) 1.

13 G.G. Yakobson, T.D. Petrova and L.S. Kobrina, Fluorine Chem. Rev., 7 (1974) 115.

14 R.E. Banks and J.C. Tatlow in R.E. Banks, D.W.A. Sharp and J.C. Tatlow (eds.) 'Fluorine : The First Hundred Years (1886-1986))', Elsevier Sequoia, Lausanne, 1986 p. 227.

15 R.D. Chambers, R.P. Corbally and W.K.R. Musgrave, J. Chem. Soc. Perkin Trans. I, (1972) 1281; C.J. Drayton, W.T. Flowers and R.N. Haszeldine, ibid., (1975) 1029.

16 M.S. Falou, Ph.D. Thesis,University of Manchester (1985).

17 R.D. Chambers, R.S. Matthews, W.K.R. Musgrave and P.G. Urben, Org. Magn. Resonance, 13 (1980) 363.

18 R.L. Lichter and R.E. Wasylishen, J. Am. Chem. Soc., 97 (1975) 1808.

19 B.E. Smart,'The Chemistry of Functional groups: Supplement D: The Chemistry of Halides, Pseudohalides and Azides' Part 1, Ed. S. Patai and Z. Rappoport, Wiley-InterScience, Chichester, (1983) p.603.

20 R.E. Banks and C. Oppenheim, J. Fluorine Chem., 12 (1978) 27.