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NITROXIDE CHEMISTRY. PART XVII [1]. REACTION OF BISTRIFLUOROMETHYL NITROXIDE WITH SOME HALOGENOALKANES AND RELATED ALKENES

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SUMMARY

The mono(bistrifluoromethylamino-oxy)alkanes $(CF_3)_2NOCXYZ$ (X = Y = F, Z = Cl; X = H, Y = F or Cl, Z = CH_3; X = Y = F, Z = CH_3; X = H, Y = Cl or Br, Z = CF_3; X = Cl, Y = Br, Z = CF_3) have been synthesised by treatment of appropriate halogenoalkanes, CHXYZ, with bistrifluoromethyl nitroxide. The 1,2-bis(bistrifluoromethylamino-oxy)-alkanes $(CF_3)_2NOCH_2CXYON(CF_3)_2$ were obtained as by-products in the reactions involving the ethanes CH_3CHXY (X = H, Y = F or Cl; X = Y = F); these products, like their analogues $(CF_3)_2NOCHFCF_2ON(CF_3)_2$ and $(CF_3)_2NOCH_2CCl_2ON(CF_3)_2$, were also prepared <u>via</u> attack of bistrifluoromethyl nitroxide on the corresponding ethenes.

INTRODUCTION

Work on reactions between bistrifluoromethyl nitroxide and halogeno-methanes and -ethanes was undertaken as part of a methodical survey of attack by the nitroxide on organic substrates [3]. In particular, the intention was to extend knowledge of the action of the nitroxide on alkanes [4].

RESULTS AND DISCUSSION

Details of the synthesis in excellent yield of the (bistrifluoromethylamino-oxy)trihalogenomethanes $(CF_3)_2NOCX_3$ (X = Cl, 99.5%; X = Br, 98%) via attack on chloroform and bromoform by bistrifluoromethyl nitroxide at room temperature were reported [5] shortly before our investigation began. As expected from knowledge of the ease of homolytic attack on chloro- and fluoro-alkanes [6,7], the nitroxide, a pseudo-halogen 'instant' radical resembling chlorine atom, proved much less capable of abstracting hydrogen from chlorodifluoromethane (see Scheme 1) and apparently incapable of doing so from fluoroform during 3 weeks at 80 °C.

$$CHF_2Cl^{\underline{a}} \xrightarrow{(CF_3)_2NO\cdot^{\underline{a}}} (CF_3)_2NOH + \cdot CF_2Cl \xrightarrow{(CF_3)_2NO\cdot} (CF_3)_2NOCF_2Cl^{\underline{b}}$$

Scheme 1

[a] Equimolar ratio. [b] Yields (based on the nitroxide) : 18% after 3 weeks at 80 °C; 23% after 1 week at 100 °C.

Deactivation of β-hydrogen by fluorine substituents [6,7] was clearly evident in reactions between bistrifluoromethyl nitroxide and the halogenoethanes CF_2ClCH_3, CF_3CH_2Cl, and CF_3CH_2Br, all of which were attacked extremely slowly at 50 °C. The first substrate underwent only ca. 5% reaction with the nitroxide at 80 °C during 3 weeks [8], and forcing conditions were employed with CF_3CH_2Cl (100 °C, 15 days) and CF_3CH_2Br (150 °C, 15 days) in order to obtain samples of the derivatives $(CF_3)_2NOCHXCF_3$ (X = Cl, Br) within a reasonable time. (In the case of the bromo-compound this caused deep-seated decomposition, as indicated by the presence of free bromine in the complex product). Replacement of hydrogen in 1-chloro-2,2,2-trifluoroethane by bromine decreased the activation energy for removal of the remaining α-hydrogen, attack of the nitroxide on $CF_3CHClBr$ occurring at room temperature to give $(CF_3)_2NOCClBrCF_3$ quantitatively after 2 weeks.

Reactions involving bistrifluoromethyl nitroxide and chloro-, fluoro-, and 1,1-difluoro-ethane also produced no surprises : attack at α-hydrogen [6] occurred smoothly at ambient temperature with the first two substrates, and at 80 °C in the case of the difluoro-compound, producing a mixture of mono- (mainly) and bis-(bistrifluoromethylamino-oxy)ethanes (see Scheme 2). The dehydrogenation leg of the reaction mechanism parallels that established for alkanes [4] and aralkanes [9]; authentic samples of the 2:1 nitroxide:olefin adducts were prepared in separate experiments, which were extended to include the halogeno-ethenes $CH_2{=}CCl_2$ and $CHF{=}CF_2$ [$\longrightarrow$ $(CF_3)_2NOCH_2CCl_2ON(CF_3)_2$ (98.5% yield) and $(CF_3)_2NOCHFCF_2ON(CF_3)_2$ (97%)] as a prelude to a kinetic study of saturation of ethenes by bistrifluoromethyl nitroxide [10].

EXPERIMENTAL

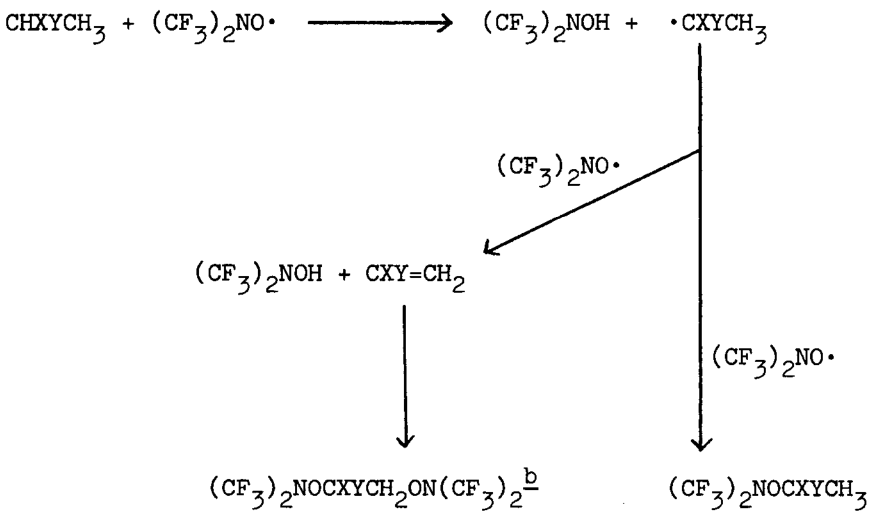
N.m.r. Data

Unless stated otherwise, n.m.r. spectra were recorded with a Perkin-Elmer R10 instrument operating at 56.46 (^{19}F) and 60 (^{1}H) MHz with trifluoroacetic acid and benzene, respectively, as external references. Absorptions to high field of reference 'spikes' have been assigned negative chemical shift values.

Reactions of Bistrifluoromethyl Nitroxide

(a) General procedure

The nitroxide was condensed, *in vacuo*, onto the frozen substrate contained in a Pyrex ampoule cooled to -196 °C; the ampoule was then sealed by fusion of the neck (for reactions at elevated temperatures) or closure of a PTFE



Yields (%)[a]		$(CF_3)_2NOCXYCH_2ON(CF_3)_2$[b]	$(CF_3)_2NOCXYCH_3$
	X = H, Y = F	17	74
	X = H, Y = Cl	15	72
	X = Y = F	5	76

Scheme 2

[a] Based on $(CF_3)_2NO\cdot$. [b] In separate experiments between ethenes and the nitroxide, these adducts were obtained in 98, 99 and 97% yield, respectively.

needle valve (Rotaflo or Fischer-Porter type for experiments at room temperature) and placed in a steel guard to warm to ambient temperature. After being kept at reaction temperature for an appropriate period in the guard (occasional inspection of the ampoule enabled the progress of reaction to be assessed owing to diminution of the purple colour of the nitroxide as it was consumed), the ampoule was re-cooled to -196 °C and opened to a vacuum system. Volatile product was transferred to the system and subjected to trap-to-trap fractional condensation at 1—2 mmHg pressure; the fractions were analysed by i.r. spectroscopy, g.l.c., and molecular weight determination (Regnault's method). In the case of a hydrogen-abstraction reaction (Table 1), final isolation of pure (bistrifluoromethylamino-oxy)-alkane material involved removal of <u>NN</u>-bistrifluoromethyl-hydroxylamine with cold aqueous sodium hydroxide.

TABLE 1

Reactions between bistrifluoromethyl nitroxide and halogenated alkanes

Substrate (g, mmol)	$(CF_3)_2NO\cdot$ (g, mmol)	Reaction period and temp (^oC) (ampoule size, cm^3)	Products (g, mmol, %)
CHF_2Cl (2.85, 32.9)	5.26, 31.3	7d, 100 (300)	$(CF_3)_2NOCF_2Cl$ (nc)[a] (0.91, 3.60, 23)
			CHF_2Cl (2.54, 29.4, 89)
			$(CF_3)_2NO\cdot$[a] (4.04, 24.0, 77)
			$(CF_3)_2NOH$ (0.61, 3.61, 23)
CH_3CH_2Cl (1.26, 19.5)	3.93, 23.4	24 h, 21 (70)	$(CF_3)_2NOCHClCH_3$ (nc)[b] (1.94, 8.4, 72)
			$(CF_3)_2NOCHClCH_2ON(CF_3)_2$[c] (0.35, 0.88, 15)
			CH_3CH_2Cl (0.62, 9.61, 49)
			$(CF_3)_2NOH$ (1.84, 10.9, 93)

(continued overleaf)

TABLE 1 *(cont.)*

CH_3CH_2F (0.96, 20.0) + $CH_2{=}CH_2$[d] (0.28, 1.00)	4.03, 24.0	5 d, 21 (70)	$(CF_3)_2NOCHFCH_3$ (nc)[b] (1.74, 8.09, 74) $(CF_3)_2NOCHFCH_2ON(CF_3)_2$[c] (0.35, 0.92, 17) CH_3CH_2F (0.45, 9.375, 47) $(CF_3)_2NOH$ (1.80, 10.65, 97) $(CF_3)_2NOCH_2CH_2ON(CF_3)_2$[c] (0.38, 1.04, 104)
CH_3CHF_2 (2.31, 35.0)	9.72, 57.9	10 d, 80 (300)	$(CF_3)_2NOCF_2CH_3$ (nc)[b] (5.13, 22.0, 76) $(CF_3)_2NOCF_2CH_2ON(CF_3)_2$[e] (0.28, 0.70, 5) CH_3CHF_2[f] $(CF_3)_2NOH$ (3.97, 23.5, 81)
CF_3CH_2Cl (1.47, 12.4)	5.29, 31.5	15 d, 100 (300)	$(CF_3)_2NOCHClCF_3$ (nc) (0.5, 1.75, 14)[g] [CF_3CH_2Cl, $(CF_3)_2NO\cdot$, $(CF_3)_2NOH$, unidentified][f]

CF_3CH_2Br (2.09, 12.9)	5.42, 32.3	15 d, 150 (300)	$(CF_3)_2NOCHBrCF_3$ (nc) (0.6, 1.8, 14)[g] [$(CF_3)_2NO\cdot$, $(CF_3)_2NOH$, Br_2, unidentified][f]
$CF_3CHClBr$[h] (3.40, 17.2)	7.75, 46.1	14 d, 21 (60)	$(CF_3)_2NOCClBrCF_3$[i] (6.28, 17.2, 100) $(CF_3)_2NO\cdot$ (1.89, 11.25, 24) $(CF_3)_2NOH$ (2.97, 17.6, 102)

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[a] The $(CF_3)_2NOCF_2Cl$ and unreacted nitroxide co-condensed at -120 °C in vacuo; the $(CF_3)_2NO\cdot$ was removed with Hg [11]. [b] Co-condensed with $(CF_3)_2NOH$ at -78 °C and purified by treatment with cold 2M-NaOH aq. [to remove $(CF_3)_2NOH$] and dried over P_2O_5. [c] A sample was isolated by g.l.c. and identified spectroscopically (i.r. and n.m.r.). [d] Produced as a byproduct during the preparation of the ethyl fluoride via treatment of p-$MeC_6H_4SO_3Et$ with KF at 180-250 °C [12] and converted into $(CF_3)_2NOCH_2CH_2ON(CF_3)_2$ [13] during the reaction. [e] Condensed at -45 °C during trap-to-trap fractional condensation of the reaction product, and identified spectroscopically (i.r. and n.m.r.). [f] Amounts not determined; unreacted $(CF_3)_2NO\cdot$ was removed with mercury [11], and, in the reaction involving CF_3CH_2Br, Br_2 with butadiene. [g] After isolation by g.l.c.; cold 0.1M-NaOH aq. was used to remove $(CF_3)_2NOH$. [h] This experiment was carried out by W.J. Nicholson. [i] Condensed at -45 °C in vacuo and subsequently washed with cold 1M-NaOH aq. to remove $(CF_3)_2NOH$.

TABLE 2

Properties of new mono(bistrifluoromethylamino-oxy)-derivatives (— indicates not determined)

Compound		Elemental analyses and mol. wt.[b]					N.m.r. parameters	
[b.p., °C (mmHg)[a]]		C	H	F	N	M	δ $(CF_3)_2NO$-	Others[c]
$(CF_3)_2NOCF_2Cl$	Found:	14.5	0.0	—	5.6	254	+9.0	δ_{CF_2} +39.1
33 (765)	Requires:	14.2	0.0		5.5	253.5	(t, 8 Hz)	(sept.)
$(CF_3)_2NOCHClCH_3$	Found:	20.8	2.1	—	—	231	+9.0	δ_{CH} -0.91 (br. q)
74 (764)	Requires:	20.7	1.7			231.5	(v.br. s[d])	δ_{CH_3} -5.05 (d, 6 Hz)
$(CF_3)_2NOCHFCH_3$	Found:	22.6	2.1	—	6.4	215	+8.3	δ_{CF} -46.6 (m),
46 (754)	Requires:	22.3	1.9		6.5	215	(br. s[d])	δ_{CH} -1.4 (dq; J^2_{HF} 60, J_{HH} 5 Hz), δ_{CH_3} -5.6 (dd; J^3_{HF} 18 Hz)
$(CF_3)_2NOCF_2CH_3$	Found:	20.8	1.4	—	6.3	234	+8.9	δ_{CF_2} +3.7 (m),
44 (754)	Requires:	20.6	1.3		6.0	233	(t, 8.5 Hz)	δ_{CH_3} -5.12 (t; J^3_{HF} 14 Hz)
$(CF_3)_2NOCHClCF_3$	Found:	—	—	59.8	—	285.5[f]	+9.0	δ_{CF_3} -2.3 (br. s),
60 (758)	Requires:			59.8		285.5	(v.br. s[d,e])	δ_{CH} (p-$C_6H_4Cl_2$) -1.38 (q; J^3_{HF} 4.5 Hz)[e]

$(CF_3)_2NOCHBrCF_3$	Found:	—	—	51.3	—	330[g]	+9.8	δ_{CF_3} +0.2 (m),
73 (758)	Requires:			51.8		330	(v.br. s[d,e])	δ_{CH} (p-$C_6H_4Cl_2$) -1.06 (q; J^3_{HF} 5 Hz)[e]
$(CF_3)_2NOCClBrCF_3$	Found:	13.6	0.0	46.0	3.9	—	+12.0	δ_{CF_3} -3.0 (m)
95.5 (760)	Requires:	13.2	0.0	46.9	3.8		(v.br. m[d])	

[a] Siwoloboff's method. [b] Regnault's method unless indicated otherwise. [c] δ_H (p.p.m.) w.r.t. C_6H_6 (ext.) unless stated otherwise. [d] The broadness of the absorption results from the presence of the chiral centre adjacent to the $(CF_3)_2NO$- group; no variable temperature studies were undertaken [cf. ref. 14]. [e] At 84.6 (^{19}F) or 90 (^1H) MHz; [f] By mass spectrometry {m/e 285 [$M^{+\cdot}$ (^{35}Cl), 1.4%], 250 ($M^{+\cdot}$-Cl·, 27.4%), 168 [$(CF_3)_2NO^+$, 14.6], 117 ($CF_3CH^{35}Cl^+$, 100%), and 69 (CF_3^+, 96.6) (correct isotopic abundances were observed for Cl-containing ions)}.

[g] By mass spectrometry {m/e 329 [$M^{+\cdot}$ (^{79}Br), 0.3%), 250 ($M^{+\cdot}$-^{79}Br·, 85.8), 168 [$(CF_3)_2NO^+$, 6.3%], 161 ($CF_3CH^{79}Br^+$, 37.7%), and 69 (CF_3^+, 100%) (correct isotopic abundances were obtained for Br-containing species)}.

TABLE 3

Reactions between bistrifluoromethyl nitroxide and halogenated ethenes

Substrate (g, mmol)	$(CF_3)_2NO\cdot$ (g, mmol)	Reaction period at room temperature (ampoule size, cm^3)	Products[a] (g, mmol, %)
CH_2=CHF (0.276, 6.00)	1.01, 6.01	21 h (60)	$(CF_3)_2NOCH_2CHFON(CF_3)_2$ (nc)[b,g] (1.12, 2.93, 98) CH_2=CHF (0.136, 2.96, 49)
CH_2=CHCl (0.375, 6.00)	1.01, 6.01	50 min (65)	$(CF_3)_2NOCH_2CHClON(CF_3)_2$ (nc)[c,h] (1.18, 2.96, 99) CH_2=CHCl (0.188, 3.00, 50)
CH_2=CF_2 (0.384, 6.00)	1.01, 6.01	30 h (60)	$(CF_3)_2NOCH_2CF_2ON(CF_3)_2$[d,i] (1.17, 2.925, 97) CH_2=CF_2 (0.192, 3.00, 50)
CH_2=CCl_2 (0.582, 6.00)	1.01, 6.01	15 min (60)	$(CF_3)_2NOCH_2CCl_2ON(CF_3)_2$ (nc)[e,j] (1.28, 2.96, 98.5) CH_2=CCl_2 (0.288, 2.97, 49.5)

$CHF{=}CF_2$ (0.492, 6.00)	1.01, 6.01	1 h (65)	$(CF_3)_2NOCHFCF_2ON(CF_3)_2$ [f,k] (1.22, 2.92, 97) $CHF{=}CF_2$ (0.234, 2.85, 48)

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[a] Separated by trap-to-trap fractional condensation, *in vacuo*; trap temperatures are stated below for each bis(bistrifluoromethylamino-oxy)-compound.

[b] -45; [c] -63; [d] -45; [e] -23; [f] -45 °C trap.

[g] B.p. 108 °C at 759 mmHg (Siwoloboff), n_D^{20} 1.2844 (Found: C, 18.7; H, 0.7; N, 7.0. $C_6H_3F_{13}N_2O_2$ requires C, 18.8; H, 0.8; N, 7.3%)

[h] B.p. 123 °C at 757 mmHg (Siwoloboff), n_D^{20} 1.3082 (Found: C, 18.4; H, 1.1; N, 6.7. $C_6H_3ClF_{12}N_2O_2$ requires C, 18.1; H, 0.75; N, 7.0%).

[i] B.p. 99 °C at 757 mmHg (Siwoloboff) (lit. [15], 98 °C), n_D^{20} 1.2787 (Found: C, 18.0; H, 0.7; N, 6.8. Calc. for $C_6H_2F_{14}N_2O_2$: C, 18.0; H, 0.5; N, 7.0%), δ_F +7.30 [s; $(C\underline{F}_3)_2NOCH_2$-], -7.65 [multiplet; $C\underline{F}_2$], and +8.75 [t; $(C\underline{F}_3)_2NOCF_2$] p.p.m., δ_H (TMS) +4.35 (t) p.p.m.

[j] B.p. 136 °C at 759 mmHg (Siwoloboff), n_D^{20} 1.3254 (Found: C, 16.8; H, 0.6; N, 6.3. $C_6H_2Cl_2F_{12}N_2O_2$ requires C, 16.6; H, 0.5; N, 6.5%), δ_F +8.12 [s; $(C\underline{F}_3)_2NOCH_2$-] and +11.62 [s; $(C\underline{F}_3)_2NOCCl_2$-] p.p.m. {*cf.* δ_F for $(CF_3)_2NOCCl_2CCl_2ON(CF_3)_2$ = +12.58 p.p.m. [10]}, δ_H (TMS) +4.55 (s) p.p.m.

[k] B.p. 105 °C at 759 mmHg (Siwoloboff) (lit. [15], 89 °C), n_D^{20} 1.2734 (Found: C, 17.1; H, 0.5; N, 6.6. Calc. for $C_6HF_{15}N_2O_2$: C, 17.2; H, 0.2; N, 6.7%).

(b) Results

(i) Hydrogen-abstraction reactions involving halogenoalkanes.- Essential experimental details are presented in Table 1. The mono(bistrifluoromethylamino-oxy)-derivatives were characterised as shown in Table 2.

(ii) Addition reactions involving halogenoalkenes.- These were carried out with equimolar ratios of reactants, as shown in Table 3, to ensure 'clean' reactions. The 1,2-bis(bistrifluoromethylamino-oxy)ethanes obtained were characterised as described in the footnotes to the table and, for $(CF_3)_2NOCH_2CHXON(CF_3)_2$ (X = F, Cl) and $(CF_3)_2NOCHFCF_2ON(CF_3)_2$, as described previously [14 ; n.m.r. data].

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3 See ref. 1 and previous parts in the Series. For reviews of knowledge of the chemistry of $(CF_3)_2NO\cdot$, see R.E. Banks in 'Fluorocarbon and Related Chemistry' (CS Specialist Periodical Reports), volumes 1 (1971, p. 109), 2 (1974, p. 223), and 3 (1976, p. 235).

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5 H.J. Emeléus, P.M. Spaziante and S.M. Williamson, J.Inorg.Nucl.Chem., 32 (1970) 3219 [the conversion $(CF_3)_2NO\cdot + CHCl_3 \longrightarrow (CF_3)_2NOCCl_3$ was first reported in 1968 (H.C. Ang, Chem.Comm., (1968) 1320]. In our hands, the reaction between equimolar quantities of $CHCl_3$ and $(CF_3)_2NO\cdot$ is complete within 3 h at 21 °C, giving $(CF_3)_2NOCCl_3$ [b.p. 95.5 °C (Siwoloboff), δ_F (CF_3CO_2H) +12.5 p.p.m.] in 96% yield; methylene chloride is more susceptible than chloroform to attack by the nitroxide, and yields $(CF_3)_2NOCHCl_2$, as will be

described later when work on $(CF_3)_2NO$-substituted carbenes is complete.

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