The reaction of bis(trifluoromethyl)amino-oxyl with t-butyl bromide, t-butyl chloride, 2,2-dichloropropane, 2-chloro-2-phenylpropane and t-butyl acetate

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(Received May 24, 1993; accepted September 7, 1993)

Abstract

Reaction of the oxyl $(CF_3)_2NO\cdot$ (**1**) with t-butyl bromide (*c.* 2:1 molar ratio) at room temperature results in initial hydrogen abstraction to give the hydroxylamine $(CF_3)_2NOH$ (**3**) and the radical $\dot{C}H_2CMe_2Br$ (**17**) which (*i*) couples with oxyl **1** to afford the compound $(CF_3)_2NOCH_2CMe_2Br$ (**6**) (33.5%) and (*ii*) eliminates a bromine atom to give the alkene $CH_2{=}CMe_2$. Addition of oxyl **1** and bromine to the alkene affords the adducts $(CF_3)_2NOCH_2CMe_2ON(CF_3)_2$ (**4**) (10%) and CH_2BrCMe_2Br (**8**) (26.5%), respectively, while allylic hydrogen abstraction from the alkene leads to the compounds $[(CF_3)_2NOCH_2]_2CMeON(CF_3)_2$ (**5**) (10%) and $(CF_3)_2NOCH_2CMe[ON(CF_3)_2]CH_2Br$ (**7**) (15.5%). Reaction with t-butyl chloride is more complex and gives a number of unidentified products together with the compounds **4** (37%), **5** (8%) and $(CF_3)_2NOCH_2CMe[ON(CF_3)_2]CH_2Cl$ (**9**) (3.5%) formed by an analogous reaction pathway, although the large amount of hydrogen chloride (61%) isolated indicates that hydrogen abstraction by chlorine atoms competes with abstraction by oxyl **1**. With 2,2-dichloropropane, reaction with the oxyl **1** is slow (even at 70–80 °C) and gives mainly hydrogen chloride, hydroxylamine **3** (32%), the substitution product $(CF_3)_2NOCH_2CCl_2CH_3$ (**10**) (42%) and the 2:1 adduct of oxyl **1** and the alkene $CH_2{=}CMeCl$, i.e. $(CF_3)_2NOCH_2CMeClON(CF_3)_2$ (**11**) (24%). In contrast, reaction involving 2-chloro-2-phenylpropane is facile at room temperature and affords hydrogen chloride (97.5%), hydroxylamine **3** (12.5%) and the 2:1 adduct $(CF_3)_2NOCH_2CMePhON(CF_3)_2$ (**12**) (78%) of oxyl **1** and the alkene $CH_2{=}CMePh$. Treatment of t-butyl acetate with oxyl **1** gives hydroxylamine **3** (49%), the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**2**) (9%) and the compounds $(CF_3)_2NOCH_2CMe_2OAc$ (**14**) (36%), $[(CF_3)_2NO]_2CHCMe_2OAc$ (**15**) (15%) and $(CF_3)_2NO_2CCMe_2OAc$ (**16**) (40%) formed via successive oxyl **1** attack on a methyl group. In these reactions, compounds arising via a 1,2-shift of bromine, chlorine or acetate were not detected in the products.

Introduction

Vicinal chlorine shifts have been observed to take place in the intermediate radicals arising from addition of the radicals $(CF_3)_2NO\cdot$ (**1**) and $(CF_3)_2N\cdot$ (generated from the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**2**)) to the alkenes $CH_2{=}CRCCl_3$ (R = H, CH_3) [1]. In an extension of this study, reactions of oxyl **1** with the halides Me_3CX (X = Cl, Br), Me_2CCl_2 and Me_2CClPh, and with the acetate Me_3COAc were investigated to determine if 1,2-shifts of halogen and acetate, i.e. $\dot{C}H_2CMeXY \rightarrow XCH_2\dot{C}MeY$ (X = Cl, Br or Ac, Y = Me; X = Y = Cl; X = Cl, Y = Ph) would occur in the intermediate radicals formed by hydrogen abstraction to give more stable radicals. A preliminary investigation of the reactions of oxadiazapentane **2** with the compounds Me_3CBr and Me_2CClPh was also undertaken.

A number of reactions of oxyl **1** with halogenoalkanes have been reported previously in which vicinal halogen shifts either could not occur or would not be expected, i.e. RCH_2Br (R = H, Me, Et) [2], CHX_3 (X = Cl, Br) [3], CHF_3, CHF_2Cl, CH_3CH_2X (X = F, Cl), CH_3CHF_2, CF_3CH_2X (X = Cl, Br) and $CF_3CHClBr$ [4] and Me_2CHCH_2X (X = Cl, Br) [5]; the reaction with the acetate Me_2CHCH_2OAc has also been carried out [5].

Results and discussion

The conditions used and the products formed from the reaction of oxyl **1** with the halogenopropanes and t-butyl acetate are shown in Table 1. In all cases a number of unidentified minor products were also formed.

$(CF_3)_2NOH$ (**3**) $(CF_3)_2NOCH_2CMe_2ON(CF_3)_2$ (**4**)

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SSDI 0022-1139(93)02980-S

TABLE 1. Reaction of oxyl **1** with halogenopropanes and t-butyl acetate

Substrate	Ratio **1**/substrate	Temp. (°C)	Time	Recovered substrate (%)	Products[a] (%)
Me_3CBr	1.85	*c.*20	30 h	25	**3**, 41[b]; **4**, 10; **5**, 10; **6**, 33.5; **7**, 15.5; **8**, 26.5[c]
Me_3CCl	1.98	*c.*20	30 d	30	HCl, 61; **3**, 13[b]; **4**, 35; **5**, 8; **9**, 3.5[d]
Me_2CCl_2	2.01	70–80	78 d	50	**3**, 32[b]; **10**, 42; **11**, 24[e]
$Me_2CHPhCl$	2.00	*c.*20	0.5 h	32.5	HCl, 97.5; **3**, 12.5[b]; **12**, 78[f]
Me_3COAc	2.13	*c.*20	41 d	51	**3**, 49[b]; **13**, 3[b]; **2**, 9[b]; **14**, 40; **15**, 15; **16**, 36[g]

[a]Based on substrate not recovered.
[b]Based on oxyl **1**.
[c]Four minor unidentified products also formed.
[d]Eight minor unidentified products also formed.
[e]A low-boiling mixture of HCl, amine **13** and CO_2, and three minor unidentified higher-boiling products also formed.
[f]Eight minor unidentified products also formed.
[g]Twelve minor unidentified products also formed.

$[(CF_3)_2NOCH_2]_2CMeON(CF_3)_2$
(5)

$(CF_3)_2NOCH_2CMe_2Br$
(6)

$(CF_3)_2NOCH_2CMe(CH_2X)ON(CF_3)_2$
(7) X = Br
(9) X = Cl

CH_2BrCMe_2Br **(8)** $(CF_3)_2NOCH_2CMeCl_2$ **(10)**

$(CF_3)_2NOCH_2CMeClON(CF_3)_2$
(11)

$(CF_3)_2NOCH_2CMePhON(CF_3)_2$
(12)

$(CF_3)_2NH$ **(13)** $(CF_3)_2NOCH_2CMe_2OAc$ **(14)**

$[(CF_3)_2NO]_2CHCMe_2OAc$ **(15)** $(CF_3)_2NO_2CCMe_2OAc$ **(16)**

The identified products from the t-butyl bromide reaction are considered to have been formed as outlined in Scheme 1.

Initial hydrogen abstraction by oxyl **1** from t-butyl bromide gave the hydroxylamine **3** and the radical $\dot{C}H_2CMe_2Br$ (**17**), which is either trapped by oxyl **1** to afford the substitution product **6** or undergoes β-scission with loss of a bromine atom to give isobutene. Radical addition of oxyl **1** and addition of bromine (probably ionic) to this alkene then gave the adducts **4** and **8**, respectively. A competing reaction of the alkene is allylic hydrogen abstraction by oxyl **1** to afford the symmetrical allyl radical **18**, which underwent coupling with oxyl **1** to give the alkene **19** and also reacted with bromine to form the allyl bromide **20**. Addition of oxyl **1** across the double bonds of alkenes **19** and **20** then gave compounds **5** and **7**, respectively.

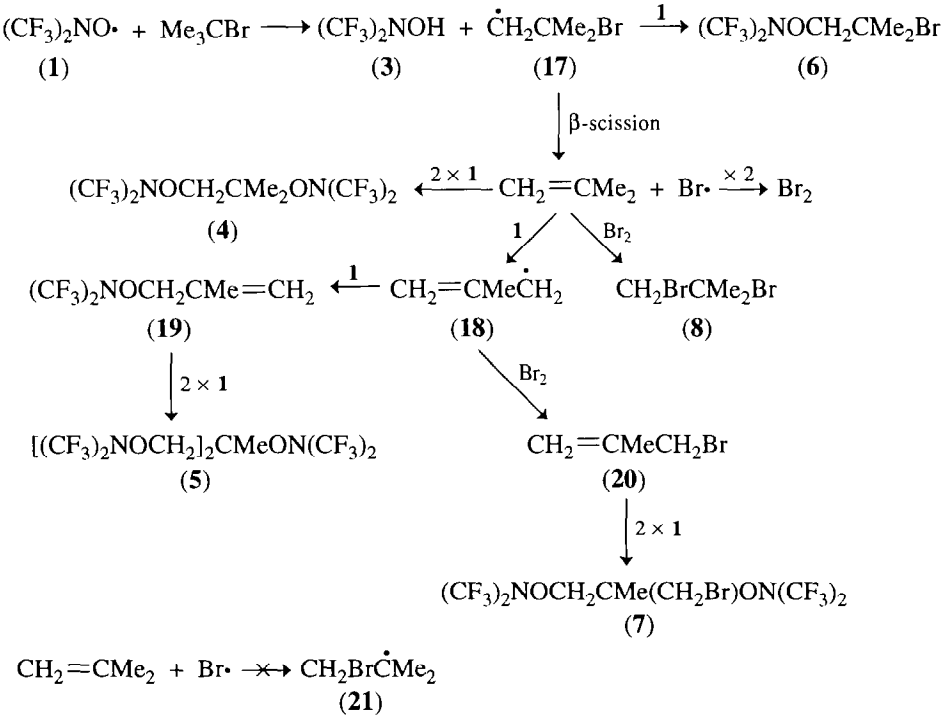
The ratio of products **6**/**4** + **5** + **7** + **8** (33.5:62) indicated that β-scission of a bromine atom from radical **17** was considerably more favourable than coupling of radical **17** with oxyl **1**.

The possibility that compound **7** (and maybe **5**) was formed via bromine atom addition to isobutene to give radical **21** was discounted, because it has been found [5] that radical **21**, generated by hydrogen abstraction from isobutyl bromide by oxyl **1**, undergoes coupling with oxyl **1** to afford compound $(CF_3)_2NOCMe_2CH_2Br$ (78%) as the major product; only a relatively low yield (7%) of compound **7** was observed in this reaction via further hydrogen abstraction by oxyl **1** and the intermediacy of the allyl bromide **20**.

It is possible that bromine atoms compete with oxyl **1** for abstraction of hydrogen atoms in this system, but if this occurs then hydrogen bromide would be expected to be oxidised by oxyl **1** to bromine with the concurrent formation of hydroxylamine **3**.

The reaction of oxyl **1** with isobutene at or below room temperature has been reported previously [6] to give the 2:1 adduct **4** and small amounts of a compound later identified [7] as the allylic substitution product **19**. Compound **19** was formed in higher yield (49%) by passage at low pressure of a preheated mixture of oxyl **1** and isobutene into a mixing chamber at 200 °C.

The product mixture from the t-butyl bromide reaction before separation showed weak IR absorptions in the



Scheme 1.

range 1720–1820 cm^{-1} (C=O str.) indicating that further oxyl **1** attack on $(CF_3)_2NOCH_2$ groups had occurred and that one or more of the minor unidentified products contained a carbonyl group.

Compounds **4** and **8** were identified by comparison of their spectral data (IR, NMR and MS) with those of authentic samples. Identification of compounds **5–7** was based on elemental analysis and the following spectral data. The ^1H NMR spectra showed absorptions (i) at δ *c.* 4.1 (AB, $2CH_2O$) and 1.27 (s, CH_3) ppm confirming the presence of two CH_2O groups adjacent to a chiral carbon bonded to methyl, i.e. an OCH_2CMeCH_2O grouping in compound **5**, (ii) at δ *c.* 3.5 (s, CH_2O) and 1.56 (s, CMe_2) ppm for compound **6** confirming an $O-CH_2CMe_2$ grouping and (iii) at δ 4.14 (s, CH_2O), *c.* 3.35 (AB, CH_2Br) and 1.35 (s, CH_3) ppm for compound **7** consistent with an OCH_2CMeCH_2Br grouping. The ^{19}F NMR spectra showed the presence of three $(CF_3)_2NO$ groups in compound **5** {δ+9.5 [s, $(CF_3)_2NOCMe$) and +7.5 [s, $2(CF_3)_2NOCH_2$] ppm}, one $(CF_3)_2NO$ group in compound **6** {δ+11.3 [s, $(CF_3)_2NO$] ppm} and two $(CF_3)_2NO$ groups in compound **7** {δ+9.4 [s, $(CF_3)_2NOCMe$] and +7.6 [s, $(CF_3)_2NOCH_2$] ppm}. The mass spectra showed peaks at *m/z* 391 $[M-(CF_3)_2NO]^+$, 377 $[M-(CF_3)_2NOCH_2]^+$ and 182 $[(CF_3)_2NOCH_2^+]$ for compound **5**, at *m/z* 303/305 (M^+), 182 $[(CF_3)_2NOCH_2^+]$ and 121/123 (CMe_2Br^+) for compound **6** and at *m/z* 302/304 $[M-(CF_3)_2NO]^+$, 288/290 $[M-(CF_3)_2NOCH_2]^+$ and 93/95 (CH_2Br^+) for compound **7**.

Reaction of oxyl **1** with t-butyl chloride was slower and more complex than with the bromide and 11 high-boiling products were formed of which only three, i.e. **4**, **5** and **9**, were isolated; these represent only 46.5% total yield based on chloride reacted. Again carbonyl absorptions were observed in the IR spectrum of the product mixture before separation.

The isolation of a large amount of hydrogen chloride and only a relatively small amount of hydroxylamine **3** from this reaction indicates that β-scission of a chlorine atom from the intermediate radical CH_2CMe_2Cl to give isobutene is facile and that chlorine atoms are more effective than oxyl **1** in abstracting hydrogen atoms. This ready loss of chlorine from the intermediate radical explains why the product of coupling of the radical with oxyl **1**, i.e. $(CF_3)_2NOCH_2CMe_2Cl$, was not isolated from the product mixture and hence, if it was formed, it was present only in relatively low yield. Oxidation of HCl by oxyl **1** to give chlorine and hydroxylamine **3** would not be expected to occur (unlike oxidation of HBr which has a much weaker bond) and so it is not surprising that the compound CH_2ClCMe_2Cl (the adduct of isobutene and chlorine) was not detected.

Compounds **4**, **5** and **9** (the chlorine analogue of compound **7**) are considered to be formed by the same pathway as outlined for compounds **4**, **5** and **7** in Scheme 1, with hydrogen abstraction mainly occurring by chlorine atom attack. Compound **9** was identified from the following spectral data: ^1H NMR absorptions at δ *c.* 4.0 (s, CH_2O), *c.* 3.4 (AB, CH_2Cl) and *c* 1.2

(s, CH_3) ppm confirming the OCH_2CMeCH_2Cl grouping; ^{19}F NMR bands at $\delta+9.2$ [s, $(CF_3)_2NOCMe$] and $+7.35$ [s, $(CF_3)_2NOCH_2$] ppm; and mass (*m/z*) 377 $[M-CH_2Cl]^+$, 258/260 $[M-CF_3)_2NO]^+$, 244/246 $[M-(CF_3)_2NOCH_2]^+$, 182 $[(CF_3)_2NOCH_2^+]$ and 49/51 $(\dot{C}H_2Cl^+)$.

The compounds Me_2CCl_2 and Me_2CPhCl showed remarkably different reactivities towards attack by oxyl **1**, with reaction of the dichloride being very slow at room temperature and relatively slow at 70–80 °C, while reaction of cumyl chloride was very fast at room temperature. At 70–80 °C the dichloride gave some hydrogen chloride, but the relatively high yield of hydroxylamine **3** (32%) indicated that loss of chlorine by β-scission from the intermediate radical **22** was less favourable than loss from the intermediate radical $\dot{C}H_2CMe_2Cl$ formed in the t-butyl chloride reaction. This less favourable β-scission of a chlorine atom resulted in a considerably higher yield of substitution product **10** than of the 2:1 adduct (**11**) of oxyl **1** and the β-scission product, i.e. the alkene **23**. Three minor unidentified products were also formed in this reaction and the crude reaction mixture showed carbonyl absorptions in the IR spectrum. The products are considered to be formed as shown in Scheme 2.

Compounds **10** and **11** were identified by elemental analysis and from the following spectral data. ^1H NMR bands at δ 4.12 (s, CH_2O) and 1.91 (s, CH_3) ppm, and a ^{19}F NMR absorption at $\delta+8.2$ [s, $(CF_3)_2NOCH_2$] ppm, confirmed that compound **10** contained a $((CF_3)_2NOCH_2CMe$ grouping, while an ion peak in the mass spectrum at *m/z* 97/99/101 confirmed the $CMeCl_2$ group. The ^1H NMR spectrum of compound **11**, with absorptions at *c*, 4.05 (AB, CH_2O) and *c*. 1.7 (s, CH_3) ppm, and the ^{19}F NMR spectrum with absorptions at $\delta+10.4$ (q, 3F, CF_3); $+9.7$ (q, 3F, CF_3) and $+7.2$ [s, 6F, $(CF_3)_2NOCH_2$] ppm, confirmed the presence of the $(CF_3)_2NOCH_2CMeON(CF_3)_2$ grouping. Mass spectral peaks at *m/z* 377 $(M-Cl)^+$, 230/232 $[(CF_3)_2NOCMeCl^+]$, 182 $[(CF_3)_2NOCH_2^+]$ and 92/94 (OCH_2CMeCl^+) confirmed the structure.

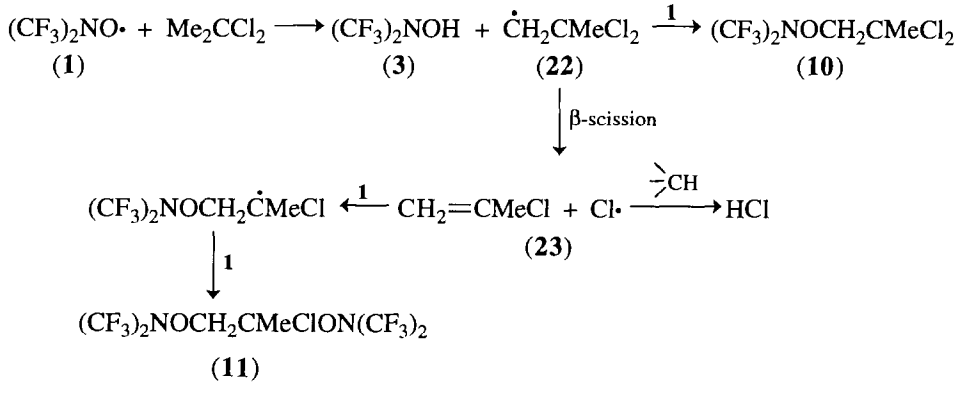
The observation that the two CF_3 groups in the $(CF_3)_2NOCMeCl$ grouping are non-equivalent and absorb as two distinct quartets in the ^{19}F NMR spectrum was somewhat unexpected, since the spectra of compounds containing a $(CF_3)_2NO$ group bonded to a chiral centre rarely show such non-equivalence and the $(CF_3)_2NO$ group in the $(CF_3)_2NOCMePh$ grouping of compound **12** (see below) absorbed as a singlet.

It was hoped that abstraction of a hydrogen atom from cumyl chloride would result in the intermediate radical **24** undergoing a vicinal chlorine shift to afford the very stable tertiary benzylic radical **25**. However, β-scission of chlorine from radical **24** was highly favoured to afford alkene **26** and hence adduct **12** (Scheme 3).

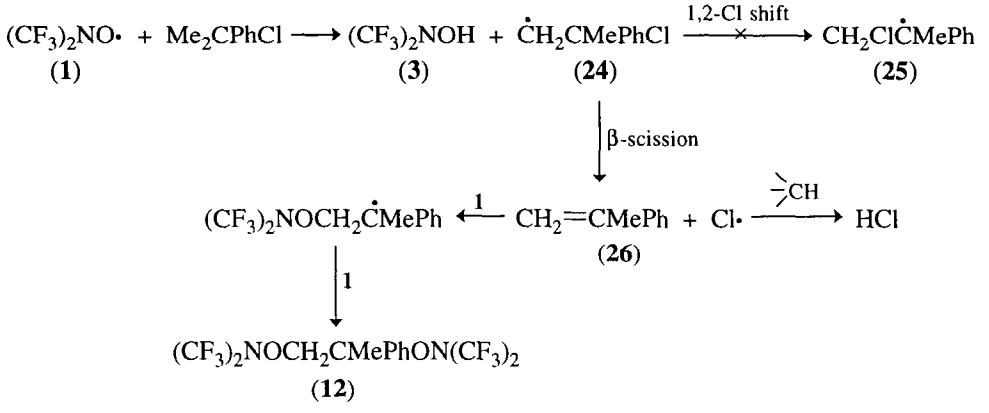
Eight minor unidentified products were also formed in the reaction and certain of these contained a carbonyl group (IR spectroscopy). The near-quantitative yield of hydrogen chloride and low yield of hydroxylamine **3** obtained show that hydrogen abstraction in this system involves mainly chlorine atoms. Also, the combined yield of hydrogen chloride and hydroxylamine **3** relative to that of the cumyl chloride reacted (1.34:1.0) demonstrated that considerable allylic hydrogen abstraction from alkene **26** and/or abstraction from adduct **12** had taken place.

Adduct **12** was identified by elemental analysis, the presence in its mass spectrum of peaks at *m/z* 272 and 182 for the ions $(CF_3)_2NOCMePh^+$ and $(CF_3)_2NOCH_2^+$, respectively, ^1H NMR absorptions at δ *c*. 7 (C_6H_5), *c*. 3.9 (AB, CH_2O) and 1.46 (s, CH_3) ppm, consistent with the grouping OCH_2CMe, and ^{19}F NMR absorptions at $\delta+9.9$ [s, $(CF_3)_2NOCMe$] and $+7.6$ [s, $(CF_3)_2NOCH_2$] ppm.

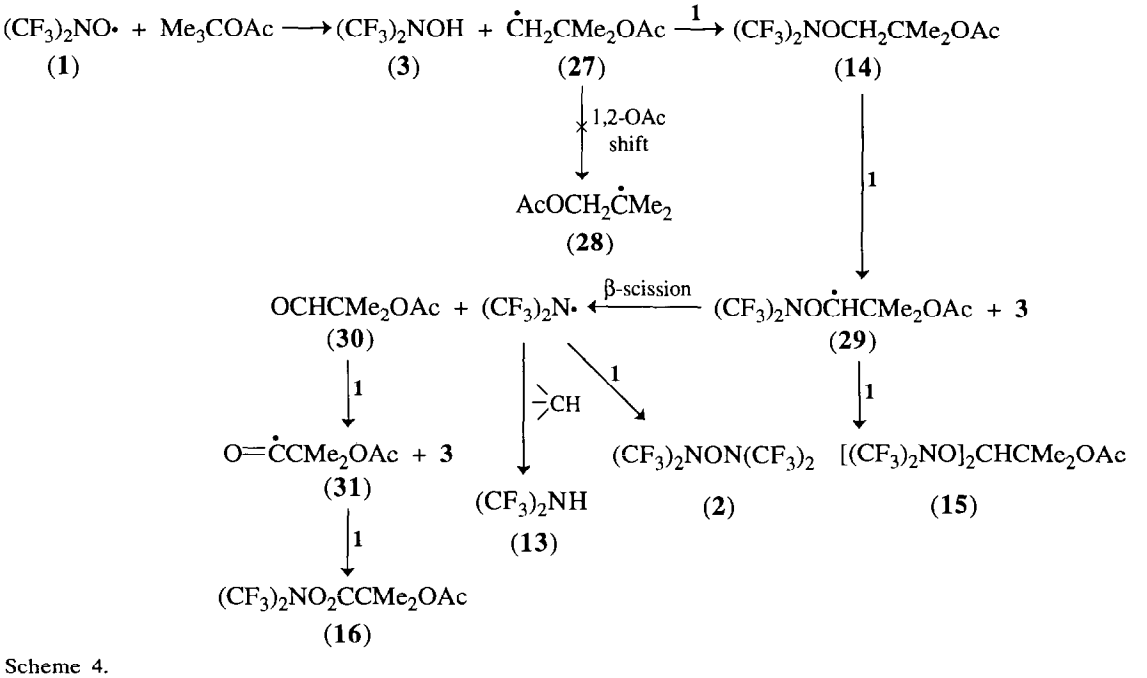
Reaction of oxyl **1** with t-butyl acetate was slow at room temperature and the pathway by which the isolated products **3** and **13–16** are considered to arise is shown in Scheme 4; a large number of minor unidentified products were also formed.



Scheme 2.



Scheme 3.



Scheme 4.

The intermediate radical **27** formed by hydrogen abstraction was scavenged by oxyl **1** to give the monosubstitution product **14**. Products resulting from the rearrangement of radical **27** to the more stable radical **28** via a 1,2-acetoxy shift, e.g. $(CF_3)_2NOCMe_2CH_2OAc$, were not isolated. Further hydrogen abstraction from the $(CF_3)_2NOCH_2$ grouping of compound **14** then took place to afford radical **29** which underwent competing reaction with oxyl **1**, to give the disubstitution product **15**, and β-scission to yield aldehyde **30** and the $(CF_3)_2N\cdot$ radical. Hydrogen abstraction from aldehyde **30**, followed by reaction of the resulting radical with oxyl **1**, gave diester **16**, while amine **13** and oxadiazapentane **2** were formed from the $(CF_3)_2N\cdot$ radicals by hydrogen abstraction and coupling with oxyl **1**, respectively.

Radicals of type $(CF_3)_2NO\dot{C}HR$ have been reported previously to undergo competing coupling with oxyl **1** and β-scission to give aldehydes [8]. The aldehydes are readily converted into esters of type $(CF_3)_2NO_2CR$ on reaction with oxyl **1** [9]. Furthermore, it has been shown conclusively that esters do not arise from β-scission of $(CF_3)_2N\cdot$ from radicals of type $[(CF_3)_2NO]_2\dot{C}R$, since the disubstituted compounds $[(CF_3)_2NO]_2CHR$ are relatively unreactive towards hydrogen abstraction by oxyl **1** [8].

Diester **16** was identified by elemental analysis, NMR absorptions at δ_H 1.69 (CH_3CO_2) and 1.29 (CMe_2) ppm and $\delta_F + 8.9$ [$(CF_3)_2NO$] ppm and mass spectral bands at *m/z* 282 $(M-Me)^+$, 129 $[M-(CF_3)_2NO]^+$ and 101 (CMe_2OAc^+). Compounds **14** and **15** were isolated as a mixture and their NMR spectra showed absorptions for compound **14** at δ_H 3.96 (CH_2O), 1.55 (CH_3CO_2) and 1.29 (CMe_2) ppm and $\delta_F + 7.6$ [$(CF_3)_2NOCH_2$] ppm (as expected for $(CF_3)_2NOCH_2CMe_2OAc$) and ab-

sorptions for compound **15** at δ_H 5.21 (OCHO), 1.55 (CH_3CO_2) and 1.13 (CMe_2) ppm and δ_F +8.5 [$(CF_3)_2NO$] ppm, consistent with $[(CF_3)_2NO]_2$-$CHCMe_2OAc$. The mass spectrum of the mixture was not very informative apart from peaks assigned to breakdown of compound **14** at *m/z* 268 $(M-Me)^+$, 224 $(M-CH_3CO_2)^+$ and 223 $(M-CH_3CO_2H)^+$.

Hence, in the above reactions evidence was not obtained for rearrangement of the intermediate radicals $\dot{C}H_2CMeXY$ (X=Br, Y=Me; X=Cl, Y=Me; X=Y=Cl; X=Cl, Y=Ph; X=OAc, Y=Me) to the more stable radicals $CH_2X\dot{C}MeY$ by 1,2-shifts of Br, Cl or OAc.

A preliminary investigation was undertaken of the reactions of the oxadiazapentane **2** with the halogenoalkanes Me_3CBr and Me_2CPhCl (*c.* 1:1 molar ratio) at room temperature in the dark. The reactions were much slower than the corresponding reactions of oxyl **1** and gave complex multicomponent product mixtures. From the t-butyl bromide reaction the lower-boiling product was the amine **13** (12%), while compound **3** (32%), unchanged t-butyl bromide (27% recovered), the substitution product **6** (6%) and the dibromide **8** (32%) were identified in the higher-boiling mixture.

Clearly both $(CF_3)_2N\cdot$ and $(CF_3)_2NO\cdot$ (**1**) radicals abstracted hydrogen atoms and the formation of compounds **6** and **8** shows that, as in the t-butyl reaction with oxyl **1**, the intermediate radical $\dot{C}H_2CMe_2Br$ (**18**) reacted with oxyl **1** [or abstracted $(CF_3)_2NO$ from oxadiazapentane (**2**)] and underwent β-scission of bromine to afford isobutene.

From the reaction with the halide Me_2CPhCl, apart from recovered reactants **2** (23% recovered) and Me_2CPhCl (40% recovered), only the hydrogen chloride (33%) and compound **3** (39%) and **13** (13%) were isolated and identified. Thus, the radicals $(CF_3)_2N\cdot$, $(CF_3)_2NO\cdot$ and $Cl\cdot$ all abstract hydrogen atoms in this system and β-scission of chlorine from the intermediate radical $\dot{C}H_2CMePhCl$ (**24**) would appear to be less favoured than in the corresponding reaction with oxyl **1**.

Experimental

Starting materials

Oxyl **1** was prepared in 96% yield by oxidation of the hydroxylamine **3** with potassium permanganate and sulphuric acid [10], and was converted into oxadiazapentane **2** by reaction with trifluoronitrosomethane (2:1 molar ratio) [10]. The other reactants Me_3CBr, Me_3CCl, Me_2CCl_2, Me_2CPhCl and Me_3COAc were commercial samples, the purity of each being checked (^1H NMR spectroscopy) before use.

General techniques

The reactions involving compounds **1** and **2** were carried out in Pyrex ampoules (*c.* 300 cm^3 unless stated otherwise). Products were separated by fractional condensation *in vacuo* into low-boiling fractions and higher-boiling material, and individual components were obtained from the latter material by preparative-scale GLC [Pye 104 instrument using columns (2 or 4 m) packed with silicone SE 30 oil, Apiezon L (APL) grease, polyethylene glycol adipate (PEGA) or trixylyl phosphate (TXP) (20%–25% w/w) on acid-washed Celite] and were examined by IR spectroscopy (Perkin-Elmer 197 instrument), ^1H NMR spectroscopy [Varian Associates HA100 (100.0 MHz) spectrometer; internal reference Me_4Si], ^{19}F NMR spectroscopy [Varian Associates HA100 (94.12 MHz) instrument; external reference CF_3CO_2H] and mass spectrometry (AEI MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded as solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

Boiling points were determined using Siwoloboff's method and molecular weights of gases were measured using Regnault's method.

The IR spectra of products containing the $(CF_3)_2NO$ group all showed bands (cm^{-1}) at 1300–1200 (C–F str.), *c.* 1050 (C–O–N str.), 960–980 (C–N str.) and *c.* 710 (CF_3 def.).

Reactions of bis(trifluoromethyl)amino-oxyl (1)

(a) With t-butyl bromide

A mixture of oxyl **1** (2.24 g, 13.3 mmol) and t-butyl bromide (0.98 g, 7.2 mmol), stored in an ampoule (*c.* 100 cm^3) (30 h), gave (i) *N,N*-bis(trifluoromethyl)hydroxylamine (**3**) (0.93 g, 5.5 mmol, 41%), (ii) unchanged t-butyl bromide (0.25 g, 1.8 mmol, 25% recovered) and (iii) higher-boiling material (2.02 g) which was shown by GLC (2 m SE30 and 2 m Kel-F at 80 °C) to contain five major (A–E) and four minor components. The major components were separated by preparative-scale GLC (2 m SE30 at 90 °C) to give: (i) 1,2-bis[bis(trifluoromethyl)amino-oxy]-2-methylpropane (**4**) (0.21 g, 0.50 mmol, 10%), which was identified by a comparison of its IR, ^1H and ^{19}F NMR and mass spectra with those previously reported [6]; (ii) 1,2,3-tris[bis(trifluoromethyl)amino-oxy]-2-methylpropane (**5**) (nc) (0.30 g, 0.51 mmol, 10%) (Analysis: Found: C, 21.6; H, 1.1; N, 7.6; F, 61.7%. $C_{10}H_7F_{18}N_3O_3$ requires: C, 21.5; H, 1.3; N, 7.5; F, 61.2%), b.p. 163 °C {^1H NMR ($CDCl_3$) δ: 4.13, 4.03 (AB, 4H, $2CH_AH_BO$, J_{AB} = 11 Hz); 1.27 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +9.5 [s, 6F, $(CF_3)_2NOCMe$]; +7.5 [s, 12F, $2(CF_3)_2NOCH_2$] ppm. MS *m/z*: 391 {1.5%, $[M-(CF_3)_2NO]^+$}; 377 {4.8 $[M-(CF_3)_2NOCH_2]^+$}; 182 [12.1, $(CF_3)_2NOCH_2^+$]; 166 (11.7, $C_3H_2F_6N^+$); 150 (13.8, $C_2HF_5NO^+$); 69 (32.8,

CF_3^+); 58 (21.6, $C_3H_6O^+$); 57 (25.0, $C_3H_5O^+$); 55 (15.6, $C_4H_7^+$ and/or $C_3H_3O^+$); 43 (100.0, $C_2H_3O^+$); 41 (32.6, $C_3H_5^+$)}; (iii) 1-[bis(trifluoromethyl)amino-oxy]-2-bromo-2-methylpropane (**6**) (nc) (0.55 g, 1.8 mmol, 33.5%) (Analysis: Found: C, 23.6; H, 2.7; Br, 25.8; N, 4.9; F, 37.6%. $C_6H_8BrF_6NO$ requires: C, 23.7; H, 2.6; Br, 26.3; N, 4.6; F, 37.5%), b.p. 132 °C {^{1}H NMR ($CDCl_3$) δ: 3.45 (s, 2H, CH_2O); 1.56 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +11.3 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 303/305 (33.7%, M^+); 288/290 [4.7, $(M-CH_3)^+$]; 182 [4.1, $(CF_3)_2NOCH_2^+$]; 150 (19.7, $C_2HF_5NO^+$); 121/123 (7.1, CMe_2Br^+); 69 (38.9, CF_3^+); 57 (40.2, $C_3H_5O^+$); 55 (26.0, $C_4H_7^+$ and/or $C_3H_3O^+$); 43 (100.0, $C_2H_3O^+$); 42 (27.2, $C_3H_6^+$); 41 (33.3, $C_3H_5^+$); 40 (13.9, $C_3H_4^+$); 39 (13.4, $C_3H_3^+$); 29 (26.7, CHO^+); (iv) 1,2-bis[bis(trifluoromethyl)amino-oxy]-3-bromo-2-methylpropane (7) (0.39 g, 0.81 mmol, 15.5%) (Analysis: Found: C, 20.7; H, 1.5; N, 6.0%. $C_8H_7BrF_{12}N_2O_2$ requires: C, 20.4; H, 1.5; N, 5.9%), b.p. 170 °C {^{1}H NMR ($CDCl_3$) δ: 4.14 (s, 2H, CH_2O); 3.43, 3.27 (AB, 2H, CH_AH_BBr, $J_{AB}=11$ Hz); 1.35 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +9.4 [s, 6F, $(CF_3)_2NOCMe$]; +7.6 [s, 6F, $(CF_3)_2NOCH_2$] ppm. The mass spectrum was comparable to that recorded previously [5], i.e. *m/z*: 377 [3.9%, $(M-CH_2Br)^+$]; 302/304 {43.0, $[M-(CF_3)_2NO]^+$}; 288/290 {9.7 $[M-(CF_3)_2NOCH_2]^+$}; 150 (22.5, $C_2HF_5NO^+$); 93/95 (3.9, CH_2Br^+); 71 (20.5, $C_4H_7O^+$); 69 (28.1, CF_3^+); 57 (44.1, $C_3H_5O^+$); 55 (29.1, $C_4H_7^+$ and/or $C_3H_3O^+$); 43 (100.0, $C_2H_3O^+$); 42 (26.7, $C_3H_6^+$ and/or $C_2H_2O^+$); 41 (35.7, $C_3H_5^+$); 39 (13.4, $C_3H_3^+$); 29 (24.7, CHO^+)}; and (v) 1,2-dibromo-2-methylpropane (**8**) (0.31 g, 1.44 mmol, 26.5%) (Analysis: Found: C, 22.0; H, 4.0; Br, 73.7%. $C_4H_8Br_2$ requires: C, 22.2; H, 3.7; Br, 74.1%), which was identified by a comparison of its IR, ^{1}H NMR and mass spectra with those of a known pure sample.

(b) With t-butyl chloride

A mixture of oxyl **1** (1.57 g, 9.3 mmol) and t-butyl chloride (0.43 g, 4.7 mmol), stored in an ampoule (*c.* 50 cm^3) (30 d), gave (i) a −196 °C fraction (0.10 g) (Analysis: Found: M, 43) which was shown (IR spectroscopy) to consist mainly of hydrogen chloride (*c.* 0.07 g, *c.* 2.0 mmol, *c.* 61%) and (ii) a higher-boiling dark yellow liquid (1.90 g), which was shown by GLC (2 m SE30 and 2 m Kel-F at 65 °C) to consist of 13 components (A–M) of which five (A, B, F, K and L) were major. The major components were separated by preparative-scale GLC (2 m SE30 at 75 °C) and were identified as hydroxylamine **3** (0.20 g, 1.2 mmol, 13%), unchanged t-butyl chloride (0.13 g, 1.4 mmol, 30% recovered), 1,2-bis[bis(trifluoromethyl)amino-oxy]-2-methylpropane (**4**) (0.46 g, 1.17 mmol, 35% on chloroalkane, 25% on oxyl), 1,2,3-tris[bis(trifluoromethyl)amino-oxy]-2-methylpropane (**5**) (0.14 g, 0.25 mmol, 8% on chloroalkane and oxyl) and 1,2-bis[bis(trifluoromethyl)-amino-oxy]-3-chloro-2-methylpropane (**9**) (0.43 g, 0.10 mmol, 3.5% on chloroalkane, 2% on oxyl) {^{1}H NMR ($CDCl_3$) δ: 4.03 (s, 2H, CH_2O); 3.44, 3.32 (AB, 2H, CH_AH_BCl, $J=12$ Hz); 1.22 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +9.2 {s, 6F, $(CF_3)_2NOC$<}; +7.35 [s, 6F $(CF_3)_2NOCH_2$] ppm. MS *m/z*: 411/413 [0.2%, $(M-CH_3)^+$]; 377 [9.2, $(M-CH_2Cl)^+$]; 258/260 {12.0, $[M-(CF_3)_2NO]^+$}; 244/246 {16.3, $[M-(CF_3)_2NOCH_2]^+$}; 182 [15.8, $(CF_3)_2NOCH_2^+$]; 166 (11.0, $C_3H_2F_6N^+$); 150 (27.8, $C_2HF_5NO^+$); 77/79 (10.7, $C_3H_6Cl^+$); 69 (65.6, CF_3^+); 57 (50.6, $C_3H_5O^+$); 55 (14.1, $C_4H_7^+$ and/or $C_3H_3O^+$); 49/51 (13.7, CH_2Cl^+); 43 (100.0, $C_2H_3O^+$ and $C_3H_7^+$); 42 (37.5, $C_3H_6^+$); 41 (51.5, $C_3H_5^+$); 39 (16.2, $C_3H_3^+$); 29 (36.5, CHO^+)}. The mass spectrum was comparable to that reported previously [5].1

(c) With 2,2-dichloropropane at 70–80 °C

A mixture of oxyl **1** (2.34 g, 13.9 mmol) and 2,2-dichloropropane (0.78 g, 6.9 mmol), heated at 70–80 °C (78 d), gave (i) a −196 °C fraction (0.42 g, 4.6 mmol) (Analysis: Found: M, 92) which was shown (IR spectroscopy) to consist of hydrogen chloride, *N,N*-bis(trifluoromethyl)amine (**13**) and carbon dioxide, and (ii) higher-boiling material (2.68 g) which was shown by GLC (2 m SE30 and 2 m Kel-F at 80 °C) to contain unchanged 2,2-dichloropropane and hydroxylamine **3** together with seven components (A–G) in the ratio 1.0:4.6:16.2:9.4:2.5:1.0:5.1. Separation of the major components by preparative-scale GLC (4 m Kel-F at 80 °C) gave hydroxylamine **3** (0.76 g, 4.5 mmol, 32%), unchanged 2,2-dichloropropane (0.40 g, 3.5 mmol, 50% recovered), 1-[bis(trifluoromethyl)amino-oxy]-2,2-dichloropropane (**10**) (component C) (nc) (0.42 g, 1.5 mmol, 42%) (Analysis: Found: C, 21.2; H, 1.9; N, 5.1; F, 40.5%. $C_5H_5Cl_2F_6NO$ requires: C, 21.4; H, 1.8; N, 5.0; F, 40.7%) {^{1}H NMR ($CDCl_3$) δ: 4.12 (s, 2H, CH_2O); 1.91 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +8.2 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 243/245 [7.0%, $(M-HCl)^+$]; 182 [0.5, $(CF_3)_2NOCH_2^+$]; 150 (12.5, $C_2HF_5NO^+$); 133 (6.4, $C_2F_5N^+$); 111/113/115 (77.2, $C_3H_5Cl_2^+$); 97/99/101 (100.0, $C_2H_3Cl_2^+$); 75/77 (70.8, $C_3H_4Cl^+$); 69 (90.7, CF_3^+); 61/63 (56.3, $C_2H_2Cl^+$); 44 (36.4, $C_2H_4O^+$); 43 (25.2, $C_2H_3O^+$); 39 (26.0, $C_3H_3^+$)} and 1,2-bis[bis(trifluoromethyl)amino-oxy]-2-chloropropane (**11**) (component D) (nc) (0.33 g, 0.8 mmol, 24%) Analysis: Found: C, 20.6; H, 1.1; N, 6.8%. $C_7H_5ClF_{12}N_2O_2$ requires: C, 20.4; H, 1.2; N, 6.8%), b.p. 135 °C {^{1}H NMR ($CDCl_3$) δ: 4.14, 3.96 (AB, 2H, CH_AH_BO, $J_{AB}=10$ Hz); 1.68 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +10.4 (q, 3F, CF_3N, $J=11$ Hz); +9.7 (q, 3F, CF_3N, $J=11$ Hz); +7.2 [s, 6F, $(CF_3)_2NO$] ppm. MS *m/z*: 377 [1.2%, $(M-Cl)^+$]; 244/246 {19.7, $[M-\{CF_3)_2NO]^+$}; 230/232 {6.1, $[M-(CF_3)_2$-

$NOCH_2]^+$}; 182 [1.3, $(CF_3)_2NOCH_2^+$]; 166 (5.1, $C_3H_2F_6N^+$); 150 (12.2, $C_2HF_5NO^+$); 92/94 (10.2, $C_3H_5ClO^+$); 76/78 (7.1, $C_3H_5Cl^+$); 69 (32.0, CF_3^+); 43 (100.0, $C_2H_3O^+$); 41 (16.0, $C_3H_5^+$); 28 (85.2, $C_2H_4^+$)}.

(d) With 2-chloro-2-phenylpropane

A mixture of oxyl **1** (1.88 g, 11.2 mmol) and 2-chloro-2-phenylpropane (0.87 g, 5.6 mmol), stored in an ampoule (*c.* 100 cm^3) (0.5 h), gave (i) a −196 °C fraction (0.17 g) (Analysis: Found: M, 38) which was shown (IR spectroscopy) to consist of hydrogen chloride (*c.* 0.14 g, 3.7 mmol, 97.5%) contaminated with traces of amine **13**, (ii) hydroxylamine **3** (0.23 g, 1.4 mmol, 12.5%) and (iii) a colourless non-volatile liquid residue (2.32 g) which was shown by GLC (2 m APL and 2 m PEGA at 150 °C) to contain two major (A and B) and eight minor components. Component B was identified (IR spectroscopy and GLC retention time) as unchanged 2-chloro-2-phenylpropane) (0.28 g, 1.8 mmol, 32.5% recovered) and component A was separated by preparative-scale GLC (4 m APL at 140 °C) and identified as 1,2-bis[trifluoromethyl]amino-oxy]-2-phenylpropane (**12**) (nc) (1.34 g, 3.0 mmol, 78%) (Analysis: Found: C, 34.4; H, 2.3; N, 6.5; F, 50.6%. $C_{13}H_{10}F_{12}N_2O_2$ requires: C, 34.4; H, 2.2; N, 6.2; F, 50.2%) {^{1}H NMR ($CDCl_3$) δ: 6.94 (mult., 5H, C_6H_5); 4.01, 3.75 (AB, 2H, CH_AH_BO, J_{AB} = 10 Hz); 1.46 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +9.9 [s, 6F, $(CF_3)_2NOC$<]; +7.6 [s, 6F, $(CF_3)_2NOCH_2$] ppm. MS *m/z*: 286 {43.0%, $[M-(CF_3)_2NO]^+$}; 272 {10.4, $[M-(CF_3)_2NOCH_2]^+$}; 182 {3.2, $[(CF_2)_3NOCH_2]^+$}; 134 (73.9, $C_9H_{10}O^+$); 118 (100.0, $C_9H_{10}^+$); 105 (71.8, $C_8H_9^+$); 103 (17.8, $C_8H_7^+$); 92 (23.4, $C_7H_8^+$); 77 (22.0, $C_6H_5^+$); 69 (37.4, CF_3^+); 43 (55.2, $C_2H_3O^+$)}.

(e) With t-butyl acetate

A mixture of oxyl **1** (2.43 g, 14.5 mmol) and t-butyl acetate (0.79 g, 6.8 mmol), stored (41 d), gave a −196 °C fraction identified (IR spectroscopy) as amine **13** (0.06 g, 0.4 mmol, 3%) and a higher-boiling liquid (3.26 g) which was shown by GLC (2 m SE30 at 90 °C) to contain five major and 12 minor components. The five major components were separated by preparative scale GLC (2 m SE30 at 90 °C) and identified as: (i) hydroxylamine **3** (1.20 g, 7.1 mmol, 49%); (ii) perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (**2**) (0.22 g, 0.7 mmol, 9%); (iii) unchanged t-butyl acetate (0.40 g, 3.5 mmol, 51% recovered); (iv) 2-[bis(trifluoromethyl)-amino-oxycarbonyl]isopropyl acetate (**16**) (nc) (0.39 g, 1.3 mmol, 40%) (Analysis: Found: C, 32.1; H, 3.2; N, 4.4%. $C_8H_9F_6NO_4$ requires: C, 32.3; H, 3.0; N, 4.7%), b.p. 163 °C {IR ($\nu_{max.}$) (cm^{-1}): 1828, 1751 (s) (C=O str.). ^{1}H NMR ($CDCl_3$) δ: 1.69 (s, 3H, CH_3CO_2); 1.29 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +8.9 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 282 [0.1%, $(M-CH_3)^+$]; 145 {2.9, $[M-(CF_3)_2N]^+$}; 133 (4.6, $C_2F_5N^+$); 129 {7.9, $[M-(CF_3)_2NO]^+$}; 101 {35.0, $[M-(CF_3)_2NO_2C]^+$}; 69 (47.0, CF_3^+); 59 (38.9, $CH_3CO_2^+$); 58 (14.5, $C_2H_2O_2$); 44 (57.7, CO_2^+); 43 (100.0, $C_2H_3O^+$); 42 (14.1, $C_2H_2O^+$); 41 (16.1, $C_3H_5^+$)}; and (v) a mixture (0.57 g) of 2-{[bis(trifluoromethyl)amino-oxy]methyl}isopropyl acetate (**14**) (nc) (0.34 g, 1.2 mmol, 36%) and 2,2-{bis[bis(trifluoromethyl)amino-oxy]methyl}isopropyl acetate (**15**) (nc) (0.23 g, 0.5 mmol, 15%) in the ratio 2.6:1.0 as shown by GLC (2 m TXP at 90 °C) and ^{19}F NMR spectroscopy. IR ($\nu_{max.}$) (cm^{-1}): 1779, 1701 (s) (C=O str.). ^{1}H NMR ($CDCl_3$) δ: (compound **14**): 3.96 (s, 2H, CH_2O); 1.55 (s, 3H, CH_3CO_2); 1.29 (s, 6H, CMe_2) ppm; and (compound **15**): 5.21 (s, 1H, −OCHO−); 1.55 (s, 3H, CH_3CO_2) ppm; 1.13 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: (compound **14**): +7.6 [s, $(CF_3)_2NO$] ppm; and (compound **15**): +8.5 [s, $2(CF_3)_2NO$] ppm. MS *m/z*: 268 (2.4%, $C_7H_8F_6NO_3^+$); 224 (11.1, $C_6H_8F_6NO^+$); 223 (25.9, $C_6H_7F_6NO^+$); 114 (13.3, $C_2F_4N^+$ and/or $C_6H_{10}O_2^+$); 111 (19.7, $C_6H_7O_2^+$); 101 (33.6, $C_5H_9O_2^+$); 69 (71.0, CF_3^+); 59 (23.4, $C_2H_3O_2^+$); 56 (34.4, $C_4H_8^+$); 55 (68.9, $C_4H_7^+$); 44 (50.6, CO_2^+); 43 (100.0, $C_2H_3O^+$ and/or $C_3H_7^+$); 42 (29.9, $C_2H_2O^+$ and/or $C_3H_6^+$); 41 (54.3, $C_3H_5^+$); 39 (40.9, $C_3H_3^+$); 29 (52.7, CHO^+); 28 (37.6, CO^+).

Reactions of perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (2)

(a) With t-butyl bromide

A mixture of oxadiazapentane **2** (1.82 g, 5.7 mmol) and t-butyl bromide (0.81 g, 5.9 mmol), stored (15 d), gave (i) a −196 °C fraction identified (IR spectroscopy) as amine **13** (0.11 g, 0.7 mmol, 12%) and (ii) higher-boiling material (2.52 g) which was shown by GLC (2 m SE30 and 2 m Kel-F at 90 °C) to contain hydroxylamine **3** (0.47 g, 2.8 mmol, 32%), unchanged t-butyl bromide (0.20 g, 1.5 mmol, 27% recovered), 1,2-dibromo-2-methylpropane (**8**) (0.31 g, 1.4 mmol, 32%), 1-[bis(trifluoromethyl)amino-oxy]-2-bromo-2-methylpropane (**6**) (0.08 g, 0.3 mmol, 6%) and 13 other components which could not be separated by GLC methods.

(b) With 2-chloro-2-phenylpropane

A mixture of oxadiazapentane **2** (2.78 g, 8.7 mmol) and 2-chloro-2-phenylpropane (1.49 g, 9.6 mmol), stored (5 d), gave (i) a −196 °C fraction (0.24 g, 2.8 mmol) (Analysis: Found: M, 74) shown (IR spectroscopy) to consist of hydrogen chloride (0.07 g, 1.9 mmol, 33%) and amine **13** (0.16 g, 0.9 mmol, 13%), (ii) a −78 °C fraction (1.14 g) shown (IR and ^{19}F NMR spectroscopy) to contain unchanged oxadiazapentane **2** (0.64 g, 2.0 mmol, 23% recovered) and hydroxylamine **3** (0.44 g, 2.6 mmol, 39%) and (iii) a non-volatile black liquid (2.89 g) which was shown by GLC (2 m TXP and 2 m APL at 150 °C) to contain unchanged 2-chloro-2-phenylpropane (0.60 g, 3.8 mmol, 40% recovered) and

12 other components which could not be separated by GLC methods.

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