Reaction of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) with propene, but-2-ene and halogeno derivatives

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Abstract

Reaction of the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**1**) with an excess of the propenes $CH_2=CXR$ (X=H or Cl, R=Me or CH_2Cl) at room temperature gives high yields (92%–97%) of mixtures of the 1:1 adducts $(CF_3)_2NCH_2CXRON(CF_3)_2$ (**3**) and $(CF_3)_2NCXRCH_2ON(CF_3)_2$ (**4**) in the ratio 87:13 to 90:10 via initial $(CF_3)_2N\cdot$ radical attack. In contrast, the corresponding reactions of the alkenes $CH_2=CClR$ (R=Me, CH_2Cl) with the *N*-bromoamine $(CF_3)_2NBr$ (**2**) under free-radical conditions results in monodirectional $(CF_3)_2N\cdot$ radical attack to give the 1:1 adducts $(CF_3)_2NCH_2CBrClR$ (**14**) (95%–98%). With the alkenes $CH_2=CHCF_3$ and $CCl_2=CHMe$, reaction with **1** affords the adducts $(CF_3)_2NCH_2CH(CF_3)ON(CF_3)_2$ (**3e**) (96%) and $(CF_3)_2NCHMeCCl_2ON(CF_3)_2$ (**10**) (86%), respectively, but 3-bromopropene gives a complex mixture of products including the alkene $(CF_3)_2NCH_2CH=CH_2$ (**7**) (4%), the compound $[(CF_3)_2NCH_2]_2CHON(CF_3)_2$ (**8**) (24%) and the dibromide $(BrCH_2)_2CHON(CF_3)_2$ (**9**) (48%). Treatment of (*E*)- or (*Z*)-but-2-ene with **1** gives in each case a mixture (*c.* 80%) of the *erythro* and *threo* 1:1 adducts $(CF_3)_2NCHMeCHMeON(CF_3)_2$ (**11**) in the ratio 75:25, while from (*E*)-1-chlorobut-2-ene the adducts $(CF_3)_2NCH(CH_2Cl)CHMeON(CF_3)_2$ (**12**) (54%) and $(CF_3)_2NCHMeCH(CH_2Cl)ON(CF_3)_2$ (**13**) (42%) are formed each as a mixture of the *erythro* and *threo* isomers.

Introduction

Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (**1**) has been reported to undergo reaction with fluoroalkenes [1], vinylsilanes [2], the alkenes $CH_2=CRCCl_3$ (R=H, Me) [3] and substituted ethenes [4] to give 1:1 adducts in high yield. Such reactions are considered to take place by a free-radical chain process involving initial $(CF_3)_2N\cdot$ radical attack followed by chain transfer of the resulting intermediate radicals with oxadiazapentane **1**, i.e.

$$(CF_3)_2N\cdot + \rangle C{=}C\langle \longrightarrow (CF_3)_2NC\text{–}C\cdot \xrightarrow{1}$$

$$(CF_3)_2NC\text{–}CON(CF_3)_2 + (CF_3)_2N\cdot$$

In an extension of this study, the reactions of the oxadiazapentane **1** with propene, but-2-ene and certain of their halogeno derivatives have been investigated and the results obtained have prompted a study of the reactions of the *N*-bromoamine $(CF_3)_2NBr$ (**2**) with the alkenes $CH_2=CClR$ (R=Me, CH_2Cl).

Results and discussion

The results obtained from reaction of the oxadiazapentane **1** with an excess of the propenes and butenes at room temperature are summarised in Table 1.

$(CF_3)_2NON(CF_3)_2$ (**1**)

$(CF_3)_2NBr$ (**2**)

$(CF_3)_2NCH_2CXYON(CF_3)_2$ (**3**) **a**, X = H, Y = Me; **b**, X = H, Y = CH_2Cl; **c**, X = Cl, Y = Me; **d**, X = Cl, Y = CH_2Cl; **e**, X = H, Y = CF_3

$(CF_3)_2NCXYCH_2ON(CF_3)_2$ (**4**) **a**, X = H, Y = Me; **b**, X = H, Y = CH_2Cl; **c**, X = Cl, Y = Me; **d**, X = Cl, Y = CH_2Cl

$(CF_3)_2NH$ (**5**)

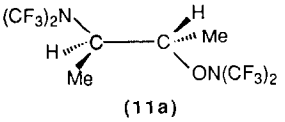
$(CF_3)_2NOH$ (**6**)

$(CF_3)_2NCH_2CH=CH_2$ (**7**)

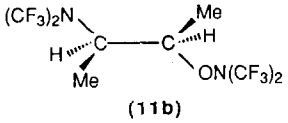
$[(CF_3)_2NCH_2]_2CHON(CF_3)_2$ (**8**)

$[BrCH_2]_2CHON(CF_3)_2$ (**9**)

$(CF_3)_2NCHMeCCl_2ON(CF_3)_2$ (**10**)



(**11a**)



(**11b**)

$(CF_3)_2NCH(CH_2Cl)CHMeON(CF_3)_2$ (**12**)

$(CF_3)_2NCHMeCH(CH_2Cl)ON(CF_3)_2$ (**13**)

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TABLE 1. Reaction of the oxadiazapentane **1** with alkenes

Alkene (g, mmol)	**1** (g, mmol)	Time (d)	Recovered alkene (g, mmol, %)	Products (g, mmol, %)[a]
CH_2=CHMe (0.58, 13.8)	(2.10, 6.56)	3	(0.30, 7.1, 51)	**3a** (2.02, 5.63, 80)[b]; **4a** (0.28, 0.77, 12)[b]
CH_2=$CHCH_2Cl$ (4.25, 54.2)	(10.0, 31.3)	2	(1.72, 22.6, 42)	**5** (0.20, 1.3, 4); **6** (0.22, 1.3, 4); **3b** (10.2, 25.7, 82)[b]; **4b** (1.38, 3.5, 11)[b]; high-boiling residue (*c.* 0.4 g)
CH_2=$CHCH_2Br$ (2.47, 20.4)	(3.58, 11.2)	5	(0.89, 7.4, 36)	**5** (0.10, 0.6, 5.5); **6** (0.04, 0.25, 2); −23 °C (2.70 g): 7 (0.1, 0.5, 4)[c]; **8** (1.61, 3.15, 24)[c]; 0 °C: **9** (2.30, 6.3, 48)
CH_2=CClMe (2.30, 30.05)	(5.68, 17.75)	4	(0.97, 12.65, 42)	**3c** (6.15, 15.5, 87)[d]; **4c** (0.69, 1.75, 10)[d]
CH_2=$CClCH_2Cl$ (1.61, 14.4)	(3.60, 11.25)	4	(1.12, 10.0, 69.5)	−78 °C: **1** (2.22, 6.9, 61); −23 °C: **3d** (1.60, 3.7, 85)[d]; **4d** (0.22, 0.5, 11)[d]
CH_2=$CHCF_3$ (4.33, 45.1)	(4.35, 13.6)	7	(3.29, 34.3, 76)	−78 °C: **1** (0.93, 2.9, 21.5); −23 °C: **3e** (4.33, 10.4, 96)
CCl_2=CHMe (3.46, 31.5)	(5.06, 15.8)	5	(1.73, 15.7, 50)	**5** (0.27, 1.8, 11); **6** (0.22, 1.3, 8); −45 °C (0.43 g)[e]; −23 °C: **10** (5.85, 13.5, 86)
(*E*)-MeCH=CHMe (1.10, 19.64)	(5.46, 17.06)	7	(0.18, 3.2, 16)	**5** (0.24, 1.5, 8.5); **6** (0.26, 1.5, 8); −45 °C (0.5 g)[e]; −23 °C: **11a** (3.84, 10.2, 60)[b]; **11b** (1.28, 3.4, 20)[b]
(*Z*)-MeCH=CHMe (0.70, 12.5)	(2.96, 9.25)	3	(0.15, 2.7, 22)	**5** (0.10, 0.7, 7.5); **6** (0.095, 0.6, 6.5); −45 °C (0.25 g)[e]; −23 °C: **11a** (2.10, 5.59, 60.5)[b]; **11b** (0.70, 1.86, 20)[b]
(*E*)-MeCH=$CHCH_2Cl$ (1.90, 21.6)	(3.60, 11.3)	7	(0.96, 10.5, 49)	**5** (0.05, 0.3, 2.5); **6** (0.05, 0.4, 3); −23 °C: **12** (2.58, 6.2, 54)[f]; **13** (1.86, 4.6, 42)[f]

[a]Yields of amine **5** and hydroxylamine **6** based on oxyl **1**: other yields based on alkene reacted, i.e. not recovered.
[b]Separated by GLC (4 m SE30 at 80 °C).
[c]Separated by GLC (4 m SE30 at 100 °C) from 10-component mixture.
[d]Separated by GLC (4 m SE30 at 100 °C).
[e]Multicomponent mixture.
[f]Not separated; yields estimated by GLC (4 m SE30 at 80 °C).

The alkenes CH_2=$CHCF_3$ and CCl_2=CHMe underwent exclusive $(CF_3)_2N\cdot$ radical attack on the CH_2 and CHMe groups, respectively, as expected, but with the other propenes studied (apart from allyl bromide, where reaction was complicated by loss of bromine) mixtures of the two 1:1 adducts were produced and these results are compared in Table 2 with those obtained from the reactions of the *N*-bromoamine **2** with these propenes.

Bidirectional addition of the oxadiazapentane **1** to the alkenes CH_2=CClR (R = Me, CH_2Cl) was most unexpected, since reaction with 1-chloroethene had resulted in stereospecific addition to give only the 1:1 adduct $(CF_3)_2NCH_2CHClON(CF_3)_2$ [4] via the radical $(CF_3)_2NCH_2\dot{C}HCl$ which is less stable than the radicals $(CF_3)_2NCH_2\dot{C}ClR$ (R = Me, CH_2Cl). Therefore, the free-radical reactions of the *N*-bromoamine **2** with the alkenes CH_2=CClR (R = Me, CH_2Cl) were investigated to determine whether bidirectional addition also took place.

$(CF_3)_2NCH_2CBrXY$	$(CF_3)_2NCXYCH_2Br$
(14) a, X = H, Y = Me	**(15) a**, X = H, Y = Me
b, X = H, Y = CH_2Cl	**b**, X = H, Y = CH_2Cl
c, X = Cl, Y = Me	**c**, X = Cl, Y = Me
d, X = Cl, Y = CH_2Cl	**d**, X = Cl, Y = CH_2Cl

TABLE 2. 1:1 Adduct ratios formed in the reactions of the oxadiazapentane **1** and the *N*-bromoamine **2** with propenes

Alkene	Addend	1:1 Adduct ratio	Yield (%)	Addend	1:1 Adduct ratio	Yield (%)
CH_2=CHMe	**1**	**3a/4a** = 87:13	92	**2**	**14a/15a** = 91:9	94[a]
CH_2=$CHCH_2Cl$	**1**	**3b/4b** = 88:12	93	**2**	**14b/15b** = 96:4	81[b]
CH_2=CClMe	**1**	**3c/4c** = 90:10	97	**2**	**14c/15c** = 100:0[c]	95[d]
CH_2=$CClCH_2Cl$	**1**	**3d/4d** = 88:12	96	**2**	**14d/15d** = 100:0	98[d]

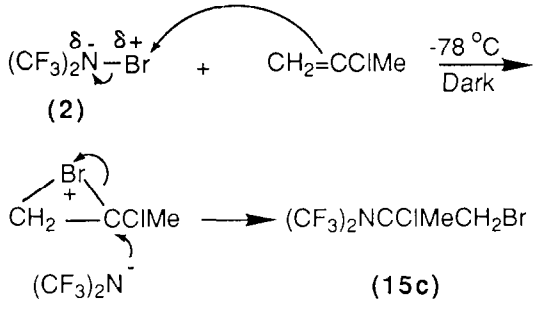
[a]Ref. 5.
[b]Ref. 6.
[c]Under ionic conditions, ratio **14c/15c** = 0:100.
[d]Present work.

The liquid-phase reaction of the *N*-bromoamine **2** with an excess of the alkene CH_2=CClMe (*c.* 1:1.3 molar ratio) at room temperature in light (1 d) gave unchanged alkene (24% recovered), small amounts of perfluoro-2-azapropene and amine **5**, and 1:1 adduct **14c** (95%); a vapour-phase reaction in light also gave compound **14c** (95%). In these reactions the alternative 1:1 adduct **15c** was not detected; this compound was synthesised by reaction under ionic conditions, i.e. treatment of the alkene with the *N*-bromoamine **2** (1.25:1 molar ratio) at −78 °C in the dark (1 d) which gave unchanged alkene (20% recovered), amine **5** (0.5%) and adduct **15c** (99%) (Scheme 1).

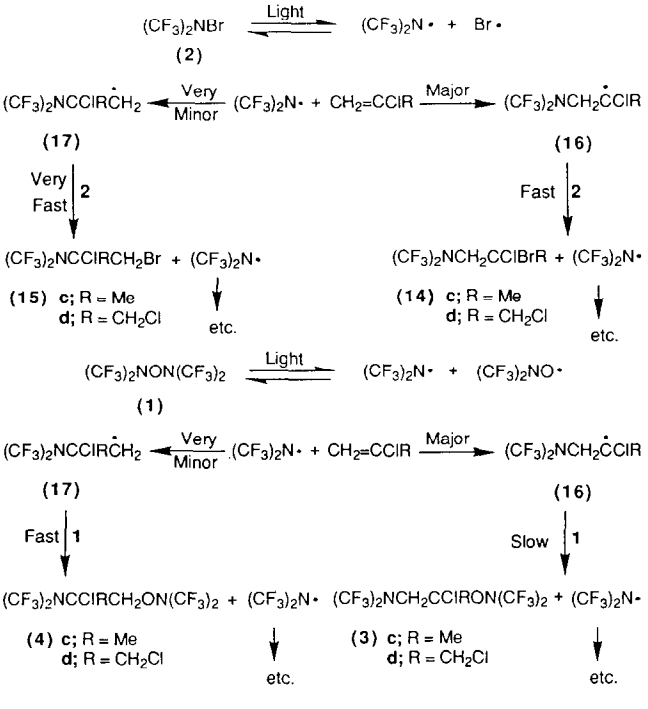
The vapour-phase reaction of the *N*-bromoamine **2** with a slight excess of the alkene CH_2=$CClCH_2Cl$ (1.05:1 molar ratio) in light (3 d) afforded unchanged alkene (6% recovered), perfluoro-2-azapropene (2%) and 1:1 adduct **14d** (98%); adduct **15d** was not detected.

The only other alkenes susceptible to bidirectional radical attack and which have been reacted with both the oxadiazapentane **1** and the *N*-bromoamine **2** are fluoroethene and trifluoroethene; almost identical 1:1 adduct ratios were reported for both addends, i.e. CH_2=CHF 94:6 [4] and 94:6 [7]; CHF=CF_2 80:20 [1] and 78:22 [8]. Thus the free-radical reactions with the chloropropenes are the first examples of addends **1** and **2** giving significantly different 1:1 adduct isomer ratios. It is considered that the reasons for the difference are (i) $(CF_3)_2N\cdot$ radical addition is reversible and (ii) the *N*-bromoamine **2** is a far more efficient chain-transfer agent than the oxadiazapentane **1**; this has been demonstrated in the reactions of the two addends with (*E*)- and (*Z*)-but-2-ene (see later).

Initial $(CF_3)_2N\cdot$ radical attack on the chloropropene CH_2=CClR (R = Me, CH_2Cl) occurs almost exclusively (but not 100%) at the terminal CH_2 groups to afford the more stable intermediate tertiary radicals **16**, and these undergo rapid chain transfer with the *N*-bromoamine **2** to give the observed 1:1 adducts **14c** and **14d**. The other adducts, **15c** and **15d**, are formed in too small an amount to be detected via $(CF_3)_2N\cdot$ radical attack at the substituted vinylic carbons to give the less stable primary radicals **17**, which undergo even more rapid chain transfer with *N*-bromoamine **2** at the unhindered CH_2 groups. In these additions, both intermediate radicals **16** and **17** are formed irreversibly (Scheme 2).



Scheme 1.



Scheme 2.

However, with the bulky addend $(CF_3)_2NON(CF_3)_2$ (**1**), chain transfer at the tertiary site in the radicals **16** is sterically hindered and therefore relatively slow, thus allowing β-scission [to regenerate the alkene and $(CF_3)_2N\cdot$ radicals] to compete effectively with chain transfer [to afford adducts **3c** and **3d**], i.e. formation of radicals **16** is reversible. The small amounts of radicals **17** formed undergo rapid chain transfer at the unhindered CH_2 groups with the oxadiazapentane **1** (as with the *N*-bromoamine **2**) to give the adducts **4c** and **4d**. Hence, in the oxadiazapentane **1** additions, the reversible formation of intermediate radicals **16** and the irreversible formation of intermediate radicals **17** allows significant quantities of the unexpected adducts **4c** and **4d** to be produced (Scheme 2).

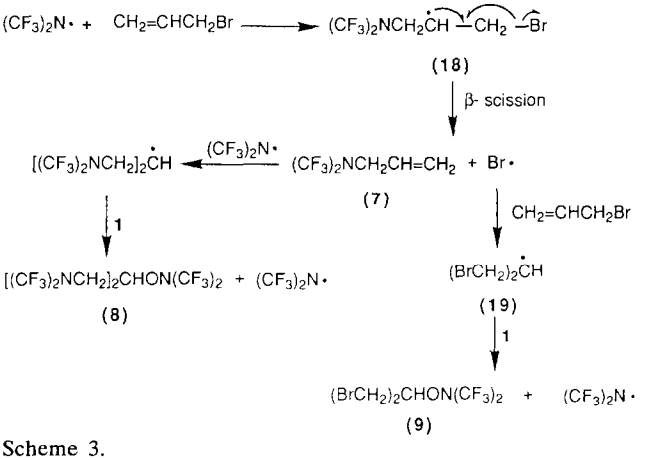
The difference in the 1:1 adduct isomer ratios observed with 3-chloropropene, although less pronounced, can be explained in a similar manner.

The structures of the adducts **3**, **4**, **14c**, **14d** and **15c** were established by elemental analysis (Table 3), NMR spectral data (Table 4) and mass spectrometry (Table 5). Each compound which contained a $(CF_3)_2NCH_2$ group, i.e. **3**, **14c**, and **14d**, showed a ^1H NMR absorption in the range δ 3.1–3.8 ppm (2H, CH_2N), a strong MS band (73%–100%) at *m/z* 166 $[(CF_3)_2NCH_2^+]$ and ^{19}F NMR absorptions in the range $\delta+8$ to $+11.5$ $[(CF_3)_2NO]$ and/or $+17.5$ to $+22$ ppm $[(CF_3)_2N]$. The ^{19}F NMR absorptions for the $(CF_3)_2NO$ group adjacent to a chiral centre in adducts **3c** and **3d** showed non-equivalence of the CF_3 groups, i.e. two quartets (1:1 ratio) with mutual coupling ($J=11$–12 Hz).

Adducts **4** showed a lower-field ^1H NMR absorption in the range δ 3.7–4.5 ppm (2H, CH_2O), ^{19}F NMR absorptions (1:1 ratio) at $+7.3$ to $+12.4$ $[(CF_3)_2NO]$ and $+18$ to $+22$ ppm $[(CF_3)_2N]$ and a weak MS band (4%–7%) at *m/z* 182 $[(CF_3)_2NOCH_2^+]$. The presence of a CH_2Br group in adduct **15c** was shown by a ^1H NMR absorption at δ 3.49 ppm and an MS band at *m/z* 214/216 [16%, $(M-CH_2Br)^+$], and the ^{19}F NMR absorption at δ $+27.4$ ppm confirmed the $(CF_3)_2N$ group.

The reaction of oxadiazapentane **1** with 3-bromopropene was complex and gave eight minor unidentified products, as well as compounds **5** and **6** formed by hydrogen abstraction, the propenylamine **7**, the 1:1 adduct **8** of the alkene **7** and the oxadiazapentane **1** and the dibromide **9**. Products **7**–**9** are considered to be formed as shown in Scheme 3.

Attack on the alkene by the $(CF_3)_2N\cdot$ radical gave the intermediate radical **18** which underwent β-scission to afford the prop-2-enylamine **7** and a bromine atom. Free-radical addition of the oxadiazapentane **1** to the alkene **7** gave the adduct **8**, while bromine atom addition afforded the intermediate radical **19** which abstracted oxyl $(CF_3)_2NO\cdot$ from the oxadiazapentane **1** to yield



Scheme 3.

the dibromide **9**. The bromine content of dibromide **9** is equivalent to 96% of that present in the reacted 3-bromopropene, and so the majority of the minor unidentified products do not contain bromine.

Analogous products to **7**–**9** have been reported to be formed in the photochemical reaction of bromotrichloromethane with 3-bromopropene, i.e. $CH_2=CHCH_2CCl_3$, $(CCl_3CH_2)_2CHBr$ and $(BrCH_2)_2CHBr$ [9,10].

The allylamine **7** has been synthesised previously in 80% yield by dehalogenation of the adduct **14b** with zinc in ethanol [6], and was identified by comparison of the ^1H and ^{19}F NMR data with those reported [6]. The structures of compounds **8** and **9** were established by elemental analysis, a low-field ^1H NMR absorption at δ 4.16–4.46 ppm (1H, CHO) and a higher-field absorption for two equivalent methylene groups (CH_2N or CH_2Br), confirmation of the presence of two equivalent $(CF_3)_2N$ groups (δ_F $+17.6$ ppm) and a $(CF_3)_2NO$ group (δ_F $+8.4$ ppm) in compound **8** and only a $(CF_3)_2NO$ group (δ_F $+10.1$ ppm) in compound **9**, and an MS band at *m/z* 166 [100%, $(CF_3)_2NCH_2^+$] in the spectrum of compound **8**.

The reaction of the oxadiazapentane **1** with (*E*)- or (*Z*)-but-2-ene gave the same 75:25 mixture of the two diastereomers of the 1:1 adduct **11** in each case. This result contrasts that of the photochemically-initiated additions of the *N*-bromoamine **2** to these (*E*)- and (*Z*)-alkenes which afforded the *erythro* and *threo* isomers in the ratios 77:23 and 17:83, respectively [11]; reaction under ionic conditions resulted in stereospecific *anti* addition [12].

Since the ^1H NMR vicinal methine coupling constants were of comparable magnitude for both the isomers of adduct **11**, it was not possible to assign unequivocally *erythro* and *threo* configurations based on the spectra, although of the two CHN absorptions (δ 3.62 and 3.74 ppm) that at higher field (major) could be assigned to the *erythro* isomer. It would be expected that the major product would have the *erythro* configuration **11a**, in

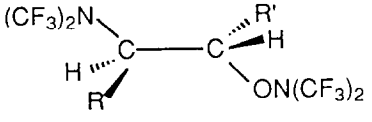
which steric interactions are at a minimum with the bulky $(CF_3)_2N$ and $(CF_3)_2NO$ groups and the two methyl groups *anti* and the minor product would be the more sterically hindered *threo* isomer **11b**. In support of this, it has been observed (i) that in the ^{19}F NMR spectra of the adducts $(CF_3)_2NCHMeCHBrMe$ [12] and $(CF_3)_2NCHClCHClON(CF_3)_2$ [4] the $(CF_3)_2N$ groups in the *erythro* isomers absorbed to higher field than those in the *threo* isomers and (ii) that the *erythro* isomers of these adducts have shorter GLC retention times than the *threo* isomers on a column packed with silicone oil on Celite. The major isomer of adduct **11** had the shorter GLC retention time and the higher-field ^{19}F NMR chemical shift for the $(CF_3)_2N$ group (δ_F +21.5 ppm) as compared to the minor isomer (δ_F +22.1 ppm).

Hence the major isomer is assigned the *erythro* configuration **11a** and the minor isomer is assigned the *threo* configuration **11b**.

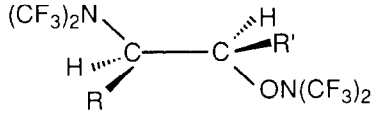
The predominance of *anti* addition in the *N*-bromoamine **2** reactions can be explained by a fast chain-transfer step between the intermediate radical $(CF_3)_2NCHMe\dot{C}HMe$ (**20**) and the *N*-bromoamine **2** (before C–C bond rotation results in equilibration of the radicals **20a** and **20b**) which for steric reasons occurs at the opposite side of the molecule to that at which initial $(CF_3)_2N\cdot$ radical addition occurred. With the corresponding oxadiazapentane **1** additions, the chain-transfer step is relatively slow and equilibration takes place between the intermediate radicals **20a** and **20b** by C–C bond rotation before chain transfer to afford the same ratio of isomer **11a** and **11b** regardless of the but-2-ene isomer employed (Scheme 4).

A preliminary investigation of the reaction of the oxadiazapentane **1** with the alkene (*E*)-MeCH=$CHCH_2Cl$ (2:1 molar ratio) gave a mixture (96%) of the four possible diastereoisomers resulting from initial bidirectional $(CF_3)_2N\cdot$ radical attack. These were identified (GLC–MS) as the *erythro* (**12a**) and *threo* (**12b**) isomers of adduct **12** (54%) in the ratio 50:50 and the *erythro* (**13a**) and *threo* (**13b**) isomers of adduct **13** (42%) in the ratio 55:45 (presuming that the *erythro* isomer has the shorter GLC retention time). Adducts **12a** and **12b** showed MS bands at *m/z* 214/216 [35%–42%, $(CF_3)_2NCHCH_2Cl^+$] and 196 [16%–19%, $(CF_3)_2NOCHMe^+$] while adducts **13a** and **13b** showed bands at *m/z* 180 [100%, $(CF_3)_2NCHMe^+$] and 242/244 {7%–8%, $[M-(CF_3)_2NO]^+$}, thus establishing the structures.

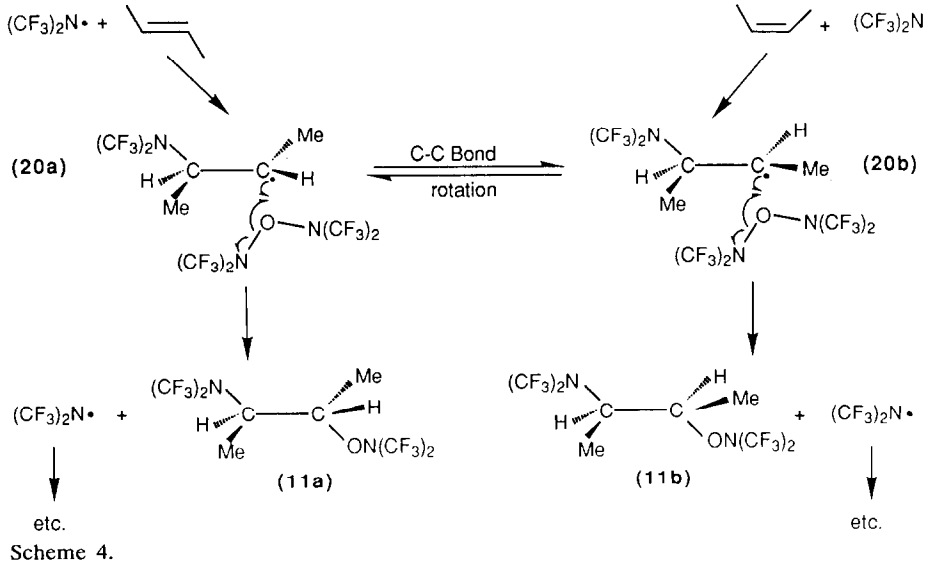
Therefore, in this reaction, initial $(CF_3)_2N\cdot$ radical attack is somewhat more favoured at the $=CHCH_2Cl$ group and, surprisingly, the *erythro* adducts are apparently not favoured, in contrast to the but-2-ene reactions.



(12a) R = CH_2Cl, R' = Me
(13a) R = Me, R' = CH_2Cl



(12b) R = CH_2Cl, R' = Me
(13b) R = Me, R' = CH_2Cl



Scheme 4.

TABLE 3. Elemental analysis and boiling point data

Adduct R=$(CF_3)_2N$	Analysis: Found (%)				Analysis: Calc. (%)				Boiling point (°C)
	C	H	N	F	C	H	N	F	
$RCH_2CHMeOR$ (**3a**)	23.4	1.7	7.6		23.2	1.7	7.7		112
$RCH_2CH(CH_2Cl)OR$ (**3b**)	21.4	1.1	7.2	57.7	21.2	1.3	7.1	57.5	138
$RCH_2CClMeOR$ (**3c**)	21.0	1.3	7.1		21.2	1.3	7.1		127
$RCH_2CCl(CH_2Cl)OR$ (**3d**)	19.5	0.9	6.6		19.5	0.9	6.5		150
$RCH_2CH(CF_3)OR$ (**3e**)	20.3	0.7	7.0		20.2	0.7	6.7		108
$RCHMeCH_2OR$ (**4a**)	23.3	2.0	7.8		23.2	1.7	7.7		
$RCH(CH_2Cl)CH_2OR$ (**4b**)	21.4	1.4	7.0		21.2	1.3	7.1		133
$RCClMeCH_2OR$ (**4c**)	21.5	1.3	7.3		21.2	1.3	7.1		127
$RCCl(CH_2Cl)CH_2OR$ (**4d**)	19.5	0.8	6.7		19.5	0.9	6.5		
$(RCH_2)_2CHOR$ (**8**)	21.3	0.9	8.3		21.1	1.0	8.3		121
$(BrCH_2)_2CHOR$ (**9**)	16.5	1.4	3.5	31.1	16.3	1.4	3.8	30.9	142
$RCHMeCCl_2OR$ (**10**)	19.5	1.1	6.4		19.5	0.9	6.5		156
$RCHMeCHMeOR$ (**11a**) (*erythro*)	25.2	2.1	7.3	60.5	25.5	2.1	7.4	60.6	125–127
$RCHMeCHMeOR$ (**11b**) (*threo*)	25.3	2.1	7.3	60.4	25.5	2.1	7.4	60.6	135–138
$RCH(CH_2Cl)CHMeOR$ (**12**) + $RCHMeCH(CH_2Cl)OR$ (**13**)	23.7	1.8	6.7	55.3	23.4	1.7	6.8	55.5	
$RCH_2CClBrMe$ (**14c**)	19.7	1.6	4.3	37.3	19.5	1.6	4.5	37.0	119
$RCH_2CClBrCH_2Cl$ (**14d**)	17.3	0.9	4.2	33.6	17.5	1.2	4.1	33.3	131
$RCClMeCH_2Br$ (**15c**)	19.9	1.6	4.5	37.1	19.5	1.6	4.5	37.0	117

Experimental

Starting materials

Oxadiazapentane **1** was prepared by reaction of bis(trifluoromethyl)amino-oxyl, $(CF_3)_2NO\cdot$, with trifluoronitrosomethane (2:1 molar ratio) [13] and the *N*-bromoamine **2** was synthesised by reaction of perfluoro-2-azapropene with mercury(II) fluoride to give the mercurial $[(CF_3)_2N]_2Hg$ which was then treated with bromine [8]. The alkene $CH_2{=}CHCF_3$ was a research sample available in the Department and the remaining alkenes were commercial samples whose purity was checked (IR and NMR spectroscopy) before use.

General techniques

Products, after initial separation by fractional condensation *in vacuo*, were further separated (where necessary) by preparative-scale GLC [Pye 104 instrument using columns (4 m) packed with silicone SE30 oil (20% 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; external reference tetramethylsilane], ^{19}F NMR spectroscopy [Varian Associates HA100 (94.12 MHz) instrument; external reference trifluoroacetic acid] and mass spectrometry (AEI MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded using solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

Boiling points were determined using Siwoloboff's method.

Reactions of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (1)

(a) With 3-chloropropene (general procedure)

A mixture of oxadiazapentane **1** (10.0 g, 31.3 mmol) and 3-chloropropene (4.15 g, 54.2 mmol) sealed *in vacuo* in a Pyrex ampoule (*c.* 300 cm^3) fitted with a Rotaflo Teflon tap, was stored at room temperature in the dark (2 d). The volatile products were separated by passage at low pressure (*c.* 1 mmHg) through traps cooled to −23, −45, −78 and −196 °C, respectively, into the following fractions.

(i) A combined −196 °C and −78 °C fraction (0.42 g) which was shown by GLC (2 m SE30 at 50 °C) and IR spectroscopy to be a mixture of *N,N*-bis-(trifluoromethyl)amine (**5**) (0.20 g, 1.3 mmol, 4% based on **1**) and *N,N*-bis(trifluoromethyl)hydroxylamine (**6**) (0.22 g, 1.3 mmol, 4% based on **1**).

(ii) A −45 °C fraction which was identified (IR and ^1H NMR spectroscopy) as unchanged 3-chloropropene (1.72 g, 22.6 mmol, 42% recovered).

(iii) A −23 °C fraction which was separated by GLC (4 m SE30 at 90 °C) into its two components, i.e. 3-chloro-1-[*N,N*-bis(trifluoromethyl)amino]-2-[*N,N*-bis-(trifluoromethyl)amino-oxy]propane (**3b**) (nc (10.2 g, 25.7 mmol, 82%) and 3-chloro-2-[*N,N*-bis(trifluoromethyl)amino]-1-[*N,N*-bis-(trifluoromethyl)amino-oxy]-propane (**4b**) (nc) (1.38 g, 3.5 mmol, 11%) present in the ratio 88:12.

TABLE 4. ^1H and ^{19}F NMR spectral data

Compound R = $(CF_3)_2N$	^1H NMR δ (ppm)	^{19}F NMR δ (ppm)
$RCH_2CHMeOR$ (**3a**)	4.27 (sextet, 1H, CHO, J=6 Hz); 3.41 and 3.11 (ABd, 2H, CH_2N, J_{AB}=16 Hz); 1.27 (d, 3H, CH_3)	+18.1 [s, $(CF_3)_2N$]; +9.4 [s, $(CF_3)_2NO$]
$RCH_2CH(CH_2Cl)OR$ (**3b**)	4.37 (mult, 1H, CHO); 3.65 (mult, 2H, CH_2N); 3.52 (mult, 2H, CH_2Cl)	+17.7 [s, $(CF_3)_2N$]; +9.4 [s, $(CF_3)_2NO$]
$RCH_2CClMeOR$ (**3c**)	3.45 (s, 2H, CH_2N); 1.41 (s, 3H, CH_3)	+19.2 [s, $(CF_3)_2N$]; +11.2 and +9.2 (2q, $2CF_3NO$, J=12 Hz)
$RCH_2CCl(CH_2Cl)OR$ (**3d**)	3.82 (2s, CH_2N and CH_2Cl)	+20.9 [s, $(CF_3)_2N$]; +10.8 and +10.5 (2q, $2CF_3NO$, J=11 Hz)
$RCH_2CH(CF_3)OR$ (**3e**)	4.35 (sextet, 1H, CHO, J=7 Hz); 3.42 (d, 2H, CH_2N)	+17.2 [s, $(CF_3)_2N$]; +8.3 [s, $(CF_3)_2NO$]; 0.3 (d, CF_3, J=7 Hz)
$RCHMeCH_2OR$ (**4a**)	3.88 (complex, 3H, CH_2O and CHN); 1.41 (d, 3H, CH_3, J=6 Hz)	+21.4 [s, $(CF_3)_2N$]; +7.3 [s, $(CF_3)_2NO$]
$RCH(CH_2Cl)CH_2OR$ (**4b**)	4.20 (mult, 1H, CHN); 3.75 (mult, 2H, CH_2O); 3.47 (mult, 2H, CH_2Cl)	+21.6 [s, $(CF_3)_2N$]; +8.4 [s, $(CF_3)_2NO$]
$RCClMeCH_2OR$ (**4c**)	3.73 (s, 2H, CH_2O); 1.21 (s, 3H, CH_3)	+18.8 [s, $(CF_3)_2N$]; +12.4 [s, $(CF_3)_2NO$]
$RCCl(CH_2Cl)CH_2OR$ (**4d**)	4.53 (s, 2H, CH_2O); 4.05 (s, 2H, CH_2Cl)	+18.0 [s, $(CF_3)_2N$]; +7.9 [s, $(CF_3)_2NO$]
$(RCH_2)_2CHOR$ (**8**)	4.16 (mult., 1H, CHO); 3.18 (mult, 4H, $2CH_2N$)	+17.6 [s, $2(CF_3)_2N$]; +8.4 [s, $(CF_3)_2NO$]
$(BrCH_2)_2CHOR$ (**9**)	4.46 (pentet, 1H, CHO, J=6 Hz); 3.76 (mult., 4H, $2CH_2Br$)	+10.1 [s, $(CF_3)_2NO$]
$RCHMeCCl_2OR$ (**10**)	5.03 (q, 1H, CHN, J=8 Hz); 1.39 (d, 3H, CH_3)	+18.9 and +12.7 (2q, $2CF_3N$, J=11 Hz); +5.1 [s, $(CF_3)_2NO$]
RCHMeCHMeOR (**11a**)	4.46 (pentet, 1H, CHO, J=7.3 Hz); 3.62 (pentet, 1H, CHN, J=7.3 Hz); 1.75 (d, 3H, CH_3); 1.62 (d, 3H, CH_3)	+21.5 [s, $(CF_3)_2N$]; +8.8 [s, $(CF_3)_2NO$]
RCHMeCHMeOR (**11b**)	4.44 (pentet, 1H, CHO, J=7 Hz); 3.74 (pentet, 1H, CHN, J=7 Hz); 1.54 (d, 3H, CH_3); 1.47 (d, 3H, CH_3)	+22.1 [s, $(CF_3)_2N$]; +8.7 [s, $(CF_3)_2NO$]
$RCH(CH_2Cl)CHMeOR$ (**12**) + $RCHMeCH(CH_2Cl)OR$ (**13**)	4.2–4.5 (CHO); 3.7–3.9 (CHN and CH_2Cl); 1.3–1.6 (CH_3)	+22.4 to +23.5 [$(CF_3)_2N$]; +9.0 to +9.8 [$(CF_3)_2NO$]
$RCH_2CClBrMe$ (**14c**)	3.19 (s, 2H, CH_2N); 1.50 (s, 3H, CH_3)	+21.8 [$(CF_3)_2N$]
$RCH_2CClBrCH_2Cl$ (**14d**)	3.40 (2s, CH_2N and CH_2Cl)	+22.3 [$(CF_3)_2N$]
$RCClMeCH_2Br$ (**15c**)	3.49 (s, 2H, CH_2Br); 1.64 (s, 3H, CH_3)	+27.4 [$(CF_3)_2N$]

A small amount (*c.* 0.4 g) of a higher-boiling residue remained in the reaction tube.

(b) With other alkenes

The conditions used and the results obtained from reaction of the oxadiazapentane **1** with the alkenes CH_2=CHMe, CH_2=$CHCH_2Cl$, CH_2=$CHCH_2Br$, CH_2=CClMe, CH_2=$CClCH_2Cl$, CH_2=$CHCF_3$, CCl_2=CHMe, (*E*)-MeCH=CHMe, (*Z*)-MeCH=CHMe and (*E*)-MeCH=$CHCH_2Cl$ are shown in Table 1.

Elemental analysis and boiling point data obtained for the products are given in Table 3, the ^1H and ^{19}F NMR spectral data are recorded in Table 4, and the MS data are summarised in Table 5.

All the products which contained $(CF_3)_2NO$ groups showed IR bands ($\nu_{max.}$) (cm^{-1}) at 1300–1160 (s) (C–F str.), *c.* 1050 (s) (C–O–N str.), 960–980 (s) (C–N str.) and *c.* 710 (m to s) (CF_3 def.).

The products **3a–e**, **4a–d**, **8–10**, **11a**, **11b**, **12** and **13** are all new compounds.

TABLE 5. MS data

Compound $R=(CF_3)_2N$	MS, *m/z* (%, assignment)[a,b]
$RCH_2CHMeOR$ (**3a**)	347 [2, $(M-Me)^+$]; 343 [6, $(M-F)^+$]; 196 [21, $(CF_3)_2NOCHMe^+$]; 194 [74, $(CF_3)_2NC_3H_6^+$]; 180 [16, $(CF_3)_2NCHMe^+$]; 179 (5, $C_4H_3F_6N^+$); 166 [73, $(CF_3)_2NCH_2^+$]; 150 (14, $C_2HF_5NO^+$); 78 (49, $C_2H_2F_2N^+$); 69 (94, CF_3^+); 61 (73, $C_3H_6F^+$); 58 (23, $C_3H_6O^+$); 43 (100, $C_2H_3O^+$/$CHNO^+$)
$RCH_2CH(CH_2Cl)OR$ (**3b**)	377 [0.2, $(M-F)^+$]; 347 [2, $(M-CH_2Cl)^+$]; 228 {17, $[M-(CF_3)_2NO]^+$}; 195 (16, $C_4H_3F_6NO^+$); 166 (100); 78 (34); 69 (36); 43 (17)
$RCH_2CClMeOR$ (**3c**)	361 [11, $(M-Cl)^+$]; 244 {5, $[M-(CF_3)_2N]^+$}; 288 {30, $[M-(CF_3)_2NO]^+$}; 166 (82); 150 (12); 95 (13, $C_2F_3N^+$); 78 (16); 69 (30); 43 (100)
$RCH_2CCl(CH_2Cl)OR$ (**3d**)	395 [11, $(M-Cl)^+$]; 278 {4, $[M-(CF_3)_2N]^+$}; 249 (6, $C_5H_4F_9N^+$); 229 (8, $C_4H_2ClF_6NO^+$); 166 (100); 150 (9); 78 (31); 69 (35); 49 (12, CH_2Cl^+); 42 (13, CNO^+)
$RCH_2CH(CF_3)OR$ (**3e**)	392 [2, $(M-F)^+$]; 264 [18, $(M-C_2F_5N)^+$]; 166 (100); 96 (27); 78 (65); 69 (75); 43 (18)
$RCHMeCH_2OR$ (**4a**)	196 (0.3); 194 (2); 182 (4, $(CF_3)_2NOCH_2^+$]; 180 (34); 166 (9); 150 (1); 124 (5, $C_4H_5F_3N^+$); 96 (2, $C_2HF_3N^+$); 78 (14); 69 (31); 43 (100)
$RCH(CH_2Cl)CH_2OR$ (**4b**)	396 (34, M^+); 311 [46, $(M-OCF_3)^+$]; 249 (100); 195 (12); 182 (7); 166 (25); 161 (23, $C_4H_4F_5N^+$); 134 (8, $C_2HF_5N^+$); 114 (6, $C_2F_4N^+$); 96 (13); 78 (15); 69 (24)
$RCClMeCH_2OR$ (**4c**)	311 (9); 249 (24); 230 (7, $C_4H_3ClF_6NO^+$); 182 (4); 166 (7); 150 (6); 133 (8, $C_2F_5N^+$); 114 (12); 96 (8); 95 (6); 69 (88); 43 (100)
$RCCl(CH_2Cl)CH_2OR$ (**4d**)	411 [1, $(M-F)^+$]; 395 (7); 345 (26, $M-OCF_3)^+$; 278 (31); 249 (100); 216 (5, $C_4H_3ClF_6N^+$); 182 (5); 166 (38); 77 (41, $C_2HF_2N^+$); 69 (86)
$(RCH_2)_2CHOR$ (**8**)	494 [1, $(M-F)^+$]; 361 {2, $[M-(CF_3)_2N]^+$}; 347 {2, $[M-(CF_3)_2NCH_2]^+$; 192 [5, $(CF_3)_2NC_3H_4^+$]; 179 (7); 166 (100); 78 (27); 69 (26); 43 (13)
$(BrCH_2)_2CHOR$ (**9**)	274 [4, $(M-CH_2Br)^+$]; 199 {100, $[M-(CF_3)_2NO]^+$}; 166 (4); 150 (9); 119 (56, $C_3H_4Br^+$); 69 (20); 43 (12); 39 (32, $C_3H_3^+$)
$RCHMeCCl_2OR$ (**10**)	394 [7, $(M-HCl)^+$]; 262 {22, $[M-(CF_3)_2NO]^+$}; 227 [6, $(CF_3)_2NC_3H_4Cl^+$]; 180 (78); 150 (11); 129 (29, $C_2Cl_2FO^+$); 92 (43, CF_2NCHMe^+); 69 (100); 63 (45, $CClO^+$)
$RCHMeCHMeOR$ (**11a**) (*erythro*)	224 {18, $[M-(CF_3)_2N]^+$}; 208 {32, $[M-(CF_3)_2NO]^+$}; 193 (8, $(CF_3)_2NC_3H_3^+$]; 180 (100); 166 (11); 150 (5); 92 (26); 75 (27, $C_3H_6FN^+$); 72 (25, $(C_3H_3FN^+$); 69 (30); 55 (45, $C_4H_7^+$); 43 (46)
$RCHMeCHMeOR$ (**11b**) (*threo*)	224(15); 208 (32); 180 (100); 166 (15); 150 (6); 92 (38); 75 (39); 72 (24); 69 (46); 55 (72); 43 (42)
$RCH(CH_2Cl)CHMeOR$ (**12a**) (*erythro*)	242 {10, $[M-(CF_3)_2NO]^+$}; 214 [35, $(CF_3)_2NCHCH_2Cl^+$]; 196 (16); 193 (14); 180 (10); 179 (23); 166 (12); 150 (12); 81 (59, $C_2H_3ClF^+$); 73 (16); 69 (100); 53 (25)
$RCH(CH_2Cl)CHMeOR$ (**12b**) (*threo*)	242 (14); 214 (42); 196 (19); 179 (29); 166 (14); 150 (12); 81 (61); 73 (16); 69 (100); 53 (20)
$RCHMeCH(CH_2Cl)OR$ (**13a**) (*erythro*)	242 (7); 192 (8); 180 (100); 166 (29); 92 (60); 78 (15); 69 (81); 57 (19, $C_2H_3NO^+$); 53 (16)
$RCHMeCH(CH_2Cl)OR$ (**13b**) (*threo*)	242 (8); 192 (12); 180 (100); 166 (30); 92 (51); 78 (13); 69 (86); 57 (17); 53 (17)
$RCH_2CClBrMe$ (**14c**)	272 [6, $(M-Cl)^+$]; 228 [64, $(M-Br)^+$]; 166 (100); 155 (34, $C_3H_5BrCl^+$); 141 (44, $C_2H_3BrCl^+$); 95 (45, $C_3H_5ClF^+$); 78 (43); 75 (46, $C_3H_4Cl^+$); 69 (72)
$RCH_2CClBrCH_2Cl$ (**14d**)	166 (100); 140 (79, $C_2H_2BrCl^+$); 78 (43); 75 (17); 69 (48); 61 (8, $C_2H_2Cl^+$); 40 (15); 39 (13)
$RCClMeCH_2Br$ (**15c**)	272 (15); 228 (7); 214 [16, $(M-CH_2Br)^+$]; 178 (12, $C_5H_2F_6N^+$); 166 (8); 154 (23, $C_3H_4BrCl^+$); 75 (19); 69 (100)

[a]Expressed as percentage of base peak.

[b]Only the ^{35}Cl and ^{79}Br isotope peaks are recorded for ions which contain Cl and/or Br, but the intensities are the total of all the isotope peaks.

Reactions of N-*bromobis(trifluoromethyl)amine (2)*

(a) With 2-chloropropene (liquid phase in light)

A mixture of the *N*-bromoamine **2** (2.52 g, 10.8 mmol) and 2-chloropropene (1.06 g, 13.8 mmol), sealed *in vacuo* in a Rotaflo tube (*c.* 150 cm^3) and kept at room temperature in light (1 d), gave volatile material which was separated by passage at low pressure (*c.* 1 mmHg) through traps cooled to −23, −45, −66, −78 and −196 °C, respectively, to afford (i) a −196 °C fraction identified (IR spectroscopy) as perfluoro-2-azapropene (0.05 g, 0.4 mmol, 3.5%), (ii) a −78 °C fraction identified (IR spectroscopy) as amine **5** (0.01 g, 0.01 mmol, 0.1%), (ii) a −66 °C fraction identified (IR spectroscopy) as unchanged 2-chloropropene (0.26 g, 3.4 mmol, 24% recovered) and (iv) a −23 °C fraction identified as 2-bromo-2-chloro-1-[*N*,*N*-bis(trifluoromethyl)amino]-propene (**14c**) (nc) (3.18 g, 10.3 mmol, 95%).

A second reaction carried out in the vapour phase in light in a Pyrex bulb (*c.* 5 dm^3) into which the *N*-bromoamine **2** (2.28 g, 9.8 mmol) and the alkene (0.77 g, 10.05 mmol) were sealed *in vacuo*, gave (i) perfluoro-2-azapropene (0.05 g, 0.4 mmol, 4%), (ii) unchanged alkene (0.05 g, 0.6 mmol, 6% recovered) and (iii) 1:1 adduct **14c** (2.90 g, 9.4 mmol, 95%).

(b) With 2-chloropropene (liquid phase in the dark)

A mixture of the *N*-bromoamine **2** (3.79 g, 15.9 mmol) and 2-chloropropene (1.52 g, 19.9 mmol), sealed *in vacuo* in a Rotaflo tube (*c.* 150 cm^3) and kept at −78 °C in the dark (1 d), gave (i) amine **5** (0.01 g, 0.1 mmol, 0.5%) which condensed at −196 °C, (ii) a −66 °C fraction identified (IR spectroscopy) as unchanged alkene (0.31 g, 4.0 mmol, 20% recovered) and (iii) a −23 °C fraction identified as 1-bromo-2-chloro-2-[*N*,*N*-bis(trifluoromethyl)amino]propane (**15c**) (nc) (4.87 g, 15.8 mmol, 99%).

(c) With 2,3-dichloropropene (vapour phase in light)

A mixture of the *N*-bromoamine **2** (2.23 g, 9.6 mmol) and 2,3-dichloropropene (1.12 g, 10.1 mmol), sealed *in vacuo* in a Pyrex bulb (*c.* 5 dm^3) and kept at room temperature in light (3 d), gave (i) perfluoro-2-azapropene (0.03 g, 0.2 mmol, 2%) when condensed at −196 °C and (ii) a colourless liquid which condensed in a trap at 0 °C and was separated by preparative-scale GLC (4 m, SE30 at 100 °C) into its two components identified as unchanged 2,3-dichloropropene (0.06 g, 0.6 mmol, 6% recovered) and 2-bromo-1,2-dichloro-3-[*N*,*N*-bis(trifluoromethyl)amino]propane (**14d**) (nc) (3.22 g, 9.4 mmol, 98%).

The elemental analysis and boiling point data for compounds **14c**, **14d** and **15c** are recorded in Table 3, the ^1H and ^{19}F NMR data in Table 4 and the MS data in Table 5.

Compounds **14c**, **14d** and **15c** all showed bands in their IR spectra ($\nu_{max.}$) (cm^{-1}) at 1290–1130 (s) (C−F str.), 950–990 (s) (C−N str.) and 690–710 (s) (CF_3 def.) as expected for the $(CF_3)_2N$ group.

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