Reaction of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) with substituted ethenes and with cyclohexene

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Abstract

The reaction of the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**1**) with the alkenes $CH_2{=}CHX$ (X = Br, Cl, Ph, CN), $CH_2{=}CX_2$ (X = Cl, F), $CHCl{=}CCl_2$ and $CF_2{=}CCl_2$ at *c.* 20 °C gives in each case a single 1:1 adduct formed via initial $(CF_3)_2N\cdot$ radical attack. With the alkene $CH_2{=}CHF$, bidirectional radical attack occurs to afford the 1:1 adducts $(CF_3)_2NCH_2CHFON(CF_3)_2$ and $(CF_3)_2NCHFCH_2ON(CF_3)_2$ in the ratio 94:6, while with (*E*)-$CHCl{=}CHCl$ a mixture of the *erythro* and *threo* 1:1 adducts is formed (ratio 70:30). Reaction of **1** with the alkene $CCl_2{=}CCl_2$ at 50 °C gives the hydrazine $(CF_3)_2NN(CF_3)_2$ (39%), the 1:1 adduct $(CF_3)_2NCCl_2CCl_2ON(CF_3)_2$ (21%) and the 2:1 adduct of the oxyl $(CF_3)_2NO\cdot$ and the alkene, i.e. $(CF_3)_2NOCCl_2CCl_2ON(CF_3)_2$ (39%), while with cyclohexene allylic hydrogen abstraction competes with addition to afford the compounds $(CF_3)_2NH$ (4%), $(CF_3)_2NOCHCH{=}CH(CH_2)_2CH_2$ (27%), $(CF_3)_2NCH(CH_2)_4CH_2$ (23%) and the 1:1 adduct $(CF_3)_2NCH(CH_2)_4CHON(CF_3)_2$ (44%). From competition experiments, the order of reactivity of alkenes, $CH_2{=}CCl_2 > CHF{=}CF_2 > CH_2{=}CHCl > CH_2{=}CH_2 > CH_2{=}CHF > CH_2{=}CF_2 > CHCl{=}CCl_2 > CCl_2{=}CCl_2$, towards $(CF_3)_2N\cdot$ radical attack is obtained.

Introduction

Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) $(CF_3)_2NON(CF_3)_2$ (**1**) was first prepared by photolysis of tris(trifluoromethyl)hydroxylamine [1], but it is more conveniently synthesised by reaction of the oxyl $(CF_3)_2NO\cdot$ (**2**) with trifluoronitrosomethane [2]. It has been found to undergo ready reaction with a variety of fluoroalkenes [3], vinylsilanes [4] and the alkenes $CH_2{=}CRCCl_3$ (R = H, Me) [5] at room temperature via initial $(CF_3)_2N\cdot$ radical attack to afford 1:1 adducts in high yield. In cases where elevated temperature is required for reaction to occur at a reasonable rate, e.g. with hexafluoropropene at 85 °C [3], 2:1 adducts of the oxyl **2** and the alkene are also formed.

In the present work, the reactions of the oxadiazapentane **1** with a series of substituted ethenes have been investigated to determine if 1:1 adducts are formed in high yield. The reaction with cyclohexene was also studied to ascertain whether allylic hydrogen abstraction could compete with addition to the double bond, and competition reactions involving the treatment of pairs of substituted ethenes with a deficiency of the oxadiazapentane **1** were carried out to obtain a reactivity order for the alkenes towards **1**.

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Results and discussion

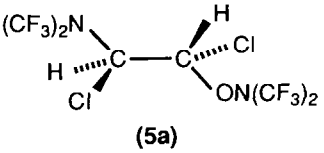
The conditions used and the products formed in the reactions of the oxadiazapentane **1** with substituted ethenes are summarised in Table 1.

$(CF_3)_2NCH_2CXYON(CF_3)_2$

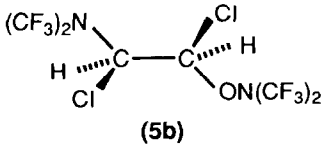
(3) **a**; X = H, Y = Br
b; X = H, Y = Cl
c; X = H, Y = Ph
d; X = H, Y = F
e; X = H, Y = CN
f; X = Y = Cl
g; X = Y = F

$(CF_3)_2NCHFCH_2ON(CF_3)_2$

(4)



(5a)



(5b)

$(CF_3)_2NCXYCCl_2ON(CF_3)_2$

(6) **a**; X = H, Y = Cl
b; X = Y = F
c; X = Y = Cl

$(CF_3)_2NOCCl_2CCl_2ON(CF_3)_2$

(7)

$(CF_3)_2NN(CF_3)_2$

(8)

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TABLE 1. Reaction of the oxadiazapentane **1** with substituted ethenes

Alkene (g, mmol)	**1** (g, mmol)	Time (h)	Recovered alkene (g, mmol, %)	Products (g, mmol, %)
CH_2=CHBr (2.26, 21.1)	(2.92, 9.12)	1	(1.20, 11.2, 53)	**3a** (3.90, 9.10, 99)
CH_2=CHCl (1.37, 21.9)	(5.10, 15.9)	120	(0.41, 6.6, 30)	**3b** (6.00, 15.7, 98)
CH_2=CHPh (1.40, 13.46)	(3.97, 12.4)	120	(0.11, 1.2, 8)	**3c** (5.17, 12.2, 98)
CH_2=CHF (0.84, 18.3)	(3.38), 10.6)	240	(0.36, 7.8, 42)	**3d** (3.58, 9.85, 93); **4** (0.24, 0.61, 6)
CH_2=CHCN[a] (0.76, 14.3)	(4.47, 14.0)	336	(0.013, 0.25, 2)	**3e** (5.16, 13.85, 99)
CH_2=CCl_2[a] (1.08, 11.1)	(3.36, 10.5)	120		**3f** (4.29, 10.35, 99); $\{CH_2-CCl_2\}_n$ (0.05)
CH_2=CF_2 1.58, 24.7)	(6.10, 19.1)	48	(0.39, 6.1, 24.5)	**3g** (7.26, 18.9, 99)
(*E*)-CHCl=CHCl (1.48, 15.3)	(1.52, 4.7)	72	(1.03, 10.6, 69)	**5a** (1.37, 3.25, 69); **5b** (0.58, 1.38, 30)
CHCl=CCl_2 (2.62, 19.9)	(4.70, 14.7)	48	(0.68, 5.2, 26)	**6a** (6.59, 14.6, 99)
CF_2=CCl_2 (2.52, 18.9)	(5.60, 17.5)	168	(0.19, 1.4, 7)	**6b** (7.88, 17.4, 99)
CCl_2=CCl_2[b] (2.59, 15.6)	(4.80, 15.0)	168	(1.10, 6.6, 42)	**6c** (1.53, 3.1, 21); **7** (2.96, 5.9, 39); **8** (1.78, 5.9, 39)

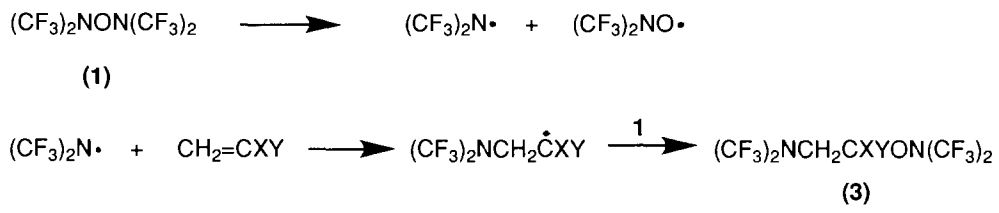
[a]Reactions carried out in Pyrex bulbs (*c.* 5 dm^3) in light; remaining reactions carried out in Pyrex ampoules (*c.* 300 cm^3) in the dark.
[b]Carried out at 50 °C; other reactions carried out at room temperature.

With the unsymmetrical substituted ethenes CH_2=CHX (X=Br, Cl, Ph, CN), CH_2=CX_2 (X=Cl, F), CHCl=CCl_2 and CF_2=CCl_2, a single 1:1 adduct was obtained in each case in high yield (98%–99%) via $(CF_3)_2N\cdot$ radical attack on the carbon atom which afforded the most stable intermediate radical (Scheme 1) in agreement with the monodirectional additions reported to these alkenes of a large variety of addends under free-radical conditions, including those of the *N*-halogenoamines $(CF_3)_2NX$ (X=Cl, Br) to the alkenes CH_2=CHCl [6], CH_2=CCl_2 [6] and CH_2=CF_2 [7]. In the present work, the free-radical addition of the *N*-bromoamine $(CF_3)_2NBr$ to the alkene CHCl=CCl_2 in light was carried out and gave the 1:1 adduct $(CF_3)_2NCHClCCl_2Br$ (98%).

The reactions were carried out in the liquid phase except with the readily polymerised alkenes CH_2=CCl_2 and CH_2=CHCN, which afforded higher yields of 1:1 adducts by reaction in the gas phase.

With vinyl fluoride, bidirectional $(CF_3)_2N\cdot$ radical attack occurred to afford the adducts **3d** and **4** in the ratio 94:6, with major attack taking place on the CH_2 group. This result compares well with the ratios of bidirectional attack on vinyl fluoride reported for the $(CF_3)_2N\cdot$ radical generated from $(CF_3)_2NCl$ (95:5) [8], $(CF_3)_2NBr$ (94:6) [9] and $(CF_3)_2NI$ (93:7) [8].

The mass spectra were most informative in assigning structures to the 1:1 adducts, i.e. the spectra of the compounds **3a–g** contained a strong peak at *m/z* 166 $[(CF_3)_2NCH_2^+]$ (40%–100%), except for compound **3c** which gave a relatively weak peak (16%), although the $[M-(CF_3)_2NCH_2]^+$ peak at *m/z* 258 was strong (82%) and the spectra of adducts **6a** and **6b** contained peaks at *m/z* 200/202 $[(CF_3)_2NCHCl^+]$ (28%) and 202 $[(CF_3)_2NCF_2^+]$ (26%), respectively. The ^{19}F NMR spectra of all the adducts showed two absorptions (1:1 ratio) at δ_F +16.9 to +25.4 $[(CF_3)_2N]$ and +17.2 to +12.0 $[(CF_3)_2NO]$ ppm, with the $(CF_3)_2N$ absorption in adduct **6a** appearing as two quartets (J=25 Hz) due to coupling between the CF_3 groups which were rendered non-equivalent by the adjacent chiral centre; surprisingly, the $(CF_3)_2N$ group absorption in adduct **4** did not show such non-equivalence. The ^1H NMR spectra were consistent with the structures proposed, i.e. adducts **3a–e** each gave two absorptions (ratio 2:1) at δ_H 2.98–3.83 ppm (N-CH_2) and 4.81–5.79 ppm (O-CHX), adducts



Scheme 1.

3f and **3g** a singlet absorption at 3.6–4.15 ppm ($N-CH_2$) and adduct **6a** a singlet absorption at 5.94 ppm (N–CHCl). The above data show unequivocally that the adducts have the structures assigned.

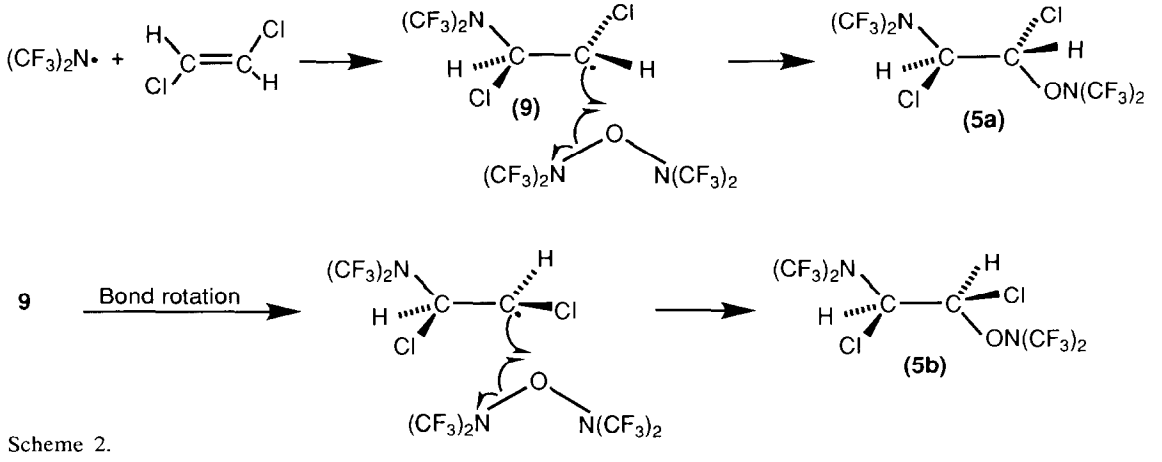
The reaction of the oxadiazapentane **1** with the alkene (*E*)-CHCl=CHCl gave a mixture of two 1:1 adducts (**5a,b**) (ratio 70:30), which were assigned on the basis of the NMR spectral data obtained for the mixture.

For the *erythro* and *threo* 1:1 adducts $(CF_3)_2NCH_DMeCH_EXMe$ (X = Cl, Br), obtained by *anti* addition of the amines $(CF_3)_2NX$ (X = Cl, Br) under ionic conditions to (*E*) and (*Z*)-but-2-ene, respectively, it was reported (i) that the ^1H NMR vicinal coupling constants J_{D-E} were larger in the *erythro* isomers (11.0 and 10.0 Hz) than in the *threo* isomers (9.7 and 9.4 Hz) and (ii) that the ^{19}F NMR chemical shifts for the $(CF_3)_2N$ group were at lower field in the *threo* isomers than in the *erythro* isomers [10].

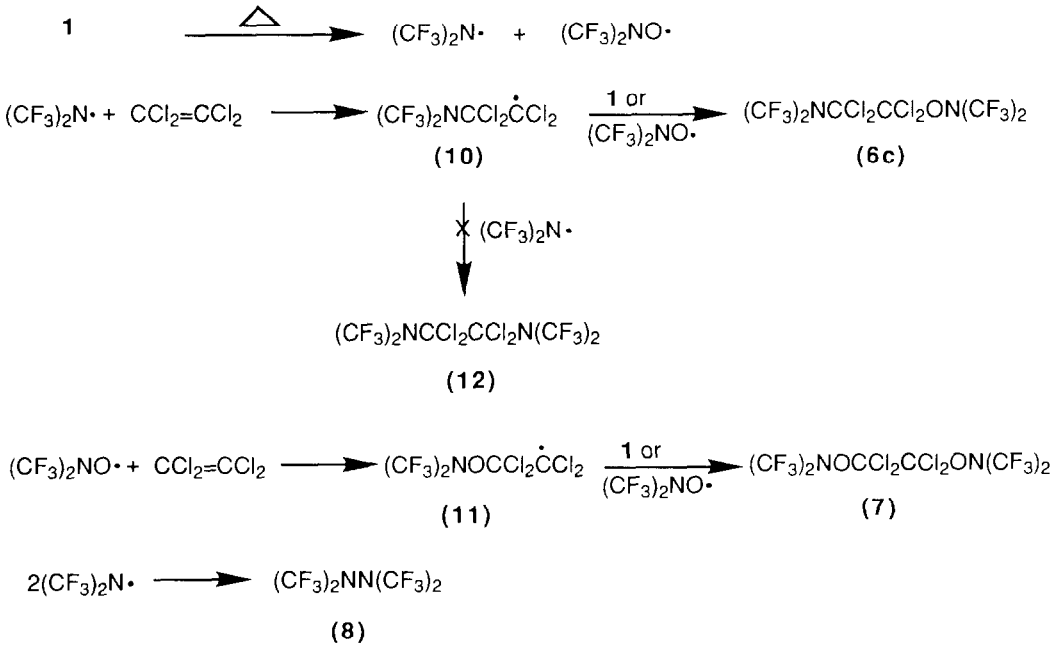
The NMR spectra of the major and minor isomers of adduct **5**, $(CF_3)_2NCH_DClCH_EClON(CF_3)_2$ showed values for J_{D-E} of 10 and 9 Hz and $(CF_3)_2N$ chemical shifts at δ_F +21.4 and +21.9 ppm, respectively. On this evidence the major isomer is assigned the *erythro* structure **5a** and the minor isomer the *threo* structure **5b**. *Anti* addition of the oxadiazapentane to (*E*)-CHCl=CHCl would afford the *erythro* isomer **5a**, which is the adduct preferred on steric grounds, with the two Cl atoms *trans* as well as the bulky $(CF_3)_2N$ and $(CF_3)_2NO$ groups. The minor *threo* isomer **5b** is the product of *syn* addition, although it is probable that C–C bond rotation in the intermediate radical **9** takes place followed by chain transfer from the opposite side of the intermediate to the $(CF_3)_2N$ group (Scheme 2).

The reaction of the oxadiazapentane **1** with tetrachloroethene was very slow at *c.* 20 °C and reaction at 50 °C gave only a low yield (21%) of the 1:1 adduct **6c**, the major products being the 2:1 adduct **7** (39%) of the oxyl **2** and the alkene and tetrakis(trifluoromethyl)hydrazine **8** (39%). This result indicates that breakdown of compound **1** to the radicals $(CF_3)_2N\cdot$ and $(CF_3)_2NO\cdot$ is relatively fast at 50 °C and dimerisation of the $(CF_3)_2N\cdot$ radicals to hydrazine **8** and $(CF_3)_2NO\cdot$ radical attack on the alkene competes with $(CF_3)_2N\cdot$ radical attack. It is possible that under these conditions attack on the intermediate radicals **10** and **11** by oxyl **2** competes with chain transfer involving oxadiazapentane **1** (Scheme 3). Compound **12**, arising from $(CF_3)_2N\cdot$ radical coupling with the intermediate radical **10**, was not detected in the products. This is in agreement with a previous report [11] that dimerisation of $(CF_3)_2N\cdot$ radicals is more favourable than reaction of the radicals with intermediate radicals of type $(CF_3)_2NCF_2CF_2\dot{C}XCl$ (X = F, Cl); the $(CF_3)_2N\cdot$ radicals were generated by decomposition of the compound $(CF_3)_2NOC(CF_3)_2N{=}NC(CF_3)_2ON(CF_3)_2$.

Storage of a mixture of the oxadiazapentane **1** and cyclohexene (1:1 molar ratio) for 3 d at room temperature in the dark gave the amine $(CF_3)_2NH$ (4%),

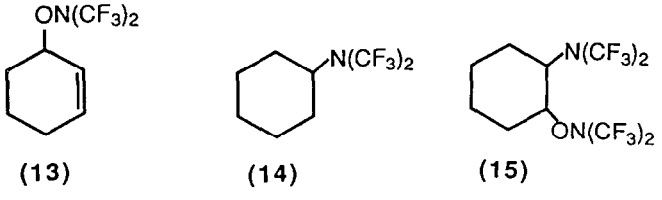


Scheme 2.



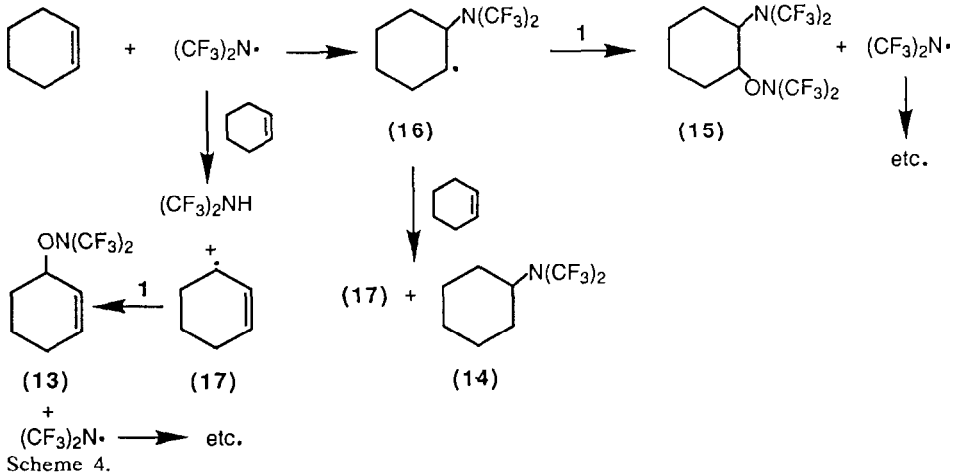
Scheme 3.

unchanged **1** (29% recovered), unchanged cyclohexene (4% recovered), the allylic substitution product **13** (27%), bis(trifluoromethyl)aminocyclohexane (**14**) (23%) and the 1:1 adduct **15** (44%). The products are considered to have been formed as shown in Scheme 4.



The yield of the substitution product **13** is equal to the combined yields of the cyclohexylamine **14** and the amine $(CF_3)_2NH$, and is best explained by competing $(CF_3)_2N\cdot$ radical addition to cyclohexene to afford the intermediate radical **16** and allylic abstraction to give the allyl radical **17**. The intermediate radical **16** then undergoes both reaction with oxadiazapentane **1** to give the 1:1 adduct **15** and allylic hydrogen abstraction from cyclohexene to give radical **17** and the aminocyclohexane **14**.

It has been reported that reaction of cyclohexene with the compounds CCl_4 and CCl_3Br under peroxide-initiated conditions gave the 1:1 adducts $CCl_3C_6H_{10}X$ and the allylic substitution products C_6H_9X (X=Cl,



Scheme 4.

Br), but a product corresponding to aminocyclohexane **14**, i.e. $C_6H_{11}CCl_3$, was not formed [12, 13]. The difference in the reactions is presumably due to chain transfer of radical **16** with the oxadiazapentane **1** being slower than chain transfer of the radical $CCl_3C_6H_{10}\cdot$ with CCl_3X, thus allowing allylic abstraction by radical **16** to compete with chain transfer.

Elemental analysis and spectral data confirmed the structures of compounds **13–15**. Thus, the ^1H NMR spectra all showed the presence of the appropriate number of CH_2 groups together with absorptions for two vinylic (δ 5.85 ppm) and a $\rangle$CHO (δ 4.45 ppm) hydrogen (compound **13**), a $\rangle$CHN (δ 3.51 ppm) hydrogen (compound **14**) and both a $\rangle$CHO (δ 4.31 ppm) and a $\rangle$CHN (δ 3.52 ppm) hydrogen (compound **15**). Compounds **13** and **15** showed ^{19}F NMR absorptions for $(CF_3)_2NO$ (δ +9 to +10 ppm) groups and compounds **14** and **15** absorptions for $(CF_3)_2N$ (δ +23 to +24 ppm) groups. The mass spectra of compounds **13** and **14** showed parent ion peaks at *m/z* 249 and 235, respectively, while adduct **15** showed ion peaks at *m/z* 250 $(M-(CF_3)_2N]^+$ and 234 $[M-(CF_3)_2NO]^+$.

The ^{19}F NMR spectrum of adduct **15** showed two $(CF_3)_2N$ and two $(CF_3)_2NO$ absorptions indicating the presence of two isomers (ratio 5:2) presumably the *trans* and *cis* adducts, respectively.

A series of competition reactions between oxadiazapentane **1** and mixtures of an excess of two substituted ethenes gave the results summarised in Table 2.

The order of alkene reactivity was $CH_2{=}CCl_2 > CHF{=}CF_2 > CH_2{=}CHCl > CH_2{=}CH_2 > CH_2{=}CHF > CH_2{=}CF_2 > CHCl{=}CCl_2 > CCl_2{=}CCl_2$.

For the fluoroalkenes the reactivity order observed, $CHF{=}CF_2 > CH_2{=}CHF > CH_2{=}CF_2$, has been noted for other radical additions [14] and the alkene $CF_2{=}CF_2$ is more reactive than trifluoroethene towards oxyl $(CF_3)_2NO\cdot$ attack [15]. Deactivation of the double bonds of the alkenes $CH_2{=}CHF$ and $CH_2{=}CF_2$ relative to ethene towards attack by the radical $(CF_3)_2N\cdot$, which is of comparable electrophilicity to the CF_3 radical [8], is presumably due to the $-I$ inductive effect of fluorine. The much increased reactivity of trifluoroethene is probably due to hybridisation and bond angle differences as has been postulated previously [16–18].

With the chloroethenes, the order observed, i.e. $CH_2{=}CCl_2 > CH_2{=}CH_2 > CHCl{=}CCl_2 > CCl_2{=}CCl_2$, can be explained by the relative importance of intermediate radical stability, steric hindrance to radical attack and double bond electron density. Substitution of H by Cl increases intermediate radical stability $(-\dot{C}Cl_2 > -\dot{C}HCl > \dot{C}H_2)$, but steric hindrance is increased and double bond electron density is decreased (by the $-I$ effect of Cl). With the alkenes $CH_2{=}CHCl$ and $CH_2{=}CCl_2$, radical attack occurs at the sterically favoured CH_2 group and it is considered that intermediate radical stability outweighs reduced double-bond electron density. However, with the alkene $CHCl{=}CCl_2$, the combined effects of increased steric hindrance to attack (at CHCl) and a further decrease in double-

TABLE 2. Reaction of the oxadiazapentane **1** with mixtures of ethenes

Reactant alkenes		**1** (g, mmol)	Time (d)	Alkenes recovered (%)		1:1 Adducts[a]	
A (g, mmol)	B (g, mmol)			A	B	From A (g, mmol, %)	From B (g, mmol, %)
$CH_2{=}CCl_2$ 1.79, 18.45	$CHCl{=}CCl_2$ 2.42, 18.45	1.50, 4.7	7	74	99	1.95, 4.65, 99	
$CH_2{=}CCl_2$ 4.33, 44.6	$CH_2{=}CHCl$ 2.79, 44.6	1.65, 5.1	3	90	98.5	1.79, 4.3, 84	0.23, 0.6, 11
$CH_2{=}CCl_2$ 4.30, 44.4	$CHF{=}CF_2$ 3.64, 44.4	1.43, 4.5	3	94	96	1.17, 2.8, 62	0.64, 1.6, 35.5
$CH_2{=}CH_2$ 1.92, 68.5	$CH_2{=}CHCl$ 4.35, 68.5	1.45, 4.5	7	97.5	95.5	0.55, 1.6, 35.5	1.09, 2.84, 63
$CH_2{=}CHCl$ 0.96, 15.3	$CHCl{=}CCl_2$ 2.01, 15.3	2.18, 6.8	7	56	100	2.52, 6.6, 97	
$CH_2{=}CH_2$ 1.12, 40.1	$CH_2{=}CHF$ 1.84, 40.1	1.62, 5.0	7	90	97	1.39, 4.0, 80	0.31, 0.85, 17
$CH_2{=}CHF$ 2.03, 44.2	$CH_2{=}CF_2$ 2.83, 44.2	2.10, 6.6	7	92	93.5	1.28, 3.5, 53	1.08, 2.8, 42
$CH_2{=}CH_2$ 1.24, 44.4	$CHCl{=}CCl_2$ 5.92, 44.4	2.10, 6.6	7	86	99	2.09, 6.0, 91	0.18, 0.4, 6
$CHCl{=}CCl_2$ 3.10, 23.6	$CCl_2{=}CCl_2$ 3.91, 23.6	1.84, 5.75	10	77	98	2.44, 5.4, 94	0.17, 0.35, 6

[a]Yields based on oxadiazapentane **1**.

bond electron density more than offset intermediate radical stability, and for the alkene $CCl_2=CCl_2$ the steric hindrance to attack (at CCl_2) is further increased and the double-bond electron density is further decreased resulting in even slower reaction.

Experimental

Starting materials

The oxadiazapentane **1** was prepared by reaction of bis(trifluoromethyl)amino-oxyl $(CF_3)_2NO\cdot$ (**2**) with trifluoronitrosomethane (2:1 molar ratio) [2], and the *N*-bromoamine $(CF_3)_2NBr$ was available in the Department having been prepared by the reaction of perfluoro-2-azapropene with mercury(II) fluoride to give the mercurial $[(CF_3)_2N]_2Hg$ followed by reaction with bromine [1]. The alkenes were commercial samples and their purities were checked (IR and NMR spectroscopy) before use.

General techniques

Reactions of the oxadiazapentane **1** and the *N*-bromoamine $(CF_3)_2NBr$ were carried out *in vacuo* in Pyrex ampoules (*c.* 300 cm^3 unless stated otherwise) fitted with Rotaflo Teflon taps, and the resulting volatile material was separated by fractional condensation into lower-boiling fractions containing unchanged reactants and higher-boiling product fractions, with further separation of product mixtures achieved by preparative-scale GLC [Pye 104 instrument using columns (4 or 10 m) packed with silicone SE30 oil (20% w/w) on acid-washed Celite]. Products were examined by IR spectroscopy (Perkin-Elmer 197 instrument), ^1H NMR spectroscopy [Varian Associates HA100 (100.0 MHz) spectrometer; external 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 using solutions of samples 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) with alkenes

(a) Bromoethene (general procedure)

A mixture of oxadiazapentane **1** (2.92 g, 9.12 mmol) and bromoethene (2.26 g, 21.1 mmol) stored in the dark (1 h), gave: (i) a −78 °C fraction identified as unchanged bromoethene (1.20 g, 11.2 mmol, 53% recovered); and (ii) a −23 °C fraction which was identified as 1-bromo-2-{[*N*,*N*-bis(trifluoromethyl)amino]-1-[*N*,*N*-bis(trifluoromethyl)amino-oxy]}ethane (**3a**) (nc) (3.90 g, 9.10 mmol, 99%).

(b) Other substituted ethenes

The conditions used and the results obtained from reaction of oxadiazapentane **1** with the alkenes $CH_2=CHCl$, $CH_2=CHPh$, $CH_2=CHF$, $CH_2=CHCN$ [in a Pyrex bulb (*c.* 5 dm^3) in light], $CH_2=CCl_2$ [in a Pyrex bulb (*c.* 5 dm^3) in light], $CH_2=CF_2$, (*E*)-$CHCl=CHCl$, $CHCl=CCl_2$ and $CF_2=CCl_2$ at room temperature and with $CCl_2=CCl_2$ at 50 °C are summarised in Table 1. In the $CCl_2=CCl_2$ reaction, the hydrazine **8** condensed at −196 °C and the mixture of compounds **6c** and **7** was separated by GLC (4 m SE30 at 120 °C) methods.

Elemental analysis and boiling point data obtained for the 1:1 adducts **3a–c**, **3f,g**, **3d+4**, **5a,b** and **6a–c**, and for compound **7** are given in Table 3, the ^1H and ^{19}F NMR spectral data are recorded in Table 4 and the mass spectral data in Table 5.

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

(c) Cyclohexene

A mixture of oxadiazapentane **1** (2.54 g, 7.9 mmol) and cyclohexene (0.65 g, 7.9 mmol) stored *in vacuo* in the dark (3 d) gave: (i) a −78 °C fraction identified (IR spectroscopy) as *N*,*N*-bis(trifluoromethyl)amine (0.6 g, 0.4 mmol, 4%); (ii) unchanged diazapentane **1** (0.74 g, 2.3 mmol, 29% recovered) which condensed at −66 °C; and (iii) a colourless liquid which condensed at −23 °C and was separated by GLC (10 m SE30 at 100 °C) methods into its four components. These were identified as (i) 3-[*N*,*N*-bis(trifluoromethyl)amino-oxy]cyclohexene (**13**) (nc) (0.55 g, 2.2 mmol, 27%) (Analysis: Found: C, 38.5; H, 3.9; N, 5.4; F, 45.7%, $C_8H_9F_6NO$ requires: C, 38.5; H, 3.6; N, 5.4; F, 45.8%) {^1H NMR ($CDCl_3$) δ: 5.85 (mult., 2H, 2 =CH); 4.45 (mult., 1H, >CHO); 1.81 (complex, 6H, $3CH_2$) ppm. ^{19}F NMR δ: +9.4 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 249 (0.3%, M^+); 166 (6.8, $C_3H_2F_6N^+$); 150 (3.1, $C_2HF_5NO^+$); 81 (100.0, $C_6H_9^+$); 79 (22.0, $C_6H_7^+$); 69 (24.2, CF_3^+); 55 (13.0, $C_4H_7^+$); 41 (39.5, $C_3H_5^+$); 39 (16.8, $C_3H_3^+$)}; (ii) *N*,*N*-bis(trifluoromethyl)amino-cyclohexane (**14**) (nc) (0.44 g, 1.8 mmol, 23%) (Analysis: Found: C, 40.6; H, 5.0; N, 5.7%. $C_8H_{11}F_6N$ requires: C, 40.8; H, 4.7; N, 5.9%) {^1H NMR ($CDCl_3$) δ: 3.51 (mult., 1H, >CHN); 2.00 (complex, 6H, $3CH_2$); 1.49 (complex, 2H, CH_2) ppm. ^{19}F NMR δ: +23.2 [s, $(CF_3)_2N$] ppm. MS *m/z*: 235 (14.8%, M^+); 192 (100.0, $C_5H_4F_6N^+$); 179 (31.4, $C_4H_3F_6N^+$); 166 (14.5, $C_3H_2F_6N^+$); 83 (38.2, $C_6H_{11}^+$); 82 (60.6, $C_6H_{10}^+$); 69 (28.6, CF_3^+); 55 (23.7, $C_4H_7^+$); 54 (16.7, $C_4H_6^+$); 41 (30.1, $C_3H_5^+$)}; (iii) 1-

TABLE 3. Elemental analysis and boiling point data for the 1:1 adducts of oxadiazapentane **1** and substituted ethenes

Compound [R = $(CF_3)_2N$]	Analysis								B.p. (°C)
	Found (%)				Calculated (%)				
	C	H	N	F	C	H	N	F	
$RCH_2CHBrOR$ (**3a**)	16.7	0.7	6.5	53.6	16.9	0.7	6.5	53.4	111
$RCH_2CHClOR$ (**3b**)	19.0	0.9	7.4	59.4	18.8	0.8	7.3	59.6	103
$RCH_2CHPhOR$ (**3c**)	33.8	1.9	7.3	54.1	34.0	1.9	6.6	53.8	171
RCH_2CHFOR (**3d**) / $RCHFCH_2OR$ (**4**)	19.7	0.7	7.9	67.5	19.7	0.8	7.7	67.5	
$RCH_2CHCNOR$ (**3e**)	22.2	0.6	11.3	61.2	22.5	0.8	11.3	61.2	129
RCH_2CCl_2OR (**3f**)	17.6	0.2	6.5	54.6	17.3	0.5	6.7	54.7	129
RCH_2CF_2OR (**3g**)	18.9	0.7	7.2	69.4	18.8	0.5	7.3	69.3	101
$RCHClCHClOR$ (**5**)	17.3	0.6	6.6	54.5	17.3	0.5	6.7	54.7	108
$RCHClCCl_2OR$ (**6a**)	16.0	0.3	6.0	50.7	15.9	0.2	6.2	50.5	137
RCF_2CCl_2OR (**6b**)	16.0	0.0	6.2	50.1	15.9	0.0	6.2	50.3	132
$RCCl_2CCl_2OR$ (**6c**)	14.5	0.0	5.7	46.4	14.8	0.0	5.8	46.9	159
$ROCCl_2CCl_2OR$ (**7**)	14.3	0.0	5.6	45.4	14.4	0.0	5.6	45.4	

TABLE 4. ^1H and ^{19}F NMR spectral data for the 1:1 adducts of oxadiazapentane **1** and substituted ethenes

Compound [R = $(CF_3)_2N$]	^1H NMR δ (ppm)	^{19}F NMR δ (ppm)
$RCH_2CHBrOR$ (**3a**)	5.68 (dd, 1H, CHBrO, J=9 and 5 Hz); 3.49 (AB mult., 2H, CH_2N)	+17.7 [s, $(CF_3)_2N$]; +9.4 [s, $(CF_3)_2NO$]
$RCH_2CHClOR$ (**3b**)	5.79 (t, 1H, CHClO, J=8 Hz); 3.60 (mult., 2H, CH_2N)	+18.6 [s, $(CF_3)_2N$]; +9.5 [s, $(CF_3)_2NO$]
$RCH_2CHPhOR$ (**3c**)	7.34 (br., 5H, C_6H_5); 4.77 (dd, 1H, CHO, J=8 and 6 Hz); 3.43 and 2.98 (ABd, 2H, CH_2N, J_{AB}=14 Hz)	+19.5 [s, $(CF_3)_2N$]; +9.9 [s, $(CF_3)_2NO$]
RCH_2CHFOR (**3d**)	5.26 (dt, 1H, CHFO, J_{F-H}=59 Hz, J_{CH_2-H}=6 Hz); 3.16 (mult., 2H, CH_2N)	+17.6 [s, $(CF_3)_2N$]; +7.8 [s, $(CF_3)_2NO$]; −56.0 (d, CHF, J=59 Hz)
$RCH_2CH(CN)OR$ (**3e**)	4.81 [t, 1H, CH(CN)O, J=6 Hz]; 3.83 (d, 2H, CH_2N, J=6 Hz)	+17.0 [s, $(CF_3)_2N$]; +7.8 [s, $(CF_3)_2NO$]
RCH_2CCl_2OR (**3f**)	4.13 (s, CH_2N)	+18.8 [s, $(CF_3)_2N$]; 11.4 [s, $(CF_3)_2NO$]
RCH_2CF_2OR (**3g**)	3.61 (mult., CH_2N)	+16.9 [s, $(CF_3)_2N$]; +8.2 [s, $(CF_3)_2NO$]; −5.3 (mult., CF_2)
$RCHFCH_2OR$ (**4**)		+20.2 [d, $(CF_3)_2N$, J=6 Hz]; +7.2 [s, $(CF_3)_2NO$]; −57.2 (mult., CHF)
$RCHClCHClOR$ (**5a**)	6.05 (mult., 1H, CHClO); 5.46 (d, 1H CHClN, J=10 Hz)	+21.4 [s, $(CF_3)_2N$]; +10.2 [s, $(CF_3)_2NO$]
$RCHClCHClOR$ (**5b**)	6.00 (mult., 1H, CHClO); 5.43 (d, 1H, CHClN, J=9 Hz)	+21.9 [s, $(CF_3)_2N$]; +10.6 [s, $(CF_3)_2NO$]
$RCHClCCl_2OR$ (**6a**)	5.94 (s, CHClN)	+23.4 (q, 3F, CF_3N; J=25 Hz); +17.3 (q, 3F, CF_3N, J=25 Hz); +11.5 [s, 6F, $(CF_3)_2NO$]
RCF_2CCl_2OR (**6b**)		+25.4 [t, $(CF_3)_2N$, J=17 Hz]; +12.0 [s, $(CF_3)_2NO$]; −18.4 (sep., CF_2, J=17 Hz)
$RCCl_2CCl_2OR$ (**6c**)		+20.2 [s, $(CF_3)_2N$]; +13.4 [s, $(CF_3)_2NO$]
$ROCCl_2CCl_2OR$ (**7**)		+13.0 [s, $(CF_3)_2NO$]

{[*N*,*N*-bis(trifluoromethyl)amino]-2-[*N*,*N*-bis(trifluoromethyl)amino-oxy]}cyclohexane (**15**) (nc) (1.40 g, 3.5 mmol, 44%) (Analysis: Found: C, 29.9; H, 2.6; N, 7.2; F, 56.2%. $C_{10}H_{10}F_{12}N_2O$ requires: C, 29.9; H, 2.5; N, 7.0; F, 56.7%), b.p. 173 °C {^1H NMR ($CDCl_3$) δ: 4.31 (mult., 1H, >CHO); 3.52 (mult., 1H, >CHN); 2.45 (complex, 2H, CH_2); 2.01 (complex, 2H, CH_2); 1.55 (complex, 4H, $2CH_2$) ppm. ^{19}F NMR δ: +23.60 [s, $(CF_3)_2N$]; +23.00 [s, $(CF_3)_2N$]; +9.8 [s, $(CF_3)_2NO$]; +9.3 [s, $(CF_3)_2NO$] ppm in the ratio 2:5:5:2. MS *m/z*: 250 {2.4%, $[M-(CF_3)_2N]^+$}; 234 {21.7, $[M-(CF_3)_2NO]^+$}; 192 (13.3, $C_5H_4F_6N^+$); 166 (47.5,

TABLE 5. MS data for the 1:1 adducts of oxadiazapentane **1** and substituted ethenes

Compound [R = $(CF_3)_2N$]	MS, *m/z* (%, assignment)[a,b]
$RCH_2CHBrOR$ (**3a**)	347 [44, $(M-Br)^+$]; 274 {18, $[M-CF_3)_2N]^+$}; 258 {27, $[M-CF_3)_2NO]^+$}; 179 (24); 166 [70, $(CF_3)_2NCH_2^+$]; 125 (14, $C_2H_2BrNO^+$); 78 (28); 69 (100, CF_3^+).
$RCH_2CHClOR$ (**3b**)	363 [2, $(M-F)^+$]; 347 [22, $(M-Cl)^+$]; 230 {37, $[M-(CF_3)_2N]^+$}; 214 {65, $[M-(CF_3)_2NO]^+$}; 179 (23); 166 (94); 81 (60, $C_2H_3FCl^+$); 78 (53); 69 (100).
$RCH_2CHPhOR$ (**3c**)	405 [1, $(M-F)^+$]; 258 [82, $(CF_3)_2NOCHPh^+$]; 259 {96, $[M-(CF_3)_2NO]^+$}; 166 (16); 123 (100, $C_8H_8F^+$); 106 (59); 105 (79); 104 (46); 103 (55); 91 (52); 77 (45, $C_6H_5^+$); 69 (44).
RCH_2CHFOR (**3d**)	347 [13, $(M-F)^+$]; 214 {8, $[M-(CF_3)_2N]^+$}; 198 {64, $[M-(CF_3)_2NO]^+$}; 179 (19); 166 (69); 110 (35); 78 (43); 69 (100).
$RCH_2CH(CN)OR$ (**3e**)	354 [2, $(M-F)^+$]; 221 {11, $[M-(CF_3)_2N]^+$}; 205 {11, $[M-(CF_3)_2NO]^+$}; 166 (93); 110 (27); 96 (30); 78 (30); 69 (100); 53 (38); 52 (19).
RCH_2CCl_2OR (**3f**)	381 [20, $(M-Cl)^+$]; 248 {31, $[M-(CF_3)_2NO]^+$}; 166 (100); 115 (27, $C_2H_2Cl_2F^+$); 78 (31); 69 (85).
RCH_2CF_2OR (**3g**)	365 [10, $(M-F)^+$]; 232 {17, $[M-(CF_3)_2N]^+$}; 216 {45, $[M-(CF_3)_2NO]^+$}; 166 (40); 128 (35); 78 (36); 69 (100).
$RCHClCHClOR$ (**5**)	264 {8, $[M-(CF_3)_2N]^+$}; 248 {16, $[M-(CF_3)_2NO]^+$}; 213 [28, $(CF_3)_2NCH{=}CHCl^+$]; 200 [16, $(CF_3)_2NCHCl^+$]; 96 (13); 69 (100).
$RCHClCCl_2OR$ (**6a**)	282 {11, $[M-(CF_3)_2NO]^+$}; 247 [27, $(CF_3)_2NCH{=}CCl_2$]; 200 [27, $(CF_3)_2NCHCl^+$]; 130 (30, $C_2HCl_3^+$); 96 (8); 69 (100).
RCF_2CCl_2OR (**6b**)	433 [1, $(M-F)^+$]; 417 [5, $(M-Cl)^+$]; 300 {9, $[M-(CF_3)_2N]^+$}; 284 {10, $[M-(CF_3)_2NO]^+$}; 202 [26, $(CF_3)_2NCF_2^+$]; 114 (44); 69 (100).
$RCCl_2CCl_2OR$ (**6c**)	465 [4, $(M-F)^+$]; 332 {9, $[M-(CF_3)_2N]^+$}; 297 [14, $[M-C_2F_7NO)^+$]; 164 (100, $C_2Cl_4^+$); 69 (100).

[a]For ion peaks which contained Cl or Br only, the ^{35}Cl and ^{79}Br ion peaks were recorded, but the intensities were the total of all the isotope peaks.
[b]Expressed as a percentage of the base peak.

$C_3H_2F_6N^+$); 98 (13.4, $C_2H_3F_3N^+$); 81 (100.0, $C_6H_9^+$); 69 (18.5, CF_3^+); 67 (18.5, $C_5H_7^+$); 55 (18.7, $C_4H_7^+$); 41 (12.6, $C_3H_5^+$)}; and (iv) unchanged cyclohexene (0.02 g, 0.3 mmol, 4% recovered).

Reaction of N-*bromobis(trifluoromethyl)amine with trichloroethene*

A mixture of the *N*-bromoamine (2.95 g, 12.7 mmol) and trichloroethene (1.89 g, 14.4 mmol) kept *in vacuo* at room temperature in light (3 d) gave: (i) (a −196 °C fraction identified (IR spectroscopy) as perfluoro-2-azapropene (0.03 g, 0.2 mmol, 2%); (ii) unchanged alkene (0.224 g, 1.7 mmol, 12% recovered) which condensed at −23 °C; and (iii) a residue identified as 1-bromo-2-*N*,*N*-bis(trifluoromethyl)amino-1,1,2-trichloroethane (nc) (4.54 g, 12.5 mmol, 98%) (Analysis: Found: C, 13.3; H, 0.4%. $C_4HBrCl_3F_6N$ requires: C, 13.2; H, 0.3%), b.p. 141 °C {^1H NMR ($CDCl_3$) δ: 3.75 (s, CHCl) ppm. ^{19}F NMR δ: +27.1 (q, 3F, CF_3N, $J = 11$ Hz); +20.0 (q, 3F, CF_3N, $J = 11$ Hz) ppm. IR ($\nu_{max.}$) (cm^{-1}): 3135 (w) (C−H str.); 1300–1180 (s), (C−F str.); 995, 970 (s) (C−N str.); 698 (s), (CF_3 def.). MS *m/z*: 282/284/286/288 [33.5% $(M-Br)^+$]; 247/249/251 [39.9, $(M-ClBr)^+$]; 200/202 [79.8, $(M-CCl_2Br)^+$]; 159/161/163/165 (66.8, CCl_2Br^+); 83/85/87 (58.1, $CHCl_2^+$); 69 (100.0, CF_3^+)}.

Competition reactions of oxadiazapentane 1 with mixtures of ethenes

(a) 1,1-Dichloroethene and trichloroethene (general procedure)

A mixture of oxadiazapentane **1** (1.50 g, 4.7 mmol), 1,1-dichloroethene (1.79 g, 18.45 mmol) and trichloroethene (2.42 g, 18.45 mmol) sealed *in vacuo* in a Pyrex bulb (*c.* 10 dm^3) and kept at room temperature in light (7 d) gave: (i) unchanged 1,1-dichlorethene (1.33 g, 13.75 mmol, 74% recovered) which condensed at −66 °C; (ii) unchanged trichloroethene (2.40 g, 18.4 mmol, 99% recovered) which condensed at −23 °C; and (iii) the 1:1 adduct **3f** of 1,1-dichloroethene (1.95 g, 4.65 mmol, 99%). GLC analysis (2 m SE30 at 70 °C) of the 1:1 adduct showed that the adduct **6a** derived from trichloroethene was absent.

(b) Other mixtures of ethenes

Reactions of oxadiazapentane **1** in *c.* 5 dm^3 bulbs (unless stated otherwise) with mixtures of the ethenes $CH_2{=}CCl_2$ and $CH_2{=}CHCl$ (10 dm^3 bulb), $CH_2{=}CCl_2$ and $CHF{=}CF_2$, $CH_2{=}CH_2$ and $CH_2{=}CHCl$, $CH_2{=}CHCl$ and $CHCl{=}CCl_2$, $CH_2{=}CH_2$ and $CH_2{=}CHF$, $CH_2{=}CHF$ and $CH_2{=}CF_2$, $CH_2{=}CH_2$ and $CHCl{=}CCl_2$ (25 dm^3 bulb), and $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ (800 cm^3 bulb) were carried out in daylight and the results obtained are summarised in Table 2. The adduct fractions were examined by GLC (2 m SE30 at 50–80 °C)

methods after calibration with adduct mixtures of known constitution.

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