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Reactions of bis(trifluoromethyl)amino-oxyl and perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) with non-conjugated dienes and with allylbenzene

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Abstract

Reaction of the oxyl $(CF_3)_2NO\cdot$ (**1**) with norbornadiene (**4**) (1.6:1 molar ratio, liquid phase or 2:1 molar ratio, solution in $CFCl_2CF_2Cl$) gave the non-rearranged 2:1 adducts 5-*exo*-6-*endo*-bis(bistrifluoromethylamino-oxy)norborn-2-ene (**13a**) (ca. 30%) and its 5-*exo*-6-*exo*-isomer (**13b**) (ca. 30%), the rearranged 2:1 adducts 3-*endo*-5-*exo*-bis(bistrifluoromethylamino-oxy)nortricyclane (**14a**) (ca. 10%) and its 3-*exo*-5-*exo* isomer (**14b**) (ca. 10%) and a mixture of four 4:1 adduct isomers of 2-*exo*-3,5,6-tetrakis(bistrifluoromethylamino-oxy)norbornane (**15**) (10%–20%); only the four 2:1 adducts were formed in solution using a large excess of the diene (1:19 molar ratio) or in the gas phase (2:1 molar ratio). In contrast, reaction of the oxadiazapentane (**3**) with diene **4** (1.1:1 molar ratio) in solution afforded only telomeric material. The reaction between oxyl **1** and cyclo-octa-1,5-diene (**5**) (1.9:1 molar ratio, −196 °C to ca. 20 °C) gave the hydroxylamine $(CF_3)_2NOH$ (**17**) (43.5%), the allylic substitution product $(CF_3)_2NOCHCH{=}CH(CH_2)_2CH{=}CHCH_2$ (**19**) (30%), two isomeric disubstitution products $[(CF_3)_2NO]_2C_8H_{10}$ (**20**) (12.5% and 15.5%) and two diastereomers of the 2:1 adduct $(CF_3)_2NOCH(CH_2)_2CH{=}CH(CH_2)_2CHON(CF_3)_2$ (13.5% and 14.5%). In the corresponding reaction of the oxadiazapentane **3** with diene **5** (ca. 1:1 molar ratio, ca. 20 °C) hydrogen abstraction leading to compound **19** (13%) was less favoured, the major product being the 1:1 adduct $(CF_3)_2NCH(CH_2)_2CH{=}CH(CH_2)_2CHON(CF_3)_2$, formed as two diastereomers (**31a**) (34%) and (**31b**) (28%); the amine $(CF_3)_2NCH(CH_2)_2CH{=}CH(CH_2)_2CH_2$ (**32**) (9%) was also formed as a minor product. Addition was also favoured in the reaction of oxyl **1** with cyclo-octene (**6**) (1.8:1 molar ratio, −196 to ca. 20 °C), leading to the 2:1 adduct (**23**) (67.5%); hydrogen abstraction led to the allylic substitution product (**22**) in low yield (20%). All of the products isolated from the reaction of oxyl **1** with penta-1,4-diene (**7**) (1.8:1 molar ratio, −78 °C), apart from the 2:1 adduct (**27**) formed in low yield (2.5%), resulted from hydrogen abstraction, i.e. the dienes $(CF_3)_2NOCH(CH{=}CH_2)_2$ (**24**) (26.5%) and $(CF_3)_2NOCH_2CH{=}CHCH{=}CH_2$ (**26**) (19%) and the alkenes *trans*- and *cis*-$(CF_3)_2NOCH_2CH[ON(CF_3)_2]CH{=}CHCH_2ON(CF_3)_2$ (**25a**) (44.5%) and (**25b**) (5%), respectively. The gas-phase reaction between the oxadiazapentane **3** and diene **7** (1:1 molar ratio, ca. 20 °C) afforded a high yield of the 1:1 adduct (**33**) (70%), while a reaction carried out mainly in the liquid phase gave as major products compound **33** (36%) and a mixture of two 1:2 adducts considered to be diastereomers of the cyclopentane derivative $CH_2{=}CHCH_2CHCH[CH_2ON(CF_3)_2]CH_2CH[CH_2N(CF_3)_2]CH_2$ (**34**) (41%). From the reaction of the oxyl **1** with allylbenzene (**8**) (2.5:1 molar ratio, −196 to ca. 20 °C) only products formed via hydrogen abstraction were isolated, i.e. the compounds $(CF_3)_2NOCHPhCH[ON(CF_3)_2]CH_2ON(CF_3)_2$ (**28**) as two diastereomers (20.5% and 10%), $(CF_3)_2NOCHPhCH{=}CH_2$ (**29**) (37%) and $(CF_3)_2NOCH_2CH{=}CHPh$ (**30**) (16.5%). In contrast to this, the corresponding reaction involving the oxadiazapentane **3** (1:1 molar ratio, ca. 20 °C) gave the 1:1 adduct (**35**) (66.5%) and only a low yield (5.5%) of the hydrogen abstraction product **30**.

Keywords: Bis(trifluoromethyl)amino-oxyl; Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane); Non-conjugated dienes; Allylbenzene; NMR spectroscopy

1. Introduction

In previous investigations, we have reported that addition of the radicals $(CF_3)_2NO\cdot$ (**1**) and $(CF_3)_2N\cdot$ (**2**) [generated from the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**3**)] to the alkenes $CH_2{=}CRCCl_3$ (R = H, Me) [1] and to α- and β-pinene [2] gave intermediate radicals which rearranged (wholly or in part) by a vicinal chlorine shift and by opening of the four-membered ring, respectively. However, evidence

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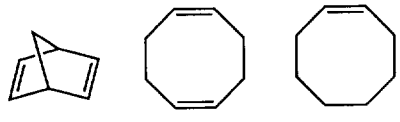
was not obtained for rearrangement involving (i) vicinal halogen shifts in the radicals $\dot{C}H_2CMe_2X$ (X = Cl, Br) and $\dot{C}H_2CMe(Ph)Cl$ [3], (ii) a vicinal OAc shift in the radical $\dot{C}H_2CMe_2OAc$ [3] and (iii) opening of the cyclopropyl ring in the radicals $\dot{C}H_2CH_2\dot{C}HCXY$ (X = H, Y = Ph; X = H, Y = OH; X = Me, Y = OH) [4]; the radicals were all generated from the corresponding saturated compounds by hydrogen abstraction involving **1** or **2**.

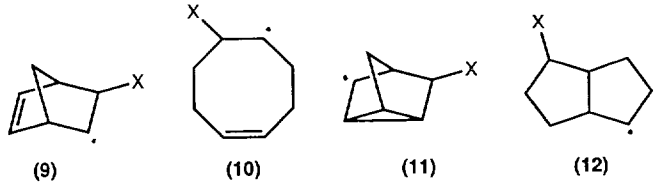
In a continuation of these studies, the reactions of oxyl **1** with norbornadiene (**4**), *cis*, *cis*-cyclo-octa-1,5-diene (**5**), cyclo-octene (**6**), penta-1,4-diene (**7**) and allylbenzene (**8**) and of the oxadiazapentane **3** with compounds **4, 5, 7** and **8** are now reported. The reactions involving compounds **4** and **5** were carried out to determine whether rearranged products were formed via the well-documented cyclisation of intermediate radicals **9** and **10** to nortricyclyl (**11**), see for example, Ref [5] and bicyclo[3.3.0]octyl (**12**) radicals, see, for example, Ref. [6], respectively. With substrate **5** the extent of allylic hydrogen abstraction relative to radical addition to a double bond was also of interest, and this was the major purpose for the investigations involving compounds **7** and **8**. The reaction of oxyl **1** with cyclo-octene (**6**) was studied to compare the results obtained with those from the corresponding reaction with diene **5**.



(4) (5) (6)

$CH_2(CH{=}CH_2)_2$ $CH_2{=}CHCH_2Ph$

(7) (8)



(9) (10) (11) (12)

2. Results and discussion

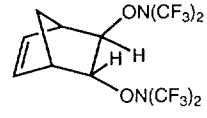
2.1. Reaction of oxyl 1 with norbornadiene (4)

The results obtained from the reaction of oxyl **1** with norbornadiene (**4**) are summarised in Table 1.

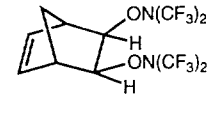
Table 1
Reaction of oxyl **1** with norbornadiene (**4**)

Experiment	1	2	3	4
Conditions	liquid	solution [a]	solution [a]	gas
Molar ratio **1/4**	1.6:1	2:1	1:19	2:1
Temp. (°C)	−64	−78	−64	ca. 20
Time (h)	2	0.67	1.5	0.1
Recovered **4** (%)	32	– [b]	– [b]	– [b]
Products [c, d]				
13a	32 [e]	34	41	20
13b	28 [e]	27	39	15.5
14a	14	8.5	9	30.5
14b	10	7.5	8	22
15 (isomer 1)	5	13		
15 (isomer 2)	2.5	4		
15 (isomer 3)	2	3		
15 (isomer 4)	2	3		

[a] Carried out in $CF_2ClCFCl_2$ as solvent.
[b] Not determined.
[c] Product ratios in order of increasing GLC retention times.
[d] Small amount of amine (**16**) and hydroxylamine (**17**) also formed.
[e] Isolated yields.

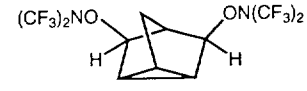


(13a)

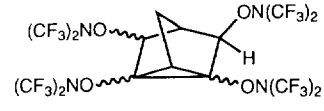


(13b)

(14a)



(14b)



(15)

$(CF_3)_2NH$ $(CF_3)_2NOH$

(16) (17)

Initial radical attack takes place on norbornadiene (**4**) from the *exo* side because of steric hindrance to attack from the *endo* side and chain transfer of the resulting 5-*exo*-norbornenyl radical **9** can occur from both the *exo* and *endo* sides with transfer from the *exo* side becoming less favoured the bulkier the 5-*exo* substituent [7]. The product ratio obtained depends therefore on the size of the attacking radical, whether the equilibrium is established between intermediate radical **9** and the more stable nortricyclyl radical **11** (which is related directly to the effectiveness of the addendum as a chain-transfer agent), and the conditions employed including the reactant ratio.

Of relevance to the present work was the previous observation that reaction of oxyl **1** with norbornene gave the corresponding 2-*exo*-3-*endo*- and 2-*exo*-3-*exo*-disubstituted norbornanes in the ratio 1.3:1 via the 2-*exo*-norbornyl radical [8]. This ratio is in good agreement with the ratio obtained (1.17 ± 0.12:1) in the present work for the formation of the 5-*exo*-6-*endo*- and 5-*exo*-

6-*exo*-disubstituted norbornenes **13a** and **13b** arising via the 5-*exo*-norbornenyl radical **9** [X = $(CF_3)_2NO$].

The isomers **13a** and **13b** were distinguished by their NMR spectra in which separate absorptions were present for both the non-equivalent $(CF_3)_2NO$ groups and the *endo*- and *exo*-hydrogens in the *trans* isomer **13a**, while only one absorption was present in each case for the equivalent $(CF_3)_2NO$ groups, vinylic hydrogens, *endo*-hydrogens and bridgehead methine hydrogens in the *cis* isomer **13b**.

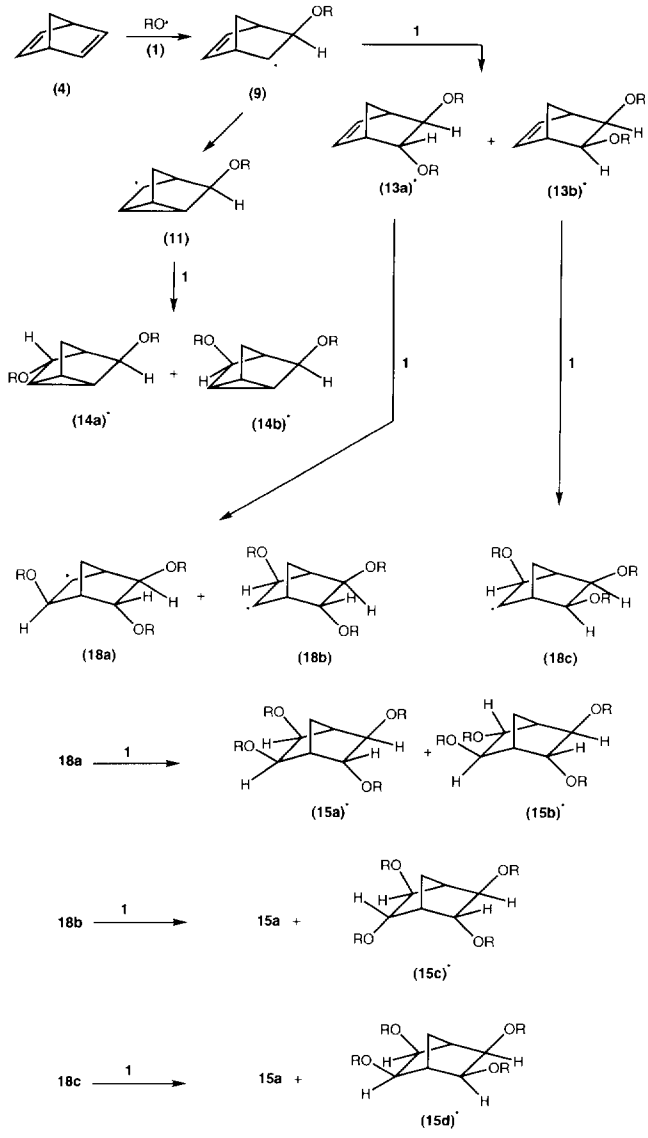
The rearranged 2:1 adducts **14a** and **14b** formed via the 5-*exo*-nortricyclic radical **11** [X = $(CF_3)_2NO$] were observed in all four experiments, but were most favoured in the gas-phase reaction (experiment 4) in which they were formed as the major products. This was expected because the lower reactant concentrations present would favour the establishment of the equilibrium between radical **9** and the more stable radical **11**. Compounds **14a** and **14b** were not isolated and were identified by coupled GLC/MS {(*m/z*): 260 $[M-(CF_3)_2NO]^+$; 108 $[M-(CF_3)_2NO-(CF_3)_2N]^+$; 92 $[M-2(CF_3)_2NO]^+$; 79 (base peak, $C_6H_7^+$)}. By comparison with the order of elution and relative yields of the non-rearranged 2:1 adducts **13a** and **13b**, it is probable that the first eluted and major compound is the 3-*endo*-5-*exo* isomer **14a** and the minor compound is the 3-*exo*-5-*exo* isomer **14b** (ratio **14a/14b** = 1.26 ± 0.13:1).

The four higher-boiling products, which were not isolated, had virtually identical mass spectra (coupled GLC/MS) {(*m/z*): 596 $[M-(CF_3)_2NO]^+$; 595 $[M-(CF_3)_2NOH]^+$; 108 ($C_7H_8O^+$); 92 ($C_7H_8^+$); 69 (base peak, CF_3^+)} which were consistent with the compounds being isomers of the 2-*exo*-3,5,6-tetrasubstituted norbornane **15** formed by further addition of oxyl **1** to the double bond in the norbornenes **13a** and **13b**; the absence of these compounds in the products from experiments 3 (large excess of diene **4** present) and 4 (gas-phase reaction) supports the assignment.

Only four isomers of the norbornane **15** can be formed, providing attack on the norbornenes **13a** and **13b** by oxyl **1** takes place from the *exo* side leading to the norbornyl radicals (**18a–c**) each of which is then scavenged by oxyl **1** from either the *endo* or *exo* side. One isomer, that with three *exo* substituents and one *endo* substituent (**15a**), could arise from each of the intermediate radicals **18a–c**, but the other three isomers (**15b–d**) can each only be formed from *one* intermediate radical and so it is considered probable that the major isomer has structure **15a**.

The ratios of non-rearranged to rearranged products ranged from 3:1 to 5.2:1 in the reactions carried out in the liquid phase or in solution (experiments 1–3), but was 0.7:1 in the gas-phase reaction (experiment 4).

The products **13–15**, of which **13a** and **13b** were isolated, are therefore considered to have been formed as shown in Scheme 1.



Scheme 1. R = $(CF_3)_2N$. * Identified products.

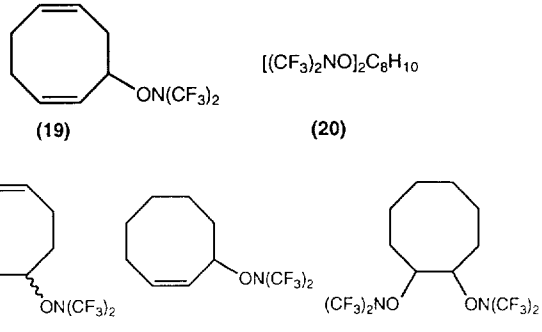
2.2. Reaction of oxadiazapentane 3 with norbornadiene (4)

The corresponding reaction of the oxadiazapentane **3** with diene **4** (1.1:1 molar ratio) in solvent $CF_2ClCFCl_2$ at room temperature (ca. 8 d) gave, on removal of the solvent and volatile material in vacuo, a yellow gelatinous substance which could not be resolved into its components by column chromatography or TLC using the eluants Me_2CO, $CHCl_3$ or $CF_2ClCFCl_2$. The IR and NMR spectra were complex and poorly resolved, but the presence of both $(CF_3)_2N$ and $(CF_3)_2NO$ groups was confirmed {^{19}F NMR δ: 20–23 [$(CF_3)_2N$]; 8–10 [$(CF_3)_2NO$]ppm} and the mass spectrum showed ion peaks containing up to three diene **4** residues. The material is therefore considered to consist of telomers of diene **4** containing $(CF_3)_2N$ and $(CF_3)_2NO$ groups.

A white solid was obtained after dissolving the gelatinous material in solvent $CF_2ClCFCl_2$ and then evaporating in vacuo to remove any residual low-boiling material, but its IR and NMR spectra were very similar to those of the original material.

Diene **4** can undergo reaction under free-radical conditions to give soluble low molecular weight telomers [9] and, since norbornene is not telomerised readily, it is considered that the nortricyclyl radical **9** is involved in the propagation step, although the resulting telomers may be composed mainly of 5,6-disubstituted norbornene units [10] or of alternating 5,6-disubstituted norbornene and 3,5-disubstituted nortricyclane units [9]. The reason for the preferred telomerisation in the present reaction involving initial $(CF_3)_2N\cdot$ (**2**) radical attack on diene **4** is that the oxadiazapentane **3** is bulky and chain transfer is slow, i.e. it is a relatively poor chain-transfer agent. The telomers of the type $(CF_3)_2N(C_7H_8)_nON(CF_3)_2$ which are formed could undergo further reaction with the oxadiazapentane **3** involving attack by radical **2** on unsaturated norbornene units present in the telomer chain followed by chain transfer with **3**.

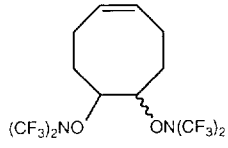
The results obtained from the reactions of the oxyl **1** with the dienes **5** and **7** and the alkenes **6** and **8** and of the oxadiazapentane **3** with compound **5**, **7** and **8** are given in Table 2.



(19)

$[(CF_3)_2NO]_2C_8H_{10}$

(20)



(21)

(22)

(23)

$(CF_3)_2NOCH(CH{=}CH_2)_2$

(24)

$(CF_3)_2NOCH_2CH[ON(CF_3)_2]CH{=}CHCH_2ON(CF_3)_2$

(25)

$(CF_3)_2NOCH_2CH{=}CHCH{=}CH_2$

(26)

$(CF_3)_2NOCH_2CH[ON(CF_3)_2]CH_2CH{=}CH_2$

(27)

$(CF_3)_2NOCH(Ph)CH[ON(CF_3)_2]CH_2ON(CF_3)_2$

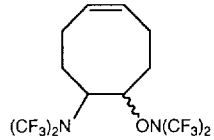
(28)

$(CF_3)_2NOCH(Ph)CH{=}CH_2$

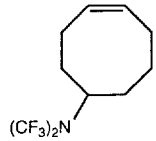
(29)

$(CF_3)_2NOCH_2CH{=}CHPh$

(30)



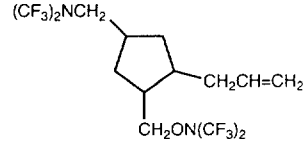
(31)



(32)

$(CF_3)_2NCH_2CH[ON(CF_3)_2]CH_2CH{=}CH_2$

(33)



(34)

$(CF_3)_2NCH_2CH[ON(CF_3)_2]CH_2Ph$

(35)

2.3. Reaction of oxyl 1 with cyclo-octa-1,5-diene (5)

The major mode of reaction between oxyl **1** and cyclo-octa-1,5-diene (**5**) was hydrogen abstraction leading to a monosubstituted diene considered to have structure **19** and two disubstituted cyclo-octadienes **20**. The two isomers **20** were each separated (GLC) as a ca. 1:1 mixture with a diastereomer of the 2:1 adduct **21**.

The identified products **19–21** are considered to have been formed as shown in Scheme 2.

Allylic hydrogen abstraction would afford radical **36** which could be scavenged by oxyl **1** to give the 3-substituted cyclo-octa-1,5-diene **19** and/or the 6-substituted cyclo-octa-1,4-diene **37**. Oxyl **1** attack on a double bond followed by hydrogen abstraction from the resulting radical also leads to the 1,4-diene **37**. The NMR spectra of the monosubstituted product did not allow an unequivocal identification to be made, but molecular models indicate that the 1,4-diene **37** is subject to considerable more ring strain than the 1,5-diene **19** and hence the product probably has structure **19**. If an analogous mechanism is operative in the formation of the two disubstituted octadienes **20** (ca. 1:1 ratio), then these compounds could be the 3,4-, 3,7- or 3,8-disubstituted cyclo-octa-1,5-dienes, **20a–c**, each of which could exist as *cis* and *trans* isomers.

The diastereomers of the 2:1 adduct **21** were also formed in a ca. 1:1 ratio, but it was not possible to assign stereochemistry to the individual isomers on the evidence available.

The molecular formula of the monosubstituted product was confirmed as $C_{10}H_{11}F_6NO$ by elemental analysis (for C, H, N) and the presence of a molecular ion peak (*m/z*: 275) in the mass spectrum. The ^1H NMR spectrum showed absorptions for four vinylic hydrogens, an allylic CH–O hydrogen and three CH_2 groups (δ: ca. 5.3 and 2.6–1.7 ppm, respectively) and the ^{19}F NMR spectrum showed a single absorption (δ: 8.8 ppm) in the region expected for a $(CF_3)_2NO$ group which are consistent with structure **19**.

Elemental analysis figures (C, H, N, F) for the two mixtures of isomers of compounds **20** and **21** were consistent with them containing compounds of molecular

Table 2
Reactions of the oxyl **1** and oxadiazapentane **3** with dienes and alkenes

1 or 3	Substrate	Molar ratio 1 or 3/ substrate	Conditions		Recovered substrate (%)	Products (%) [c]
			Temp. (°C)	Time (h)		
1	**5**	1.9:1	−196 to ca. 20	ca. 0.5	35	**17** (43.5) [d]; **19** (30); **20a** (12.5) [e]; **20b** (15.5) [e]; **21a** (13.5) [e]; **21b** (14.5) [e]
1	**6**	1.8:1	−196 to ca. 20	ca. 0.5	18	**17** (10) [d]; **22** (20); **23** (67.5)
1	**7**	1.8:1	−78	0.5	44	**17** (30) [d]; **24** (26.5); **25a** (44.5); **25b** (5) [f]; **26** (19); **27** (2.5) [f]
1	**8**	2.5:1	−196 to ca. 20	ca. 0.5	17	**16** (6) [d]; **17** (32) [d]; **28a** (20.5); **28b** (10); **29** (37); **30** (16.5)
3	**5**	ca. 1:1	20	144	10	**16** [g]; **17** [g]; **19** (13); **31a** (34); **31b** (28); **32** (9) [h]
3	**7**	ca. 1:1	20	48	13	**16** [g]; **17** [g]; **33** (70)
3	**7**	ca. 1:1	20	48 [a]	7	**16** [g]; **17** [g]; **33** (36); **34** (41)
3	**8**	ca. 1:1	20	144 [b]	6	**16** (5); **17** (7); **30** (5.5); **35** (66.5) [i]

[a] Gas-phase reaction.
[b] Mainly liquid-phase reaction.
[c] Product yields based on substrate reacted, i.e. not recovered.
[d] Product yields based on **1** or **3** reacted, i.e. nor recovered.
[e] Mixtures of compounds **20a**+**21a** and **20b**+**21b** were obtained.
[f] Not isolated; identified by coupled GLC/MS.
[g] Yields not determined.
[h] Tentatively identified.
[i] Unchanged reactant **2** (7% recovered) also obtained.

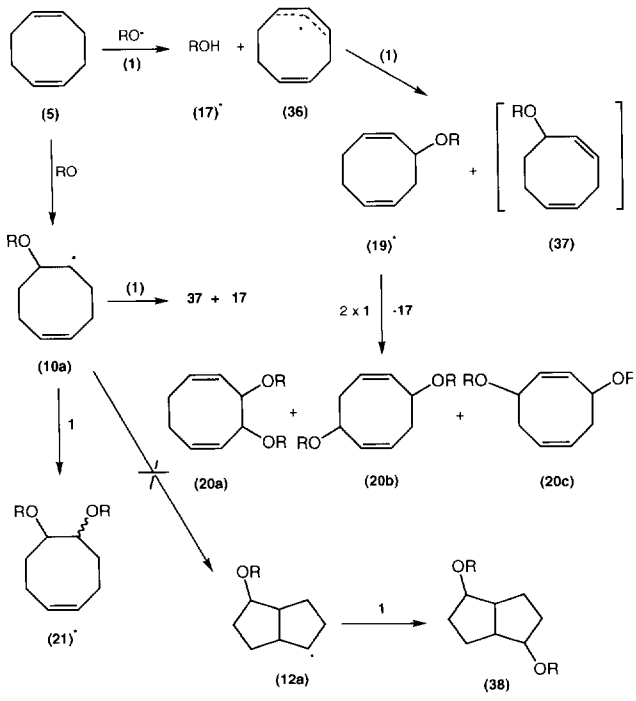
formulae $C_{12}H_{10}F_{12}N_2O_2$ and $C_{12}H_{12}F_{12}N_2O_2$ (ca. 1:1 ratio). The NMR and mass spectra of the two mixtures were also very similar {^{1}H NMR δ: 5.8–5.2 (5.8–5.2) (6H, 4 =CH in **20**; 2 =CH in **21**); 5.0–4.6 (5.0–4.5) (2H, 2 allylic >CH–O in **20**); 4.2 (4.17) (2H, 2 non-allylic >CH–O in **21**); 2.6–1.0 (2.6–1.0) (12H, 2 CH_2 in **20**; 4 CH_2 in **21**) ppm. ^{19}F NMR δ: 8.6–8.4 (8.6–8.4) [$(CF_3)_2NO$] ppm. MS (*m/z*) for **20**: 290 $[M-(CF_3)_2N]^+$; 274 $[M-(CF_3)_2NO]^+$; 260 ($C_9H_8F_6NO^+$); 122 ($C_8H_{10}O^+$); 106 ($C_8H_{10}^+$). MS (*m/z*) for **21**: 276 $[M-(CF_3)_2NO]^+$; 124 ($C_8H_{12}O^+$); 108 ($C_8H_{12}^+$)} and these data confirmed the presence of a disubstituted cyclo-octadiene and a 2:1 adduct in each mixture.

The isolated products accounted for 86% of the diene **5** which had reacted and so rearrangement of intermediate radical **10a** to the corresponding bicyclo[3.3.0]octyl radical **12a**, the precursor of the 2:1 adduct **38**, was not favoured although compound **38** could be present in the five minor unidentified products also formed in the reaction.

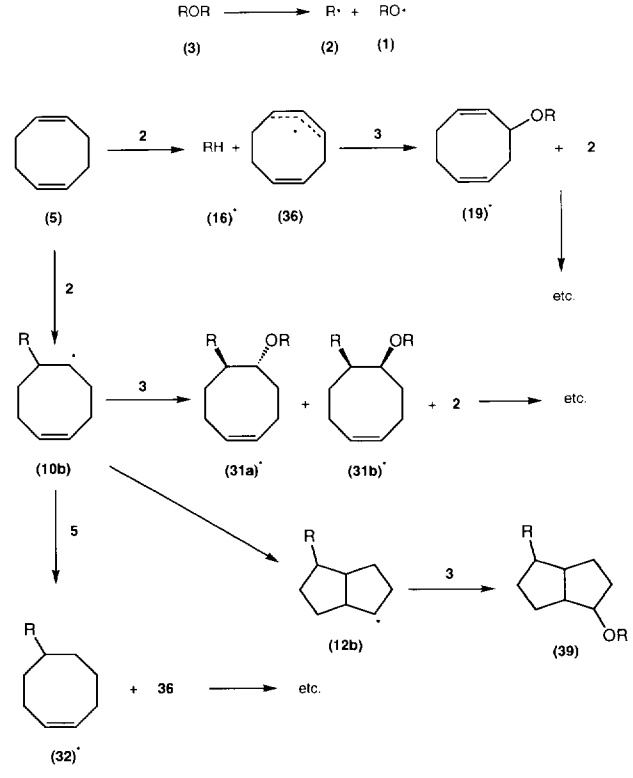
2.4. Reaction of oxadiazapentane 3 with cyclo-octa-1,5-diene (5)

The corresponding reaction between the oxadiazapentane **3** and diene **5** resulted mainly in addition across one of the double bonds to afford two diastereomers of the 1:1 adduct **31** via the intermediate radical **10b**. Hydrogen abstraction by the $(CF_3)_2N\cdot$ radical (**2**) leading to the allylic substitution product **19** was only a minor reaction and the remaining identified product, the alkenylamine **32**, arose by allylic hydrogen abstraction from reactant diene **5** by the intermediate radical **10b**. These routes to the isolated products **19**, **31** and **32** are shown in Scheme 3.

Analogous allylic hydrogen abstractions by intermediate radicals have been reported to take place in the reaction of the oxadiazapentane **3** with cyclohexene [11] and 2(10)-pinene [2]. The hydrogen abstractions occur because the oxadiazapentane **3** is a relatively poor chain-transfer agent and it is surprising that rearrangement of radical **10b** to the bicyclo[3.3.0]octyl radical **12b** and hence the 1:1 adduct **39** (which was not detected)



Scheme 2. R = $(CF_3)_2N$. * Identified products 9two of the isomers **20a–c** also formed).



Scheme 3. R = $(CF_3)_2N$. * Identified products.

was less favoured than hydrogen abstraction by **10b** to give **32**.

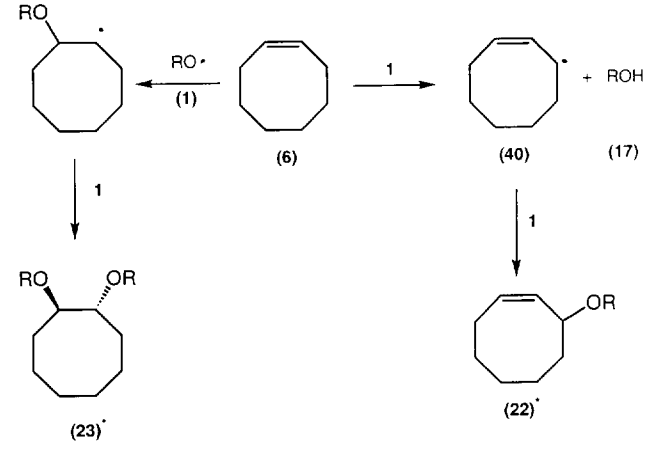
The two isomers of 1:1 adduct **31** each gave expected elemental analysis figures (for C, H, N) and the spectral data obtained confirmed the structures proposed {^{1}H NMR bands for two vinylic protons, a >CH–O hydrogen, a >CH–N hydrogen and four CH_2 groups. ^{19}F NMR bands for $(CF_3)_2N$ and $(CF_3)_2NO$ groups (1:1 ratio). MS (*m/z*): 276 $[M-(CF_3)_2N]^+$; 260 $[M-(CF_3)_2NO]^+$; 124 ($C_8H_{12}O^+$); 108 ($C_8H_{12}^+$)}. The ^{19}F NMR spectrum of the minor isomer showed a non-equivalence of the two CF_3 groups in the $(CF_3)_2N$ grouping, presumably caused by restricted rotation, which indicates the isomer has the *cis* structure **31b** and hence the major isomer, which showed an absence of such non-equivalence, has the *trans* structure **31a**.

The alkenylamine **32** was not obtained completely pure but the NMR spectra {^{1}H NMR δ: ca. 5.7 (2H, 2 =CH); 3.7 (1H, >CH–N); 2.6–1.2 (10H, 5 CH_2) ppm. ^{19}F NMR δ: 23.1 $[(CF_3)_2N]$ ppm} confirmed the assignment.

2.5. Reaction of oxyl 1 with cyclo-octene (6)

From the reaction of the oxyl **1** with cyclo-octene (**6**) only the allylic substitution product **22** and the 2:1 adduct **23** (Scheme 4) were isolated, accounting for 87.5% of alkene **6** which had reacted. Hydrogen abstraction (20%) was less favoured than in the corresponding reaction with diene **5** and the reactions with C_5–C_7 cycloalkenes (66%–93%) [8], and this is considered to be due to the ring strain in cyclo-octene resulting in acute ring skewing and hence poor resonance stabilisation of the allylic cyclo-octenyl radical **40**. The isolated products **22** and **23** are considered to have been formed as shown in Scheme 4.

The substituted alkene **22** was identified by elemental analysis (for C, H, N), the presence of a molecular ion peak (*m/z*: 277) in its mass spectrum and the NMR spectra [^{1}H NMR bands for two vinylic hydrogens, a >CH–O hydrogen and five CH_2 groups. ^{19}F NMR band (δ: 8.8 ppm) for a $(CF_3)_2NO$ group]. The 2:1 adduct **23** gave expected elemental analysis figures (for C, H,



Scheme 4. R = $(CF_3)_2N$. * Identified products.

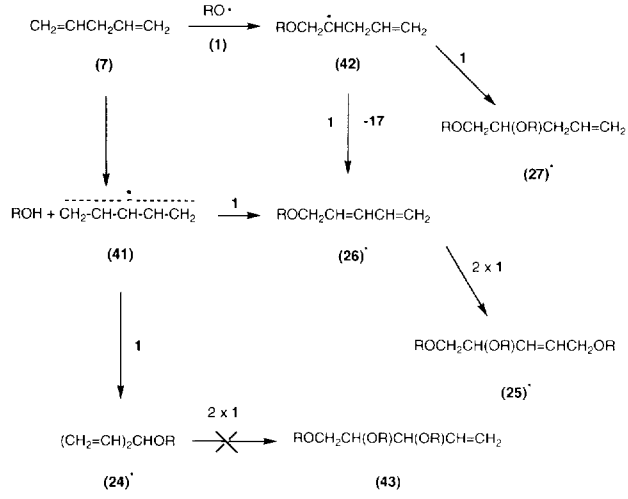
N, F) and the NMR spectra showed absorptions for two non-equivalent >CH–O hydrogens [δ: 4.18 (1H); 4.06 (1H) ppm], two CH_2–CH–O groups, four other CH_2 groups and two non-equivalent $(CF_3)_2NO$ groups (δ: 9.0 and 8.7 ppm in the ratio 1:1) which confirmed the structure and was consistent with the presence of one isomer, presumably the sterically-favoured *trans* isomer. It has been reported that reaction of oxyl **1** with the C_4–C_7 cycloalkenes afforded mixtures of *cis* and *trans* 2:1 adduct in the ratio ca. 1:3 except with cyclopentene which gave a ratio of ca. 1:10 [8].

2.6. Reaction of oxyl 1 with penta-1,4-diene (7)

The reaction of oxyl **1** with penta-1,4-diene (**7**) gave the monosubstituted dienes **24** and **26** and the trisubstituted alkene **25** as the *trans* and *cis* isomers **25a** (major) and **25b** (minor), respectively, all formed via allylic hydrogen abstraction, together with the 2:1 adduct **27** in very low yield (2.5%). Allylic hydrogen abstraction is very favoured in this system presumably because the resulting radical **41** is stabilised by two allyl groups. The identified products **24**–**27** are considered to be formed as shown in Scheme 5.

Allyl radical **41** was scavenged by oxyl **1** at both the 3- and 1-positions to afford the monosubstitution products **24** and **26**, respectively. Further oxyl **1** addition to compound **26** (1,2 or 1,4) then afforded alkene **25**. The 2:1 adduct **27** arose by oxyl **1** attack on diene **7** to give the intermediate radical **42** which was then scavenged by oxyl **1**. It is also possible that intermediate radical **42** underwent hydrogen abstraction by oxyl **1** to some extent to give the 1,3-diene **26**.

The identified products account for 97.5% of diene **7** which had reacted and evidence was not obtained for further oxyl **1** attack on compound **24** leading to the 3,4,5-trisubstituted pent-1-ene **43**, showing clearly the greater reactivity of the 1,3-diene system in **26**



Scheme 5. R = $(CF_3)_2N$. * Identified products.

relative to the 1,4-diene system in **24**. Therefore, scavenging of allyl radical **41** by oxyl **1** is preferred at the more reactive and less hindered primary terminal carbons (C-1 and C-5) than the more hindered secondary carbon (C-3) in the ratio 68.5:26.5.

The monosubstitution compound **24** and the major isomer of alkene **25** were separated by GLC and were identified by elemental analysis (for C, H, N, F) and the following spectral evidence {**24**: ^{1}H NMR δ: 5.37–4.78 (6H, 6 =CH); 4.33 (1H, >CH–O) ppm. ^{19}F NMR δ: 8.3 [$(CF_3)_2NO$ ppm. **25**: ^{1}H NMR δ: 5.51 (2H, 2 =CH); 4.19 (3H, allylic CH_2O and >CH–O); 3.84 (2H, CH_2O) ppm. ^{19}F NMR δ: 8.1, 7.4, 7.1 [3 $(CF_3)_2NO$] ppm}; the alkene was presumed to be the sterically favoured *trans* isomer **25a**. The remaining products **25b, 26** and **27** could not be separated adequately by GLC and they were identified by a consideration of their mass spectra (obtained by coupled GLC/MS); the spectrum of compound **25b** {*m/z*: 552 $(M-F)^+$; 403 $[M-(CF_3)_2NO]^+$; 234 $[M-(CF_3)_2NO-(CF_3)_2NOH]^+$; 221 $[M-(CF_3)_2NO-(CF_3)_2NOCH_2]^+$; 182 $[(CF_3)_2NOCH_2]$; 69 (base peak, CF_3^+)} was almost identical to its *trans* isomer **25a** and the spectrum of compound **26** [*m/z*: 235 (M^+); 81 $(C_5H_5O^+)$; 69 (CF_3^+); 67 (base peak, $C_5H_7^+$)] was very similar to its isomer compound **24**, while the 2:1 adduct **27** showed ion peaks at *m/z*: 403 $(M-H)^+$; 363 $(M-C_3H_5)^+$; 208 $[M-(CF_3)_2NOH-C_2H_3]^+$; 182 $[(CF_3)_2NOCH_2^+]$; 60 (base peak, CF_3^+); 68 $(C_5H_8^+)$.

2.7. Reaction of oxadiazapentane 3 with penta-1,4-diene (7)

The gas-phase reaction between the oxadiazapentane **3** and diene **7** afforded the 1:1 adduct **33** as the major product together with 20 minor components which could not be separated or identified. A second reaction carried out mainly in the liquid phase gave a much lower yield of the 1:1 adduct **33**, together with two other components and a number of minor components. The two other major components were separated together admixed with some of the minor components and were tentatively identified on the basis of the NMR and mass spectra of the mixture as two diastereomers of the 1:2 adduct **34**.

The 1:1 adduct **33** gave expected elemental analysis figures (for C, H, N, F) and the following spectral data confirmed the structure {^{1}H NMR δ: 5.33–4.71 (3H, CH=CH_2); 3.87 (1H, >CH–O); 2.99 (2H, CH_2N); 2.10 (2H, CH_2CH=) ppm. ^{19}F NMR δ: 18.0 [6F, $(CF_3)_2N$]; 8.3 [6F, $(CF_3)_2NO$] ppm. MS (*m/z*): 346 $(M-H-C_3H_5)^+$; 220 $[M-(CF_3)_2NO]$; 179 $[(CF_3)_2NC_2H_3^+]$; 166 [base peak, $(CF_3)_2NCH_2^+$]}. The impure mixture of isomers of compound **34** showed ^{1}H NMR absorptions for CH=CH_2, CH_2O, CH_2N, 3 CH_2 and 3 >CH groups, ^{19}F NMR absorptions at δ: 19.0 [$(CF_3)_2N$]; 9.4 [$(CF_3)_2NO$]; 8.2 [$(CF_3)_2NO$] ppm (ratio 2:1:1) and

MS peaks at *m/z*: 288 $[M-(CF_3)_2NO]^+$; 182 $[(CF_3)_2NOCH_2^+]$; 166 $[(CF_3)_2NCH_2^+]$; 136 $(C_{10}H_{16}^+)$ in agreement with the proposed structure.

The identified products **33** and **34** are considered to have been formed as shown in Scheme 6.

Addition of radical **2** to a double bond afforded intermediate radical **44** which underwent chain transfer with oxadiazapentane **3** to give the 1:1 adduct **33**. In the liquid phase, competing reaction of the intermediate radical **44** with diene **7** took place to afford the dimer radical **45** which underwent intramolecular cyclisation of the 5-*exo* type to give the cyclopentylmethyl radical **46**, the precursor of the 1:2 adduct **34**. It has been reported [12] that with hexen-6-yl radicals 5-*exo* cyclisation to afford a primary cyclopentylmethyl radical is favoured over 6-*endo* cyclisation to give a more stable secondary cyclohexyl radical; the observed ratio is ca. 50:1 and a ca. 10:1 ratio is predicted from stereoelectronic requirements and calculations of the relative steric and angle strain imposed on the transition states [13].

Small amounts of the amine **16** and the hydroxylamine **17** were also formed in both reactions indicating that hydrogen abstraction from the allylic position had taken place to some extent.

2.8. Reaction of oxyl 1 with allylbenzene (8)

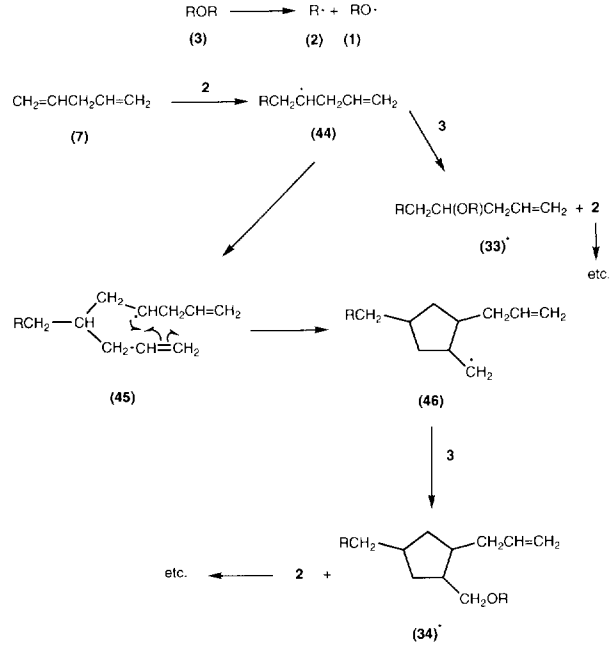
From the reaction of oxyl **1** with allylbenzene (**8**) (2.5:1 molar ratio) a high-boiling mixture was obtained comprising of eight components. Four components were major and these were separated by GLC and identified as two diastereomers of the trisubstituted compound **28** and the monosubstituted alkenes **29** and **30** (yields 20.5%, 10%, 37% and 16.5%, respectively). Use of a higher molar ratio (4.3:1) afforded compounds **28a, 28b, 29** and a new product (yields ca. 46%, 22%, 24% and 3%), together with two of the minor components formed in the first reaction; compound **30** was not detected. The IR spectrum of the crude high-boiling mixture from the second experiment showed a weak band [λ_{max} (cm^{-1}): ca. 1700 (C=O str.)] which was not present in the crude mixture from the first experiment, and this indicated that further oxyl **1** attack had taken place on a $CH_2ON(CF_3)_2$ group [14] to give the new component, i.e.

$$RCH_2ON(CF_3)_2 \xrightarrow{1} R\dot{C}HON(CF_3)_2 \longrightarrow$$

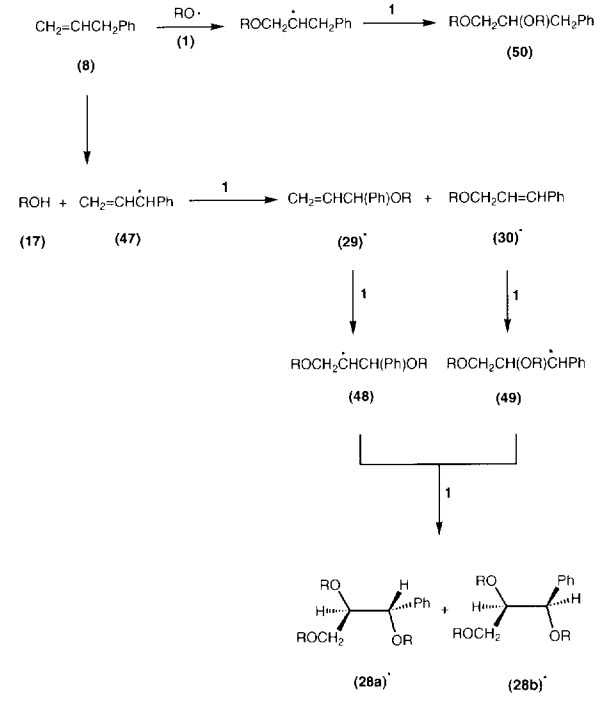
$$(CF_3)_2N\cdot + RCHO \xrightarrow{1} R\dot{C}{=}O \xrightarrow{1} RCO_2N(CF_3)_2$$

The higher yields of compound **28a** and **28b** obtained in the second experiment were at the expense of both the monosubstituted alkenes **29** and **30**, but mainly **30**, so these are the precursors to **28a** and **28b**. The identified products **28–30** are considered to be formed as shown in Scheme 7.

Initial hydrogen abstraction afforded the radical **47**, which is highly stabilised being both allylic and benzylic, and this was scavenged by oxyl **1** at both the primary and secondary sites leading to compounds **30** and **29**, respectively. Further oxyl **1** attack on the double bonds in alkenes **29** and **30** then takes place to give the intermediate radicals **48** and **49** which couple with oxyl **1** to afford the diastereomers **28a** and **28b**. Oxyl **1** attack on alkene **30** would be expected to be faster



Scheme 6. R = $(CF_3)_2N$. * Identified products.



Scheme 7. R = $(CF_3)_2N$. * Identified products.

than attack on alkene **29** because it leads to the stabilised benzylic radical **49** rather than a less stable secondary radical **48**.

The 2:1 adduct **50** was not isolated and so it can only be a minor product if it is formed at all.

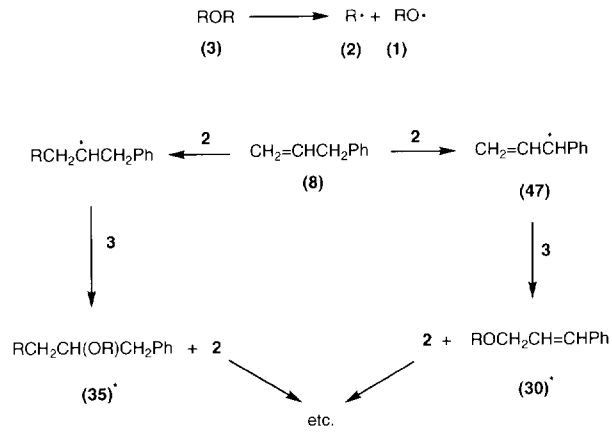
The diastereomers **28a** and **28b** were identified by elemental analysis (for C, H, N, F), the presence in the NMR spectra of each isomer of absorptions for the groups C_6H_5, two $\rangle$CH–O and CH_2O (integrated intensities 5:1:1:2) and also for three $(CF_3)_2NO$ groups (^{19}F NMR δ: 8.8–7.5 ppm) and MS peaks at *m/z*: 453 $[M-(CF_3)_2NO]^+$; 285 $[M-2(CF_3)_2NO]^+$; 258 $[M-(CF_3)_2NOCH_2-(CF_3)_2NOCH]^+$; 182 $[(CF_3)_2NOCH_2^+]$; 117 (base peak, $C_9H_9^+$). It is suggested that the major isomer has the *erythro* configuration **28a** in which the bulky $(CF_3)_2NO$ groups and the phenyl and $CH_2ON(CF_3)_2$ groups are *anti*, while the minor isomer has the less sterically favoured *threo* configuration **28b**.

The monosubstitution products **29** and **30** gave correct elemental analysis figures (for C, H, N, F) and the presence of a molecular ion peak (*m/z*: 275) in the mass spectrum of each isomer confirmed the molecular formula. The structures were assigned by a consideration of the NMR spectra with ^1H NMR absorptions for a phenyl group, three vinylic hydrogens and a $\rangle$CH–O hydrogen and a ^{19}F NMR absorption for a $(CF_3)_2NO$ group (δ: 9.3 ppm) in the spectra of compound **29** and ^1H NMR absorptions for a phenyl group, a *trans* –CH=CH– group (J=15 Hz) and a CH_2O group and a ^{19}F NMR absorption for a $(CF_3)_2NO$ group (δ: 8.3 ppm) in the spectra of compound **30**; the *cis* isomer of compound **30** was not detected in the products.

2.9. Reaction of oxadiazapentane 3 with allylbenzene (8)

The reaction between the oxadiazapentane **3** and allylbenzene (**8**) gave a high-boiling mixture comprising of four major and six minor components. The substituted alkene **30** was identified by a comparison of its GLC retention time and mass spectrum (obtained by coupled GLC/MS) with those of a pure sample obtained from the oxyl **1**/alkene **8** reaction. A second major product was separated by GLC and identified as the 1:1 adduct **35** (66.5%), while the remaining two major products (ca. 16%) could not be separated by GLC and remain identified. Surprisingly, the 3-substituted alkene **29** was not detected in the products.

The products **30** and **35** are considered to have been formed as shown in Scheme 8 and the 1:1 adduct **35** was identified by elemental analysis (for C, H, N, F), ^1H NMR absorptions for the groups C_6H_5, $\rangle$CH–O, CH_2N and CH_2, ^{19}F NMR absorptions for a $(CF_3)_2N$ and a $(CF_3)_2NO$ group (δ: 18.45 and 8.45 ppm in a 1:1 ratio) and mass spectral bands at *m/z*: 438 (M^+); 272 $[M-(CF_3)_2NCH_2]^+$; 270 $[M-(CF_3)_2NO]^+$; 166 $[(CF_3)_2NCH_2^+]$; 91 (base peak, $C_7H_7^+$).



Scheme 8. R=$(CF_3)_2N$. * Identified products.

The notable difference observed between reactions involving the oxyl **1** and the corresponding reactions involving the oxadiazapentane **3** was that allylic hydrogen abstraction was favoured by oxyl **1** [except with cyclooctene (**6**)] while addition to a double bond was favoured by the $(CF_3)_2N\cdot$ radical (**2**). This difference can be attributed mainly to greater steric crowding in radical **2** (branching at the radical centre) than in radical **1** (branching at the atom adjacent to the radical centre), thus favouring reaction of radical **2** at the more accessible double bonds. The greater electrophilicity of radical **2** as compared to oxyl **1** could be a further factor favouring reaction of radical **2** at the electron-rich double bonds.

3. Experimental details

3.1. Starting materials

The oxyl **1** was prepared by oxidation of the hydroxylamine **17** with potassium permanganate and sulphuric acid [15] and was converted into the oxadiazapentane **3** by reaction with trifluoronitrosomethane (2:1 molar ratio) [15]. Dienes ***4***, ***5*** and **7** and alkenes **6** and **8** were commercial samples and the purity of each was checked (^1H NMR spectroscopy) before use.

3.2. General techniques

Reactions were carried out in vacuo in Pyrex ampoules (ca. 50 cm^3 capacity unless stated otherwise) fitted with Rotaflo Teflon taps and the volatile products were removed in vacuo and were separated by fractional condensation in vacuo at low pressure (1–2 mmHg) where necessary. High-boiling product mixtures were separated into their components by preparative-scale GLC [Pye 104 instrument using columns (2–4 m) packed with Silicone SE30 oil, Apiezon L (APL) grease, trixylyl phosphate (TXP) or Kel-F oil (20%–25% w/w) on acid-

washed Celite] and were examined by IR spectroscopy (Perkin-Elmer 197 instrument), ^{1}H NMR spectroscopy [Varian Associates HA-100 (100.0 MHz) spectrometer; internal reference Me_4Si], ^{19}F NMR spectroscopy [Varian Associates HA-100 (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 run as solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

Boiling points were determined by Siwoloboff's method.

All of the isolated products containing $(CF_3)_2NO$ groups showed IR bands at ν_{max} (cm^{-1}): 1300–1235 (vs) (C–F str.); 1045–1030 (s) (C–O–N str.); 968–960 s) (C–N str.); 710–705 (s) (CF_3 def.) together with bands at 1690–1640 (m) (C=C str.) and 3125–3030 (w) (aryl and vinyl C–H str.) and/or 2940–2860 (m) (aliph. C–H str.).

The ^{1}H and ^{19}F NMR spectra of compounds **13a, 13b, 19, 22–24, 25a, 28a, 28b, 29, 30, 31a, 31b, 32, 33** and **35** are given in Table 3 and the MS data are listed in Table 4.

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

(a) With norbornadiene (4)

A mixture of the oxyl **1** (1.72 g, 10.2 mmol) and norbornadiene (**4**) (0.58 g, 6.3 mmol), stored at −64 °C (2 h), gave (i) a highly volatile combined −78 and −196 °C fraction (0.35 g) shown (IR and NMR) to contain mainly bis(trifluoromethyl)amine (**16**), *N,N*-bis(trifluoromethyl)hydroxylamine (**17**) and carbon dioxide; and (ii) a higher-boiling light brown liquid (2.25 g) (combined −23 °C fraction, 0 °C fraction and non-volatile residue) which was shown by GLC (2 m Kel-F at 95 °C) to contain nine major components (A–I) in the ratio 21.3:15.5:13.6:7.0:5.0:2.5:1.3:1.0:1.0 and six very minor components.

Components A–C were separated by preparative-scale GLC (as above) and were identified as unchanged diene **4** (0.18 g, 2.0 mmol, 32% recovered), 5-*exo*-6-*endo*-bis(*N,N*-bistrifluoromethylamino-oxy)norborn-2-ene (**13a**) (nc) (0.60 g, 1.4 mmol, 32%) (Analysis: Found: C, 30.6; H, 1.9; N, 6.6; F, 53.8%. $C_{11}H_8F_{12}N_2O_2$ requires: C, 30.8; H, 1.9; N, 6.5; F, 53.3%) and 5-*exo*-6-*exo*-bis(*N,N*-bistrifluoromethylamino-oxy)norborn-2-ene (**13b**) (nc) (0.53 g, 1.24 mmol, 28%) (Analysis: Found: C, 30.5; H, 2.1; N, 6.5; F, 53.6%. $C_{11}H_8F_{12}N_2O_2$ requires: C, 30.8; H, 1.9; N, 6.5; F, 53.3%).

On the basis of coupled GLC (as above)/MS, components D and E were identified a the *endo,exo* (**14a**) (nc) and *exo,exo* (**14b**) (nc) isomers of 3,5-bis(*N,N*-bistrifluoromethylamino-oxy)nortricyclane (0.46 g, 1.07 mmol, 25%) {MS (*m/z*): 260 [35.1% (33.5), $(M-CF_3)_2NO)^+$]; 108 [50.0 (83.8), $C_7H_8O^+$]; 107 [14.4 (17.2), $C_7H_7O^+$]; 92 [16.2 (20.5), $C_7H_8^+$]; 91 [32.5 (29.1), $C_7H_7^+$]; 80 [18.1 (20.6), $C_5H_4O^+$]; 79 [100.0 (100.0), $C_6H_7^+$]; 77 [55.1 (43.7), $C_6H_5^+$]; 69 [43.3 (17.5), CF_3^+]; 66 [92.6 (28.5), $C_5H_6^+$]; 39 [12.9 (10.9), $C_3H_3^+$]} while components F–I were identified as four stereoisomers of 2-*exo*-3,5,6,-tetrakis(*N,N*-bis(trifluoromethylamino-oxy)norbornane (**15**) (0.38 g, 0.52 mmol, 12%) {MS (*m/z*: 596 {6%, $[M-(CF_3)_2NO]^+$} 595 {41, $[M-(CF_3)_2NOH]^+$}; 427 {74, $[M-(CF_3)_2NO-(CF_3)_2NOH]^+$}; 260 (34, $C_9H_8F_6NO^+$); 259 (66, $C_9H_7F_6NO^+$); 246 (28, $C_8H_6F_6NO^+$); 124 (43, $C_7H_8O_2^+$); 123 (70, $C_7H_7O_2^+$); 108 (46, $C_7H_8O^+$); 107 (80, $C_7H_7O^+$); 94 (38, $C_6H_6O^+$); 93 (23, $C_6H_5O^+$); 92 (22, $C_7H_8^+$); 82 (50, $C_5H_6O^+$); 81 (62, $C_5H_5O^+$); 80 (29, $C_5H_4O^+$); 79 (84, $C_6H_7^+$); 78 (31, $C_6H_6^+$); 69 (100, CF_3^+); 67 (63, $C_5H_7^+$); 66 (52, $C_5H_6^+$); 55 (50, $C_3H_3O^+$); 41 (29, $C_3H_5^+$); 28 (73, $C_2H_4^+$)}.

Three further experiments were carried out as follows:

(i) A mixture of the oxyl **1** (3.65 g, 21.7 mmol), diene **4** (1.02 g, 11.1 mmol) and 1,1,2-trichlorotrifluoroethane (12.1 g), maintained at −78 °C (40 min), gave volatile material (13.0 g) and a colourless non-volatile liquid (4.58 g) shown by GLC (2 m Kel-F at 95 °C) to contain components B–I in the ratio 8.9:7.1:2.2:2.0:3.5:1.1:1.0:1.0.

(ii) A mixture of the oxyl **1** (0.60 g, 3.6 mmol), diene **4** (6.22 g, 67.5 mmol) and 1,1,2-trichlorotrifluoroethane (14.2 g), maintained at −64 °C (1.5 h), gave volatile material (20.34 g) and a colourless non-volatile liquid (0.62 g) shown by GLC (as above) to contain components B–E in the ratio 5.1:4.8:1.1:1.0 and six very minor components (components F–I were not detected).

(iii) A mixture of the oxyl **1** (3.45 g, 20.5 mmol) and diene **4** (1.0 g, 10.9 mmol) kept in the gas phase in vacuo in a Pyrex bulb (ca. 10 dm^3) underwent almost instantaneous reaction to give a light yellow, non-volatile liquid (4.41 g), which was shown by GLC (as above) to consist of components B–E in the ratio 1.3:1.0:2.0:1.4 and 11 very minor components (components F–I were not detected).

(b) With cis,cis-cyclo-octa-1,5-diene (5)

A mixture of the oxyl **1** (2.58 g, 15.4 mmol) and diene **5** (0.89 g, 8.2 mmol) underwent reaction on warming from −196 °C to room temperature to give a volatile fraction identified (IR) as hydroxylamine **17** (1.13 g, 6.7 mmol, 43.5%) and a non-volatile liquid (2.34 g) which was shown by GLC (2 m TXP at 150 °C) to contain six major components (J–O) in the ratio 1.0:1.2:1.1:1.2:2.4:4.3 and five very minor components. The major components were separated by preparative-scale GLC (2 m SE30 at 140 °C) to afford (i) unchanged diene **5** (0.31 g, 2.9 mmol, 35% recovered) (component O)); (ii) 3-(*N,N*-bistrifluoromethylamino)cyclo-octa-1,5-diene (component N) (**19**) (nc) (0.44 g, 1.6 mmol, 30%) (Analysis: Found: C, 43.4; H, 4.0; N, 5.1%. $C_{10}H_{11}F_6NO$ requires: C, 43.6; H, 4.0; N, 5.1%), b.p. 179 °C; (iii)

Table 3
^1H and ^{19}F NMR data for the isolated products

Compound	^1H NMR δ (ppm)	^{19}F NMR δ (ppm)
13a	5.91 (mult., 2H, 2 =CH); 4.37 (br., 1H, *endo* >CH–O); 3.85 (s, 1H, *exo* >CH–O); 2.79 (complex, 2H, 2 >CH); 1.54 (mult., 2H, CH_2)	8.3 [s, 6F, $(CF_3)_2NO$]; 8.1 [s, 6F, $(CF_3)_2NO$]
13b	5.86 (mult., 2H, 2 =CH); 4.02 (s, 2H, 2 >CH–O); 2.90 (br., 2H, 2 >CH); 1.70 (mult., 2H, CH_2)	8.4 [br., 2 $(CF_3)_2NO$]
19	5.3 (complex, 4H, 4 =CH); 4.8 (mult., 1H, allylic >CH–O); 2.6–1.7 (complex, 6H, 3 CH_2)	8.8 [s, $(CF_3)_2NO$]
22	5.39 (mult., 2H, 2 =CH); 4.73 (mult., 1H, >CH–O); 1.9 (complex, 4H, 2 CH_2); 1.35 (complex, 6H, 3 CH_2)	8.8 [s, $(CF_3)_2NO$]
23	4.18 (mult., 1H, >CH–O); 4.06 (mult., 1H, >CH–O); 1.75 (complex, 4H, 2 CH_2–CH–O); 1.39 (complex, 8H, 4 CH_2)	9.0 [s, 6F, $(CF_3)_2NO$]; 8.7 [s, 6F, $(CF_3)_2NO$]
24	5.37 (mult., 2H, 2 =CH); 4.92 [d mult., 2H, 2 =CH, $J(trans)=15$ Hz]; 4.78 [d mult., 2H, 2 =CH, $J(cis)=8.5$ Hz]; 4.33 [t, 1H, >CH–O, $J=5$ Hz]	8.3 [s, $(CF_3)_2NO$]
25a	5.51 (mult., 2H, 2 =CH); 4.19 (complex, 3H, =CHCH_2O and >CH–O); 3.84 (d, CH_2O, $J=5$ Hz)	8.1 [br., 6F, $(CF_3)_2NOCH$]; 7.4 [s, 6F, $(CF_3)_2NOCH_2CH=$]; 7.1 [s, 6F, $(CF_3)_2NOCH_2$]
28a	6.95 (br., 5H, C_6H_5); 4.89 (mult., 1H, Ph*CH*–O); 4.46 (mult., 1H, >CH–O); 3.95 (AB mult., 2H, CH_AH_BO)	8.8 [s, 6F, $(CF_3)_2NOCH$]; 8.4 [s, 6F, $(CF_3)_2NOCH$]; 7.25 [s, 6F, $(CF_3)_2NOCH_2$]
28b	6.97 (br., 5H, C_6H_5); 4.85 (d, 1H, Ph*CH*–O, $J=7.0$ Hz); 4.34 (mult., 1H, >CH–O); 3.99, 3.60 (AB mult., 2H, CH_AH_BO)	8.65 [br., 12F, 2 $(CF_3)_2NOCH$]; 7.55 [s, 6F, $(CF_3)_2NOCH_2$]
29	6.66 (mult., 5H, C_6H_5); 5.49 [ddd, 1H, PhCH–*CH*=, $J(trans)=16$, $J(cis)=8$, $J=1.5$ Hz]; 4.75 (mult., 2H, PhC*H* and =CH); 4.60 [dd, 1H, =CH, $J(cis)=8$, $J(gem)=2$ Hz]	9.3 [s, $(CF_3)_2NO$]
30	6.58 (br., 5H, C_6H_5); 5.80 [d, 1H, PhC*H*=CH, $J(trans)=15$ Hz]; 5.44 [dt, 1H, =*CH*CH_2, $J(trans)=15$, $J=5$ Hz]; 3.92 [d, 2H, CH_2O, $J=5$ Hz]	8.3 [s, $(CF_3)_2NO$]
31a	5.5 (mult., 2H, 2 =CH); 4.25 (mult., 1H, >CH–O); 4.02 (mult., 1H, >CH–N); 2.5–1.2 (complex, 8H, 4 CH_2)	21.6 [s, 6F $(CF_3)_2N$]; 9.3 [br., 6F, $(CF_3)_2NO$]
31b	5.4 (mult., 2H, 2 =CH); 4.3–3.8 (complex, 2H, >CH–O and >CH–N); 2.5–1.3 (complex, 8H, 4 CH_2)	25.4, 18.6 [2 mult., 2×3F, $(CF_3)_2N$]; 9.2 [br., 6F, $(CF_3)_2NO$]
33	5.33 [dd mult., 1H, CH_2CH=, $J(trans)=15$, $J(cis)=6$ Hz]; 4.84 [d mult., 1H, =CH, $J(trans)=15$ Hz]; 4.71 [d mult., 1H, =CH, $J(cis)=6$ Hz]; 3.87 (mult., 1H, >CH–O); 2.99 (mult., 2H, CH_2N); 2.10 (mult., 2H, CH_2CH=)	18.0 [s, 6F, $(CF_3)_2N$]; 8.3 [br., 6F, $(CF_3)_2NO$]
35	6.77 (mult., 5H, C_6H_5); 3.99 (mult., 1H, >CH–O); 2.86 (mult., 2H, CH_2N), 2.76 and 2.24 (AB d, 2H, CH_AH_B, $J_{A-B}=14$, $J_{CH-A}=8$, $J_{CH-B}=6$ Hz)	18.45 [s, 6F, $(CF_3)_2N$]; 8.85 [br., 6F, $(CF_3)_2NO$]

a mixture of components J and K identified as a bis(*N*,*N*-bistrifluoromethylamino-oxy)cyclo-octadiene (**20a**) and 5,6-bis(*N*,*N*-bistrifluoromethylamino-oxy)cyclo-oct-1-ene (**21a**) (nc) present in the ratio 1:1.2) (0.66 g, 1.5 mmol, 28%) (Analysis: Found: C, 32.5; H, 2.5; N, 6.3; F, 51.7%. $C_{12}H_{12}F_{12}N_2O_2$ requires: C, 32.4; H, 2.7; N, 6.3; F, 51.4% and $C_{12}H_{10}F_{12}N_2O_2$ requires: C, 32.6; H, 2.3; N, 6.3; F, 51.6%). ^1H NMR ($CDCl_3$) δ: 5.8–5.2 (complex, 6H, 6 =CH); 5.0–4.6 (complex, 2H, 2 =CHC*H*–O); 4.2 (mult., 2H, 2 >CH–O); 2.6–1.0 (complex, 12H, 6 CH_2) ppm. ^{19}F NMR δ: 8.6–8.4 [$(CF_3)_2NO$] ppm. MS (*m*/*z*): **20a**: 290 {1%, $[M-(CF_3)_2N]^+$}; 274

Table 4
MS data for isolated products

Compound	MS *m/z* (% [a], assignment)
13a	260 {1, $[M-(CF_3)_2NO]^+$}; 108 (12, $C_7H_8O^+$); 107 (4, $C_7H_7O^+$); 92 (3, $C_7H_8^+$); 91 (4, $C_7H_7^+$); 80 (6, $C_5H_4O^+$); 79 (14, $C_6H_7^+$); 77 (6, $C_6H_5^+$); 69 (6, CF_3^+); 66 (100, $C_5H_6^+$); 65 (5, $C_5H_5^+$); 41 (3, $C_3H_5^+$); 39 (5, $C_3H_3^+$); 28 (5, CO^+)
13b	427 [0.1, $(M-H)^+$]; 260 (4); 108 (25); 107 (7); 92 (10); 91 (15); 80 (11); 79 (49); 77 (31); 69 (27); 66 (100); 65 (8); 41 (10); 39 (10); 28 (31)
19	275 (2, M^+); 221 (77, $C_6H_5F_6NO^+$); 107 (100, $C_8H_{11}^+$); 105 (14, $C_8H_9^+$); 91 (43, $C_7H_7^+$); 80 (18); 79 (94); 77 (29); 69 (67); 68 (26, $C_5H_8^+$); 67 (25, CH_7^+); 55 (18, $C_4H_7^+/C_3H_3O^+$); 54 (30, $C_4H_6^+/C_3H_2O^+$); 53 (25, $C_4H_5^+$); 41 (93); 39 (60)
22	277 (0.2, M^+); 276 [2, $(M-H)^+$]; 109 (55, $C_8H_{13}^+$); 107 (9, $C_8H_{11}^+$); 81 (27, $C_6H_9^+/C_5H_5O^+$); 79 (16); 69 (23); 67 (100, $C_5H_7^+$); 55 (60); 53 (10); 43 (18, $C_2H_3O^+$); 41 (54); 39 (25); 29 (22, CHO^+)
23	278 {2, $[M-(CF_3)_2)NO]^+$}; 150 (11, $C_2HF_5NO^+$); 126 (5, $C_8H_{14}O^+$); 109 (100, $C_8H_{13}^+$); 98 (15, $C_6H_{10}O^+$); 83 (15, $C_6H_{11}^+/C_5H_7O^+$); 81 (17); 69 (31); 67 (54); 55 (55); 43 (22); 41 (35); 28 (11)
24	235 (0.5, M^+); 150 (1.5); 69 (43); 67 (100, $C_5H_7^+$); 65 (11); 55 (7); 53 (9); 41 (33); 39 (18); 28 (42)
25a	552 [1, $(M-F)^+$]; 403 {14, $(M-(CF_3)_2NO]^+$}; 234 (7, $C_7H_6F_6NO^+$); 208 (11, $C_5H_4F_6NO^+$); 192 (17, $C_5H_7F_5NO^+$); 182 [8, $(CF_3)_2NOCH_2^+$]; 150 (8); 83 (6); 82 (12, $C_5H_6O^+$); 81 (10); 69 (100, CF_3^+); 67 (32); 66 (54); 55 (25); 41 (30); 40 (20, $C_3H_4^+$); 39 (14); 29 (27)
28a	453 {2, $[M-(CF_3)_2NO]^+$}; 452 {10, $[M-(CF_3)_2NOH]^+$}; 301 {5, $[M-(CF_3)_2NO-(CF_3)_2N]^+$}; 284 (5, $C_{11}H_8F_6NO^+$); 258 (19, $C_9H_6F_6NO^+$); 133 (11, $C_9H_9O^+$); 132 (19, $C_9H_8O^+$); 119 (30, $C_8H_7O^+$); 117 (100, $C_9H_9^+$); 106 (23, $C_7H_6O^+$); 105 (53, $C_7H_5O^+$); 91 (78); 77 (23); 69 (88)
28b	452 (6); 301 (4); 284 (4); 258 (32); 133 (12); 132 (20); 119 (31); 117 (100); 106 (29); 105 (56); 91 (80); 77 (23); 69 (69)
29	285 (0.3, M^+); 131 (1, $C_9H_7O^+$); 117 (100); 116 (8, $C_9H_8^+$); 115 (31, $C_9H_7^+$); 91 (16); 77 (9); 69 (20); 51 (7); 39 (6)
30	285 (1); 131 (3); 117 (100); 116 (8); 115 (31); 91 (15); 77 (11); 69 (10); 51 (9); 39 (7)
31a	400 [5, $(M-C_2H_4)^+$]; 276 {4, $[M-(CF_3)_2N]^+$}; 260 {8, $[M-(CF_3)_2NO]^+$}; 218 (10, $C_7H_6F_6N^+$); 192 (41, $C_5H_4F_6N^+$); 166 (32, $C_3H_2F_6N^+$); 124 (7, $C_8H_{12}O^+$); 108 (7, $C_8H_{12}^+$); 107 (52, $C_8H_{11}^+$); 95 (18, $C_7H_{11}^+$); 91 (13); 81 (100, $C_5H_5O^+/C_6H_9^+$); 80 (19); 79 (75); 69 (48); 67 (37); 55 (20); 53 (15); 43 (11); 41 (58); 39 (15)
31b	276 (2); 260 (16); 218 (12); 192 (36); 166 (25); 124 (7); 108 (6); 107 (50); 95 (10); 91 (12); 81 (100); 80 (13); 79 (80); 69 (49); 67 (32); 55 (19); 53 (14); 43 (9); 41 (55); 39 (15)
33	346 [6, $(M-C_3H_6)^+$]; 220 {18, $[M-(CF_3)_2NO]^+$}; 219 {8, $[M-(CF_3)_2NOH]^+$}; 179 (11, $C_4H_3F_6N^+$); 166 [100, $(CF_3)_2NCH_2^+$]; 78 (36, $C_2H_2F_2N^+$); 69 (47); 67 (17); 54 (7); 43 (6); 42 (19, $C_2H_2O^+/C_3H_6^+$); 41 (56); 39 (19)
35	438 (2.5, M^+); 272 {1, $[M-(CF_3)_2NCH_2]^+$}; 270 {12, $[M-(CF_3)_2NO]^+$}; 269 {5, $[M-(CF_3)_2NOH]^+$}; 166 [68, $(CF_3)_2NCH_2^+$]; 117 (10); 104 (7); 91 (100); 78 (14); 69 (17); 65 (9)

[a] Intensities expressed as percentage of the base peak.

{4, $[M-(CF_3)_2NO]^+$}; 260 (1, $C_9H_8F_6NO^+$); 122 (13, $C_8H_{10}O^+$); 106 (51, $C_8H_{10}^+$). **21a**: 416 [0.5, $(M-C_2H_4)^+$]; 276 {1, $[M-(CF_3)_2NO]^+$}; 262 (1, $C_9H_{10}F_6NO^+$); 124 (21, $C_8H_{12}O^+$); 108 (11, $C_8H_{12}^+$); 107 (53, $C_8H_{11}^+$). **20a** and **21a**: 248 (23, $C_8H_8F_6NO^+$); 150 (9, $C_2HF_5NO^+$); 81 (42, $C_6H_9^+$); 80 (41, $C_6H_8^+$); 79 (100, $C_6H_7^+$); 69 (19, CF_3^+); 67 (48, $C_5H_7^+$); 41 (45, $C_3H_5^+$); 28 (92, $C_2H_4^+$). IR (ν_{max}) (cm^{-1}): 1645 (m, C=C str.); and (iv) a mixture of components L and M identified as a second (*N,N*-bistrifluoromethylamino-oxy)cyclo-octadiene (**20b**) and 5,6-bis(*N,N*-bistrifluoromethylamino-oxy)cyclo-oct-1-ene (**21b**) (nc) (present in the ratio 1.1:1.2) (0.66 g, 1.5 mmol, 28%). (Analysis: Found: C, 32.7; H, 2.4; N, 6.6; F, 51.5%). ^1H NMR ($CDCl_3$) δ: 5.8–5.2 (complex, 6H, 6 =CH); 5.0–4.5 (complex, 2H, 2 =CHC*H*–O); 4.17 (mult., 2H, 2 >CH–O); 2.6–1.0 (complex, 12H, 6 CH_2) ppm. ^{19}F NMR δ: 8.6–8.4 [$(CF_3)_2NO$] ppm. MS (*m/z*): **20b**: 290 {0.5%, $[M-(CF_3)_2N]^+$}; 274 {1, $[M-(CF_3)_2NO]^+$}; 122 (2, $C_8H_{10}O^+$). **21b**: 425 [0.5, $(M-F)^+$]: 292 {0.5, $[M-(CF_3)_2N]^+$}; 276 {0.5, $[M-(CF_3)_2NO]^+$}; 124 (1, $C_8H_{12}O^+$); 108 (9, $C_8H_{12}^+$). **20b** and **21b**: 133 (9, $C_2F_5N^+$); 81 (10, $C_6H_9^+$); 79 (9, $C_6H_7^+$); 69 (100, CF_3^+); 55 (10, $C_4H_7^+$); 44 (19, $C_2H_4O^+$); 41 (11, $C_3H_5^+$). IR (ν_{max}) (cm^{-1}): 1645 (m, C=C str.).

(c) With cyclo-octene (6)

A mixture of the oxyl **1** (1.76 g, 10.5 mmol) and alkene **6** (0.64 g, 5.8 mmol) on reaction while warming from −196 °C to room temperature gave a volatile fraction identified (IR) as hydroxylamine **17** (0.17 g, 1.0 mmol, 10%) and a colourless non-volatile liquid residue (2.23 g) shown by GLC (2 m SE30 at 130 °C) to contain three major components. These were separated by preparative-scale GLC (2 m SE30 at 130 °C) and identified as (i) unchanged alkene **6** (0.12 g, 1.1 mmol, 18% recovered); (ii) 3-(*N,N*-bistrifluoromethyl

amino-oxy)cyclo-oct-1-ene (**22**) (nc) (0.26 g, 0.9 mmol, 20%) (Analysis: Found: C, 43.3; H, 4.4; N, 5.2%. $C_{10}H_{13}F_6NO$ requires: C, 43.3; H, 4.7; N, 5.0%), b.p. 175–176 °C; and (iii) 1,2-bis(*N*,*N*-bistrifluoromethylamino-oxy)cyclo-octane (**23**) (nc) (1.43 g, 3.2 mmol, 67.5%) (Analysis: Found: C, 32.1; H, 3.2; N, 6.0; F, 51.5%. $C_{12}H_{14}F_{12}N_2O_2$ requires: C, 32.3; H, 3.1; N, 5.3; F, 51.1%), b.p. 200 °C.

(d) With penta-1,4-diene (7)

A mixture of the oxyl **1** (2.67 g, 15.9 mmol) and diene **7** (0.59 g, 8.7 mmol), maintained at −78 °C (30 min) in an ampoule (ca. 50 cm^3), gave volatile material (1.55 g) which was shown [IR, NMR and GLC (2 m SE30 at 70 °C)] to consist of three components (A′–C′). Component A′ was identified as unchanged diene **7** (0.27 g, 3.9 mmol, 44% recovered) and component B′ was identified as hydroxylamine **17** (0.80 g, 4.8 mmol, 30%). Component C′ was separated by preparative-scale GLC (2 m SE30 at 70 °C) and was identified as 3-(*N*,*N*-bistrifluoromethylamino-oxy)penta-1,4-diene (**24**) (nc) (0.30 g, 1.3 mmol, 26.5%) (Analysis: Found: C, 35.9; H, 2.9; N, 6.1; F, 48.6%. $C_7H_7F_6NO$ requires: C, 35.7; H, 3.0; N, 6.0; F, 48.5%). A colourless non-volatile residue (1.71 g) was also obtained which was shown by GLC (2 m SE30 at 70 °C) to contain four components (D′–G′) in the ratio 8.2:2.0:1.0:19.3. Component G′ was separated by preparative-scale GLC (2 m SE30 at 70 °C) and was identified as *trans*-1,4,5-tris(*N*,*N*-bistrifluoromethylamino-oxy)pent-2-ene (**25a**) (nc) (1.22 g, 2.1 mmol, 44.5%) (Analysis: Found: C, 23.2; H, 1.1; N, 7.4; F, 60.2%. $C_{11}H_7F_{18}N_3O_3$ requires: C, 23.1; H, 1.2; N, 7.4; F, 59.9%), b.p. 185 °C On the basis of coupled GLC (as above)/MS, components D′–F′ were identified as (i) 5-(*N*,*N*-bistrifluoromethylamino-oxy)penta-1,3-diene (**26**) (nc) (0.20 g, 0.9 mmol, 19%). MS (*m/z*): 235 (3%, M^+); 150 (3, $C_2HF_5NO^+$); 81 (3, $C_5H_5O^+$); 69 (39, CF_3^+); 67 (100, $C_5H_7^+$); 65 (8, $C_5H_5^+$); 53 (6, $C_4H_5^+$); 41 (30, $C_3H_5^+$); 40 (11, $C_3H_4^+$); 39 (16, $C_3H_3^+$); (ii) 4,5-bis(*N*,*N*-bistrifluoromethylamino-oxy)pent-1-ene (**27**) (nc) (0.06 g, 0.1 mmol, 2.5%). MS (*m/z*): 403 [6%, $(M-H)^+$]; 363 [0.5, $(M-C_3H_5)^+$]; 208 (23, $C_5H_4F_6NO^+$); 192 (20, $C_5H_7F_5NO^+$); 182 [14, $(CF_3)_2NOCH_2^+$]; 94 (10, $C_2H_2F_2NO^+$); 82 (12, $C_5H_6O^+$); 69 (100, CF_3^+); 68 (12, $C_5H_8^+$); 67 (29, $C_5H_7^+$); 55 (39, $C_4H_7^+/C_3H_3O^+$); 41 (35, $C_3H_5^+$); 39 (16, $C_3H_3^+$); 29 (26, CHO^+); and (iii) *cis*-1,4,5-tris(*N*,*N*-bistrifluoromethylamino-oxy)pent-2-ene (**25**) (0.1 g, 0.2 mmol, 5%). MS (*m/z*): 552 [1.5%, $(M-F)^+$]; 403 {12, $[M-(CF_3)_2NO]^+$}; 234 {8, $[M-2(CF_3)_2NO-H]^+$}; 221 {2, $[M-(CF_3)_2NO-(CF_3)_2NOCH_2]^+$}; 208 (9, $C_5H_4F_6NO^+$); 192 (16, $C_5H_7F_5NO^+$); 182 [14, $(CF_3)_2NOCH_2^+$]; 150 (14, $C_2HF_5NO^+$); 83 (10, $C_5H_7O^+$); 82 (21, $C_5H_6O^+$); 81 (13, $C_5H_5O^+$); 69 (100, CF_3^+); 68 (15, $C_4H_4O^+$); 67 (39, $C_5H_7^+/C_4H_3O^+$); 66 (26, $C_5H_6^+$); 55 (32, $C_3H_3O^+$); 41 (36, $C_3H_5^+$); 39 (19, $C_3H_3^+$); 29 (19, CHO^+).

(e) With allylbenzene (8)

A mixture of the oxyl **1** (1.96 g, 11.7 mmol) and alkene **8** (0.56 g, 4.7 mmol) on reaction while warming from −196 °C to room temperature gave a volatile mixture of hydroxylamine **17** (0.64 g, 3.8 mmol, 32%) and amine **16** (0.06 g, 0.35 mmol, 6%) as shown by IR and ^{19}F NMR spectroscopy and a light yellow, non-volatile liquid (1.82 g), which was shown by GLC (2 m TXP and 2 m APL at 150 °C) to contain nine components (P–X) in the ratio 2.3:10.6:1.0:5.2:19.3:10.7:2.1:8.6.

Components Q, S, U, V and X were separated by preparative-scale GLC (4 m TXP a 130 °C) and were identified as follows:

(i) *erythro*-1,2,3-Tris(*N*,*N*-bistrifluoromethylamino-oxy)-3-phenylpropane (**28a**) (nc) (0.50 g, 0.80 mmol, 20.5%) (Analysis: Found: C, 28.7; H, 1.1; N, 7.0; F, 54.7%. $C_{15}H_9F_{18}N_3O_3$ requires: C, 29.0; H, 1.4; N, 6.8; F, 55.1%).

(ii) *threo*-1,2,3-Tris(*N*,*N*-bistrifluoromethylamino-oxy)-3-phenylpropane (**28b**) (nc) (0.25 g, 0.40 mmol, 10%) (Analysis: Found: C, 28.9; H, 1.3; N, 6.7; F, 55.2%. $C_{15}H_9F_{18}N_3O_3$ requires: C, 29.0; H, 1.4; N, 6.8; F, 55.1%).

(iii) 3-(*N*,*N*-Bistrifluoromethylamino-oxy)-3-phenylpropene (**29**) (nc) (0.41 g, 1.4 mmol, 37%) (Analysis: Found: C, 46.6; H, 3.2; N, 5.2; F, 40.1%. $C_{11}H_9F_6NO$ requires: C, 46.3; H, 3.2; N, 4.9; F, 40.0%), b.p. 173 °C.

(iv) Unchanged allylbenzene (**8**) (0.09 g, 0.8 mmol, 17% recovered).

(v) *trans*-3-(*N*,*N*-Bistrifluoromethylamino-oxy)-1-phenylpropene (**30**) (nc) (0.18 g, 0.60 mmol, 16.5%) (Analysis: Found: C, 46.6; H, 3.1; N, 4.9; F, 40.3% $C_{11}H_9F_6NO$ requires: C, 46.3; H, 3.2; N, 4.9; F, 40.0%), m.p. 32–34 °C.

A second experiment using a mixture of oxyl **1** (3.12 g, 18.6 mmol) and alkene **8** (0.51 g, 4.3 mmol), which was maintained at room temperature (20 min), gave (i) volatile material (1.08 g), which was shown (IR and ^{19}F NMR spectroscopy) to consist of hydroxylamine **17** (0.88 g, 5.2 mmol, 28%) and perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane (**3**) (ca. 0.13 g, ca. 0.4 mmol, ca. 2%); and (ii) a non-volatile liquid (2.55 g) which was shown by GLC (2 m TXP and APL at 150 °C to contain components Q–U obtained in the first experiment and a new component Y in the ratio 20.8:1.0:9.6:1.1:10.8:1.5. The IR spectrum of the non-volatile liquid showed an absorption (ν_{max}) (cm^{-1}): ca. 1700 (w) (C=O str.).

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

(a) With norbornadiene (4)

A mixture of the oxadiazapentane **3** (3.46 g, 10.8 mmol), diene **4** (0.90 g, 9.8 mmol) and 1,1,2-trichlorotrifluoroethane (7.25 g) was stored at room temper-

ature (8 d). The volatile material was then removed in vacuo to give a non-volatile gelatinous residue (4.0 g) (Analysis: Found: C, 33.4; H, 2.1; N, 4.9; F, 49.4%). ^{19}F NMR ($CDCl_3$) δ: 20–23 [$(CF_3)_2N$]; 8–10 [$(CF_3)_2NO$] ppm. MS (*m/z*): 675 (0.6%); 597 (1, $C_{25}H_{25}F_{12}N_2O^+$); 581 (3, $C_{25}H_{25}F_{12}N_2^+$); 580 (0.5, $C_{25}H_{24}F_{12}N_2^+$); 411 (4, $C_{11}H_7F_{12}N_2O^+$); 350 (6); 327 (19); 259 (3, $C_9H_7F_6NO^+$); 249 (11, $C_{15}H_{16}F_2N^+$); 244 (22, $C_9H_8F_6N^+$); 243 (6, $C_9H_7F_6N^+$); 192 (27, $C_5H_7F_5NO^+$); 166 (72, $C_3H_2F_6N^+$); 109 (13, $C_7H_9O^+$); 108 (14, $C_7H_8O^+$); 107 (14, $C_7H_7O^+$); 91 (50, $C_7H_7^+$); 79 (53, $C_6H_7^+$); 78 (30, $C_6H_6^+$); 77 (38, $C_6H_5^+$); 69 (100, CF_3^+); 66 (21, $C_5H_6^+$); 65 (21, $C_5H_5^+$). Attempts to separate the material by GLC (eluants $CHCl_3$, Me_2CO and $CFCl_2CF_2Cl$) were unsuccessful and so it was dissolved in 1,1,2-trichlorotrifluoroethane (30 cm^3) and the solvent then removed in vacuo (to remove any residual low-boiling material) to afford a white solid (3.5 g) (Analysis: Found: C, 42.4; H, 3.6; N, 5.5; F, 49.3%) the IR, NMR and mass spectra of which were very similar to those of the original material.

(b) With cis,cis-cyclo-octa-1,5-diene (5)

A mixture of the oxadiazapentane **3** (3.69 g, 11.5 mmol) and diene **5** (1.29 g, 11.9 mmol) maintained at room temperature (6 d), gave a volatile mixture (0.71 g) of amine **16** and hydroxylamine **17**, as shown by IR spectroscopy, and a non-volatile liquid residue (4.26 g) which was shown by GLC (2 m SE30 and TXP at 150 °C) to contain eight components (H′–O′). The four major components (H′ and M′–O′) were separated by preparative-scale GLC (2 m SE30 followed by 2 m TXP at 125 °C) to give:

(i) Unchanged diene **5** (0.13 g, 1.2 mmol, 10% recovered).

(ii) 3-(*N*,*N*-Bistrifluoromethylamino-oxy)cyclo-octa-1,5-diene (**19**) (0.39 g, 1.4 mmol, 13%).

(iii) *trans*-5-(Bistrifluoromethylamino)-6-(*N*,*N*-bistrifluoromethylamino-oxy)cyclo-oct-1-ene (**31a**) (nc) (1.55 g, 3.6 mmol, 34%) (Analysis: Found: C, 33.7; H, 2.9; N, 6.8; F, 53.8%. $C_{12}H_{12}F_{12}N_2O$ requires: C, 33.6; H, 2.8; N, 6.5; F, 53.5%).

(iv) *cis*-5-(Bistrifluoromethylamino)-6-(*N*,*N*-bistrifluoromethylamino-oxy)cyclo-oct-1-ene (**31b**) (nc) (1.24 g, 3.0 mmol, 28%) (Analysis: Found: C, 33.8; H, 3.0; N, 6.5%. $C_{12}H_{12}F_{12}N_2O$: requires C, 33.6; H, 2.8; N, 6.5%).

Component J′ was partially separated by preparative-scale GLC (as above) and was tentatively identified as 5-(bistrifluoromethylamino)cyclo-oct-1-ene (**32**) (nc) (0.30 g, 0.12 mmol, 9%). ^{1}H NMR ($CDCl_3$) δ: ca. 5.7 (complex, 2H, 2 =CH); 3.7 (mult., 1H, >CH–N); 2.6–1.2 (complex, 10H, 5 CH_2) ppm. ^{19}F NMR δ: 23.1 [$(CF_3)_2N$] ppm.

(c) With penta-1,4-diene (7) in the gas phase

A mixture of the oxadiazapentane **3** (3.20 g, 10.0 mmol) and diene **7** (0.71 g, 10.4 mmol), sealed in vacuo in a Pyrex bulb (ca. 10 dm^3) and kept at room temperature (2 d), gave a complex mixture shown by GLC (2 m SE30 at 90–150 °C) to contain unchanged diene **7**, one major component and 20 minor components. The volatile material (0.45 g) was shown by IR and NMR spectroscopy and GLC (2 m SE30 at 90 °C) to contain unchanged diene **7** (0.09 g, 1.4 mmol, 13% recovered), amine **16** and hydroxylamine **17** and a number of other components with ^{19}F NMR absorptions δ: 6–21 ppm. The non-volatile liquid residue (3.46 g) contained one major and 14 minor components as shown by GLC (2 m SE30 at 130 °C) and the major component was separated by preparative-scale GLC (2 m SE30 at 130 °C) and was identified as 5-(bistrifluoromethylamino)-4-(*N*,*N*-bistrifluoromethylamino-oxy)pent-1-ene (**33**) (nc) (2.41 g, 6.2 mmol, 70%) (Analysis: Found: C, 27.5; H, 2.2; N, 7.2; F, 58.3%. $C_9H_8F_{12}N_2O$ requires: C, 27.8; H, 2.1; N, 7.2; F, 58.8%).

(d) With penta-1,4-diene (7) (gas and liquid phases present)

A mixture of the oxadiazapentane **3** (2.79 g, 8.7 mmol) and diene **7** (0.57 g, 8.4 mmol), sealed in vacuo in an ampoule (ca. 50 cm^3) and kept at room temperature (2 d), gave a volatile fraction (0.80 g) which was shown [IR, NMR, GLC (2 m SE30 at 90 °C)] to contain unchanged diene **7** (0.04 g, 0.56 mmol, 7% recovered), amine **16** and hydroxylamine **17** and a number of other components (13 ^{19}F NMR absorptions in the range δ: 6–23 ppm). The colourless non-volatile liquid residue (2.56 g) was shown by GLC (2 m SE30 at 150 °C) to contain three major (U′–W′) and 10 minor components. Component U′ and a mixture of components V′ and W′ (contaminated with minor components) were separated by preparative-scale GLC (2 m SE30 at 150 °C).

Component U′ was identified as 5-(bistrifluoromethylamino)-4-(*N*,*N*-bis(trifluoromethylamino-oxy)pent-1-ene (**33**) (1.07 g, 2.8 mmol, 36%) while components V′ and W′ were tentatively identified as 2:1 adducts (**34**) of the diene **7** and the oxadiazapentane **3** (ca. 0.73 g, ca. 1.6 mmol, ca. 41%). ^{1}H NMR ($CDCl_3$) δ: 5.7–4.8 (complex, 3H, CH=CH_2); 4.3–3.8 (complex, 2H, CH_2–O); 2.9 (2H, CH_2–N); 2.2–1.1 (complex, 9H, 3 CH_2 and 3 CH) ppm. ^{19}F NMR δ: 19.0 [complex overlapping absorptions, 6F, $(CF_3)_2N$]; 9.4, 8.2 [6F, $(CF_3)_2NO$] ppm. MS (*m/z*): 288 {5%, $[M-(CF_3)_2NO]^+$}; 287 {3 $[M-(CF_3)_2NOH]^+$}; 246 (2, $C_7H_{10}F_6N^+$); 182 [3, $(CF_3)_2NOCH_2^+$]; 166 [48, $(CF_3)_2NCH_2^+$]; 136 (2, $C_{10}H_{16}^+$); 135 (7, $C_{10}H_{15}^+$); 134 (6, $C_{10}H_{14}^+$); 133 (8, $C_2F_5N^+$); 130 (15, $C_9H_6O^+/C_{10}H_{10}^+$); 121 (49, $C_9H_{13}^+$); 111 (11, $C_7H_{11}O^+$); 95 (11, $C_7H_{11}^+$); 93 (33, $C_7H_9^+$); 91 (34, $C_7H_7^+$); 81 (15, $C_6H_9^+$); 79 (42, $C_6H_7^+$); 78 (26, $C_6H_6^+$); 69 (100, CF_3^+); 67 (24, $C_5H_7^+$); 44 (96, $C_2H_4O^+$); 41 (22, $C_3H_5^+$); 39 (16, $C_3H_3^+$).

(e) With allylbenzene (8)

A mixture of the oxadiazapentane **3** (2.30 g, 7.2 mmol) and alkene **8** (0.89 g, 7.5 mmol), maintained at room temperature (6 d), gave a volatile fraction (0.27 g) which was shown by IR and ^{19}F NMR spectroscopy to consist of the unchanged oxadiazapentane **3** (0.14 g, 0.5 mmol, 7% recovered), amine **16** (0.05 g, 0.3 mmol, 5%) and hydroxylamine **17** (0.08 g, 0.5 mmol, 7%). The light yellow liquid residue (2.92 g) was shown by GLC (2 m TXP and APL at 150 °C) to contain five major components (P′–T′) present in the ratio 12.5:1.1:1.3:2.3:1.0 and six minor components.

Components R′ and T′ were identified by a comparison of their GLC retention times and coupled GLC/MS with those of pure samples as the unchanged alkene **8** (0.05 g, 0.5 mmol, 6% recovered) and *trans*-3-(*N*,*N*-bistrifluoromethylamino-oxy)-1-phenylpropene (**30**) (0.11 g, 0.4 mmol, 5.5%).

Component P′ was separated by preparative-scale GLC (2 m APL at 150 °C) and was identified as 1-(bistrifluoromethylamino)-2-(*N*,*N*-bistrifluoromethylamino-oxy)-3-phenylpropane (**35**) (nc) (2.07 g, 4.7 mmol, 66.5%) (Analysis: Found: C, 35.9; H, 2.3; N, 6.5; F, 51.7%. $C_{13}H_{10}F_{12}N_2O$ requires: C, 35.6; H, 2.3; N, 6.4; F, 52.1%).

Attempts to separate compounds Q′ and S′ by preparative-scale GLC were unsuccessful.

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