The reactions of bis(trifluoromethyl)amino-oxyl and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) with α- and β-pinene

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Abstract

The reaction of the oxyl $(CF_3)_2NO\cdot$ (**7**) with α-pinene (**1**) (2:1 molar ratio) on warming from −196 °C to room temperature gives the hydroxylamine $(CF_3)_2NOH$ (**9**) (37% based on oxyl), 3-[*N,N*-bis(trifluoromethyl)amino-oxy]pin-2(10)-ene (**10**) (66.5% based on α-pinene) as a mixture of the *exo* and *endo* isomers (ratio 50:50) and 2,3-bis[*N,N*-bis(trifluoromethyl)amino-oxy]pinane (**11**) (20.5% based on α-pinene) as a mixture of several diastereomers. A corresponding reaction with β-pinene (**2**) on warming from −196 °C to room temperature affords hydroxylamine **9** (21% based on oxyl), 10-[*N,N*-bis(trifluoromethyl)amino-oxy]pin-2-ene (**12**) (48% based on β-pinene), 1-{[*N,N*-bis(trifluoromethyl)amino-oxy]methyl}-4-{2-[*N,N*-bis(trifluoromethyl)amino-oxy]isopropyl}cyclohex-1-ene (**13**) (10% based on β-pinene) and 2,10-bis[*N,N*-bis(trifluoromethyl)amino-oxy]pinane (**14**) (40.5% based on β-pinene) as a mixture of two diastereomers (ratio 59:41). A second reaction involving slow passage of the oxyl **7** in nitrogen through a solution of pinene **2** in $CF_2ClCFCl_2$ as a solvent gave compounds **12** (64%), **13** (7%) and **14** (29%). The room temperature reactions of the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**8**) with pinenes **1** and **2** (1:1 molar ratio) afforded complex product mixtures. The reaction with pinene **1** yields hydroxylamine **9** (22% based on compound **8**), the amine $(CF_3)_2NH$ (**15**) (23% based on compound **8**) and an inseparable higher-boiling mixture containing *c.* 14 components, while the reaction of pinene **2** gives compounds **9** and **15** and a higher-boiling mixture (*c.* 11 components) from which compound **12** (7% based on β-pinene), 10-[*N,N*-bis(trifluoromethyl)amino]pin-2-ene (**16**) (15% based on β-pinene) and the rearrangement products 1-{[*N,N*-bis(trifluoromethyl)amino]methyl}-4-{2-[*N,N*-bis(trifluoromethyl)amino-oxy]isopropyl}cyclohex-1-ene (**17**) (10% based on β-pinene) and 1-{[*N,N*-bis(trifluoromethyl)amino]methyl}-4-isopropylcyclohex-1-ene (**18**) (20% based on β-pinene) could be separated and identified.

Introduction

With certain addends, e.g. $CHCl_3$, CCl_4, CCl_3Br, n-C_3F_7I and Cl_3SiH, reaction with α-pinene (**1**) and β-pinene (**2**) under free-radical conditions leads to the rearranged 1:1 adducts **3** and **4**, respectively, via opening of the strained four-membered ring [1]. However, if the addend is a highly efficient chain-transfer agent, e.g. RSH, rearrangement does not occur and the products are the 1:1 adducts **5** and **6**, respectively [1] (Scheme 1).

Reaction of pinenes **1** and **2** with *N*-bromosuccinimide and t-butyl hypochlorite resulted mainly in allylic halogenation [2–4] and, in the reaction of the compound CCl_3Br with pinene **1**, allylic bromination competed to some extent with rearrangement [1].

We have reported previously that reaction of the oxyl $(CF_3)_2NO\cdot$ (**7**) and the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**8**) with alkenes $CH_2{=}CRCCl_3$ (R = H, Me) afforded intermediate radicals of type $XCH_2\dot{C}RCCl_3$ which rearranged to the radicals $XCH_2CRCl\dot{C}Cl_2$ [X = $(CF_3)_2NO$ and $(CF_3)_2N$] by a vicinal chlorine shift [5]. However, the radicals $\dot{C}H_2CMe_2X$ (X = Cl, Br, OAc), $\dot{C}H_2CMeCl_2$ and $\dot{C}H_2CMePhCl$ [generated by hydrogen abstraction from the corresponding substituted alkanes by the radicals **7** and $(CF_3)_2N\cdot$] did not undergo rearrangement [6].

In a continuation of this study of rearrangements induced by attack of the radicals $(CF_3)_2NO\cdot$ (**7**) and $(CF_3)_2N\cdot$ on organic substrates, the reactions of oxyl **7** and oxadiazapentane **8** with pinenes **1** and **2** have been investigated.

Results and discussion

The results obtained from the reactions of oxyl **7** and oxadiazapentane **8** with pinenes **1** and **2** are summarised in Table 1.

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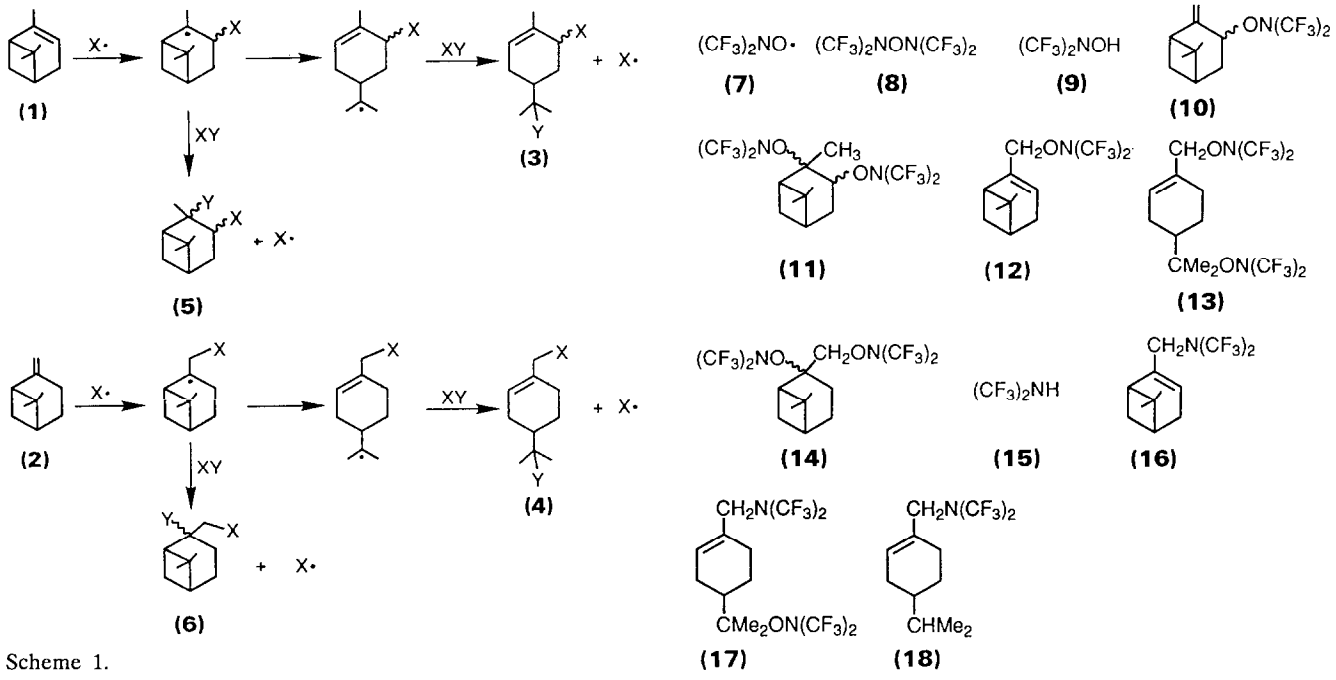


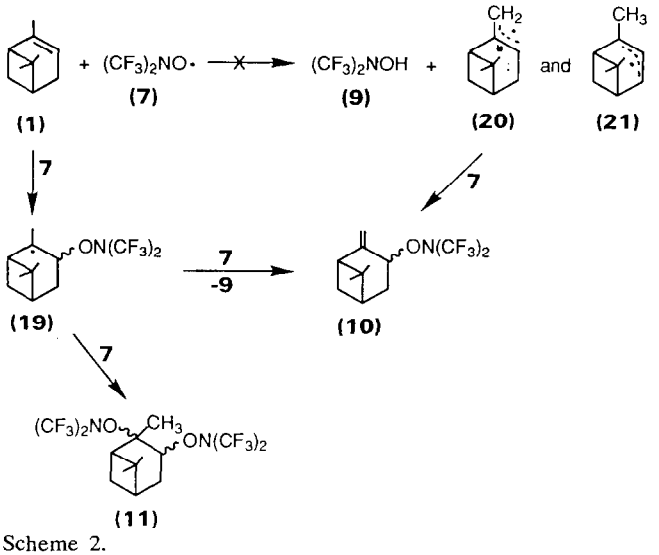
Scheme 1.

Reaction of oxyl **7** with α-pinene (**1**) was complete on warming from −196 °C to room temperature, but the rearrangement product of type 3 (Scheme 1) resulting from opening of the four-membered ring was not detected. The formation of the observed products, the hydroxylamine **9**, the substituted pin-2(10)-ene **10** and the 2:1 adduct **11** can be explained by initial attack of oxyl **7** on pinene **1** at the 3-position to afford the intermediate tertiary radical **19**. This was followed either by scavenging of the radical **19** with oxyl **7** to give the 2:1 adduct **11** [isolated as a mixture of several diastereomers (^{19}F NMR spectroscopy)] or by hydrogen abstraction from the methyl group bonded to the radical centre by oxyl **7** to afford hydroxylamine **9** and the substituted β-pinene **11** [isolated as a mixture of two diastereomers in the ratio 50:50 (^{1}H NMR spectroscopy)] (Scheme 2.)

TABLE 1. Reactions of oxyl **7** and oxadiazapentane **8** with pinenes **1** and **2**

Pinene	Reactant	Molar ratio 7 or 8: 1 or 2	Temperature (°C)	Time	Recovered pinene (%)	Products (%)[a]
1	**7**	*c.* 2:1	−196 to 20	0.5 h	4.5	**9**, 37[b]; **10**, 66.5; **11**, 20.5[c]
2	**7**	*c.* 2:1	−196 to 20	0.5 h	19	**9**, 21[b]; **12**, 48; **13**, 10; **14a**, 16.5; **14b**, 24
2[d]	**7**	2:1	20	0.5 h	11.5	**9**[e]; **12**, 64; **13**, 7; **14a**, 11; **14b**, 18
1	**8**	1:1	20	15 d	0	**9**, 22[b]; **15**, 23[b,f]
2	**8**	1.2:1	20	6 d	0	**9**[e]; **15**[e]; **12**, 7; **16**, 15; **17**, 10; **18**, 20[g]

[a]Yields based on pinene **1** or **2** not recovered.
[b]Yields based on compounds **7** or **8**.
[c]Four minor high-boiling products also formed.
[d]Carried out in $CF_2ClCFCl_2$.
[e]Yields not determined.
[f]Complex high-boiling mixture of *c.* 14 components also formed.
[g]Products separated from mixture of *c.* 11 components.



Scheme 2.

The possibility that compound **10** was formed via initial hydrogen abstraction from the methyl group to give the allyl radical **20** (Scheme 2) was discounted for the following reasons. Firstly, abstraction of a secondary allylic hydrogen from the 4-position of pinene **1** to give the strained allyl radical **21** would be expected to compete with abstraction of a primary hydrogen from the 10-position to give the allyl radical **20**; products arising from the allyl radical **21** were not isolated. Secondly, the isomeric 10-substituted pin-2-ene **12**, isolated from reaction of oxyl **7** with β-pinene (**2**) (see later), could have been formed via the same allyl radical **20**, but it is inconceivable that if allyl radical **20** was formed in both reactions its scavenging by oxyl **7** would lead to a different product in these two reactions.

The absence of rearranged products indicates that reaction of the intermediate radical **19** with oxyl **7** is fast relative to opening of the four-membered ring, and the favourable hydrogen abstraction from the methyl group of intermediate **19** to afford compound **10** relative to coupling with oxyl **7** to give the 2:1 adduct **11** is presumably due to the steric hindrance at carbon 2 towards oxyl **7** attack.

Compounds **10** and **11** were identified by elemental analysis and the following spectral data. Compound **10** was shown to be a 3-substituted pin-2(10)-ene, present as a mixture of the *exo* and *endo* isomers in the ratio 50:50, from (i) ^{1}H NMR absorptions for the two vinylic protons in each isomer at 4.88 and 4.75 ppm, two distinct methine absorptions (1:1 ratio) in the region expected for >CH−O (4.37 and 4.31 ppm), six ring hydrogens (1.4–2.3 ppm) and non-equivalent methyl groups in a CMe_2 grouping (1.07 and 0.44 ppm) and (ii) ^{19}F NMR absorptions at δ +8.5 and +10.7 ppm (1:1 ratio) in the region expected for $(CF_3)_2NO$ groups. The MS peak at *m/z* 135 (37%, $C_{10}H_{15}^+$), i.e. $[M-(CF_3)_2NO]^+$ provided further confirmation of the structure. The ^{1}H NMR spectrum of compound **11** showed an absence of absorptions for vinylic hydrogens, but absorptions were present for a >CH−O group (4.56 ppm), six ring hydrogens (1.4–2.3 ppm), a methyl group (1.38 ppm) and two non-equivalent methyl groups in a CMe_2 grouping (1.18 and 0.86 ppm), consistent with a 2,3-disubstituted pinane. The presence of two non-equivalent $(CF_3)_2NO$ groups was confirmed by the absorptions centred on δ +9.5 and +10.3 ppm in the ^{19}F NMR spectrum, each consisting of several overlapping singlets which indicated the presence of diastereomers. The MS peaks at *m/z* 304 {4%, $[M-(CF_3)_2NO]^+$} and 136 (35, $C_{10}H_{16}^+$), i.e. $[M-2(CF_3)_2NO]^+$ were consistent with the proposed structure.

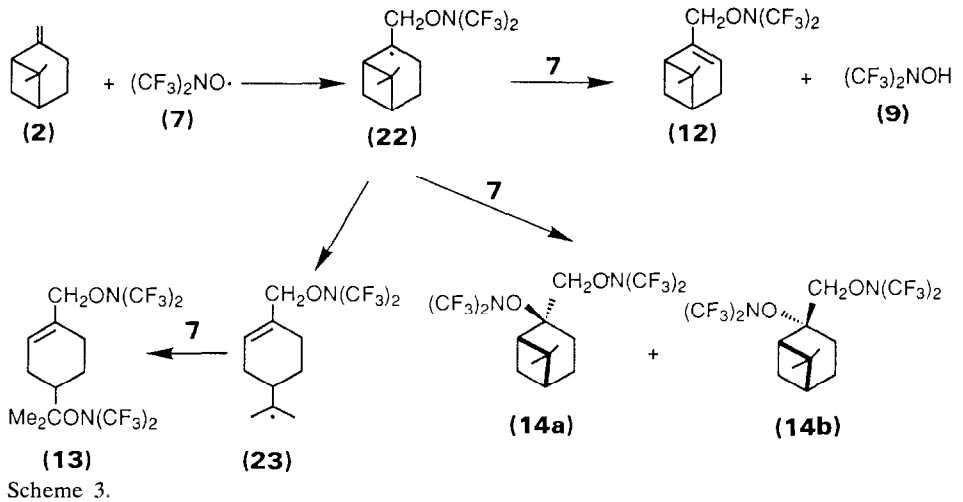
The reaction of oxyl **7** with β-pinene (**2**) was also complete on warming from −196 °C to room temperature and gave the expected rearranged 2:1 adduct **13**, but only as a minor product. All of the products formed, i.e. hydroxylamine **9**, the 2:1 adduct **13** and the non-rearranged compounds **12** and **14**, can be explained by initial addition of oxyl **7** to alkene **2** at the 10-position to afford the tertiary radical **22**. Radical **22** then underwent (i) hydrogen abstraction from the 3-position by oxyl **7** to give the 10-substituted pin-2-ene **12** as the major product, (ii) addition of oxyl **7** to the 2-position to yield the 2:1 adduct **14** as the *exo*- and *endo*-diastereomers **14a** and **14b** (ratio 40:60) which were separated, and (iii) opening of the four-membered ring to afford the rearranged tertiary radical **23** and hence the 2:1 adduct **13** (Scheme 3).

Surprisingly, an attempt to increase the yield of the rearranged 2:1 adduct **13** by carrying out the reaction in a solvent ($CF_2ClCFCl_2$) was unsuccessful; instead, the yield of the substitution product **12** was increased mainly at the expense of the non-rearranged 2:1 adducts **14a** and **14b**.

Thus, as in the reaction of pinene **1**, rearrangement of the initial intermediate radical **22** was not favoured because of the facile reaction of radical **22** with oxyl **7** to yield compounds **12**, **14a** and **14b**.

It is considered probable that approach of the oxyl **7** to the intermediate radical **22** would be preferred from the opposite side of the molecule to the hydrocarbon bridge for steric reasons, and therefore the major 2:1 adduct would be the *endo* isomer **14b** and the minor adduct the *exo* isomer **14a**.

The structures of the products **12–14** were confirmed by elemental analysis and the following spectral data. The ^{1}H NMR spectrum of compound **12** showed that it was a substituted pin-2-ene by absorptions for one vinylic hydrogen (5.37 ppm), a CH_2O group (4.11 ppm), six ring hydrogens (1.4–2.3 ppm) and a ring CMe_2 group (0.62 and 1.08 ppm) and the ^{19}F NMR spectrum con-



Scheme 3.

firmed the $(CF_3)_2NO$ group (+8.8 ppm). MS peaks at *m/z* 303 (M^+), 182 [$(CF_3)_2NOCH_2^+$] and 135 ($C_{10}H_{15}^+$), i.e. [$M-(CF_3)_2NO$]$^+$, were consistent with the structure proposed. The rearranged 2:1 adduct **13** showed ^{1}H NMR absorptions for a 1,4-disubstituted cyclohex-1-ene, i.e. one vinylic hydrogen (5.50 ppm) and seven ring hydrogens (1.4–2.4 ppm), together with a CH_2O group (4.20 ppm) and a CMe_2X group adjacent to a chiral centre (0.63 and 1.15 ppm). Two absorptions in the ^{19}F NMR spectrum at δ +8.3 and +9.4 ppm confirmed the presence of two non-equivalent $(CF_3)_2NO$ groups and MS peaks at *m/z* 471 $(M-H)^+$, 304 [$M-(CF_3)_2NO$]$^+$, 290 [$M-CH_2ON(CF_3)_2$]$^+$, 262 [$M-CMe_2ON(CF_3)_2$]$^+$, 210 [$Me_2CON(CF_3)_2^+$] and 136 ($C_{10}H_{16}^+$) afforded further structural proof. The spectra of the two isomers **14a** and **14b** were very similar and the pinane structure was demonstrated by ^{1}H NMR absorptions for eight ring hydrogens (1.2–2.4) ppm, a ring CMe_2 group (*c.* 0.9 and *c.* 1.1 ppm) together with a CH_2O group (*c.* 4.1 ppm). The presence of two non-equivalent $(CF_3)_2NO$ groups, as shown by ^{19}F NMR absorptions at *c.* +8.5 and *c.* +10 ppm and MS bands at *m/z* 471 $(M-H)^+$, 304 [$M-(CF_3)_2NO$]$^+$, 290 [$M-CH_2ON(CF_3)_2$]$^+$, 262 [$M-CMe_2ON(CF_3)_2$]$^+$, 210 [$Me_2CON(CF_3)_2^+$] and 136 ($C_{10}H_{16}^+$) gave final proof of the structure.

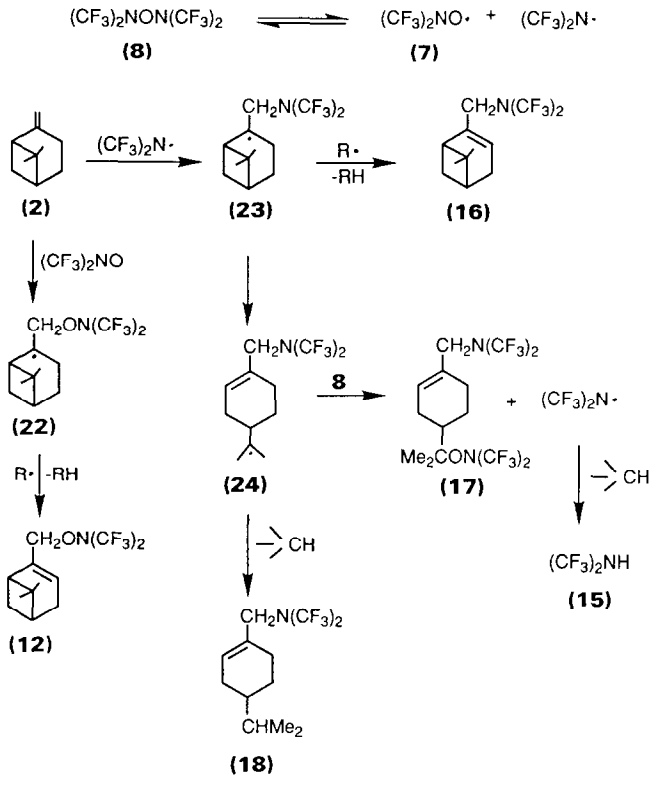
The reactions of the oxadiazapentane **8** with pinenes **1** and **2** were far more complex than the corresponding reactions of oxyl **7** and gave multicomponent, high-boiling, product mixtures together with the volatile hydroxylamine **9** and amine **15** formed by hydrogen abstraction. The high-boiling mixture (*c.* 14 components) arising from pinene **1** could not be separated into pure components or simple mixtures by GLC methods and so the products remain unidentified. However, the formation of a complex product mixture indicates that rearrangement involving opening of the four-membered ring was a major process, as found for pinene **2** (see later). Rearrangement would be expected to be more favourable in the reaction involving oxadiazapentane **8** than in the reaction involving oxyl **7**, as observed in their reactions with the alkenes $CH_2{=}CRCCl_3$ (R = H, CH_3) [5], because oxadiazapentane **8** is bulky and a relatively poor chain-transfer agent.

Four products were isolated by GLC from the multicomponent high-boiling mixture formed in the reaction of oxadiazapentane **8** with pinene **2**, i.e. a mixture of the non-rearranged 10-substituted pin-2-enes **12** and **16** and the ring-opened cyclohexene derivatives **17** and **18**.

Compounds **16–18** are considered to have been formed via $(CF_3)_2N\cdot$ radical attack at the 10-position of pinene **2** to give the intermediate tertiary radical **24**, followed either by hydrogen abstraction from the 3-position by oxyl **7** and $(CF_3)_2N\cdot$ radicals to give the pin-2-ene **16** or by ring opening to afford the rearranged tertiary radical **25**. Chain transfer of radical **25** with oxadiazapentane **8** yields the rearranged adduct **17**, and hydrogen abstraction (possibly from radical **24**) gives the cyclohexene derivative **18** which was not an expected product (Scheme 4).

The remaining product **12** probably arose via oxyl attack at the 10-position of pinene **2** as shown previously in Scheme 3.

Although the isolated products account for only 52% of the reactant **2**, the ratio of rearranged to non-rearranged compounds (30:22) is a clear indication that the intermediate radicals **22** and **24** formed by radical attack at the 10-position undergo slow reaction with the bulky oxadiazapentane **8**, thus allowing ring opening to be favoured. This contrasts with the corresponding reaction of oxyl **7** in which attack on the intermediate radical **22** by the less bulky oxyl **7** is favoured and ring opening is only a minor pathway. Of the two rear-



Scheme 4.

rangement products isolated, the yield of compound **18** was much greater than that of compound **17**. This shows that reaction of the rearranged tertiary radical **25** with oxadiazapentane **8** is slow, thus allowing hydrogen abstraction by radical **25** to compete with chain transfer.

Compound **16** was identified admixed with compound **12** by a consideration of the spectral data obtained, i.e. ^{1}H NMR absorptions at δ 5.23 (mult., 1H, =CH), 3.37 (br., 2H, CH_2N), 2.4–1.4 (complex, 6H, 6 ring CH) and 1.06 and 0.61 (2s, 6H, CMe_2) ppm, which showed the product was a 10-substituted pin-2-ene, a ^{19}F NMR absorption at $\delta+19.5$ ppm, which confirmed the 10-substituent was a $(CF_3)_2N$ group, and MS peaks at *m/z* 287 (M^+), 272 $(M-Me)^+$ and 166 [100%, $(CF_3)_2NCH_2^+$].

The ring-opened products **17** and **18** were identified by elemental analysis and the following spectral data. The ^{1}H NMR spectra of both compounds showed that they were 1,4-disubstituted cyclohex-1-enes containing a $(CF_3)_2NCH_2$ group in the 1-position and a CMe_2X group in the 4-position, i.e. absorptions for one vinylic hydrogen (*c.* 5.4 ppm), CH_2N (*c.* 3.4 ppm), seven ring hydrogens (2.1–1.2 ppm) and a CMe_2 group (1.04 ppm for **17** and 0.70 and 0.64 ppm for **18**); a $CHMe_2$ group was confirmed in the spectrum of compound **18** by an additional hydrogen in the range 2.1–1.2 ppm and by each of the non-equivalent methyl groups (adjacent to a chiral centre) appearing as a doublet ($J=6$ Hz). The ^{19}F NMR spectra showed that both compounds contained a $(CF_3)_2N$ group ($\delta+18.9$ ppm) and that compound **17** also contained a $(CF_3)_2NO$ group ($\delta+10.7$ ppm), while the MS data, i.e. peaks for compound **17** at *m/z* 288 $[M-(CF_3)_2NO]^+$, 246 $[M-(CF_3)_2NOCMe_2]^+$, 210 $[(CF_3)_2NOCMe_2^+]$, 166 [100%, $(CF_3)_2NCH_2^+$] and 136 ($C_{10}H_{16}^+$) and for compound **18** at *m/z* 289 (M^+), 246 $(M-CHMe_2)^+$, 166 [91%, $(CF_3)_2NCH_2^+$] and 137 ($C_{10}H_{17}^+$) afforded further conclusive structural proof.

Experimental

Starting materials

Oxyl **7** was prepared by oxidation of hydroxylamine **9** with potassium permanganate and sulphuric acid [7], and was converted into oxadiazapentane **8** by reaction with trifluoronitrosomethane (2:1 molar ratio) [7]. Pinenes **1** and **2** were commercial samples and the purity of each was checked [^{1}H NMR spectroscopy] before use.

General techniques

Sealed-tube reactions were carried out *in vacuo* in Pyrex ampoules (volume stated in the text) fitted with Rotaflo Teflon taps and the volatile products were removed *in vacuo*. High-boiling mixtures of products were separated into their individual components by preparative-scale GLC [Pye 104 instrument using columns (2–4 m) packed with silicone SE30 oil, Apiezon L (APL) grease or trixylyl phosphate (TXP) (20%–25% w/w) on acid-washed Celite] and were examined by IR spectroscopy (Perkin-Elmer 197 instrument), ^{1}H NMR spectroscopy [Varian Associates HA100 (100.0 MHz) spectrometer; internal reference Me_4Si], ^{19}F NMR spectroscopy [Varian Associates HA100 (94.12 MHz) instrument; external reference CF_3CO_2H] and mass spectrometry (AEI MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were run as solutions in $CDCl_3$ and chemical shifts to low field of the reference are designated positive.

Boiling points were determined using Siwoloboff's method.

Reactions of bis(trifluoromethyl)amino-oxyl (7)

(a) With α-pinene (1)

A mixture of oxyl **7** (1.73 g, 10.3 mmol) and pinene **1** (0.76 g, 5.6 mmol), warmed from −196 °C to room temperature (*c.* 0.5 h) in an ampoule (*c.* 100 cm^3), gave a volatile fraction identified (IR spectroscopy) as

N,N-bis(trifluoromethyl)hydroxylamine (**9**) (0.65 g, 3.8 mmol, 37% based on oxyl) and a light brown, liquid residue (1.84 g) which was shown by GLC methods (2 m SE30 at 145 °C) to consist of unchanged pinene **1** and two major and four minor components. Separation of the major components by preparative-scale GLC (4 m SE30 then 2 m TXP at 140 °C) afforded (i) unchanged pinene **1** (0.03 g, 0.3 mmol, 4.5% recovered); (ii) 3-[*N,N*-bis(trifluoromethyl)amino-oxy]pin-2(10)-ene (**10**) (nc) (1.09 g, 3.6 mmol, 66.5% based on pinene) (Analysis: Found: C, 47.8; H, 5.1; N, 4.9; F, 37.9%. $C_{12}H_{15}F_6NO$ requires: C, 47.5; H, 5.0; N, 4.6; F, 37.6%) as a 1:1 mixture of the *exo* and *endo* isomers {^{1}H NMR δ: 4.88 (mult., 2H, $=CH_2$); 4.75 (mult., 2H, $=CH_2$); 4.37 (mult., 1H, CH−O); 4.31 (mult., 1H, CH−O); 2.3–1.4 (complex, 12H, 12 ring CH); 1.07 (s, 6H, $2CH_3$); 0.44 (s, 6H, $2CH_3$) ppm. ^{19}F NMR δ: +10.7 [s, 6F, $(CF_3)_2NO$]; +8.5 [s, 6F, $(CF_3)_2NO$] ppm. Mass spectrum *m/z*: 135 (37%, $C_{10}H_{15}^+$, i.e. $[M-(CF_3)_2NO]^+$); 107 (33, $C_8H_{11}^+$ and/or $C_7H_7O^+$); 93 (92, $C_7H_9^+$ and/or $C_6H_5O^+$); 91 (49, $C_7H_7^+$); 79 (72, $C_6H_7^+$); 77 (35, $C_6H_5^+$); 69 (100, CF_3^+); 57 (20, $C_3H_5O^+$); 55 (20, $C_4H_7^+$ and/or $C_3H_3O^+$); 53 (20, $C_4H_5^+$); 43 (60, $C_3H_7^+$ and/or $C_2H_3O^+$); 41 (91, $C_3H_5^+$); 39 (28, $C_3H_3^+$); 29 (15, CHO^+). IR (ν_{max}) (cm^{-1}): 2976, 2932 (m) (C−H str.); 1645 (w) (C=C str.); 1466 (m); 1453 (m); 1437 (m); 1412 (m); 1385 (m); 1370 (m); 1350 (m); 1299–1200 (vs) (C−F str.); 1083 (m); 1037, 1025 (s) (C−O−N str.); 966 (s) (C−N str.); 913 (s); 710 (s) (CF_3 def.)}; and (iii) 2,3-bis[*N,N*-bis(trifluoromethyl)amino-oxy]-pinane (**11**) (nc) (0.52 g, 1.1 mmol, 20.5% based on pinene) (Analysis: Found: C, 35.9; H, 3.5; N, 5.8; F, 47.8%. $C_{14}H_{16}F_{12}N_2O_2$ requires: C, 35.6; H, 3.4; N, 5.9; F, 48.3%) {^{1}H NMR δ: 4.56 (mult., 1H, CH−O); 2.5–1.5 (complex, 6H, 6 ring CH); 1.38 (s, 3H, CH_3); 1.18, 0.86 (2s, 6H, ring CMe_2) ppm. ^{19}F NMR δ: +10.4 to +10.2 [6F, $(CF_3)_2NO$] and +9.55 to +9.45 [6F, $(CF_3)_2NO$] ppm. Mass spectrum *m/z*: 304 (4%, $[M-(CF_3)_2NO]^+$); 250 (31, $C_8H_{10}F_6NO^+$); 136 (35, $C_{10}H_{16}^+$); 135 (38, $C_{10}H_{15}^+$); 93 (98, $C_7H_9^+$ and/or $C_6H_5O^+$); 83 (39, $C_5H_7O^+$); 80 (20, $C_6H_8^+$); 69 (100, CF_3^+); 55 (23, $C_4H_7^+$ and/or $C_3H_3O^+$); 43 (91, $C_3H_7^+$ and/or $C_2H_3O^+$); 41 (32, $C_3H_3^+$). IR ($\nu_{max.}$) (cm^{-1}): 3003, 2941, 2882 (m) (C−H str.); 1475 (m); 1460 (m); 1397 (m); 1383 (m); 1370 (m); 1295–1199 (vs) (C−F str.); 1136 (m); 1083 (s); 1058, 1023 (s) (C−O−N str.); 991 (m); 960 (s) (C−N str.); 701 (s) (CF_3 def.)}.

A second reaction carried out at −78 °C (3 h) gave almost identical results.

(b) With β-pinene (2)

A mixture of oxyl **7** (1.79 g, 10.7 mmol) and pinene **2** (0.77 g, 5.7 mmol), warmed from −196 °C to room temperature (*c.* 0.5 h) in an ampoule (*c.* 100 cm^3), gave volatile material identified (IR spectroscopy) as hydroxylamine **9** (0.39 g, 2.3 mmol, 21% based on oxyl) and a colourless liquid residue (2.10 g), which was shown by GLC methods (2 m SE30 at 130 °C) to contain unchanged pinene **2** and four major components in the ratio 5.4:1.0:1.7:2.9. Separation of the mixture by preparative-scale GLC (as above) afforded (i) unchanged pinene **2** (0.15 g, 1.1 mmol, 19% recovered); (ii) 10-[*N,N*-bis(trifluoromethyl)amino-oxy]pin-2-ene (**12**) (nc) (0.67 g, 2.2 mmol, 48% based on pinene) (Analysis: Found: C, 47.7; H, 5.1; N, 4.7; F, 38.0%. $C_{12}H_{15}F_6NO$ requires: C, 47.5; H, 5.0; N, 4.6; F, 37.6%); b.p. 184 °C {^{1}H NMR δ: 5.37 (mult., 1H, =CH); 4.11 (s, 2H, CH_2O); 2.3–1.4 (complex, 6H, 6 ring CH); 1.08, 0.62 (2s, 6H, ring CMe_2) ppm. ^{19}F NMR δ: +8.8 [s, $(CF_3)_2NO$] ppm. Mass spectrum *m/z*: 303 (3%, M^+); 182 [1, $(CF_3)_2NOCH_2^+$]; 135 (37, $C_{10}H_{15}^+$, i.e. $[M-(CF_3)_2NO]^+$); 119 (11, $C_9H_{11}^+$); 107 (45, $C_7H_7O^+$); 93 (69, $C_7H_9^+$); 91 (100, $C_7H_7^+$); 79 (88, $C_6H_7^+$); 77 (69, $C_6H_5^+$); 69 (44, CF_3^+); 55 (26, $C_4H_7^+$ and/or $C_3H_3O^+$); 43 (46, $C_3H_7^+$ and/or $C_2H_3O^+$); 41 (53, $C_3H_5^+$); 39 (19, $C_3H_3^+$). IR ($\nu_{max.}$) (cm^{-1}): 2924, 2841 (m) (C−H str.); 1468 (m); 1433 (m); 1289–1200 (vs) (C−F str.); 1083 (m); 1036 (m) (C−O−N str.); 962 (s) (C−N str.); 702 (s) (CF_3 def.)}; (iii) 1-{[*N,N*-bis(trifluoromethyl)amino-oxy]methyl}-4-{[2-*N,N*-bis-(trifluoromethyl)amino-oxy]isopropyl}cyclohex-1-ene (**13**) (nc) (0.22 g, 0.47 mmol, 10% based on pinene) (Analysis: Found: C, 35.4; H, 3.2; N, 6.1; F, 48.1%. $C_{14}H_{16}F_{12}N_2O_2$ requires: C, 35.6; H, 3.4; N, 5.9; F, 38.3%), b.p. 215 °C {^{1}H NMR δ: 5.50 (mult., 1H, =CH); 4.20 (s, 2H, CH_2O); 2.4–1.4 (complex, 7H, 7 ring CH); 1.15, 0.63 (2s, 6H, CMe_2) ppm. ^{19}F NMR δ: +9.4 [s, 6F, $(CF_3)_2NOC-$]; +8.3 [s, 6F, $(CF_3)_2NOCH_2$] ppm. Mass spectrum *m/z*: 471 [0.1%, $(M-H)^+$]; 304 {1, $[M-(CF_3)_2NO]^+$}; 302 (8, $C_{12}H_{14}F_6NO^+$); 290 (2, $[M-(CF_3)_2NOCH_2^+]$); 262 (1, $[M-(CF_3)_2NOCHMe_2]^+$); 210 [9, $(CF_3)_2NOCMe_2^+$]; 150 (15, $C_2HF_5NO^+$); 136 (3, $C_{10}H_{16}^+$); 134 (20, $C_{10}H_{14}^+$); 119 (25, $C_9H_{11}^+$); 91 (54, $C_7H_7^+$); 69 (100, CF_3^+); 43 (80, $C_3H_7^+$ and/or $C_2H_3O^+$); 41 (26, $C_3H_5^+$). IR ($\nu_{max.}$) (cm^{-1}): 2959, 2899 (m) (C−H str.); 1462 (m); 1300–1205 (vs) (C−F str.); 1114 (m); 1088 (m); 1061, 1040 (s) (C−O−N str.); 967 (s) (C−N str.); 703 (s) (CF_3 def.)}; (iv) *exo*-2,10-bis[*N,N*-bis(trifluoromethyl)amino-oxy]-pinane (**14a**) (nc) (0.36 g, 0.8 mmol, 16.5% based on pinene) (Analysis: Found: C, 35.5; H, 3.5; N, 6.2; F, 48.7%. $C_{14}H_{16}F_{12}N_2O_2$ requires: C, 35.6; H, 3.4; N, 5.9; F, 48.3%), b.p. 218 °C {^{1}H NMR δ: 4.09 (mult., 2H, CH_2O); 2.4–1.2 (complex, 8H, 8 ring CH); 1.05, 0.91 (2s, 6H, ring CMe_2) ppm. ^{19}F NMR δ: +10.0 [s, 6F, $(CF_3)_2NOC-$]; +8.3 [s, 6F, $(CF_3)_2NOCH_2$] ppm. Mass spectrum *m/z*: 472 (0.1%, M^+); 471 [2, $(M-H)^+$]; 304 (23, $[M-(CF_3)_2NO]^+$); 290 (6, $[M-(CF_3)_2NOCH_2^+]$); 248 (27, $C_8H_8F_6NO^+$); 136 (36, $C_{10}H_{16}^+$); 135 (33, $C_{10}H_{15}^+$); 95 (39, $C_7H_{11}^+$); 93 (26, $C_7H_9^+$); 83 (23,

$C_6H_{11}^+$ and/or $C_5H_7O^+$); 81 (18, $C_6H_9^+$ and/or $C_5H_5O^+$); 80 (23, $C_6H_8^+$ and/or $C_5H_4O^+$); 79 (26, $C_6H_7^+$); 69 (100, CF_3^+); 67 (22, $C_5H_7^+$ and/or $C_4H_3O^+$); 55 (29, $C_4H_7^+$ and/or $C_3H_3O^+$); 43 (54, $C_3H_7^+$ and/or $C_2H_3O^+$); 41 (41, $C_3H_5^+$). IR ($\nu_{max.}$) (cm^{-1}): 2915, 2874 (m) (C–H str.); 1484 (m); 1471 (m); 1393 (m); 1300–1205 (vs) (C–F str.); 1124 (m); 1086 (m); 1055, 1045 (s) (C–O–N str.); 964 (s, C–N str.); 702 (m) (CF_3 def.)}; and (v) *endo*-2,10-bis[*N*,*N*-bis(trifluoromethyl)amino-oxy]pinane (**14b**) (nc) (0.52 g, 1.1 mol, 24% based on pinene) (Analysis: Found: C, 35.3; H, 3.7; N, 5.6; F, 48.5%. $C_{14}H_{16}F_{12}N_2O_2$ requires: C, 35.6; H, 3.4; N, 5.9; F, 48.3%), b.p. 220 °C {^{1}H NMR δ: 4.05 (mult., 2H, CH_2O); 2.3–1.2 (complex, 8H, 8 ring CH); 1.13, 0.84 (2s, 6H, ring CMe_2) ppm. ^{19}F NMR δ: +10.3 [s, 6F, $(CF_3)_2NOC$–]; +8.4 [s, 6F, $(CF_3)_2NOCH_2$] ppm. Mass spectrum *m/z*: 471 (1%); 304 (22); 290 (5); 248 (22); 136 (31); 135 (31); 95 (17); 93 (24); 83 (21); 81 (16); 80 (18); 79 (20); 69 (100); 67 (19); 55 (27); 43 (42); 41 (40). IR ($\nu_{max.}$) (cm^{-1}): 2912, 2870 (m) (C–H str.); 1481 (m); 1474 (m); 1390 (m); 1298–1200 (vs) (C–F str.); 1130 (m); 1090 (m); 1052 (s) (C–O–N str.); 960 (s) (C–N str.); 700 (s) (CF_3 def.)}.

A second reaction in which oxyl **7** (3.38 g, 20.1 mmol) in a stream of nitrogen was passed slowly (0.5 h) through a solution of pinene **2** (1.36 g, 10.0 mmol) in 1,1,2-trichlorotrifluoroethane (38 g), and the volatile material then removed *in vacuo*, gave a high-boiling liquid residue (3.52 g) which was shown by GLC methods (2 m SE30 at 130 °C) to consist of unchanged pinene **2** (11.5% recovered) and compounds **12**, **13**, **14a** and **14b** in the ratio 64:7:11:18.

Reactions of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (8)

(a) With α-pinene (1)

A mixture of oxadiazapentane **8** (2.54 g, 7.9 mmol) and pinene **1** (1.05 g, 7.7 mmol), stored in an ampoule (*c.* 300 cm^3) at room temperature (15 d), gave volatile material (0.66 g) which was shown (IR and NMR spectroscopies) to consist mainly of hydroxylamine **9** (0.29 g, 1.7 mmol, 22% based on **8**) and *N*,*N*-bis(trifluoromethyl)amine (**15**) (0.28 g, 1,8 mmol, 23% based on **8**) and a colourless liquid residue (2.93 g) which was shown by GLC methods (2 m APL and 2 m SE30 at 130 °C) to contain *c.* 14 components. Attempts to separate the material into pure components on a variety of GLC columns were unsuccessful.

(b) With β-pinene (2)

A mixture of oxadiazapentane **8** (3.06 g, 9.6 mmol) and pinene **2** (1.12 g, 8.2 mmol), stored in an ampoule (*c.* 300 cm^3) at room temperature (6 d), gave volatile material (0.58 g) which was shown (IR spectroscopy) to be a mixture of hydroxylamine **9** and amine **15**, and a non-volatile liquid residue (3.60 g) which was shown by GLC methods (2 m TXP and 2 m SE30 at 150 °C) to contain *c.* 11 components. Separation of certain of the components was achieved by preparative-scale GLC (4 m SE30 then 2 m APL at 140 °C) and afforded (i) a mixture (0.52 g) of compound **12** (0.17 g, 0.6 mmol, 7% based on pinene) and 10-[*N*,*N*-bis(trifluoromethyl)amino]pin-2-ene (**16**) (nc) (0.35 g, 1.2 mmol, 15% based on pinene) {^{1}H NMR (compound **16**) δ: 5.23 (mult., 1H, =CH); 3.37 (br., 2H, CH_2N); 2.4–1.4 (complex, 6H, 6 ring CH); 1.06, 0.61 (2s, 6H, ring CMe_2) ppm. ^{19}F NMR δ: +19.15 [s, $(CF_3)_2N$] ppm. Mass spectrum *m/z*: 287 (3%, M^+); 272 [3, $(M-Me)^+$]; 243 (23, $C_9H_{10}F_5NO^+$); 166 [100, $(CF_3)_2NCH_2^+$]}; (ii) 1–{[*N*,*N*-bis(trifluoromethyl)amino]methyl}-4-{2-[*N*,*N*-bis(trifluoromethyl)amino-oxy]isopropyl}cyclohex-1-ene (**17**) (nc) (0.37 g, 0.8 mmol, 10% based on pinene) (Analysis: Found: C, 37.1; H, 3.8; N, 5.9%. $C_{14}H_{16}F_{12}N_2O$ requires: C, 36.8; H, 3.5; N, 6.1%) {^{1}H NMR δ: 5.43 (mult., 1H, =CH); 3.44 (s, 1H, CH_2N); 2.1–1.3 (complex, 7H, 7 ring CH); 1.04 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +18.9 [s, 6F, $(CF_3)_2N$]; +10.7 [s, 6F, $(CF_3)_2NO$] ppm. Mass spectrum *m/z*: 288 (19%, $[M-(CF_3)_2NO]^+$); 287 (16, $[M-(CF_3)_2NOH]^+$); 246 (4, $[M-(CF_3)_2NOCMe_2^+]$); 243 (10, $C_9H_{10}F_5NO^+$); 232 (54, $C_8H_8F_6N^+$); 210 [22, $(CF_3)_2NOCMe_2^+$]; 166 [100, $(CF_3)_2NCH_2^+$]; 136 (5, $C_{10}H_{16}^+$); 135 (23, $C_{10}H_{15}^+$); 121 (36, $C_9H_{13}^+$); 93 (51, $C_7H_9^+$ and/or $C_6H_5O^+$); 91 (36, $C_7H_7^+$); 79 (67, $C_6H_7^+$); 78 (28, $C_2H_2F_2N^+$); 69 (80, CF_3^+); 58 (34, $C_3H_6O^+$); 43 (93, $C_3H_7^+$ and/or $C_2H_3O^+$); 41 (34, $C_3H_5^+$)}; and (iii) 1-{[*N*,*N*-bis(trifluoromethyl)amino]methyl}-4-isopropylcyclohex-1-ene (**18**) (nc) (0.47 g, 1.6 mmol, 20% based on pinene) (Analysis: Found: C, 49.6; H, 6.0; N, 4.7%. $C_{12}H_{17}F_6N$ requires: C, 49.8; H, 5.9; N, 4.8%) {^{1}H NMR δ: 5.39 (mult., 1H, =CH); 3.40 (s, 2H, CH_2N); 2.0–1.2 (complex, 8H, 7 ring CH and $CHMe_2$); 0.70, 0.64 (2d, 6H, $CHMe_2$, J=6 Hz) ppm. ^{19}F NMR δ: +18.9 [s, $(CF_3)_2N$] ppm. Mass spectrum *m/z*: 289 (14%, M^+); 246 [5, $(M-CHMe_2)^+$]; 166 [91, $(CF_3)_2NCH_2^+$]; 137 (13, $C_{10}H_{17}^+$); 136 (18, $C_{10}H_{16}^+$); 123 (82, $C_9H_{15}^+$); 121 (22, $C_9H_{13}^+$); 95 (22, $C_7H_{11}^+$); 93 (100, $C_7H_9^+$); 91 (39, $C_7H_7^+$); 81 (68, $C_6H_9^+$); 79 (75, $C_6H_7^+$); 78 (39, $C_2H_2F_2N^+$); 77 (34, $C_6H_5^+$); 69 (96, CF_3^+); 68 (33, $C_5H_8^+$); 67 (100, $C_5H_7^+$); 55 (48, $C_4H_7^+$); 53 (21, $C_4H_5^+$); 43 (49, $C_3H_7^+$); 41 (65, $C_3H_5^+$)}.

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