Reaction of bis(trifluoromethyl)amino-oxyl with t-butylbenzene, 2,2-diphenylpropane, benzylcyclopropane and some related alcohols

Gregory D. Connelly and Anthony E. Tipping*

Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD (UK)

(Received July 16, 1993; accepted September 28, 1993)

Abstract

Reaction of the oxyl $(CF_3)_2NO\cdot$ (**1**) with t-butylbenzene (*c.* 3:1 molar ratio) at room temperature gives the hydroxylamine $(CF_3)_2NOH$ (**3**) (43% on oxyl) and a multicomponent higher-boiling mixture containing the substitution product $(CF_3)_2NOCH_2CMe_2Ph$ (**3**) (28% on arene), and the compounds 3-$(CF_3)_2NC_6H_4CMe_3$ (**5**) (8% on arene) and 4-$(CF_3)_2NC_6H_4CMe_3$ (**6**) (6% on arene). The reaction with 2,2-diphenylpropane (*c.* 4:1 molar ratio) at 70–80 °C affords hydroxylamine **3** (45% on oxyl) and a complex higher-boiling mixture, from which only the substitution product $(CF_3)_2NOCH_2CMePh_2$ (**7**) (36% on arene) could be isolated. In contrast, the reaction of oxyl **1** with benzylcyclopropane at room temperature is clean and gives hydroxylamine **3** (49% on oxyl) and the substitution product $\dot{C}H_2CH_2\dot{C}HCH(Ph)ON(CF_3)_2$ (**8**) (95% on cyclopropane). From the reactions of oxyl **1** with 2-phenylpropan-2-ol (2:1 molar ratio), cyclopropylmethanol (*c.* 4:1 molar ratio) and 1-cyclopropylethanol (2:1 molar ratio) at room temperature, apart from hydroxylamine **3**, the isolated products are a mixture of dimers of α-methylstyrene (**10–12**) (30% on ol) and the 2:1 adduct of oxyl **1** and α-methylstyrene, i.e. $(CF_3)_2NOCH_2CMe(Ph)ON(CF_3)_2$ (**9**) (50% on ol); the ester $\dot{C}H_2CH_2\dot{C}HCO_2N(CF_3)_2$ (**13**) (99% on ol); and the ketone $\dot{C}H_2CH_2\dot{C}HCOMe$ (**15**) (60% on ol), respectively.

Introduction

We have reported previously that addition of the radicals $(CF_3)_2NO\cdot$ (**1**) or $(CF_3)_2N\cdot$ (**2**) [formed from the oxadiazapentane $(CF_3)_2NON(CF_3)_2$] to the alkenes $CH_2{=}CRCCl_3$ (R = H, Me) [1] and to α- and β-pinene [2] gave intermediate radicals which underwent rearrangement (wholly or in part) involving a vicinal chlorine shift and opening of the four-membered ring, respectively. However, the intermediate radicals $\dot{C}H_2CMe_2X$ (X = Cl, Br, OAc), $\dot{C}H_2CMeCl_2$ and $\dot{C}H_2CMePhCl$ [generated by hydrogen abstraction by radicals **1** or **2** from the corresponding substituted alkanes] did not undergo rearrangement by 1,2-shifts involving halogen or the OAc group [3].

In a continuation of this investigation, the reactions of oxyl **1** with (i) the substituted arenes $PhCMe_3$, Ph_2CMe_2 and $PhCMe_2OH$, and (ii) the cyclopropane derivatives $\dot{C}H_2CH_2\dot{C}HCHXY$ (X = H, Y = Ph; X = H, Y = OH; X = Me, Y = OH) have been studied to determine whether the intermediate radicals $\dot{C}H_2CMe(Ph)X$ (X = Me, Ph and OH) and $\dot{C}H_2CH_2\dot{C}HCXY$ (X = H, Y = Ph; X = H, Y = OH; X = Me, Y = OH) formed by hydrogen abstraction would undergo a 1,2-phenyl shift or opening of the cyclopropane ring, respectively, before further reaction with oxyl **1** took place, i.e.

$$\dot{C}H_2CMe(Ph)X \longrightarrow PhCH_2\dot{C}MeX;$$

$$\dot{C}H_2CH_2\dot{C}HCXY \longrightarrow \dot{C}H_2CH_2CH{=}CXY$$

Results and discussion

The conditions used and the results obtained are summarized in Table 1.

Reactions of oxyl **1** with the arenes $PhCMe_3$ and Ph_2CMe_2 gave complex high-boiling mixtures from which the major product in each case was separated by GLC methods and identified as the monosubstituted compounds **4** and **7**, respectively. These products were formed by hydrogen abstraction from a methyl group by oxyl **1** to give the hydroxylamine **3** and the intermediate radicals $\dot{C}H_2CMe(Ph)X$ (**16**) (X = Me and Ph) which were then scavenged by oxyl **1** (Scheme 1).

The structures of compounds **4** and **7** were established from their NMR spectra [^{1}H NMR absorptions at δ 6.78 (5H, Ph), 3.63 (2H, CH_2O) and 0.95 (6H, CMe_2) ppm for compound **4** confirming the $PhCMe_2CH_2O$ grouping and at δ 6.62 (10H, 2Ph), 3.97 (2H, CH_2O)

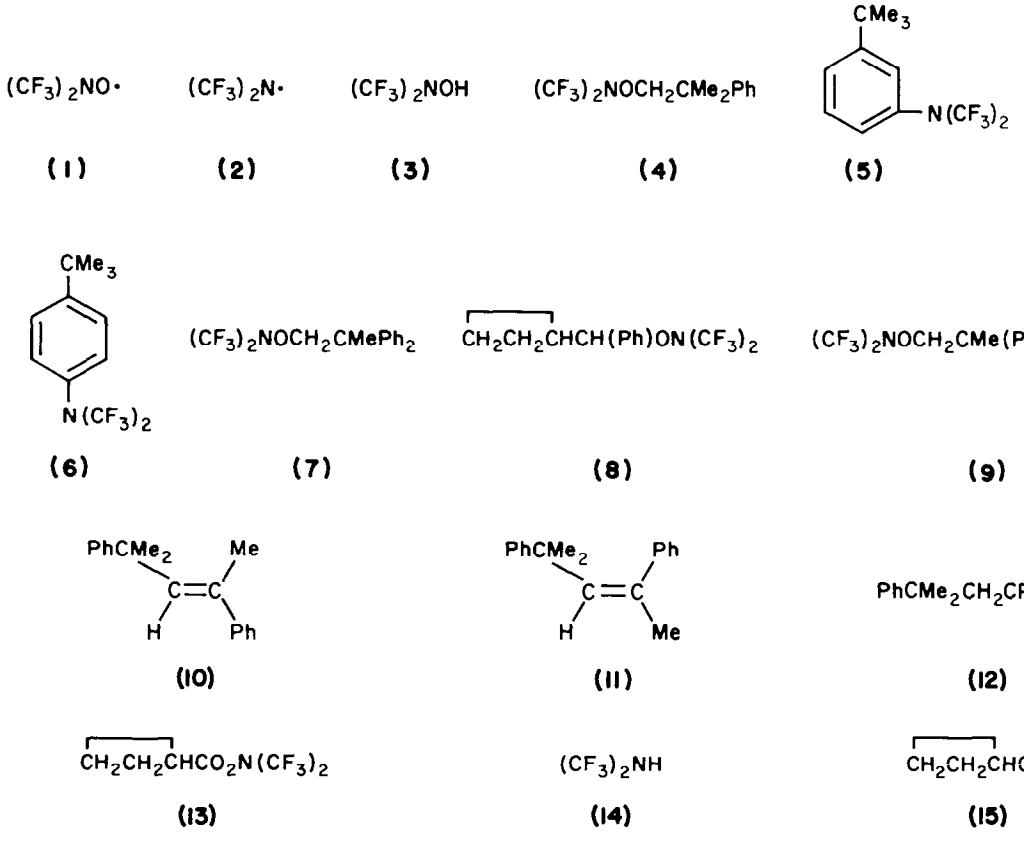
*Author to whom correspondence should be addressed.

0022-1139/94/$07.00
SSDI 0022-1139(93)02988-Q

TABLE 1. Reactions of oxyl **1** with substituted arenes and substituted cyclopropanes

Substrate	Ratio 1/substrate	Temperature (°C)	Time	Recovered substrate (%)	Products (%)[a]
$PhCMe_3$	*c.* 3:1	20	3 d	21	**3**, 43[b]; **4**, 28; **5**, 8; **6**, 6[c]
Ph_2CMe_2	*c.* 4:1	70–80	3 d	11	**3**, 45[b]; **7**, 36[c]
$\overline{CH_2CH_2CHCH_2Ph}$	2:1	20	10 min	9	**3**, 49[b]; **8**, 95[c]
$PhCMe_2OH$	2:1	20	3 d		**9**, 50; **10–12**, 30[c]
$\overline{CH_2CH_2CHCH_2OH}$	*c.* 4:1	20	10 min	2.5	**3**, 75[b]; **13**, 99
$\overline{CH_2CH_2CHCHMeOH}$	*c.* 2:1	20	5 min		**3**, 55.5[b]; **14**, 1.5[b]; **15**, 60[c]

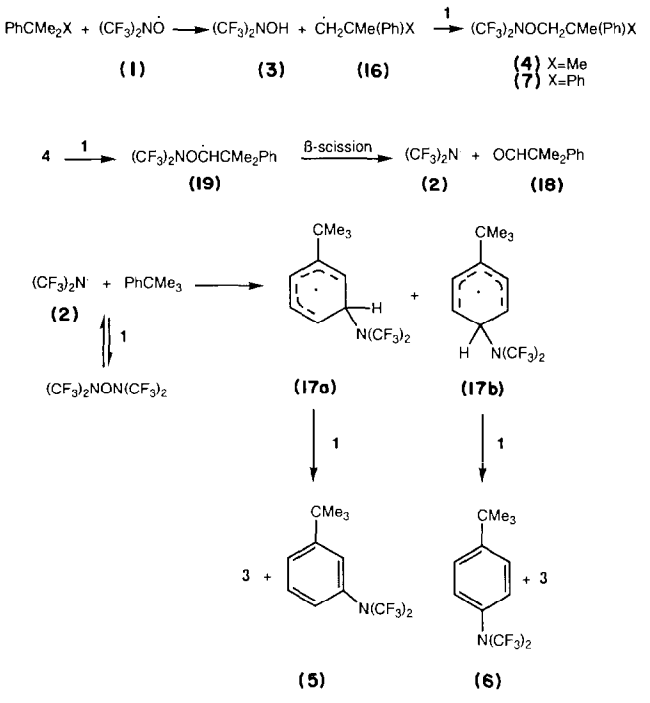
[a]Yields based on substrate reacted, i.e. not recovered.
[b]Yields based on oxyl **1**.
[c]Complex mixtures of unidentified minor products also formed.



and 1.35 (3H, CH_3) ppm for compound **7** confirming the Ph_2CMeCH_2O grouping. ^{19}F NMR absorptions in the range δ +8.8 to +10.0 ppm confirmed that each compound contained one $(CF_3)_2NO$ group].

Two minor products were also isolated from the t-butylbenzene reaction and found to be the $(CF_3)_2N$-substituted arenes **5** and **6** from a comparison of their IR, NMR and MS data with those of pure samples formed as major products in the reaction of the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ with t-butylbenzene [4]. These were unexpected products and they are considered to have arisen from the attack of the radical $(CF_3)_2N\cdot$ (**2**) on the arene ring followed by hydrogen abstraction from the resulting σ complexes **17a** and **17b** by oxyl **1** (Scheme 1) as proposed previously [5]; analogous compounds were probably also formed in the reaction involving the arene Ph_2CMe_2, but they were not isolated.

The $(CF_3)_2N\cdot$ (**2**) radicals required for the formation of compounds **5** and **6** are considered to have been generated together with aldehyde **18** from β-scission of the intermediate radical **19**, produced by hydrogen abstraction from the $(CF_3)_2NOCH_2$ group of compound **4** by oxyl **1** (Scheme 1). It has been reported previously



Scheme 1.

that radicals of type **19**, i.e. $(CF_3)_2NOCHR$, undergo competing β-scission, to give $(CF_3)_2N\cdot$ (**2**) radicals and aldehydes RCHO, and scavenging by oxyl **1** to afford compounds of type $[(CF_3)_2NO]_2CHR$ [6]. Aldehyde **18** would not be expected to be isolable, because aldehydes RCHO are highly susceptible to abstraction of the aldehydic hydrogen by oxyl **1** leading to the esters $RCO_2N(CF_3)_2$ [6, 7]; carbonyl absorptions were present in the IR spectra of the high-boiling mixtures formed in both reactions before attempted GLC separation.

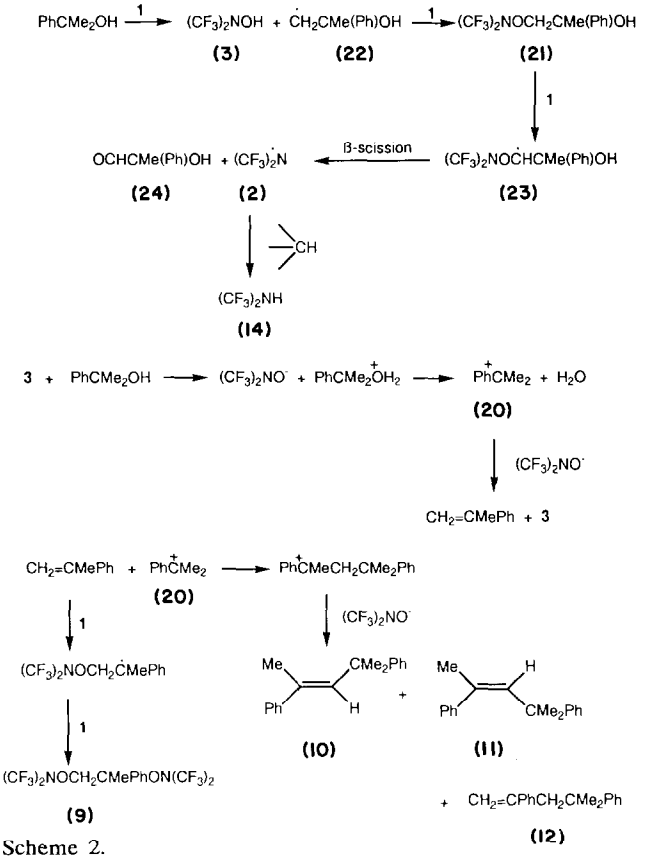
Since the complex product mixtures could not be separated adequately, it was not possible to determine whether the intermediate radicals **16** had rearranged to any extent via a 1,2-phenyl shift. The high-boiling products **4–7** identified from the two reactions account for only a moderate proportion of oxyl **1** which had reacted and of hydroxylamine **3** product. The high molar ratios of **1**/substrate and **3**/substrate not accounted for indicate that in the formation of the unidentified products considerable hydrogen abstraction resulting in substitution of H by $(CF_3)_2NO$, and also addition of oxyl **1** presumably to the aromatic rings, had occurred. The σ complexes **17a** and **17b** would be expected to react with oxyl **1** by addition (as well as abstraction of hydrogen) to afford cyclohexadienes which would be susceptible to further attack by oxyl **1**.

In contrast to these reactions, treatment of the cyclopropane derivative $\overline{CH_2CH_2}\overline{CHCH_2Ph}$ with oxyl **1** resulted in a clean and fast reaction to give the monosubstitution product **8** in excellent yield via the intermediate benzyl radical $\overline{CH_2CH_2}\dot{C}HCHPh$. Hence, it is clear that scavenging of the benzyl radical by oxyl **1** is highly favoured relative to rearrangement involving opening of the cyclopropyl ring.

Compound **8** showed ^1H NMR absorptions for a phenyl group (δ 7.2 ppm, 5H), a methine hydrogen adjacent to oxygen (δ 4.45 ppm, 1H) and five cyclopropyl hydrogens (δ 1.42 ppm, 1H and δ 0.8 ppm, 4H) and a ^{19}F NMR absorption for a $(CF_3)_2NO$ group (δ +9.5 ppm) which confirmed the structure.

The isolated high-boiling products from the reaction of oxyl **1** with 2-phenylpropan-2-ol all arose via the intermediacy of the dehydrated α-methylstyrene compound, i.e. the 2:1 adduct **9** of oxyl **1** and the styrene and the alkene dimers **10–12**. It was shown in a separate experiment that hydroxylamine **3** catalysed both the dehydration of the alcohol to the styrene and the dimerisation of the alkene via the cumyl carbocation (Scheme 2).

The hydroxylamine **3** necessary for the catalysis must have arisen by hydrogen abstraction, and so it is considered that initial reaction of oxyl **1** with the alcohol resulted in the formation of the monosubstitution compound **21** via hydrogen abstraction and the intermediacy of the radical **22**. The presence of amine **14** in the low-boiling products can be explained by further oxyl **1** attack on compound **21** at the $(CF_3)_2NOCH_2$ group



Scheme 2.

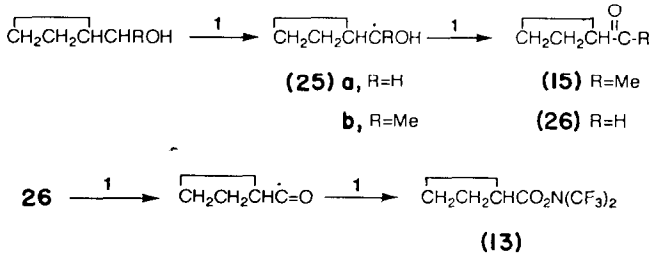
to afford the radical **23** which underwent β-scission with the formation of aldehyde **24** and $(CF_3)_2N\cdot$ (**2**) radicals (Scheme 2); further reaction of aldehyde **24** with oxyl **1** would lead to the formation of the ester $(CF_3)_2NO_2CCMePhOH$. Although neither the ester nor the monosubstitution compound **21** were isolated, the presence of bands for O–H and C=O stretch in the IR spectrum of the mixture of minor unidentified products is consistent with this reaction pathway.

It has been observed [8] that hydroxylamine **3** undergoes reaction with carbocations, e.g. Me_3C^+, to give $(CF_3)_2NO$ derivatives, but compounds arising from reaction of hydroxylamine **3** with the cumyl carbocation **20** or the carbocation precursors to the α-methylstyrene dimers **10–12**, e.g. $(CF_3)_2NOCMe_2Ph$, were not isolated in the present work.

The 2:1 adduct **9** was identified by a comparison of its IR and NMR spectra with those of the same compound formed in the reaction of oxyl **1** with 2-chloro-2-phenylpropane [3].

Treatment of the cyclopropylcarbinols $\overline{CH_2CH_2CH}$-CHROH (R = H and Me) with oxyl **1** resulted in very fast reactions and gave ester **13** and ketone **15**, respectively. Ester **13** was formed in very high yield via the intermediate radical **25a** and the aldehyde **26**, but the reaction involving 1-cyclopropylethanol gave a complex mixture of products from which only the major product ketone **15** (formed via radical **25b**) could be isolated (Scheme 3). The mixture of minor unidentified products was shown (IR spectroscopy) to contain $(CF_3)_2NO$, OH, C=O and possibly C=C groups, the complexity of the mixture suggesting that rearrangement of the intermediate radical **25b** involving opening of the cyclopropyl ring occurred to some extent. Direct oxyl **1** attack on the cyclopropyl ring is unlikely because oxyl **1** attack on cyclopropane has been shown to be very slow [9].

Ester **13** was identified by elemental analysis and its various spectra: IR (1808 cm^{-1}, ester C=O str.), ^1H NMR (five cyclopropyl hydrogens) and ^{19}F NMR [δ +8.8 ppm in the region expected for a $(CF_3)_2NO$ group].



Scheme 3.

Experimental

Starting materials

Oxyl **1** was prepared by oxidation of hydroxylamine **3** with potassium permanganate and sulfuric acid [10], the arenes and substituted cyclopropanes being commercial samples whose purities were checked (^1H NMR spectroscopy) before use.

General techniques

Reactions were carried out *in vacuo* in Pyrex ampoules (*c.* 100 cm^3 capacity) fitted with Rotaflo Teflon taps and the volatile products were removed *in vacuo* where necessary. High-boiling mixtures of products were separated into their individual components by preparative-scale GLC [Pye 104 instrument using columns (2 m) packed with silicone SE30 oil, Apiezon L (APL) grease, trixylyl phosphate (TXP) or poly(ethylene glycol adipate) (PEGA) (20%–25% w/w) on acid-washed Celite] and were examined by IR spectroscopy (Perkin-Elmer 197 instrument), ^1H NMR spectroscopy [Varian Associates HA100 (100.0 MHz) spectrometer; internal reference Me_4Si], ^{19}F NMR spectroscopy [Varian Associates HA100 (94.12 MHz) instrument; external reference CF_3CO_2H] and mass spectrometry (AEI MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were run as solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

Boiling points were determined using Siwoloboff's method.

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

(a) With t-butylbenzene

A mixture of oxyl **1** (2.43 g, 14.5 mmol) and t-butylbenzene (0.61 g, 4.5 mmol), stored (3 d) gave volatile material identified (IR spectroscopy) as *N,N*-bis(trifluoromethyl)hydroxylamine (**3**) (1.07 g, 6.3 mmol, 43% based on oxyl) and a light-yellow, non-volatile liquid (1.97 g), which was shown by GLC methods (2 m TXP and 2 m APL at 140 °C) to contain two major and 16 minor components; the IR spectrum showed bands in the range 1730–1670 cm^{-1} (C=O str.). The major components and two of the minor components were separated by preparative-scale GLC (2 m TXP at 140 °C) to give (i) unchanged t-butylbenzene (0.13 g, 0.9 mmol, 21% recovered); (ii) 1-[*N,N*-bis(trifluoromethyl)amino-oxy]-2-methyl-2-phenylpropane (**4**) (nc) (0.30 g, 1.0 mmol, 28%) (Analysis: Found: C, 47.7; H, 4.2; N, 4.8; F, 37.9%. $C_{12}H_{13}F_6NO$ requires: C, 47.8; H, 4.3; N, 4.7; F, 37.9%) {^1H NMR δ: 6.78 (mult., 5H, Ph); 3.63 (s, 2H, CH_2O); 0.95 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +8.85 [s $(CF_3)_2NO$] ppm. Mass spectrum (*m/z*): 301 (1%, M^+); 169 (7, $C_2HF_6NO^+$); 150 (6, $C_2HF_5NO^+$); 199 (21, $[M-(CF_3)_2NOCH_2]^+$); 91 (13,

$C_7H_7^+$); 88 (17, $C_7H_4^+$); 81 (13, $C_5H_5O^+$); 69 (100, CF_3^+); 58 (15, $C_3H_6O^+$); 31 (11, CF^+). IR ($\nu_{max.}$) (cm^{-1}): 3096–3058 (m) (arom. C–H str.); 2976, 2898 (m) (aliph. C–H str.); 1600, 1497 (m) (arom. C=C str.); 1447 (m); 1398 (m); 1372–1200 (vs) (C–F str.); 1178 (s) 1050 (s) (C–O–N str.); 1010 (m); 965 (s) (C–N str.); 760, 704 (s) (arom. C–H out-of-plane bend)}; and (iii) the two minor components which were identified as 3-[*N*,*N*-bis(trifluoromethyl)amino]-t-butylbenzene (**5**) (0.08 g, 0.3 mmol, 8%) and 4-[*N*,*N*-bis(trifluoromethyl)amino]-t-butylbenzene (**6**) (0.06 g, 0.23 mmol, 6%) by a comparison of their NMR spectra and GLC retention times with those of authentic samples [4].

(b) With 2,2-diphenylpropane

A mixture of oxyl **1** (2.45 g, 14.6 mmol) and 2,2-diphenylpropane (0.65 g, 3.3 mmol), heated at 70–80 °C (3 d), gave volatile material (1.14 g), which was shown (^{19}F NMR and IR spectroscopy) to consist of hydroxylamine **3** (1.12 g, 6.6 mmol, 45% based on oxyl) and *N*,*N*-bis(trifluoromethyl)amine (**14**) (0.02 g, 0.01 mmol, <1% based on oxyl) together with a brown, non-volatile liquid (1.96 g), which was shown by GLC methods (2 m SE30 and 2 m APL at 190 °C) to contain 15 components [IR ($\nu_{max.}$ (cm^{-1}): 1770–1690 (C=O str.)]. Two components were separated by preparative-scale GLC (2 m APL at 180 °C) to give unchanged 2,2-diphenylpropane (0.07 g, 0.4 mmol, 11% recovered) and a mixture (0.43 g) which consisted [^{19}F NMR spectroscopy] of an unidentified $(CF_3)_2NO$-containing compound (*c.* 0.06 g) and 1-[*N*,*N*-bis(trifluoromethyl)-amino-oxy]-2,2-diphenylpropane (**7**) (nc) (*c.* 0.37 g, *c.* 1.0 mmol, *c.* 36%). ^1H NMR δ: 6.62 (mult., 10H, 2Ph); 3.97 (s, 2H, CH_2O); 1.35 (s, 3H, Me) ppm. ^{19}F NMR δ: +10.0 [s, $(CF_3)_2NO$] ppm.

(c) With benzylcyclopropane

A mixture of oxyl **1** (3.16, 18.8 mmol) and benzylcyclopropane (1.25 g, 9.5 mmol), stored for 10 min, gave hydroxylamine **3** (1.60 g, 9.2 mmol, 49% based on oxyl) and a high-boiling liquid (2.81 g) which was shown by GLC methods (2 m APL at 150 °C) to contain two major components and six very minor components. Separation of the major components by preparative-scale GLC (2 m APL at 150 °C) afforded (i) cyclopropyl-[*N*,*N*-bis(trifluoromethyl) amino-oxy]phenylmethane (**8**) (nc) (2.47 g, 8.3 mmol, 95%) (Analysis: Found: C, 48.3; H, 3.8; N, 4.9; F, 38.3%. $C_{12}H_{11}F_6NO$ requires: C, 48.2; H, 3.7; N, 4.7; F, 38.1%), b.p. 201–202 °C {^1H NMR δ: 7.2 (mult., 5H, Ph); 4.45 (d, 1H, >CHO, J=9 Hz); 1.42 (mult., 1H, ring CH); 0.80 (complex, 4H, 4 ring CH) ppm. ^{19}F NMR δ: +9.5 [s, $(CF_3)_2NO$] ppm. Mass spectrum (*m/z*): 298 [0.3%, $(M-H)^+$]; 131 (100, $[M-(CF_3)_2NO]^+$); 129 (13, $C_{10}H_9^+$); 116 (13, $C_9H_8^+$); 115 (11, $C_9H_7^+$); 105 (10, $C_8H_9^+$ and/or $C_7H_5O^+$); 91 (51, $C_7H_7^+$), 77 (15, $C_6H_5^+$); 69 (11, CF_3^+); 51 (11, $C_4H_3^+$); 44 (5, $C_2H_4O^+$); 39 (8, $C_3H_3^+$). IR ($\nu_{max.}$) (cm^{-1}): 3058, 3040 (m) (arom. C–H str.); 3003, 2976 (m) (aliph. C–H str.); 1605, 1493 (m) (arom. C=C str.); 1449 (s); 1429 (m); 1290–1190 (vs) (C–F str.); 1070 (m); 1021 (s) (C–O–N str.); 950 (s) (C–N str.); 900 (s); 862 (s); 850 (m); 740 (m) (arom. C–H out-of-plane bend); 685 (s)}; and (ii) unchanged benzylcyclopropane (0.11 g, 0.8 mmol, 9% recovered).

(d) With 2-phenylpropan-2-ol

A mixture of oxyl **1** (2.55 g, 15.2 mmol) and the alcohol (1.05 g, 7.7 mmol), stored (3 d), gave volatile material (0.56 g; Found: M, 104), which was shown (IR spectroscopy) to consist of hydroxylamine **3**, amine **14** and carbon dioxide, and a light brown, non-volatile liquid (2.94 g) [IR ($\nu_{max.}$) (cm^{-1}): 3600–3195 (O–H str.); 1750–1680 (C=O str.)], which was shown by GLC methods (2 m PEGA and 2 m SE30 at 190 °C) to contain one major, 11 minor and three components with long GLC retention times.

The three compounds with long GLC retention times were identified as α-methylstyrene dimers (**10–12**) (combined yield *c.* 30%) by a comparison of their retention times with the products of the reaction of hydroxylamine **3** with 2-phenylpropan-2-ol (see later).

Separation of the major reaction product by preparative-scale GLC (2 m PEGA at 130 °C) gave 1,2-bis-[*N*,*N*-bis(trifluoromethyl)amino-oxy]-2-phenylpropane (**9**) (1.75 g, 3.9 mmol, 50%) which was identified by a comparison of its IR, ^1H NMR, ^{19}F NMR and mass spectra with those reported [3].

(e) With cyclopropylmethanol

A mixture of oxyl **1** (2.90 g, 17.3 mmol) and the alcohol (0.32 g, 4.4 mmol), stored for 10 min, gave hydroxylamine **3** (1.98 g, 11.7 mmol, 68% based on oxyl) and higher-boiling material (1.24 g), which was shown by GLC methods (2 m SE30 and 2 m PEGA at 80 °C) to contain two minor and one major component. Separation of the components by preparative-scale GLC (2 m PEGA at 80 °C) afforded unchanged cyclopropylmethanol (0.07 g, 0.1 mmol, 2.5% recovered), hydroxylamine **3** (0.20 g, 1.2 mmol, 7% based on oxyl) and [*N*,*N*-bis(trifluoromethyl)amino-oxycarbonyl]-cyclopropane (**13**) (nc) (1.04 g, 4.2 mmol, 99%) (Analysis: Found: C, 30.2; H, 2.2; N, 5.9; F, 48.5%. $C_6H_5F_6NO_2$ requires: C, 30.4; H, 2.1; N, 5.9; F, 48.1%) {^1H NMR δ: 2.12 (mult., 1H, ring CH); 1.15 (d, 4H, 2 ring CH_2, J=6 Hz) ppm. ^{19}F NMR δ: +8.2 [s, $(CF_3)_2NO$] ppm. Mass spectrum (*m/z*): 218 [0.1%, $(M-F)^+$]; 133 (1, $C_2F_5N^+$); 69 (100, CF_3^+); 68 (1, $C_4H_4O^+$); 55 (2, $C_3H_3O^+$); 44 (3, CO_2^+); 41 (52, $C_3H_5^+$); 40 (7, $C_3H_4^+$); 39 (32, $C_3H_3^+$); 29 (5, CHO^+). IR ($\nu_{max.}$) (cm^{-1}):

3020–2920 (m), (aliph. C–H str.); 1808 (m) (ester C=O str.); 1453 (m); 1425 (m); 1379–1205 (vs) (C–F str.); 1111 (m); 1064, 1043 (s) (C–O–N str.); 1026 (s); 1000 (m); 971 (s) (C–N str.); 909 (m); 888 (m); 863 (m); 784 (m); 734 (m); 709 (s) (CF_3 def.)}.

(f) With 1-cyclopropylethanol

A mixture of oxyl **1** (3.95 g, 23.6 mmol) and the alcohol (0.95 g, 11.0 mmol), stored for 5 min, gave a volatile mixture (2.24 g) identified (IR and ^{19}F NMR spectroscopy) as consisting of hydroxylamine **3** (2.19 g, 13.1 mmol, 55.5% based on oxyl), amine **14** (0.05 g, 1.5% based on oxyl) and high-boiling material (2.66 g), which was shown by GLC methods (2 m PEGA at 80 °C) to contain one major and 11 minor components. The major component was separated by preparative-scale GLC (2 m PEGA at 80 °C) and identified as cyclopropyl methyl ketone (**15**) (0.53 g, 6.3 mmol, 60%) from a comparison of its IR and ^1H NMR spectra with those of an authentic sample. The minor components were also collected and the IR spectrum showed bands ($\nu_{max.}$) (cm^{-1}) at 3510–3200 (O–H str.), 1755–1675 (C=O str.) and 1600–1500 (C=C str.), as well as bands due to $(CF_3)_2NO$ groups.

Reaction of N,N-*bis(trifluoromethyl)hydroxylamine (3) with 2-phenylpropan-2-ol*

A mixture of hydroxylamine **3** (1.68 g, 10.0 mmol) and the alcohol (1.34 g, 10.0 mmol), stored (1 d), gave a volatile mixture (1.84 g) of hydroxylamine **3** and water, and a yellow non-volatile liquid (1.18 g) which showed an absence of IR absorption ($\nu_{max.}$) (cm^{-1}) in the range 3570–3200 (O–H str.). The liquid was dissolved in diethyl ether (25 cm^3) and shaken with dilute aqueous sodium hydroxide (1 M, 10 cm^3) to remove traces of hydroxylamine **3**. The ether layer was then separated, dried ($CaSO_4$) and the ether removed *in vacuo* to give a colourless liquid (1.14 g), which was shown by GLC methods (2 m PEGA and 2 m APL at 190 °C) to contain three components with long retention times in the ratio 1.0:1.4:1.1. These were identified as α-methylstyrene dimers **10–12** (1.14 g, 4.83 mmol, 97%). ^1H NMR δ: 6.7 (br., 10H, Ph); 4.8–4.3 (br., 1.8H, =CH); 1.6 (br., 1H, CH_2); 1.4–0.7 (br., 8H, Me) ppm. Mass spectrum (*m/z*): 236 (20%, M^+); 221 [67, $(M-Me)^+$]; 154 (100, $C_{12}H_{10}^+$); 143 (23, $C_{11}H_{11}^+$); 119 (98, $C_9H_{11}^+$]; 91 (53, $C_7H_7^+$); 77 (23, $C_6H_5^+$). IR ($\nu_{max.}$) (cm^{-1}): 3096–2857 (arom. and aliph. C=H str.); 1597–1440 (arom. and aliph. C=C str.); 760, 700 (arom. C–H out-of-plane bend).

References

1 G.D. Connelly and A.E. Tipping, *J. Fluorine Chem., 67* (1994) 153.
2 G.D. Connelly and A.E. Tipping, *J. Fluorine Chem., 68* (1994) 103.
3 G.D. Connelly and A.E. Tipping, *J. Fluorine Chem., 68* (1994) 83.
4 G.D. Connelly, *Ph.D. Thesis,* University of Manchester, 1979.
5 G.D. Connelly, R.N. Haszeldine, A. Kenny, C.M. Irvin and A.E. Tipping, *J. Fluorine Chem., 17* (1981) 191.
6 R.E. Banks, J.M. Birchall, R.N. Haszeldine, R.A. Hughes, S. Nona and C.W. Stephens, *J. Chem. Soc., Perkin Trans., 1* (1981) 455.
7 R.E. Banks, D.R. Choudhury and R.N. Haszeldine, *J. Chem. Soc., Perkin Trans., 1* (1973) 80.
8 C.A. Nwadinigwe, *Ph.D. Thesis,* University of Manchester, 1977.
9 A.K. Brown, *Ph.D. Thesis,* University of Manchester, 1974.
10 R.E. Banks, R.N. Haszeldine and M.J. Stevenson, *J. Chem. Soc. C,* (1966) 901.