ELSEVIER

Journal of Fluorine Chemistry 69 (1994) 163–169

JOURNAL OF FLUORINE CHEMISTRY

Some further reactions of bis(trifluoromethyl)amino-oxyl with alkenes

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Received 11 September 1993; accepted 25 January 1994

Abstract

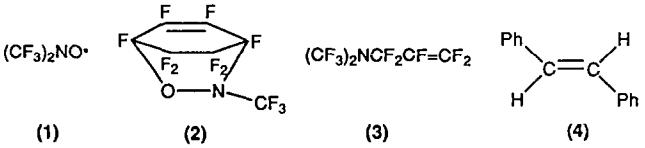
The reaction of the oxyl $(CF_3)_2NO\cdot$ (**1**) with the alkene $CF_3NOCF(CF_2)_2CFCF{=}CF$ (**2**) at 100 °C and with the alkenes $(CF_3)_2NCF_2CF{=}CF_2$ (**3**), (*E*)-PhCH=CHPh (**4**), $CH_2{=}CHCOCl$ (**5**) and $(CF_3)_2NCF_2CF{=}CFCF_2ON(CF_3)_2$ (**6**) (prepared in 76% yield by reaction of the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**7**) with the diene $CF_2{=}CFCF{=}CF_2$) at room temperature gave high yields (92%–100%) of the corresponding 2:1 adducts **8–12**; hydrolysis of the acid chloride **11** gave the acid **14** (100%). A mixture of the oxyl **1** and 3-bromopropene (4:5 molar ratio) on reaction at room temperature afforded a complex mixture of products of which the major compounds were identified by GLC–MS as $(CF_3)_2NCH_2CH{=}CH_2$ (**15**), $(CH_2Br)_2CHON(CF_3)_2$ (**16**), $(CF_3)_2NOCH_2CH(CH_2Br)ON(CF_3)_2$ (**17**), $(CF_3)_2NCH_2CH(CH_2Br)ON(CF_3)_2$ (**18**) and possibly $[(CF_3)_2NOCH_2]_2CHBr$ (**19**). The following order of reactivity of ethenes towards oxyl **1** attack was obtained; $CH_2{=}CCl_2 > CHF{=}CF_2 > CHCl{=}CCl_2 > CH_2{=}CHCl > CH_2{=}CH_2 > CH_2{=}CHF > CH_2{=}CF_2 > CCl_2{=}CCl_2$.

Keywords: Reactions; Bis(trifluoromethyl)amino-oxyl; Alkenes; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

The reaction of bis(trifluoromethyl)amino-oxyl (**1**) with both hydrocarbon alkenes and fluoroalkenes at room temperature to give high yields of 2:1 adducts has been investigated widely, e.g. refs. 1–4; with perfluorocycloalkenes more forcing conditions (ca. 80 °C) are required [1,5]. With certain hydrocarbon alkenes, e.g. $CH_2{=}CMe_2$, reaction can also occur via allylic hydrogen abstraction [6], and in the reaction of the alkenes $CH_2{=}CRCCl_3$ (R = H, Me) rearrangement of the intermediate radicals $(CF_3)_2NOCH_2\dot{C}RCCl_3$ by a 1,2-chlorine shift took place to some extent to afford both rearranged and non-rearranged 2:1 adducts [7].

In the present work, the reactions of the oxyl **1** with the alkenes **2–6** have been studied to determine if the corresponding 2:1 adducts are formed in high yield, and a preliminary investigation of the reaction of the oxyl **1** with 3-bromopropene has been carried out in order to compare the results obtained with those reported previously for reaction of the oxadiazapentane **7** with the alkene [8]. Competition reactions involving treatment of equimolar quantities of pairs of ethenes with a deficiency of the oxyl **1** have also been investigated to obtain a reactivity order for the alkenes towards oxyl **1** attack.



$(CF_3)_2NO\cdot$ (1) (2) $(CF_3)_2NCF_2CF{=}CF_2$ (3) (4)

$CH_2{=}CHCOCl$ (5) $(CF_3)_2NCF_2CF{=}CFCF_2ON(CF_3)_2$ (6) $(CF_3)_2NON(CF_3)_2$ (7)

2. Results and discussion

Alkene **6** was prepared in good yield (76%) by reaction of the oxadiazapentane **7** with the diene $CF_2{=}CFCF{=}CF_2$. The 1,4-addition observed at room temperature via initial $(CF_3)_2N\cdot$ radical attack, i.e.

$$(CF_3)_2N\cdot + CF_2{=}CFCF{=}CF_2 \longrightarrow$$

$$(CF_3)_2NCF_2{-}\dot{C}F{-}CF{-}CF_2 \xrightarrow{7}$$

$$(CF_3)_2NCF_2CF{=}CFCF_2ON(CF_3)_2$$

(6)

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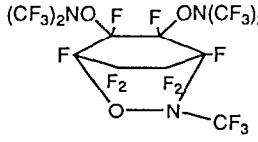
SSDI 0022-1139(94)03073-9

parallels the reaction of the oxyl **1** with the diene at 80 °C which gave the thermodynamic bis-1,4-adduct (95%), while at −72 °C the kinetic bis-1,2-adduct (98%) was produced [9].

The results obtained from reaction of the oxyl **1** with the alkenes **2–6** are summarized in Table 1.



(8)

$(CF_3)_2NCF_2CF[ON(CF_3)_2]CF_2ON(CF_3)_2$

(9)

$(CF_3)_2NOCHPhCHPhON(CF_3)_2$

(10)

$(CF_3)_2NOCH_2CHXON(CF_3)_2$

(11), X=COCl

(14), X=CO_2H

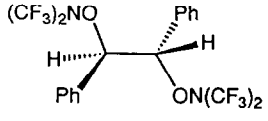
$(CF_3)_2NCF_2CF[ON(CF_3)_2]CF[ON(CF_3)_2]CF_2ON(CF_3)_2$

(12)

$(CF_3)_2NOH$

(13)

The 2:1 adducts **8–12** were each obtained in high yield (92%–100%), but the small amount of the hydroxylamine **13** from the *trans*-stilbene reaction indicated that some hydrogen abstraction by oxyl **1** had occurred in this case. The NMR spectra of the stilbene adduct **10** were consistent with it being present as a single diastereomer, since only one $(CF_3)_2NO$ absorption (δ_F 10.2 ppm) and one methine absorption [δ_H 5.27 (br.) ppm] were observed. In this case, it is probably the *meso* compound **10a** formed by *anti* addition to the alkene.



(10a)

Oxyl **1** addition to the alkene **6** occurred smoothly at room temperature, which contrasts with the report [9] that the corresponding 1,4-adduct of oxyl **1** and hexafluorobuta-1,4-diene required high temperature (200 °C) and an excess of oxyl **1** for reaction to take place to afford 1,2,3,4-tetrakis [bis(trifluoromethyl)-amino-oxy]hexafluorobutane.

The bicyclic alkene **2** was resistant to oxyl **1** attack at room temperature, but addition occurred readily at 100 °C.

The adduct **11** formed from acryloyl chloride (**5**) was hydrolysed by water at room temperature to afford the corresponding carboxylic acid **14** in quantitative yield.

The structures of the alkene **6**, the 2:1 adducts **8–12** and the acid **14** were established by elemental analysis and a consideration of their NMR spectra.

Alkene **6** was identified as the 1,4-adduct of the oxadiazapentane **7** and hexafluorobuta-1,3-diene, and not the 1,2-adduct, by the presence of two vinylic fluorine [δ −76.2 (1F) and −79.6 (1F) ppm] and two difluoromethylene [δ −3.3 (2F) and −6.1 (2F) ppm] absorptions in its ^{19}F NMR spectrum; the spectrum of the 1,2-adduct would show absorptions for three vinylic fluorines and one difluoromethylene group. The NMR spectra of adducts **8–12** showed that the vinylic fluorines or hydrogens in the reactant alkenes **2–6** had been replaced by saturated $\geq CF$, $\geq CF_2$ and $\geq CH$ groups, and that only additional $(CF_3)_2NO$ groups (δ 8–10.5 ppm) were present. The NMR spectra of the acid chloride **11** and the corresponding acid **14** were very similar, apart from the CO_2H absorption (δ 10.45 ppm) present in the ^1H NMR spectrum of compound **14**.

The reaction of oxyl **1** with 3-bromopropene (4:5 molar ratio) at room temperature (7 d) gave unchanged alkene (63% recovered), hydroxylamine **13** (14%) and a complex mixture of 15 higher-boiling components (GLC).

The five major components of the higher-boiling mixture were examined by coupled GC–MS and two were identified as the allylamine **15** (ca. 8%) and the dibromide **16** (ca. 21%) by a comparison of their GLC

Table 1
Reaction of bis(trifluoromethyl)amino-oxyl (**1**) with alkenes

Alkene (g, mmol)	**1** (g, mmol)	Time (h)	Recovered reactants (%)		Products (g, mmol, %)
			alkene	**1**	
2; 3.15, 9.76	3.22, 19.05	12[a]	3	3	**8**; 6.15, 9.40, 99
3; 0.51, 1.80	0.93, 5.5	24		34.5	**9**; 1.11, 1.8, 100
4; 0.93, 5.17	1.68, 10.0	24[b]	6		**10**; 2.40; 4.6, 92[c] **13**; 0.10, 0.06, 6
5; 3.97, 43.9	5.00, 29.8	96	66		**11**; 6.31, 14.8, 99
6; 2.68, 5.5	4.15, 24.7	336		55.5	**12**; 4.50, 5.5, 100

[a]Carried out at 100 °C; other reactions carried out at room temperature.
[b]Carried out in solvent (CCl_4).
[c]Separated from unchanged alkene **4** by preparative-scale GLC (4 m SE30 at 150 °C).

retention times and mass spectra with those of authentic samples isolated from the reaction of the oxadiazapentane **7** with 3-bromopropene [8]. Two further components were identified as the 2:1 adduct **17** (ca. 5%) {MS (*m/z*): 437/439, $(M-F)^+$; 288/290, (100%) $[M-(CF_3)_2NO]^+$; 274/276, $[M-(CF_3)_2NOCH_2]^+$; 182, $(CF_3)_2NOCH_2^+$; 120/122, $C_3H_5Br^+$; 93/95, CH_2Br^+} and the adduct **18** (ca. 9%) of the oxadiazapentane **7** and the alkene [MS (*m/z*): 347, $(M-CH_2Br)^+$; 166, (100%) $(CF_3)_2NCH_2^+$; 120/122, $C_3H_5Br^+$; 93/95, CH_2Br^+]. The remaining component was a mixture containing a 2:1 adduct probably compound **19** {MS (*m/z*): 455/457, $(M-H)^+$; 288/290, $[M-(CF_3)_2NO]^+$, 182, $(CF_3)_2NOCH_2^+$; 92/94, $CHBr^+$} together with compounds containing a $(CF_3)_2NOCHN(CF_3)_2$ grouping (*m/z*: 333) and a $(CF_3)_2NCH_2C_2H_3Br$ grouping [*m/z*: 272/274, $(CF_3)_2NC_3H_5Br^+$; 258/260, $(CF_3)_2NCH_2CHBr^+$; 179, $(CF_3)_2NC_2H_3^+$; 166, (56%) $(CF_3)_2NCH_2^+$].

$(CF_3)_2NCH_2CH{=}CH_2$ (15)

$(BrCH_2)_2CHON(CF_3)_2$ (16)

$(CF_3)_2NOCH_2CH(CH_2Br)ON(CF_3)_2$ (17)

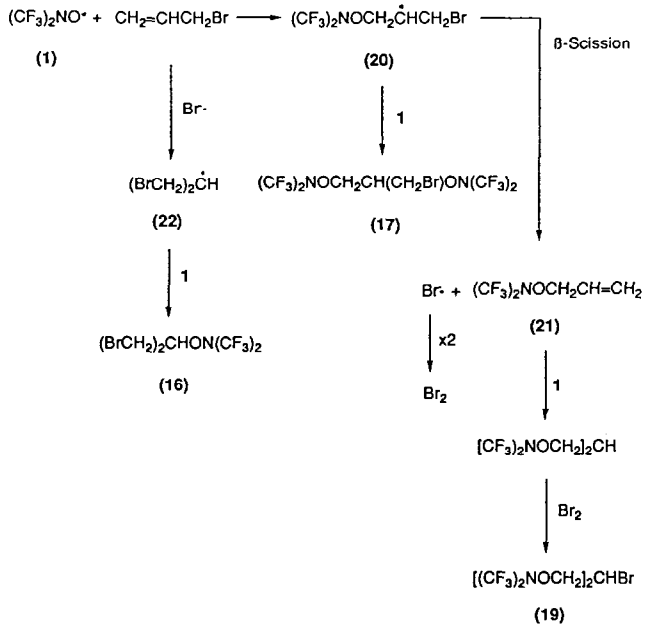
$(CF_3)_2NCH_2CH(CH_2Br)ON(CF_3)_2$ (18)

$[(CF_3)_2NOCH_2]_2CHBr$ (19)

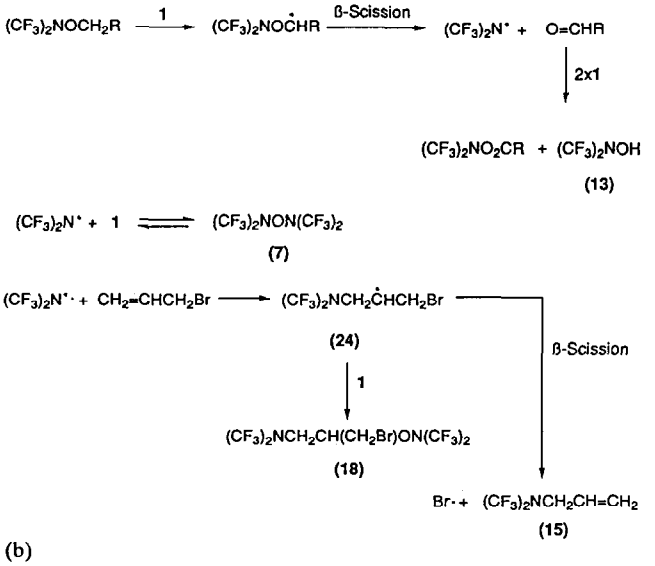
These products are considered to have been formed as shown in Scheme 1.

The intermediate radical **20** resulting from oxyl **1** attack on the alkene undergoes competing scavenging by oxyl **1** to give the 2:1 adduct **17** and β-scission of bromine to afford the allylhydroxylamine **21** which is the precursor of the rearranged 2:1 adduct **19**. Bromine attack on the reactant alkene affords the intermediate radical **22**, which is scavenged by oxyl **1** to give the dibromide **16**. The remaining products **15** and **18** contain a $(CF_3)_2N$ group and these are considered to have arisen via the intermediacy of $(CF_3)_2N\cdot$ radicals which attacked the reactant alkene. Further oxyl **1** attack on products containing a $(CF_3)_2NOCH_2-$ grouping would give intermediate radicals of type **23**, which would undergo β-scission to afford $(CF_3)_2N\cdot$ radicals and aldehydes [10]. Aldehydes RCHO are reported to undergo rapid reaction with oxyl **1** to produce hydroxylamine **13** and esters $(CF_3)_2NO_2CR$ [11]. Although such esters were not major products, the IR spectrum of the high-boiling product mixture showed a strong carbonyl absorption [(ν_{max}): 1740 cm^{-1}] consistent with their formation.

The identified products compare favourably with those formed in the corresponding reaction of oxadiazapentane **7** with 3-bromopropene [8] with two exceptions. Firstly, the 1:1 adduct **18** of the oxadiazapentane **7** and 3-bromopropene was only detected in the oxyl **1** reaction. This can be explained by the much slower reaction of



(a)



(b)

Scheme 1.

the intermediate radical **24** with oxadiazapentane **7** than with oxyl **1**, which favours competing β-scission to give alkene **15** in the oxadiazapentane **7** reaction. Secondly, the 2:1 adduct of the oxyl **1** and the allylhydroxylamine **21**, i.e. $[(CF_3)_2NOCH_2]_2CHON(CF_3)_2$, was not a major product in the oxyl **1** reaction, but the 1:1 adduct of the oxadiazapentane **7** and the allylamine **15**, i.e. $[(CF_3)_2NCH_2]_2CHON(CF_3)_2$, was a major product in the oxadiazapentane **7** reaction.

A series of competition reactions between equimolar mixture of two ethenes and a deficiency of oxyl **1** gave the results summarized in Table 2.

Table 2
Reaction of bis(trifluoromethyl)amino-oxyl (**1**) with mixtures of ethenes

Reactant alkenes		**1** (g, mmol)	Time (d)	Alkenes recovered (%)		1:1 Adducts[a]	
A (g, mmol)	B (g, mmol)			A	B	From A (g, mmol, %)	From B (g, mmol, %)
$CH_2=CH_2$	$CH_2=CHCl$						
1.60, 58.7	3.67, 58.7	1.93, 11.5	2	99.5	91	0.10, 0.30, 5	2.15, 5.4, 94
$CH_2=CCl_2$	$CHCl=CCl_2$						
1.79, 18.45	2.42, 18.45	0.98, 5.80	1	85	98	1.15, 2.65, 92	0.11, 0.2, 6
$CH_2=CHCl$	$CHCl=CCl_2$						
1.18, 18.9	2.48, 18.9	1.23, 7.32	1	96	83.5	0.27, 0.7, 19	1.37, 2.9, 81
$CH_2=CH_2$	$CH_2=CHF$						
1.25, 44.5	2.05, 44.5	1.36, 8.10	3	95.5	96.5	0.88, 2.4, 60	0.54, 1.4, 35
$CH_2=CHF$	$CH_2=CF_2$						
2.05, 44.5	2.85, 44.5	1.15, 6.84	5	95.5	96.5	0.71, 1.85, 54	0.60, 1.5, 43
$CH_2=CH_2$	$CH_2=CF_2$						
1.25, 44.5	2.85, 44.5	1.72, 10.24	6	93.5	96	1.08, 3.0, 58	0.70, 1.74, 34
$CH_2=CHCl$	$CH_2=CCl_2$						
2.14, 34.4	3.33, 34.3	1.40, 8.3	2	99	88.5	0.12, 0.3, 7	1.65, 3.8, 92
$CHCl=CCl_2$	$CCl_2=CCl_2$						
2.19, 16.7	2.78, 16.7	1.32, 7.9	1	76.5	99	1.84, 3.90, 99	0.05, 0.01, 0.5
$CH_2=CF_2$	$CCl_2=CCl_2$						
0.61, 9.8	1.62, 9.8	0.89, 5.3	14	93	96	0.28, 0.7, 58	0.25, 0.5, 41
$CH_2=CCl_2$	$CHF=CF_2$						
4.29, 44.2	2.63, 44.2	1.92, 11.4	3	94.5	92.5	1.35, 3.2, 57	0.96, 2.3, 42

[a]Yields based on oxyl **1**

The observed order of alkene reactivity, i.e. $CH_2=CCl_2 > CHF=CF_2 > CHCl=CCl_2 > CH_2=CHCl > CH_2=CH_2 > CH_2=CHF > CH_2=CF_2 > CCl_2=CCl_2$, was identical to the order obtained for $(CF_3)_2N\cdot$ radical attack (generation from the oxadiazapentane **7**) on the same alkenes, except for the position of the alkene $CHCl=CCl_2$ which came between the alkenes $CH_2=CF_2$ and $CCl_2=CCl_2$ [12]. Possible reasons for the difference in reactivity of the alkene $CHCl=CCl_2$ towards $(CF_3)_2NO\cdot$ (**1**) and $(CF_3)_2N\cdot$ radical attack are (i) the $(CF_3)_2N\cdot$ radical is more electrophilic than the $(CF_3)_2NO\cdot$ (**1**) radical and so $(CF_3)_2N\cdot$ radical attack on the highly electron-deficient alkene would be less favoured and hence slower, and (ii) the $(CF_3)_2N\cdot$ radical is branched at the radical centre while the $(CF_3)_2NO\cdot$ (**1**) radical is branched at the atom adjacent to the radical centre; the former radical would be expected to encounter more steric hindrance to attack. The factors involved in determining the reactivity of an ethene towards $(CF_3)_2N\cdot$ radical attack have been discussed previously [12] and the same factors are considered to apply to $(CF_3)_2NO\cdot$ (**1**) radical attack, i.e. steric effects, intermediate radical stability, electron density at the alkene double bond and hybridization effects.

3. Experimental

3.1. Starting materials

The oxyl **1** was prepared by oxidation of the hydroxylamine **13** with potassium permanganate and sulphuric acid [1] and was converted into the oxadiazapentane **7** by reaction with trifluoronitrosomethane (2:1 molar ratio) [1]. The alkenes employed were either research samples available in the Department or commercial samples. The purity of each was checked (IR and/or NMR) before use.

3.2. General techniques

The reactions of oxyl **1** and oxadiazapentane **7** were carried out in vacuo in Pyrex ampoules or bulbs (volumes as stated in the text) fitted with Rotaflo Teflon taps. Volatile products were separated by fractional condensation in vacuo and non-volatile products were purified where necessary by GLC [Pye 104 instrument using columns (4 m) packed with Silicone SE30 oil (20% w/w) on acid-washed Celite]. Products were examined by IR spectroscopy (Perkin-Elmer 197 instrument), ^1H NMR spectroscopy [Varian Associates HA100 (100.0 MHz) spectrometer; external reference Me_4Si], ^{19}F NMR spectroscopy [Varian Associates HA100 (94.12 MHz) instrument; external reference CF_3CO_2H] and mass spectrometry (AEI MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded using solutions of products in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

Boiling points were determined using Siwoloboff's method and melting points are uncorrected.

3.3. The reaction of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane (7) with hexafluorobuta-1,3-diene

A mixture of oxadiazapentane **7** (7.82 g, 24.4 mmol) and the diene (7.31 g, 45.1 mmol), stored in an ampoule (800 cm^3) in the dark (7 d), gave (i) unchanged hexafluorobuta-1,3-diene (3.08 g, 19.03 mmol, 42% recovered) which condensed at −196 °C, (ii) a −45 °C fraction (2.98 g) which was shown by GLC (2 m SE30 at 60 °C) to contain ca. 10 components, and (iii) a −23 °C fraction which was identified as 1-[*N*,*N*-bis(trifluoromethyl)amino]-4-[*N*,*N*-bis(trifluoromethyl)amino-oxy]hexafluorobut-2-ene (**6**) (nc) (8.95 g, 18.6 mmol, 76%).

3.4. Reactions of bis(trifluoromethyl)amino-oxyl (1) with alkenes

(a) With 1,4,5,6,7,7,8,8,-octafluoro-3-trifluoromethyl-2-oxa-3-azabicyclo[2.2.2]oct-5-ene (2) (general procedure)

A mixture of oxyl **1** (3.22 g, 19.05 mmol) and the alkene **2** (3.15 g, 9.76 mmol) heated in an ampoule (ca. 150 cm^3) at 100 °C in the dark (12 h), gave (i) unchanged oxyl **1** (0.10 g, 0.6 mmol, 3% recovered) which condensed at −120 °C, (ii) unchanged alkene (0.10 g, 0.30 mmol, 3% recovered) which condensed at −45 °C and (iii) a −23 °C fraction which was identified as 5,6-bis[*N*,*N*-bis(trifluoromethyl)amino-oxy]-1,4,5,6,7,7,8,8-octafluoro-3-trifluoromethyl-2-oxa-3-azabicyclo[2.2.2]octane (**8**) (nc) (6.15 g, 9.4 mmol, 99%).

(b) With other alkenes

The results of the reaction of oxyl **1** with the alkenes $(CF_3)_2NCF_2CF{=}CF_2$ (**3**) (ca. 300 cm^3 ampoule), (*E*)-PhCH=CHPh (**4**) in solvent CCl_4 (ca. 300 cm^3 ampoule) and $CH_2{=}CHCOCl$ (**5**) (ca. 300 cm^3 ampoule) in the dark, and with the alkene $(CF_3)_2NCF_2CF{=}CFCF_2ON(CF_3)_2$ (**6**) (ca. 150 cm^3 ampoule) in light are summarized in Table 1. All of the 2:1 adducts are new compounds.

(c) With 3-bromopropene

A mixture of oxyl **1** (3.36 g, 20.0 mmol) and 3-bromopropene (3.03 g, 25.0 mmol), stored in an ampoule (ca. 150 cm^3) in the dark (7 d), gave (i) a −78 °C fraction which was identified (IR) as *N*,*N*-bis(trifluoromethyl)hydroxylamine (**13**) (0.47 g, 2.8 mmol, 14%), (ii) unchanged 3-bromopropene (1.91 g, 15.8 mmol, 63% recovered) which condensed at −45 °C and (iii) a −23 °C and 0 °C fraction (3.98 g) which was shown by GLC (4 m SE30 at 100 °C) to contain five major components and 10 minor components.

The major components were examined by coupled GLC (as above)–MS and were identified as (i) 3-[*N*,*N*-bis(trifluoromethyl)amino]propene (**15**) (ca. 0.14 g, ca. 0.75 mmol, ca. 8%), (ii) 1,2-bis[*N*,*N*-bis(trifluoromethyl)-amino-oxy]-3-bromopropane (**17**) (ca. 0.21 g, ca. 0.45 mmol, ca. 5%) {MS (*m/z*: 437/349 [0.3% $(M-F)^+$]; 436/438 [4, $(M-HF)^+$]; 288/290 {100, $[M-(CF_3)_2NO]^+$}; 274/276 {7, $[M-(CF_3)_2NOCH_2]^+$}; 182 [18, $(CF_3)_2NOCH_2^+$]; 166 (28, $C_3H_2F_6N^+$); 136/138 (23, $C_3H_3OBr^+$); 122/124 (9, $C_3H_5Br^+$); 107/109 (26, $C_2H_4Br^+$); 93/95 (13, CH_2Br^+); 69 (68, CF_3^+); 57 (40, $C_3H_5O^+$); 43 (52, $C_2H_3O^+$); 41 (31, $C_3H_5^+$)}, (iii) a mixture (ca. 0.62 g, ca. 1.2 mmol, ca. 13%) containing a 2:1 adduct which was probably 1,3-bis[*N*,*N*-bis(trifluoromethyl)amino-oxy]-2-bromopropane (**19**) {MS (*m/z*): 455/457 (2%, $C_7H_4BrF_{12}N_2O_2^+$); 333 [15, $(CF_3)_2NOCHN(CF_3)_2^+$]; 288/290 (6, $C_5H_5BrF_6NO^+$); 272/274 (9, $C_5H_5BrF_6N^+$); 258/260 (25, $C_4H_3BrF_6N^+$); 195 (4, $C_4H_3F_6NO^+$); 182 [33, $(CF_3)_2NOCH_2^+$]; 179 [7, $(CF_3)_2NC_2H_3^+$]; 166 [57, $(CF_3)_2NCH_2^+$]; 120/122 (9, $C_3H_5Br^+$); 111 (12, $C_3H_2F_3O^+$); 107/109 (6, $C_2H_4Br^+$); 92/94 (22, $CHBr^+$); 78 (22, $C_2H_2F_2N^+$); 69 (100, CF_3^+); 57 (20, $C_3H_5O^+$); 44 (92, CO_2^+ and/or CH_2NO^+); 43 (60, $CHNO^+$); 41 (40, $C_3H_5^+$)}, (iv) 1-[*N*,*N*-bis(trifluoromethyl)amino]-2-[*N*,*N*-bis(trifluoromethyl)amino-oxy]-3-bromopropane (**18**) (ca. 0.37 g, ca. 0.83 mmol, ca. 9%) {MS (*m/z*): 347 [3, $(M-CH_2Br)^+$]; 258/260 [3, $(CF_3)_2NC_2H_3Br^+$]; 192 [6, $(CF_3)_2NC_3H_4^+$]; 182 [6, $(CF_3)_2NOCH_2^+$]; 179 [6, $(CF_3)_2NC_2H_3^+$]; 166 [100, $(CF_3)_2NCH_2^+$]; 120/122 (11, $C_3H_5Br^+$); 93/95 (8, CH_2Br^+); 78 (18, $C_2H_2F_2N^+$); 69 (33, CF_3^+); 43 (36, $C_2H_3O^+$); 41 (58, $C_3H_5^+$ and/or $C_2H_3N^+$); 39 (18, $C_3H_3^+$)}, and (v) 2-[*N*,*N*-bis(trifluoromethylamino-oxy]-1,3-dibromopropane (**16**) (ca. 0.69 g, ca. 1.86 mmol, ca. 21%).

3.5. Competition reactions of bis(trifluoromethyl)amino-oxyl (1) with mixtures of ethenes

(a) Ethene and chloroethene (general procedure)

A mixture of oxyl **1** (1.93 g, 11.5 mmol), ethene (1.60 g, 58.7 mmol) and chloroethene (3.67 g, 58.7 mmol), sealed in vacuo in a Pyrex bulb (ca. 5 dm^3) and stored at room temperature in light (2 d), gave (i) a −196 °C fraction (4.97 g) which was shown by IR and analytical GLC (8 m SE30 at 20 °C) to consist of unchanged ethene (1.64 g, 58.4 mmol, 99% recovered) and unchanged chloroethene (3.33 g, 53.3 mmol, 91% recovered) and (ii) a −23 °C fraction (2.25 g) which was shown by analytical GLC (2 m SE30 at 80 °C) and ^1H and ^{19}F NMR spectroscopy to consist of 1,2-bis[*N*,*N*-bis(trifluoromethyl)amino-oxy]ethane (0.10 g, 0.30 mmol, 5%) and 1,2-bis[*N*,*N*-bis(trifluoromethyl)-amino-oxy]chloroethane (2.15 g, 5.4 mmol, 94%).

Table 3
Elemental analysis and boiling point data

Compound	Found (%)				Calculated (%)				B.p. (°C)
	C	H	N	F	C	H	N	F	
6	19.7		5.7		19.9		5.8		121
8	20.2		6.4	66.3	20.0		6.4	66.3	86
9	17.2		7.0	70.3	17.45		6.8	70.6	127
10	41.7	2.3	5.2		41.9	2.3	5.4		195
11	19.6	0.5	6.8		19.7	0.7	6.6		118
12	17.3		7.1		17.3		6.8		190
14	20.8	0.9	7.2		20.6	1.0	6.9		84[a]

[a]Melting point.

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

Compound	^1H NMR δ (ppm)	^{19}F NMR δ (ppm)
6		22.0 [s, 6F, $(CF_3)_2N$]; 8.4 [s, 6F, $(CF_3)_2NO$]; −3.3 (mult., 2F, CF_2): −6.1 (mult., 2F, CF_2); −76.2 (mult., 1F, =CF); −79.6 (mult., 1F, =CF)
8		12.8 (s, 3F, NCF_3); 10.3 [br., 12F, $2(CF_3)_2NO$][a]
9		24.6 [s, 6F, $(CF_3)_2N$]; 10.0 [d, 6F, $(CF_3)_2NOCF$, J=12 Hz]; 9.2 [t, 6F, $(CF_3)_2NOCF_2$, J=9 Hz]; −8.4 (mult., 4F, CF_2N and CF_2O); −33.5 (mult., 1F, CFO)
10	7.06 (mult., 2H, o−C_6H_5); 6.94 (mult., 3H, *m*- and *p*-C_6H_5); 5.27 (br., 1H, CH−O)	10.2 [s, $(CF_3)_2NO$]
11	4.74 (t, 1H, CH−O, J=6 Hz); 4.36 (d, 1H, CH_2O, J=6 Hz)	8.95 [s, 6F, $(CF_3)_2NO$]; 8.15 [s, 6F, $(CF_3)_2NO$]
12		24.1 [s, 6F $(CF_3)_2N$]; 10.3 [br., 18F, $3(CF)_3)_2NO$]; −3.0 (mult., 2F, CF_2); −6.1 (mult., 2F, CF_2); −42.8 (mult., 1F, CF−O); −45.5 (mult., 1F, CF−O)
14	10.45 (s, 1H, CO_2H); 4.71 (t, 1H, CH−O, J=6 Hz); 4.26 (d, 1H, CH_2O, J=6 Hz)	9.7 [s, 6F, $(CF_3)_2NO$]; 9.0 [s, 6F, $(CF_3)_2NO$]

[a]Complex bands were also present for CF_2, CFO and CFN groups.

(b) Other mixtures of ethenes

Reactions of oxyl **1** in Pyrex bulbs (ca. 5 dm^3 unless stated otherwise) with mixtures of the ethenes CH_2=CCl_2 and CHCl=CCl_2 (10 dm^3 bulb), CH_2=CHCl and CHCl=CCl_2 (10 dm^3 bulb), CH_2=CH_2 and CH_2=CHF, CH_2=CHF and CH_2=CF_2, CH_2=CH_2 and CH_2=CF_2, CH_2=CHCl and CH_2=CCl_2, CHCl=CCl_2 and CCl_2=CCl_2 (300 cm^3 ampoule), CH_2=CF_2 and CCl_2=CCl_2 (10 dm^3 bulb) and CH_2=CCl_2 and CHF=CF_2 (10 dm^3 bulb) were carried out in light and the results are summarized in Table 2. The adduct fractions were examined by ^1H and ^{19}F NMR spectroscopy and by analytical GLC (2 m or 8 m SE30 at 20–80 °C) after calibration with adduct mixtures of known constitution.

3.6. Hydrolysis of 2,3-bis[N,N-bis(trifluoromethyl)amino-oxy]propanoyl chloride (11)

A mixture of the acid chloride **11** (1.21 g, 2.90 mmol) and water (25 cm^3), stirred vigorously (4 h) and the water removed in vacuo, gave a white acetone-soluble solid which was identified as 2,3-bis[*N*,*N*-bis-(trifluoromethyl)amino-oxy]propanoic acid (**14**) (nc) (1.18 g, 2.90 mmol, 100%).

For the new compounds, elemental analysis and boiling point data are given in Table 3, ^1H and ^{19}F NMR data in Table 4, and MS data in Table 5. The new compounds all showed bands in their IR spectra at (ν_{max}) (cm^{-1}): 1350–1190 (s, C−F str.); 1070–1030 (s, C−O−N str.); 980–960 (s, C−N str.); and ca. 710

Table 5
Mass spectra data

Compound	MS (*m/z*) (%, assignment)
6	330 {16, $[M-(CF_3)_2N]^+$}; 314 {18, $[M-(CF_3)_2NO]^+$}; 178 (10, $C_4F_6O^+$); 162 (23, $C_4F_6^+$); 131 (55, $C_3F_5^+$); 114 (17, $C_2F_4N^+$); 69 (100, CF_3^+)
8	659 [7, $(M-F)^+$]; 640 [9, $(M-2F)^+$]; 168 (19, $C_2F_6NO^+$); 130 (9, $C_2F_4NO^+$); 114 (16); 100 (10, $C_2F_4^+$); 69 (100); 47 (26, COF^+)
9	417 {22, $[M-(CF_3)_2NCF_2]^+$}; 401 {27, $[M-(CF_3)_2NOCF_2]^+$; 351 (10, $C_6F_{15}N_2O^+$); 268 (15, $C_4F_{10}NO^+$); 180 (10, $C_3F_6NO^+$); 69 (100)
10	257 (59, $C_9H_5F_6NO^+$); 180 (47, $C_{14}H_{12}^+$); 179 (21, $C_{14}H_{11}^+$); 178 (13, $C_{14}H_{10}^+$); 165 (11, $C_3HF_6N^+$); 105 (100, $C_7H_5O^+$); 77 (21, $C_6H_5^+$); 69 (29)
11	363 [28, $(M-COCl)^+$]; 230/232 (18, $C_4H_3ClF_6NO^+$); 182 (24, $C_3H_2F_6NO^+$); 168 (10); 114 (11); 94 (12, $C_2H_2F_2NO^+$); 69 (100), 63 (17, $C_2HF_2^+$); 50 (12, CF_2^+); 49/51 (16, CH_2Cl^+); 43 (18, $CHNO^+$)
12	799 [2, $(M-F)^+$]; 666 {3, $[M-(CF_3)_2N]^+$}; 650 {2, $[M-(CF_3)_2NO]^+$}; 429 (8, $C_7F_{15}N_2O_2^+$); 268 (9, $C_4F_{10}NO^+$); 218 [12, $(CF_3)_2NOCF_2^+$]; 202 [59, $(CF_3)_2NCF_2^+$]; 180 (18, $C_3F_6NO^+$); 168 (58); 130 (21); 114 (64); 69 (100)
14	363 [2, $(M-CO_2H)^+$]; 240 {3, $[M-(CF_3)_2NO]^+$}, 153 (12, $C_2F_6NH^+$); 133 (46, $C_2F_5N^+$); 114 (49); 69 (100); 50 (25); 44 (71, CH_2NO^+/CO_2^+) 43 (24, $CHNO^+$)

(m–s, CF_3 def.); compounds **11** and **14** also showed bands at 1790 and 1745 (s, C=O str.) cm^{-1}, respectively, and compound **14** an additional band at 3310 (s, O–H str.) cm^{-1}.

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