

Nitroxide Chemistry. Part 20.¹ *N,N*-Bis(trifluoromethyl)hydroxylamine as a Carbocation Trapping Agent

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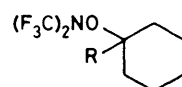
Aliphatic and alicyclic alkenes and alcohols react with an excess of *N,N*-bis(trifluoromethyl)hydroxylamine in the presence of either a catalytic or a stoichiometric amount of 98% sulphuric acid to give (bistrifluoromethylamino-oxy)-derivatives in good yields. Under the conditions of these reactions, products arising from carbocation rearrangement are obtained from cycloheptene, 1-methylcycloheptene, cyclo-octene, 1-methylcyclo-octene, 3-methylbutan-2-ol, 2-methylbut-1-ene, 2-methylpent-1-ene, and 4-methylpent-1-ene, but not from cyclopentene, 1-methylcyclopentene, cyclohexene, 1-methylcyclohexene, or norbornene. Norbornadiene gives 3-(bistrifluoromethylamino-oxy)nortricyclene as the major product, together with *exo*-5-(bistrifluoromethylamino-oxy)-norborn-2-ene. 2,2-(Bistrifluoromethylamino-oxy)butane is the sole product from the reaction of but-2-yne.

INTEREST in *N,N*-bis(trifluoromethyl)hydroxylamine² has centred mainly on its oxidation to the stable radical bis(trifluoromethyl)nitroxide,³⁻⁵ the formation of complexes with amines⁶ and caesium fluoride,⁷ and the fact that, being a weak acid,⁷ it can be converted into a sodium salt on treatment with sodium hydroxide,² or sodium hydride.⁸ The isolated observation in 1975⁹ that the hydroxylamine reacts with isobutene in the presence of sulphuric acid to give 2-(bistrifluoromethylamino-oxy)-2-methylpropane in 85% yield suggested that trapping of a carbocation by $(\text{CF}_3)_2\text{NOH}$ could provide an efficient route to $(\text{CF}_3)_2\text{NO}$ -substituted hydrocarbons. Previously this type of compound has been prepared by attack of bistrifluoromethylnitroxide on acyclic and alicyclic alkanes, but complex product mixtures are frequently observed due to disubstitution and formation of carbonyl compounds.^{9,10} We now describe some reactions of alkenes and alcohols with the hydroxylamine in the presence of 98% sulphuric acid.

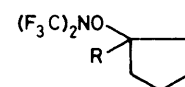
RESULTS AND DISCUSSION

Dropwise addition of cyclohexene into a mixture of *N,N*-bis(trifluoromethyl)hydroxylamine (2 mol equiv.) and 98% sulphuric acid (1 mol equiv.) at room temperature gave bis(trifluoromethylamino-oxy)cyclohexane (1),

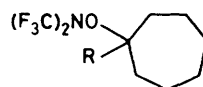
together with a small amount of a dark-brown oil shown by ¹H n.m.r. spectroscopy and mass spectrometry to be a mixture of dimers and some trimers of cyclohexene. The yield of (1) was 90% after 8 h, and this did not improve significantly after a further 28 h. When a catalytic amount of acid was used under similar conditions the yield of (1) was reduced considerably, and the alkene telomers became the major products (see Table).



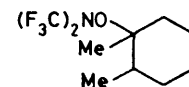
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(2) R = Me



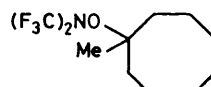
(3) R = H
(4) R = Me



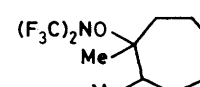
(5) R = H
(6) R = Me



(7)

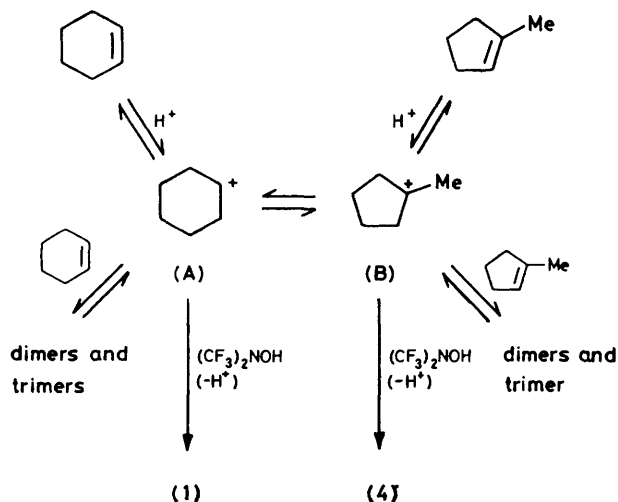


(8) R = H
(10) R = Me



(9)

SCHEME



Under conditions of high acid concentration the concentration of cyclohexyl cation will increase and that of the cyclohexene will decrease favouring capture of the carbocation by the hydroxylamine, which is not protonated even in strongly acidic media (see Scheme). At low acid concentration the more nucleophilic alkene competes effectively for the carbocation even though the hydroxylamine is still present in slightly more than 2 : 1

molar excess. Under similar conditions of low acid concentration 1-methylcyclohexene gives a high yield of 1-(bistrifluoromethylamino-oxy)-1-methylcyclohexane (2), reflecting the increased stability of the tertiary carbocation. Similar trends can be seen in the results obtained with cyclopentene and methylcyclopentene which give bis(trifluoromethylamino-oxy)cyclopentane (3) and 1-(bistrifluoromethylamino-oxy)-1-methylcyclopentane (4), respectively (see Table). In none of the reactions of cyclohexene, 1-methylcyclohexene, and 1-methylcyclopentene was there any evidence of Wagner-Meerwein rearrangement products. The interconversion of the methylcyclopentyl cation (A) (see Scheme) and the cyclohexyl cation (B) is a well studied reaction in strong acid media,¹¹ and $\Delta H^\ddagger_{B \rightarrow A}$ is *ca.* 17–18 kcal mol⁻¹.^{*} A recent calorimetric study¹² suggests that the tertiary cation (B) may only be 5–6 kcal mol⁻¹ more stable than the secondary cation (A), implying a value of $\Delta H^\ddagger_{A \rightarrow B}$ of 12–13 kcal mol⁻¹. There are many approximations implicit in arriving at this value, but the results suggest that rearrangement reactions having ΔH^\ddagger values of this magnitude will be quenched by (CF₃)₂NOH under the conditions employed. It is noticeable that cycloheptene under conditions of both low and stoichiometric acid concentrations gives a mixture of (bistrifluoromethylamino-oxy)cycloheptane (5) and the rearrangement product 1-(bistrifluoromethylamino-oxy)-1-methylcyclohexane (2). This implies that ΔH^\ddagger for the rearrangement of cycloheptyl cation to 1-methylcyclohexyl cation is considerably less than $\Delta H^\ddagger_{A \rightarrow B}$. Accurate data are not available for the relative energies of the cycloheptyl and 1-methylcyclohexyl cations, but if the increase in strain energy on going from a C₆ to a C₇ ring is similar in magnitude to that determined for cyclohexane and methylcyclohexane (*i.e.* *ca.* 7 kcal mol⁻¹),¹³ then the 1-methylcyclohexyl cation could be at least 12 kcal mol⁻¹ more stable than the cycloheptylium ion. This could have the effect of reducing ΔH^\ddagger for the cycloheptyl to methylcyclohexyl cation rearrangement to <10 kcal mol⁻¹. A mixture of 1-(bistrifluoromethylamino-oxy)-1-methylcycloheptane (6) and the rearrangement product 1-(bistrifluoromethylamino-oxy)-1,2-dimethylcyclohexane (7) is also obtained from the reaction between 1-methylcycloheptene and (CF₃)₂NOH with a catalytic amount of sulphuric acid. Cyclo-octene, under similar conditions, gives mainly 1-(bistrifluoromethylamino-oxy)cyclo-octane (8) and some 1-(bistrifluoromethylamino-oxy)-1-methylcycloheptane (6), together with a trace of a second rearrangement product believed to be 1-(bistrifluoromethylamino-oxy)-1,2-dimethylcyclohexane (7). The rearrangement product 1-(bistrifluoromethylamino-oxy)-1,2-dimethylcycloheptane (9) and 1-(bistrifluoromethylamino-oxy)-1-methylcyclo-octane (10) have also been isolated from the reaction of 1-methylcyclo-octane. These results imply that the ΔH^\ddagger values for the rearrangement of a cyclic secondary C₈ cation to a cyclic tertiary C₇ cation and of a cyclic tertiary C₈ cation

to a cyclic tertiary C₇ cation are both small, and probably <10 kcal mol⁻¹.

Norbornene reacts with (CF₃)₂NOH and sulphuric acid (molar ratio 1 : 2 : 1) at room temperature to give mainly *exo*-2-(bistrifluoromethylamino-oxy)norbornane (11) and only a trace of the *endo*-isomer (12). This product distribution is similar to those reported for additions of hydrogen chloride¹⁴ and acetic acid¹⁵ to norbornene. Reaction between norbornadiene and (CF₃)₂NOH (molar ratio 1 : 2) in the presence of a catalytic amount of sulphuric acid gives 3-(bistrifluoromethylamino-oxy)nortricyclene (13) as the major product, together with *exo*-5-(bistrifluoromethylamino-oxy)norborn-2-ene (14). An increase in the molar ratio of norbornadiene to hydroxylamine to 1 : 4 caused no significant change in the product distribution. Surprisingly, when the reaction between norbornadiene and (CF₃)₂NOH (molar ratio 1 : 2) was carried out under conditions of high acid concentration (1 mol equiv. of H₂SO₄), the major product was a dark brown oil, shown by i.r. spectroscopy and mass spectrometry to be mainly dimers of norbornadiene having some (CF₃)₂NO- groups incorporated, and mixed with trimers and tetramers of the diene; the yield of (13) from this reaction was <2% and 74% of the hydroxylamine was recovered. Authentic samples of compounds (13) and (14) were synthesised by reaction of a mixture containing 5-chloronorborn-2-ene (76%) and 3-chloronortricyclene (24%) with di(bistrifluoromethylamino-oxy)mercury.

Secondary and tertiary, but not primary, alcohols can also be used for these reactions with *N,N*-bistrifluoromethylhydroxylamine (see Table). A 76% yield of 2-(bistrifluoromethylamino-oxy)-2-methylpropane is obtained from 2-methylpropan-2-ol and the hydroxylamine in the presence of sulphuric acid at room temperature. Under similar conditions 2-methylpropan-1-ol gave <1% yield of the same product and 99% of the starting materials were recovered. The major isomer from 3-methylbutan-2-ol was the rearrangement product 2-(bistrifluoromethylamino-oxy)-2-methylbutane (15) and the yield of 2-(bistrifluoromethylamino-oxy)-3-methylbutane (16) was only 14%. Compound (15) has been prepared in almost quantitative yield by reaction of 2-methylbut-1-ene and (CF₃)₂NOH in the presence of sulphuric acid. Enthalpy data for the cations Me₂CH- \dot{C} HMe and Me₂ \dot{C} CH₂Me are not available, but it seems reasonable that their relative energies will be close to those of the *t*-butyl and *s*-butyl cations. Experimental determination by two independent methods^{16,17} indicates that in solution the *s*-butyl cation is *ca.* 14.5 kcal mol⁻¹ less stable than the *t*-butyl cation. Isomerization of the initially formed cation Me₂CH \dot{C} HMe to the cation Me₂ \dot{C} CH₂Me involves an extremely facile secondary-tertiary 1,2-H shift (ΔH^\ddagger 3–4 kcal mol⁻¹¹⁸), and it is not surprising that this cannot be quenched in the presence of (CF₃)₂NOH. Conversely, the isomerisation of Me₂ \dot{C} CH₂Me to Me₂CH \dot{C} HMe will have an energy barrier of *ca.* 17 kcal mol⁻¹, accounting for the virtual absence of

* 1 cal = 4.184 J.

compound (19) among the products from 2-methylbut-1-ene. For similar reasons 2-methylpent-1-ene gives a 98% yield of 2-(bistrifluoromethylamino-oxy)-2-methylpentane (17), and only a trace of 3-(bistrifluoromethylamino-oxy)-2-methylpentane (18). In the reaction of 4-methylpent-1-ene with $(\text{CF}_3)_2\text{NOH}$ the initially formed cation $\text{Me}_2\text{CHCH}_2\overset{\ddagger}{\text{C}}\text{HMe}$ can undergo a rapid secondary-secondary cation 1,2-H shift (ΔH^\ddagger 2—4 kcal mol⁻¹¹⁸) to the ion $\text{Me}_2\text{CH}\overset{\ddagger}{\text{C}}\text{HCH}_2\text{Me}$, which can rearrange further either by a secondary-tertiary 1,2-H shift (ΔH^\ddagger 3—4 kcal mol⁻¹¹⁴) to $\text{Me}_2\overset{\ddagger}{\text{C}}\text{CH}_2\text{CH}_2\text{Me}$, or by a methide shift (ΔH^\ddagger 3—4 kcal mol⁻¹¹⁸) to $\text{Me}\overset{\ddagger}{\text{C}}\text{HCHMeCH}_2\text{Me}$. These reactions are too fast to be quenched by $(\text{CF}_3)_2\text{NOH}$ and the product mixture contained mainly compound (17), and smaller amounts of (18) and 2-(bistrifluoromethylamino-oxy)-4-methylpentane (19), under conditions of both catalytic and stoichiometric acid concentrations.

But-2-yne reacts slowly with *N,N*-bistrifluoromethylhydroxylamine in the presence of sulphuric acid (molar ratio 1 : 2 : 1), and after 4 days at room temperature gives 2,2-(bistrifluoromethylamino-oxy)butane (20) in 81% yield. G.l.c. monitoring of this reaction showed no evidence for the intermediate formation of $\text{MeCH}=\text{CMe}\{[\text{ON}(\text{CF}_3)_2]^+\}$, implying that this is protonated rapidly under the reaction conditions.

EXPERIMENTAL

N,N-Bistrifluoromethylhydroxylamine¹⁹ and di(bistrifluoromethylamino-oxy)mercury(II)²⁰ were prepared by previously reported procedures. Cycloheptene²¹ and 1-methylcyclopentene²¹ were synthesised by dehydration of the corresponding alcohols; other alkenes used were commercial samples purified by passage down a column of

activated alumina followed by distillation and storage over sodium.

Typical Procedure for the Reactions of N,N-Bistrifluoromethylhydroxylamine with Alkenes and Alcohols.—The alkene or alcohol was added dropwise over 3—4 h to a magnetically stirred mixture of 98% sulphuric acid and *N,N*-bistrifluoromethylhydroxylamine contained in a 200 cm³ three-necked flask fitted with a cold-finger condenser maintained at -78 °C. Volatile products were transferred to a conventional vacuum apparatus and were separated by fractional condensation through traps cooled at -42, -78, -130, and -196 °C. The products collected in the -42 and -78 °C traps and pure samples were obtained by preparative g.l.c. (Pye 104 instrument, 4 m SE 30 or 5 m TXP columns), before examination by i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer), n.m.r. (Perkin-Elmer R20 or R32 or Varian HA 100 spectrometers; ¹⁹F n.m.r. chemical shifts are in p.p.m. to low field of external trifluoroacetic acid), and mass spectrometry (AEI MS 902 instrument). The results are given in the Table and the products were identified from the following data. (*Bistrifluoromethylamino-oxy*)cyclohexane (1)²² (Found: C, 38.05; H, 4.3; F, 45.35; N, 5.65. C₆F₆H₁₁NO requires C, 38.25; H, 4.44; F, 45.4; N, 5.6%; ¹H n.m.r. δ (CDCl₃; p.p.m. to low field of external Me₄Si) 0.9—1.9 (10 H, complex multiplet, CH₂), 3.65 (1 H, br, CH); ¹⁹F n.m.r. δ -9.05 (s); *m/z* (no molecular ion) 83 {[M - (CF₃)₂NO]⁺, 95.4%}, 69 [(CF₃)⁺ and (C₅H₉)⁺, 25.2%], and 55 [(C₄H₇)⁺, 100%].

1-(*Bistrifluoromethylamino-oxy*)-1-methylcyclohexane (2)²² (Found: C, 40.9; H, 5.2; F, 42.9; N, 5.5. C₉F₆H₁₃NO requires C, 40.8; H, 4.9; F, 43.0; N, 5.3%; ¹H n.m.r. δ (neat liquid; p.p.m. relative to external *p*-dichlorobenzene) +5.2 to +5.6 (10 H, complex m, CH₂) and +5.8 (3 H, s, CH₃); ¹⁹F n.m.r. δ -11.45 (s); *m/z* (no parent ion) 97 {[M - (CF₃)₂NO]⁺, 93.5%}, 69 [(CF₃)⁺ and (C₅H₉)⁺, 56.0%], 55 [(C₄H₇)⁺, 100%], 43 [(C₃H₇)⁺, 88.3%], and 41 [(C₃H₅)⁺, 38.2%].

Reactions of alkenes and alcohols with *N,N*-bistrifluoromethylhydroxylamine

Cycloalkene (mmol)	98% H ₂ SO ₄ (mmol)	(CF ₃) ₂ NOH (mmol)	Reaction time (h)	Alkene Conversion (%) ^a	1 : 1 Adducts [%] ^b	Telomers (%) ^b
Cyclohexene (48.77)	0.18	58.17	36	72	(1) [20]	50
Cyclohexene (50.0)	50.0	100.0	8	99	(1) [90]	8
Cyclohexene (50.0)	50.0	100.0	36	99	(1) [94]	5
1-Methylcyclohexene (50.0)	0.18	100.0	6	82	(2) [66]	34
Cyclopentene (50.0)	0.18	100.0	6	70	(3) [50]	50
Cyclopentene (50.0)	50.0	100.0	6	99	(3) [90]	10
1-Methylcyclopentene (49.15)	0.18	61.42	36	60	(4) [22]	78
1-Methylcyclopentene (43.0)	0.18	148.0	6	65	(4) [83]	17
1-Methylcyclopentene (50.0)	50.0	100.0	6	86	(4) [61]	38
Cycloheptene (50.0)	0.18	100.0	6	84	(5) [65], (2) [10]	20
Cycloheptene (50.0)	50.0	100.0	6	99	(5) [78], (2) [17]	5
1-Methylcycloheptene (6.36)	0.1	12.72	6	89	(6) [75], (7) [15]	9
Cyclo-octene (50.0)	0.18	100.0	6	92	(8) [81], (6) [11], (7) [trace]	7
1-Methylcyclo-octene (14.52)	0.1	28.99	6	83	(9) [8], (10) [76]	16
Norbornene (50.0)	50.0	100.0	6	97	(11) [81], (12) [≤1]	18
Norbornadiene (50.0)	0.18	100.0	6	67	(13) [77], (14) [17]	6
Norbornadiene (50.0)	50.0	100.0	6	100	(13) [2]	98
Norbornadiene (37.5)	0.18	150.0	0.5	42	(13) [80], (14) [18]	2
3-Methylbutan-2-ol (50.0)	50.0	100.0	6	90	(15) [75], (16) [14]	11
2-Methylbut-1-ene (50.0)	50.0	100.0	6	99	(15) [99], (16) [≤1]	<1
2-Methylpent-1-ene (50.0)	0.18	100.0	6	99	(17) [98], (18) [1]	1
4-Methylpent-1-ene (50.0)	0.18	100.0	6	34	(17) [93], (18) [1], (19) [2]	4
4-Methylpent-1-ene (50.0)	50.0	100.0	6	88	(17) [48], (18) [10], (19) [7] ^c	29

^a Based on alkene recovered. ^b Based on alkene consumed. ^c Two other (CF₃)₂NO-substituted compounds of molecular formula C₈H₁₃F₆NO were also detected in the mixture from this reaction.

(Bistrifluoromethylamino-oxy)cyclopentane (3)²² (Found: C, 35.6; H, 4.1; N, 6.0; F, 48.6. $C_7F_6H_9NO$ requires C, 35.4; H, 3.8; N, 5.9; F, 48.1%); 1H n.m.r. δ (neat liquid; p.p.m. relative to external *p*-dichlorobenzene) +2.56 (1 H, br, CH) and +5.1 to +5.7 (8 H, complex m, CH_2); ^{19}F n.m.r. δ -9.5 (s); m/z 237 (M^{++} , 0.1%), 69 $[(CF_3)^+ \text{ and } (C_5H_9)^+]$, 100%, and 41 $[(C_3H_5)^+]$, 75.7%.

1-(Bistrifluoromethylamino-oxy)-1-methylcyclopentane (4)²² (Found: C, 37.7; H, 4.3; F, 44.1; N, 5.5. $C_8F_6H_{11}NO$ requires C, 38.25; H, 4.4; F, 45.4; N, 5.6%); 1H n.m.r. (neat liquid; p.p.m. relative to external *p*-dichlorobenzene) +5.1 to +5.8 (8 H, complex m, CH_2) and +5.9 (3 H, s, CH_3); ^{19}F n.m.r. δ -11.1 (s); m/z (no molecular ion) 83 $\{[M - (CF_3)_2NO]^+, 98.2\%\}$, 69 $[(CF_3)^+ \text{ and } (C_5H_9)^+]$, 43.1%, 55 $[(C_4H_7)^+]$, 82.6%, 43 $[(C_3H_7)^+]$, 100%, and 41 $[(C_3H_5)^+]$, 64.9%. This compound was identical with that obtained in 74% yield from the reaction of 1-chloro-1-methylcyclopentane (20 mmol) and di(bistrifluoromethylamino-oxy)mercury (17 mmol) at room temperature.

(Bistrifluoromethylamino-oxy)cycloheptane (5)²² 1H n.m.r. δ (neat liquid; p.p.m. relative to external *p*-dichlorobenzene) +2.98 (1 H, br, CH) and +4.9 to +5.9 (12 H, complex m, CH_2); ^{19}F n.m.r. δ -10 (s); m/z (no molecular ion) 97 $\{[M - (CF_3)_2NO]^+, 58.0\%\}$, 69 $[(CF_3)^+ \text{ and } (C_7H_{13})^+]$, 19.8%, 55 $[(C_4H_7)^+]$, 100%, 43 $[(C_3H_7)^+]$, 13.4%, and 41 $[(C_3H_5)^+]$, 31.0%.

1-(Bistrifluoromethylamino-oxy)-1-methylcycloheptane (6), 1H n.m.r. δ (neat liquid; p.p.m. to low field of external Me_4Si) 1.3 (3 H, s, CH_3) and 1.6 (12 H, complex m, CH_2); ^{19}F n.m.r. δ -13.2 (s); m/z (no molecular ion) 111 $\{[M - (CF_3)_2NO]^+, 57.4\%\}$, 97 $[(C_7H_{13})^+]$, 18.7%, 69 $[(CF_3)^+ \text{ and } (C_7H_{13})^+]$, 100%, 55 $[(C_4H_7)^+]$, 72.5%, 43 $[(C_3H_7)^+]$, 94.3%, and 41 $[(C_3H_5)^+]$, 49.3%.

1-(Bistrifluoromethylamino-oxy)-1,2-dimethylcyclohexane (7), m/z (no molecular ion) 111 $\{[M - (CF_3)_2NO]^+, 4.8\%\}$, 96 $[(C_6H_{12})^+]$, 1.8%, 95 $[(C_6H_{11})^+]$, 30.2%, 82 $[(C_6H_{10})^+]$, 12.4%, 81 $[(C_6H_9)^+]$, 23.4%, 79 $[(C_6H_7)^+]$, 11.0%, 71 $[(C_5H_{11})^+]$, 100%, 55 $[(C_4H_7)^+]$, 31.4%, 43 $[(C_3H_7)^+]$, 75.4%, and 41 $[(C_3H_5)^+]$, 43.5%.

Bis(trifluoromethylamino-oxy)cyclo-octane (8), 1H n.m.r. δ (neat liquid; p.p.m. relative to external *p*-dichlorobenzene) +2.98 (1 H, br, CH), +5.23 (4 H, complex m, CH_2), and +5.52 (10 H, br, s, CH_2); ^{19}F n.m.r. δ -10 (s); m/z (no molecular ion) 111 $\{[M - (CF_3)_2NO]^+, 25.1\%\}$, 69 $[(CF_3)^+ \text{ and } (C_8H_{15})^+]$, 100%, 55 $[(C_4H_7)^+]$, 51.7%, 43 $[(C_3H_7)^+]$, 12.2%, and 41 $[(C_3H_5)^+]$, 37.5%.

1-(Bistrifluoromethylamino-oxy)-1,2-dimethylcycloheptane (9), m/z (no molecular ion) 125 $\{[M - (CF_3)_2NO]^+, 44.1\%\}$, 109 $[(C_7H_{13})^+]$, 2.5%, 69 $[(CF_3)^+ \text{ and } (C_7H_{13})^+]$, 93.9%, 55 $[(C_4H_9)^+]$, 59.9%, 43 $[(C_3H_7)^+]$, 100%, 41 $[(C_3H_5)^+]$, 44.3%.

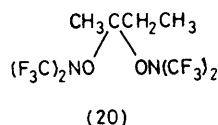
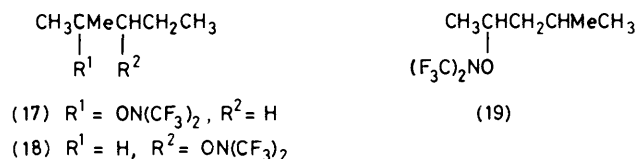
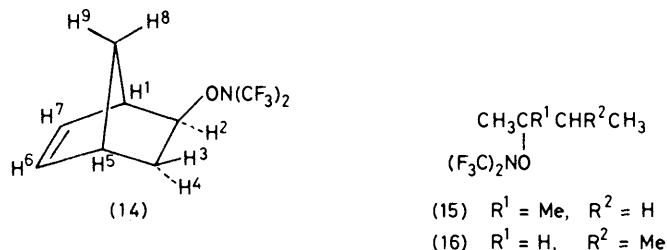
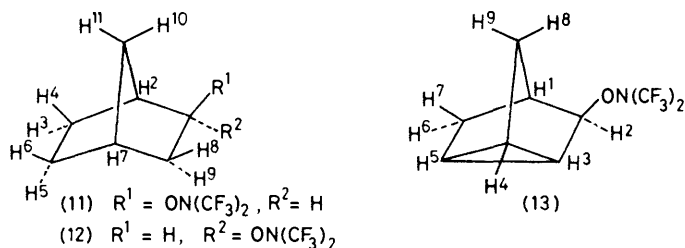
1-(Bistrifluoromethylamino-oxy)-1-methylcyclo-octane (10), 1H n.m.r. δ (neat liquid, p.p.m. to low field of external Me_4Si) 1.22 (3 H, singlet, CH_3) and 1.34 to 2.26 (14 H, complex m, CH_2); ^{19}F n.m.r. δ -11.75 (s); m/z (no molecular ion) 125 $\{[M - (CF_3)_2NO]^+, 32.8\%\}$, 109 $[(C_8H_{13})^+]$, 4.1%, 83 $[(C_6H_{11})^+]$, 34.2%, 69 $[(C_6H_9)^+ \text{ and } (CF_3)^+]$, 81.1%, 55 $[(C_4H_7)^+]$, 52.7%, 43 $[(C_3H_7)^+]$, 100%, and 41 $[(C_3H_5)^+]$, 40.8%.

exo-2-(Bistrifluoromethylamino-oxy)norbornane (11)²² (Found: C, 40.9; H, 4.1; F, 43.2; N, 5.4. $C_9F_6H_{11}NO$ requires C, 41.1; H, 4.2; F, 43.4; N, 5.3%); 1H n.m.r. δ (neat liquid; p.p.m. to low field of external Me_4Si) 1.08 (2 H, t, 10-H and 11-H), 1.28 to 1.72 (6 H, complex m, 3-H, 4-H, 5-H, 6-H, 8-H, and 9-H), 2.25 (1 H, s, 7-H), 2.51 (1 H, s,

2-H), and 4.0 (1 H, t, 1-H); ^{19}F n.m.r. δ -9.6 (s); m/z (no molecular ion) 95 $\{[M - (CF_3)_2NO]^+, 100\%\}$, 81 $[(C_6H_9)^+]$, 1.7%, 67 $[(C_5H_7)^+]$, 39.2%, 53 $[(C_4H_5)^+]$, 3.9%, and 39 $[(C_3H_3)^+]$, 8.0%.

endo-2-(Bistrifluoromethylamino-oxy)norbornane (12)²² m/z (no molecular ion) 95 $\{[M - (CF_3)_2NO]^+, 100\%\}$, 81 $[(C_6H_9)^+]$, 2.3%, 67 $[(C_5H_7)^+]$, 41.4%, 53 $[(C_4H_5)^+]$, 4.5%, and 39 $[(C_3H_3)^+]$, 10.5%.

3-(Bistrifluoromethylamino-oxy)nortricyclene (13) (Found: C, 41.0; H, 3.7; F, 43.4; N, 5.5. $C_9F_6H_9NO$ requires C, 41.4; H, 3.5; F, 43.6; N, 5.35%); 1H n.m.r. δ (neat liquid; p.p.m. relative to external *p*-dichlorobenzene) +2.8 (1 H, s, 2-H), +5.01 (2 H, m, 1-H and 4-H), and +5.65 (6 H, m, 3-H, 5-H, 6-H, 7-H, 8-H, and 9-H); ^{19}F n.m.r. δ -9.8 (s); m/z 261 (M^{++} 0.2%), 93 $\{[M - (CF_3)_2NO]^+, 100\%\}$, 91 $[(C_7H_7)^+]$, 39.5%, 81 $[(C_6H_9)^+]$, 10.4%, 79 $[(C_6H_7)^+]$, 16.6%, 77 $[(C_6H_5)^+]$, 41.9%, 69 $[(C_5H_9)^+]$ and $(CF_3)^+$, 18.8%, 66 $[(C_5H_6)^+]$, 7.3%, 41 $[(C_3H_3)^+]$, 11.3%, and $[(C_3H_3)^+]$, 100%.



exo-5-(Bistrifluoromethylamino-oxy)norborn-2-ene (14), 1H n.m.r. δ (CCl_4 ; p.p.m. to low field of external Me_4Si) 1.4 to 2.0 (4 H, m, 3-H, 4-H, 8-H, and 9-H), 2.9 (2 H, m, 1-H and 5-H), 3.67 (1 H, m, 2-H), and 6.05 (2 H, m, 6-H and 7-H); ^{19}F n.m.r. δ -11.12 (s); m/z 261 (M^{++} , 0.6%), 93 $\{[M - (CF_3)_2NO]^+, 52.4\%\}$, 91 $[(C_7H_7)^+]$, 19.5%, 79 $[(C_6H_7)^+]$,

15.5%], 77 [(C₆H₅)⁺, 22.0%], 69 [(CF₃)⁺ and (C₅H₉)⁺, 40.1%], 67 [(C₅H₉)⁺, 19.6%], 66 [(C₅H₉)⁺, 100%], 65 [(C₅H₉)⁺, 12.3%], 41 [(C₃H₇)⁺, 10.6%], and 39 [(C₃H₇)⁺, 13.4%].

2-(Bistrifluoromethylamino-oxy)-2-methylbutane (15) showed spectroscopic data identical with those reported previously.¹⁰

2-(Bistrifluoromethylamino-oxy)-3-methylbutane (16), *m/z* 239 (*M*⁺, 0.5%), 223 {[*M* - CH₃]⁺, 0.4%}, 196 {[*M* - C₃H₇]⁺, 3.9%}, 71 {[*M* - (CF₃)₂NO]⁺, 8.7%}, 69 [(CF₃)⁺ and (C₅H₉)⁺, 21.5%], 57 [(C₄H₉)⁺, 18.3%], 55 [(C₄H₉)⁺, 9.6%], 43 [(C₃H₇)⁺, 100%], 41 [(C₃H₇)⁺, 34.5%], and 39 [(C₃H₇)⁺, 10.8%].

2-(Bistrifluoromethylamino-oxy)-2-methylpentane (17), ¹H n.m.r. δ (neat liquid; p.p.m. relative to external *p*-dichlorobenzene) + 5.44 to + 5.86 (4 H, A₂B₂ m, CH₂CH₂), + 5.91 [6 H, s, (CH₃)₂C], and + 6.25 (3 H, t, CH₃CH₂, *J* 7 Hz); ¹⁹F n.m.r. δ - 11.4 (s); *m/z* (no molecular ion) 238 [(*M* - CH₃)⁺, 23.1%], 210 [(*M* - C₃H₇)⁺, 57.7%], 85 [(*M* - (CF₃)₂NO)⁺, 45.0%], 71 [(C₅H₁₁)⁺, 10.8%], 69 [(CF₃)⁺ and (C₅H₉)⁺, 23.6%], 58 [(C₄H₁₀)⁺, 44.5%], 57 [(C₄H₉)⁺, 13.7%], and [(C₃H₇)⁺, 100%].

3-(Bistrifluoromethylamino-oxy)-2-methylpentane (18), ¹H n.m.r. δ (CCl₄; p.p.m. relative to external *p*-dichlorobenzene) + 3.47 [1 H, q, CHON(CF₃)₂, *J* 7 Hz], + 5.06 [1 H, m, CH(CH₃)₂, + 5.5 (2 H, q, CH₂CH₃, *J* 7 Hz), + 5.87 [6 H, d, (CH₃)₂CH, *J* 7 Hz], and + 6.2 (3 H, t, CH₃CH₂); ¹⁹F n.m.r. δ - 12.6 (s); *m/z* (no molecular ion) 224 [(*M* - C₂H₅)⁺, 7.8%], 210 [(*M* - C₃H₇)⁺, 21.1%], 85 [(*M* - (CF₃)₂NO)⁺, 12.6%], 71 [(C₅H₁₁)⁺, 7.0%], 69 [(CF₃)⁺ and (C₅H₉)⁺, 22.1%], 58 [(C₄H₁₀)⁺, 34.4%], 57 [(C₄H₉)⁺, 55.5%], and 43 [(C₃H₇)⁺, 100%].

2-(Bistrifluoromethylamino-oxy)-4-methylpentane (19), ¹H n.m.r. δ (CCl₄; p.p.m. relative to *p*-dichlorobenzene) + 3.1 [1 H, quint, CHON(CF₃)₂], + 5.4 [1 H, sept, CH(CH₃)₂, *J* 2 Hz], + 5.7 (2 H, m, CH₂), + 5.9 (3 H, d, (CH₃)₂CH), + 6.28 (3 H, doublet, (CH₃)₂CH), and + 6.28 (3 H, d, CH₃CH, *J* 7 Hz); ¹⁹F n.m.r. δ - 11.3 (s); *m/z* (no molecular ion) 252 [(*M* - H)⁺, 9.1%], 238 [(*M* - CH₃)⁺, 3.3%], 210 [(*M* - C₃H₇)⁺, 67.4%], 85 [(*M* - (CF₃)₂NO)⁺, 1.7%], 72 [(C₅H₁₂)⁺, 10.9%], 69 [(CF₃)⁺ and (C₅H₉)⁺, 10.5%], 58 [(C₄H₁₀)⁺, 55.2%], 57 [(C₄H₉)⁺, 100%], 43 [(C₃H₇)⁺, 60.6%], and 41 [(C₃H₇)⁺, 20.3%].

2,2-(Bistrifluoromethylamino-oxy)butane (20), ¹H n.m.r. δ (neat liquid; p.p.m. relative to external *p*-dichlorobenzene) + 5.0 (2 H, q, CH₂CH₃, *J* 7 Hz), + 5.25 (3 H, s, CH₃), and + 6.37 (3 H, t, CH₂CH₃); ¹⁹F n.m.r. δ - 7.1 (s); *m/z* (no molecular ion) 150 [(C₂HF₅NO)⁺, 14.7%], 81 [(C₂F₃)⁺, 20.5%], 69 [(CF₃)⁺, 100%], and 57 [(C₄H₉)⁺, 12.6%].

Reaction of a Mixture of 5-Chloronorborn-2-ene and 3-Chloronortricyclene with Di(bistrifluoromethylamino-oxy)mercury(II).—A mixture (8.10 g, 63.0 mmol) containing 5-chloronorborn-2-ene (76%) and 3-chloronortricyclene (24%) [prepared by bubbling HCl gas during 0.5 h into a solution of norbornadiene (12.0 g, 130.4 mmol) in *n*-pentane according to a previously reported procedure²³] was added to di-

(bistrifluoromethylamino-oxy)mercury(II) (16.91 g, 31.51 mmol) contained in a Pyrex reaction tube (300 cm³), which was then sealed under vacuum. After 5 days at room temperature the volatile products were distilled by fractional condensation and the components were separated by preparative g.l.c. to give (14) (7.70 g, 29.52 mmol, 78%) and (13) (2.12 g, 8.14 mmol, 22%), having i.r. and n.m.r. spectra identical with those of the compounds isolated from the reaction of norbornene with bistrifluoromethylhydroxylamine.

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