The synthesis of [bis(trifluoromethyl)amino-oxy]-substituted bromoalkanes and their conversion into Grignard reagents

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Abstract

Reaction of the nitroxide $(CF_3)_2NO\cdot$ (**1**) with the bromoalkanes RBr (R = Me, Et and Pr^n) (1:1 molar ratio) gives the compounds $(CF_3)_2NOCH_2Br$ (**4a**) (69%), $(CF_3)_2NOCHBrMe$ (**4b**) (93%) + $(CF_3)_2NOCHBrCH_2ON(CF_3)_2$ (**6**) (6%) and $(CF_3)_2NOCHBrEt$ (**4c**) (16%) + $(CF_3)_2NOCHMeCH_2Br$ (**7**) (76%) + $(CF_3)_2NOCH_2CHBrMe$ (**8**) (3%), respectively, together with the hydroxylamine $(CF_3)_2NOH$ (**3**). Treatment of the sodium salt $(CF_3)_2NONa$ (**2**) with the dibromoalkanes $Br(CH_2)_nBr$ ($n = 2$ and 3) (1:1 molar ratio) in diglyme affords mixtures of elimination and substitution products, i.e. $H_2C{=}CHBr$ + $(CF_3)_2NOCH_2CH_2Br$ (**9a**) + $(CF_3)_2NOCH_2CH_2ON(CF_3)_2$ (**10a**) (ratio 21:39:7) and $(CF_3)_2NOCH_2CH{=}CH_2$ (**12**) + $(CF_3)_2NO(CH_2)_3Br$ (**9b**) + $(CF_3)_2NO(CH_2)_3ON(CF_3)_2$ (**10b**) (ratio 22:43:9). The α-substituted compounds **4a** and **4b** do not form Grignard reagents in diethyl ether, those formed from the β-substituted compounds **7** and **9a** undergo elimination to give propene and ethene respectively, while that produced from the γ-substituted compound **9b** is stable at room temperature and reacts with the chlorosilane $MeSiCl_3$ to afford the compound $(CF_3)_2NO(CH_2)_3SiCl_2Me$ (**20**) (53%).

Introduction

The synthesis in excellent yield of the compounds $(CF_3)_2NOCX_3$ (X = Cl, 99.5%; X = Br, 98%) by reaction of the nitroxide $(CF_3)_2NO\cdot$ (**1**) with chloroform and bromoform, respectively, has been reported [1]. A general investigation of attack by nitroxide **1** on organic substrates [2] has been carried out in this Department; as part of this study, the reactions of **1** with the methanes CHF_3 and CHF_2Cl, the ethanes CH_3CH_2X (X = F and Cl) and CH_3CHF_2, and the 1,1,1-trifluoroethanes CF_3CH_2X (X = Cl and Br) and $CF_3CHClBr$ were carried out [3].

In the present work, the reactions of nitroxide **1** with the monobromoalkanes RBr(R = Me, Et and Pr^n) and of the dibromoalkanes $Br(CH_2)_nBr$ ($n = 2$ and 3) have been investigated with the object of synthesising [bis(trifluoromethyl)amino-oxy]-substituted bromoalkanes, which could be converted via their Grignard reagents into dichlorosilyl compounds for use in polymerisation studies.

Experimental

Starting materials

The bromoalkanes and methyltrichlorosilane were commercial samples and the purity of each was checked (IR, NMR spectroscopy) before use. The nitroxide **1** was prepared by oxidation of the hydroxylamine **3** with silver(II) oxide [4] and the sodium salt **2** was made by dropwise addition of a solution of hydroxylamine **3** in anhydrous diethyl ether to a stirred suspension of sodium hydride in diethyl ether followed by removal of the ether *in vacuo* [5].

General techniques

The reactions involving nitroxide 1 were carried out *in vacuo* in Rotaflo tubes (*c.* 300 cm^3). Products were separated by fractional condensation *in vacuo* or GLC [Perkin-Elmer F21 or Aerograph Autoprep instruments using columns (2–6 m) of silicone SE30 or OVI oils (10–20% w/w) on Celite as indicated in the text] and were examined by IR spectroscopy (Perkin-Elmer 257 spectrophotometer), ^1H NMR spectroscopy [Perkin-Elmer R10 (60.0 MHz), Hitachi R20A (60.0 MHz) or Varian Associates HA100 (100.0 MHz) spectrometers; internal reference tetramethylsilane], ^{19}F NMR spectroscopy [Perkin-Elmer R10 (56.46 MHz) or Varian Associates HA100 (94.12 MHz) instruments; external reference trifluoroacetic acid] and mass spectrometry (AEI MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded using neat liquids or solutions in $CDCl_3$ (as stated in the text); chemical shifts to low field of reference are designated positive.

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Molecular weights of gases were determined by Regnault's method and boiling points were measured by Siwoloboff's method.

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

(a) Bromomethane

A mixture of oxyl **1** (3.36 g, 20.0 mmol) and bromomethane (1.90 g, 20.0 mmol), heated *in vacuo* at 60 °C (7 d), gave only volatile material (5.05 g) which on fractional condensation *in vacuo* afforded (i) a non-condensable gas, identified (IR spectroscopy) as carbon monoxide (0.06 g, 2.1 mmol, 10%) (Analysis: Found: M, 28. Calc. for CO: M, 28); (ii) a −196 °C fraction (1.40 g), identified by coupled GLC (2 m SE30 at 20 °C)–IR methods as a mixture of *N,N*-bis(trifluoromethyl)amine (**5**) (0.25 g, 1.7 mmol, 9%) and unchanged bromomethane (1.15 g, 12.1 mmol, 60% recovered); and (iii) a red–brown liquid (3.59 g) which condensed at −78 °C and was reacted with styrene to estimate the bromine (0.16 g, 1.0 mmol, 25%); the remaining colourless liquid was separated by preparative-scale GLC (3.5 m SE30 at 40 °C) into its two components, *N,N*-bis(trifluoromethyl)hydroxylamine (**3**) (1.99 g, 11.8 mmol, 59%) and [bis(trifluoromethyl)amino-oxy]bromomethane (**4a**) (nc) (1.44 g, 5.5 mmol, 69%) (Analysis: Found: C, 13.7; H, 1.1%. $C_3H_2BrF_6NO$ requires: C, 13.8; H, 0.9%), b.p. 67 °C. ^{1}H NMR (neat) δ: 6.14 (s, CH_2) ppm. ^{19}F NMR δ: +9.45 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 261/263 (0.8%, M^+); 260/262 [1.0, $(M-H)^+$]; 182 [100.0, $(M-Br)^+$]; 109/111 (27.7, CH_2BrO^+); 93/95 (64.0, CH_2Br^+); and 69 (67.8, CF_3^+). IR ($\nu_{max.}$) (cm^{-1}): 3086 and 3067 (w) (C–H str.); 1351–1199 (vs) (C–F str.); 1046 (s) (C–O–N str.); 968 (s) (C–N str.); and 712 (s) (CF_3 def.).

(b) Bromoethane

A mixture of oxyl **1** (3.36 g, 20.0 mmol) and bromoethane (2.18 g, 20.0 mmol), stored *in vacuo* at room temperature (12 h), gave only volatile material (5.54 g) which on fractional condensation *in vacuo* afforded (i) a −196 °C fraction (0.1 g) which was identified (IR spectroscopy) as a mixture of *N,N*-bis(trifluoromethyl)-amine (**5**) and perfluoro-2-azapropene; (ii) a −78 °C fraction (3.91 g) which was separated by preparative-scale GLC (3.5 m SE30 at 65 °C) into its three components identified as *N,N*-bis(trifluoromethyl)hydroxylamine (**3**) (1.64 g, 9.7 mmol, 48%), unchanged bromoethane (1.16 g, 10.6 mmol, 53% recovered) and 1-[bis(trifluoromethyl)amino-oxy]-1-bromoethane (**4b**) (nc) (1.11 g, 4.0 mmol, 43%) (Analysis: Found: C, 17.6; H, 1.6; F, 41.6; N, 5.0%. $C_4H_4BrF_6NO$ requires: C, 17.4; H, 1.5; F, 41.3; N, 5.1%), b.p. 105 °C. ^{1}H NMR (neat) δ: 6.12 (q, 1H, CHO, J=7 Hz); and 2.02 (d, 3H, CH_3, J=7 Hz) ppm. ^{19}F NMR δ: +9.13 (mult., 3F, CF_3); and +10.8 (mult., 3F, CF_3) ppm. MS *m/z*: 212/214 (11.5%, $C_2H_3BrF_4NO^+$); 196 [100.0, $(M-Br)^+$]; 107/109 (48.3, $C_2H_4Br^+$); 69 (84.5, CF_3^+); 65 (38.4, CHF_2N^+); 63 (77.7, $C_2H_4FO^+$); and 44 (69.1, $C_2H_4O^+$). IR ($\nu_{max.}$) (cm^{-1}): 3003 and 2941 (w) (C–H str.); 1362–1210 (vs) (C–F str.); 1086 and 1040 (s) (C–O–N str.); 969 (s) (C–N str.); and 712 (s) (CF_3 def.); (iii) a −45 °C fraction identified as the substituted bromoethane **4b** (1.07 g, 3.8 mmol, 41%); and (iv) a −23 °C fraction (0.46 g) which was separated by preparative-scale GLC (3.5 m SE30 at 70 °C) into its components, substituted-bromoethane **4b** (0.23 g, 0.8 mmol, 9%) and 1,2-bis[bis(trifluoromethyl)amino-oxy]-1-bromoethane (**6**) (nc) (0.23 g, 0.5 mmol, 6%) (Analysis: Found: C, 16.5; H, 0.9%. $C_6H_3BrF_{12}N_2O_2$ requires: C, 16.3; H, 0.7%), b.p. 154 °C. ^{1}H NMR ($CDCl_3$) δ: 6.17 (mult., 1H, CHO); and 4.51 and 4.53 (AB mult., 2H, CH_AH_BO) ppm. ^{19}F NMR δ: +9.6 [s, 6F, $(CF_3)_2NO$]; and +7.6 [s, 6F, $(CF_3)_2NO$] ppm. MS *m/z*: 441/443 [1.0%, $(M-H)^+$]; 363 [80.1, $(M-Br)^+$]; 276/274 {45.2, $[M-(CF_3)_2NO]^+$}; 212/214 (23.5, $C_2F_5BrN^+$); 169 (10.3, $C_2HF_6NO^+$); 150 (24.6, $C_2HF_5NO^+$); 122/124 (16.0, $CHBrNO^+$); 107/109 (13.8, CH_2BrN^+); 94/96 (43.0, CH_3Br^+); and 69 (100.0, CF_3^+). IR ($\nu_{max.}$) (cm^{-1}): 3030 and 2967 (w) (C–H str.); 1298–1210 (vs) (C–F str.); 1058 and 1040 (s) (C–O–N str.); 971 (s) (C–N str.); and 712 (s) (CF_3 def.).

(c) 1-Bromopropane

A mixture of oxyl **1** (3.36 g, 20.0 mmol) and 1-bromopropane (2.46 g, 20.0 mmol), stored *in vacuo* at room temperature (8 h), gave only volatile material (5.82 g) which on fractional condensation *in vacuo* afforded (i) a −196 °C fraction (0.17 g) shown (IR spectroscopy) to be a mixture of *N,N*-bis(trifluoromethyl)amine (**5**) and perfluoro-2-azapropene; (ii) a −78 °C fraction (3.21 g) which was separated by preparative-scale GLC (3.5 m SE30 at 60 °C) into its two components, *N,N*-bis(trifluoromethyl)hydroxylamine (**3**) (1.80 g, 10.6 mmol, 53%) and unchanged 1-bromopropane (1.41 g, 11.5 mmol, 57% recovered); (iii) a combined −45 °C and −23 °C fraction (2.44 g) which was separated by preparative-scale GLC (3.5 m SE30 at 70 °C) into its two components identified as 2-[bis(trifluoromethyl)amino-oxy]-1-bromopropane (**7**) (nc) (1.89 g, 6.5 mmol, 76%) (Analysis: Found: C, 20.8; H, 2.1; F, 39.1% $C_5H_6BrF_6NO$ requires: C, 20.6; H, 2.1; F, 39.4%), b.p. 119 °C. ^{1}H NMR (neat) δ: 4.27 (sextet, 1H, >CHO, J=6 Hz); 3.45 (mult., 2H, CH_2Br); and 1.40 (d, 3H, CH_3, J=6 Hz) ppm ^{19}F NMR δ: +9.55 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 274/276 [3.0%, $(M-CH_4)^+$]; 196 (9.6, $C_4H_4F_6NO^+$); 150 (21.8, $C_2HF_5NO^+$); 121/123 {100.0, $[M-(CF_3)_2NO]^+$}; 93/95 (15.0, CH_2Br^+); 69 (35.4, CF_3^+); 43 (27.5, $C_2H_3O^+$);

and 41 (56.5, $C_3H_5^+$). IR ($\nu_{max.}$) (cm^{-1}); 2994 and 2959 (w) (C–H str.); 1353–1210 (vs) (C–F str.); 1069 (s) (C–O–N str.); 971 (s) (C–N str.); and 714 (s) (CF_3 def.); and (iv) a mixture (0.53 g, 1.9 mmol) (Analysis: Found: C, 20.8; H, 1.9%. Calc. for $C_5H_6BrF_6NO$: C, 20.6; H, 2.1%) of 1-[bis(trifluoromethyl)amino-oxy]-1-bromopropane (**4c**) (nc) (0.39 g, 1.4 mmol, 16%) {^{1}H NMR ($CDCl_3$) δ: 5.99 (t, 1H, $-CHBrO$, $J=6$ Hz); 2.18 (pentet, 2H, CH_2, $J=6$ Hz); and 1.10 (t, 3H, CH_3, $J=6$ Hz) ppm. ^{19}F NMR δ: +10.5 [s, $(CF_3)_2NO$] ppm} and 1-[bis(trifluoromethyl)amino-oxy]-2-bromopropane (**8**) (nc) (0.14 g, 0.5 mmol, 3%) {^{1}H NMR ($CDCl_3$) δ: 4.19 (mult., 3H, CHBr and CH_2O); and 1.68 (d, 3H, CH_3, $J=6$ Hz) ppm. ^{19}F NMR δ: +8.4 [s, $(CF_3)_2NO$] ppm}.

Reactions of sodium bis(trifluoromethyl)amino-oxyl (2) with dibromoalkanes

(a) 1,2-Dibromoethane

A solution of *N,N*-bis(trifluoromethyl)hydroxylamine (**3**) (28.7 g, 0.17 mol) in anhydrous diethyl ether (25 cm^3) was added dropwise to a stirred suspension of sodium hydride (3.84 g, 0.16 mol) under nitrogen in a flask fitted with a cold finger (−78 °C) and stirring was continued (0.5 h). The ether was then removed *in vacuo* and the sodium salt **2** dissolved in anhydrous diglyme (50 cm^3) and added dropwise to a stirred solution of 1,2-dibromoethane (24.4 g, 0.13 mol) in diglyme (20 cm^3) at 50 °C and stirring was continued (1 h). After cooling to room temperature, the volatile reaction products were removed *in vacuo* and separated by fractional condensation *in vacuo* to afford (i) a −196 °C fraction identified (IR spectroscopy) as bromoethene **11** (2.36 g, 22.1 mmol, 21%) (Analysis: Found: M, 107. Calc. for C_2H_3Br: M, 107); (ii) a −23 °C fraction which was separated by preparative-scale GLC (6 m OVI at 60 °C) into its two components, 1,2-bis[bis(trifluoromethyl)amino-oxy]ethane (**10a**) (2.8 g, 7.6 mmol, 7%) and 1-[bis(trifluoromethyl)amino-oxy]-2-bromoethane (**9a**) (nc) (11.5 g, 42.0 mmol, 39%) (Analysis: Found: C, 17.6; H, 1.5; F, 41.0%; M^+, 256/258. $C_4H_4BrF_6NO$ requires: C, 17.4; H, 1.5; F, 41.3%; M, 257), b.p. 103 °C. ^{1}H NMR (neat) δ: 4.29 (t, 2H, CH_2O, $J=6$ Hz); and 3.40 (t, 2H, CH_2Br, $J=6$ Hz) ppm. ^{19}F NMR δ: +8.5 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 256/258 (0.5%, M^+); 168 (1.4, $C_2F_6NO^+$); 122/124 (4.2, $C_2H_3BrO^+$); 107/109 (100.0, $C_2H_4Br^+$), 93/95 (14.0, CH_2Br^+); 69 (38.0, CF_3^+); and 43 (37.2, $C_2H_3O^+$). IR ($\nu_{max.}$) (cm^{-1}): 2976 and 2890 (w) (C–H str.); 1351–1205 (vs) (C–F str.); 1070 and 1052 (s) (C–O–N str.); 964 (s) (C–N str.); and 710 (s) (CF_3 def.); and (iii) unchanged 1,2-dibromoethane (5.87 g, 31.0 mmol, 24% recovered) which condensed at 0 °C.

(b) 1,3-Dibromopropane

A solution of the sodium salt **2** [prepared from hydroxylamine **3** (7.6 g, 45.0 mmol) and sodium hydride (0.96 g, 40.0 mmol) as in the previous experiment] in diglyme (25 cm^3) was added dropwise to a stirred solution of 1,3-dibromopropane (8.1 g, 40.0 mmol) in diglyme (20 cm^3) at 50 °C and stirring was continued (1 h). The volatile reaction products were removed *in vacuo* to afford (i) a −78 °C fraction which was identified (IR and NMR spectroscopy) as 3-[bis(trifluoromethyl)-amino-oxy]propene (**12**) (1.25 g, 6.0 mmol, 22%) [6, 7]; and (ii) a −23 °C fraction which was separated by preparative-scale GLC (6 m OVI at 80 °C) into its two components, 1-[bis(trifluoromethyl)amino-oxy]-3-bromopropane (**9b**) (nc) (3.34 g, 11.5 mmol, 43%) (Analysis: Found: C, 21.0; H, 2.1; F, 38.9; N, 4.8%. $C_5H_6BrF_6NO$ requires: C, 20.7; H, 2.1; F, 39.3; N, 4.8%), b.p. 131 °C. {^{1}H NMR (neat) δ: 4.20 (t, 2H, CH_2O, $J=6$ Hz); 3.41 (t, 2H, CH_2Br, $J=6$ Hz); and 2.14 (pentet, 2H, CH_2, $J=6$ Hz) ppm. ^{19}F NMR δ: +8.35 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 182 [1.9%, $(M-C_2H_4Br)^+$]; 121/123 {100.0, $[M-(CF_3)_2NO]^+$}; 107/109 (12.4, $C_2H_4Br^+$); 93/95 (11.7, CH_2Br^+); 69 (26.5, CF_3^+); 58 (10.0, $C_3H_6O^+$); 43 (21.4, $C_2H_3O^+$); and 41 (73.5, $C_3H_5^+$). IR ($\nu_{max.}$) (cm^{-1}): 2994 and 2882 (w) (C–H str.); 1360–1205 (vs) (C–F str.); 1059 (s) (C–O–N str.); 971 (s) (C–N str.); and 709 (s) (CF_3 def.)} and 1,3-bis[bis(trifluoromethyl)amino-oxy]-propane (**10b**) (nc) (1.89 g, 2.5 mmol, 9%) (Analysis: Found: C, 22.0; H, 1.6; F, 60.2%. $C_7H_6F_{12}N_2O_2$ requires: C, 22.2; H, 1.6; F, 60.3%], b.p. 130 °C. {^{1}H NMR (neat) δ: 4.14 (t, 4H, $2CH_2O$, $J=6$ Hz); and 1.96 (pentet, 2H, CH_2, $J=6$ Hz) ppm. ^{19}F NMR δ: +7.5 [s, $2(CF_3)_2NO$] ppm. MS *m/z*: 210 {100.0%, $[M-(CF_3)_2NO]^+$}; 182 (17.4, $C_3H_2F_6NO^+$); 150 (9.9, $C_2HF_5NO^+$); 94 (13.9, $C_2H_2F_2NO^+$); 69 (79.7, CF_3^+); 58 (92.3, $C_3H_6O^+$); 43 (27.6, $C_2H_3O^+$); and 41 (43.5, $C_3H_5^+$). IR ($\nu_{max.}$) (cm^{-1}): 2994 and 2924 (w) (C–H str.); 1305–1205 (vs) (C–F str.); 1059 (s) (C–O–N str.); and 709 (s) (CF_3 def.)}.

The flask residue was filtered to remove sodium bromide and examination of the filtrate by GLC (6 m OVI at 130 °C) showed the presence of unchanged 1,3-dibromopropane (4.65 g, 23.0 mmol, 46% recovered).

Attempted preparation of Grignard reagents

(a) From [bis(trifluoromethyl)amino-oxy]bromomethane (4a) and 1-[bis(trifluoromethyl)amino-oxy]-1-bromoethane (4b)

Solutions of the bromo compounds **4a** or **4b** in diethyl ether, added dropwise to a stirred suspension of powdered magnesium in ether (24 h and 5 h, respectively), gave unchanged bromides **4a** (90% recovered) and **4b** (92% recovered).

(b) From 1-[bis(trifluoromethyl)amino-oxy]-2-bromoethane (9a) and 2-[bis(trifluoromethyl)amino-oxy]-1-bromopropane (7)

A solution of the bromoethane ***9a*** (1.75 g, 6.3 mmol) in diethyl ether (2 cm^3) was added dropwise to a stirred suspension of powdered magnesium (0.13 g) in ether (2 cm^3) contained in a flask (*c.* 10 cm^3) connected to a gas burette and the mixture heated under reflux (1 h). This gave ethene (0.12 g, 4.2 mmol, 66%) (Analysis: Found: M, 28. Calc. for C_2H_4: M, 28) and unchanged bromide **9a** (0.27 g, 1.0 mmol, 16% recovered).

Similar treatment of a solution of bromopropane **7** (5.0 g, 17.0 mmol) in diethyl ether (2 cm^3) with a stirred suspension of magnesium (0.48 g) in ether (2 cm^3) and the mixture heated under reflux (1 h), gave propene (0.18 g, 4.2 mmol, 24%) (Analysis: Found: M, 43. Calc. for C_3H_6: M, 42) and unchanged bromopropane **7** (0.33 g, 1.1 mmol, 8.5% recovered).

(c) From 3-[bis(trifluoromethyl)amino-oxy]-1-bromopropane (9b)

A solution of the bromopropane **9b** (2.59 g, 8.9 mmol) in diethyl ether (1 cm^3) was added dropwise to a stirred suspension of magnesium (0.50 g) in ether (2 cm^3). The resulting material was then filtered under an atmosphere of nitrogen and the filtrate added dropwise to a stirred solution of methyltrichlorosilane (1.50 g, 10.0 mmol) in ether (1 cm^3) and the mixture heated under reflux (1 h). After cooling to room temperature and filtering under nitrogen, the filtrate was fractionally distilled to remove the ether and the residue separated by preparative-scale GLC (6 m OVI at 100 °C) to give (i) unreacted methyltrichlorosilane (0.57 g, 3.8 mmol, 38% recovered); (ii) unchanged bromopropane **9b** (trace); and (iii) {3-[bis(trifluoromethyl)amino-oxy]-propyl}dichloromethylsilane (**19**) (1.53 g, 4.7 mmol, 53%), which was identified by a comparison of its IR and NMR spectra with those of an authentic sample [6].

Results and discussion

The reactions of nitroxide **1** with the bromoalkanes RBr (R = Me, Et and Pr^n) (1:1 molar ratio) and of the sodium salt **2** with dibromoalkanes (1:1 molar ratio) are summarised in Table 1.

The major products **3**–**7** obtained from the reactions of nitroxide **1** are considered to be formed as shown in Scheme 1.

Of the three monobromoalkanes studied, bromomethane was the least reactive presumably because attack by nitroxide **1**, a pseudo-halogen radical resembling Cl·, involved abstraction of a primary methyl hydrogen, while with bromoethane and 1-bromopropane a secondary methylene hydrogen was abstracted. All of the intermediate radicals **13**, formed by α-hydrogen abstraction, are stabilised by the bromine atom and the radicals MeĊHBr (**13b**) and EtĊHBr (**13c**) are further stabilised by hyperconjugation involving the methyl and methylene hydrogens, respectively. However, with 1-bromopropane, β-hydrogen abstraction was major, i.e. formation of the secondary radical MeĊHCH$_2$Br (**14**) (hyperconjugatively stabilised by five hydrogen atoms) is more favoured than formation of radical **13c**, showing that the α-position is deactivated towards attack by the weakly eletrophilic radical **1**. Such deactivation could be steric in origin, as has been postulated for alkyltrihalogenosilanes [8], or due to the $-I$ effect of bromine or a combination of the two effects.

The formation of amine **5**, carbon monoxide and bromine in the bromomethane reaction can be accounted for by further attack by nitroxide **1** on the initial product **4a**. Dehydrogenation of bromoethane to vinyl bromide, the precursor of the disubstitution product **6**, parallels that established for alkanes [9], aralkanes [10] and the halogenoalkanes EtCl, EtF and MeCHF$_2$ [3].

The absence of disubstitution products (via dehydrogenation) and the presence of the minor rearranged monosubstitution product **8** in the 1-bromopropane reaction were unexpected. It is considered that compound **8** arose by elimination of a bromine atom from radical **15** (resulting from attack by nitroxide **1** on the dehydrogenation product $H_2C{=}CHCH_2Br$) to give alkene **16** followed by electrophilic addition of hydrogen bromide (Scheme 2).

The reactions of the sodium salt **2** with the dibromides $Br(CH_2)_nBr$ ($n = 2$ and 3) provided no surprises; S_N2 substitution gave the compounds **9** and **10** and $E2$ elimination resulted in the formation of the alkenes **11** and **12** (Scheme 3).

As expected, the vinyl halide **11** was unreactive towards salt **2**, but 3-bromopropene **17** underwent allylic S_N2 substitution to give compound **12**.

The α-substituted compounds **4a** and **4b** did not form Grignard reagents on treatment with magnesium in diethyl ether under reflux; certain alkyl halides substituted in the α-position by an electron-withdrawing group have also been observed not to form Grignard reagents [11]. In contrast, on treatment of the β-substituted compounds **7** and **9a** with magnesium in diethyl ether at room temperature, a vigorous reaction occurred and propene (24%) and ethene (66%), respectively, were isolated, i.e.

$$(CF_3)_2NOCHRCH_2Br \xrightarrow[Et_2O]{Mg}$$

$$(CF_3)_2NO{-}CHR{-}CH_2{-}MgBr \longrightarrow$$

$$RCH{=}CH_2 + (CF_3)_2NOMgBr$$

TABLE 1. Synthesis of [bis(trifluoromethyl)amino-oxy]-substituted bromoalkanes

Substrate	Reactant	Conditions		Substrate recovered (%)	Products (%)
		Temp. (°C)	Time (h)		
MeBr	**1**	60	168	60	**3**, 59[b]; **4a**, 69; **5**, 9; CO, 10[c]
EtBr	**1**	20	12	53	**3**, 48[b]; **4b**, 93; **6**, 6[d]
Pr^nBr	**1**	20	8	57	**3**, 53[b]; **4c**, 16; **7**, 76; **8**, 3[d]
$Br(CH_2)_2Br$[a]	**2**	50	1	24	**9a**, 39; **10a**, 7; **11**, 21
$Br(CH_2)_3Br$[a]	**2**	50	1	46	**9b**, 43; **10b**, 9; **12**, 22

[a]Carried out in diglyme.
[b]Based on oxyl **1**; other yields based on substrate reacted (not recovered).
[c]Bromine also formed.
[d]Minor amounts of compound **5** and $CF_3N{=}CF_2$ also formed.

$(CF_3)_2NOH$ **(3)**

$(CF_3)_2NOCHRBr$ **(4)** (a) R = H (b) R = Me (c) R = Et

$(CF_3)_2NH$ **(5)**

$(CF_3)_2NOCHBrCH_2ON(CF_3)_2$ **(6)**

$(CF_3)_2NOCHMeCH_2Br$ **(7)**

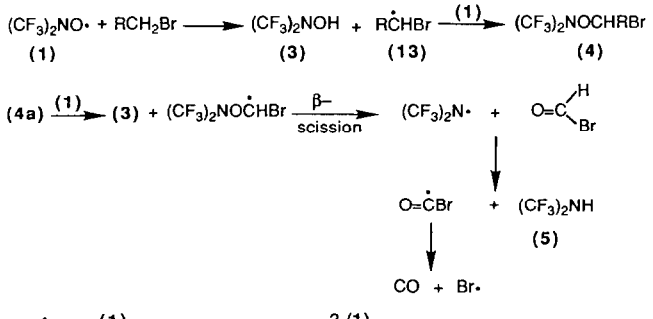
$(CF_3)_2NOCH_2CHBrMe$ **(8)**

$(CF_3)_2NO(CH_2)_nBr$ **(9)** (a) $n=2$ (b) $n=3$

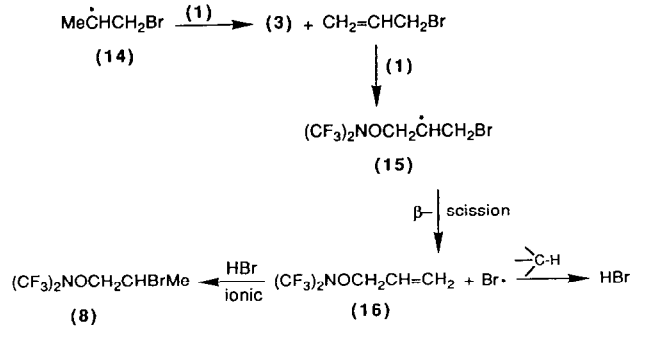
$(CF_3)_2NO(CH_2)_nON(CF_3)_2$ **(10)** (a) $n=2$ (b) $n=3$

$H_2C{=}CHBr$ **(11)**

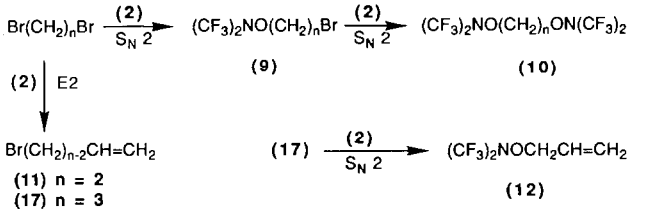
$(CF_3)_2NOCH_2CH{=}CH_2$ **(12)**



Scheme 1.



Scheme 2.



Scheme 3.

Many other β-substituted Grignard reagents are also unstable, e.g. treatment of 1-bromo-2-ethoxy-5-methylhexane with magnesium to give 5-methylhex-1-ene [11].

Reaction of the γ-substituted compound **9b** with magnesium in diethyl ether gave a solution of the corresponding Grignard reagent **18** which, after removal of unreacted magnesium, underwent facile reaction with methyltrichlorosilane to afford the methyldichlorosilyl derivative **19** (53%). This compound has also been prepared by the Speier-catalysed addition of dichloromethylsilane across the double bond of the alkene $(CF_3)_2NOCH_2CH{=}CH_2$ **(12)** [6].

$$(CF_3)_2NO(CH_2)_3Br \xrightarrow[Et_2O]{Mg} (CF_3)_2NO(CH_2)_3MgBr \xrightarrow{MeSiCl_3}$$

(18)

$(CF_3)_2NO(CH_2)_3SiCl_2Me$

(19)

Grignard reagents have been reported to be formed readily from reaction of the γ-alkoxypropyl halides $MeO(CH_2)_3X$ (X = Br or I) with magnesium [11].

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