

Hydrogen-abstraction reactions of bistrifluoromethyl nitroxide

Substrate (g, mmol)	(CF ₃) ₂ NO· (g, mmol)	Reaction period and temp. (°C) (ampoule size, cm ³)	Products ^a [R = (CF ₃) ₂ NO] (g, mmol, %)	Elemental analyses Found (required) (%)
Me ₂ O (0.46, 10.0)	3.36, 20.0	15 h, 20 (200)	RCH ₂ OMe (2.02, 9.50, 95) ^{b,c} (RCH ₂) ₂ O (0.21, 0.55, 5.5) ^{b,d} RH (1.54, 9.10, 92) Me ₂ O RON(CF ₃) ₂ unidentified MeCHROEt (1.59, 6.60, 76) ^{f,g} RCH ₂ CHROEt (0.60, 1.46, 17) ^{f,h} (MeCHR) ₂ O (0.05, 0.12, 1) ⁱ RH (1.68, 9.94, 102) Et ₂ O (0.12, 1.62, 16) unidentified (0.04 g)	C, 22.3; H, 2.6; N, 6.4 (C, 22.5; H, 2.3; N, 6.6) C, 19.0; H, 1.1; N, 7.7 (C, 18.9; H, 1.05; N, 7.4)
Et ₂ O (0.76, 10.25)	3.29, 19.6	30 min, 20 (300)	MeCHROEt (1.59, 6.60, 76) ^{f,g} RCH ₂ CHROEt (0.60, 1.46, 17) ^{f,h} (MeCHR) ₂ O (0.05, 0.12, 1) ⁱ RH (1.68, 9.94, 102) Et ₂ O (0.12, 1.62, 16) unidentified (0.04 g)	C, 29.8; H, 3.4; N, 5.7 (C, 29.9; H, 3.7; N, 5.8) C, 23.6; H, 2.0; N, 6.9 (C, 23.6; H, 2.0; N, 6.9)
PhOMe (1.08, 10.0)	3.30, 19.6	24 h, 20 (300)	PhOCH ₂ R (2.17, 7.89, 93) ^{j,k} RH (1.55, 9.18, 94) PhOMe (0.16, 1.48, 15) R· (CF ₃) ₂ NH CF ₃ N=CF ₂ unidentified (0.44 g) ^l	C, 39.6; H, 2.7; N, 5.4 (C, 39.3; H, 2.5; N, 5.1)
CHFClCF ₂ OMe (6.96, 46.9)	14.46, 86.07	6 d, 50 (300)	RCH ₂ OCF ₂ CHFCl (9.10, 28.8, 67) ^m RCFCICF ₂ OMe (1.29, 4.09, 9.5) ^{n,o} CHFClCF ₂ OMe (1.63, 11.0, 23) RH (6.81, 40.3, 94) R· (traces) RCFCICF ₂ OMe RCH ₂ OCOCFCl CHFClCF ₂ OMe unidentified	C, 19.2; H, 1.1; N, 4.4 (C, 19.0; H, 0.95; N, 4.4) C, 19.3; H, 1.1; N, 4.5 (C, 19.0; H, 0.95; N, 4.4)
CHFClCO ₂ Me (3.00, 23.7)	9.04, 53.8	27 d, 20 (300)	RCFCICO ₂ Me ^{q,r} (4.17, 14.2, 60) RH CHFClCO ₂ Me R· unidentified	C, 21.5; H, 1.3; N, 4.4 (C, 20.4; H, 1.0; N, 4.8)

^a B.p.s were determined by Siwoloboff's method; ¹⁹F n.m.r. chemical shift values (p.p.m.) refer to external CF₃CO₂H (upfield negative). ^b Isolated by g.l.c. (2 m SE30, 21 °C). ^c B.p. 70 °C at 753 mmHg; δ_F + 8.40 (s), δ_H (ext. C₆H₆) -1.92 (s; CH₂), and -3.20 (s; CH₃); *m/e* 213 (*M*⁺, <1), 212 (*M*⁺ - H·, 3), 182 [(CF₃)₂NOCH₂⁺, 15], 94 (CF₂=NOCH₂⁺, 7), 69 (CF₃⁺, 24), 45 (MeOCH₂⁺, 100), and 15 (Me⁺, 22%). ^d B.p. 127-128 °C at 740 mmHg; δ_F (30% soln. in CCl₄) +10.20 (s), δ_H (ext. C₆H₆) -1.41; *m/e* 212 [top mass peak; (CF₃)₂NOCH₂OCH₂⁺, 31], 182 [(CF₃)₂NOCH₂⁺, 100], 150^e [(CF₂=N(OH)CF₃)⁺, 2], 94 (CF₂=NOCH₂⁺, 24), and 69 (CF₃⁺, 49%). ^e This peak (assignment tentative) features prominently in the mass spectra of numerous bistrifluoromethylamino-oxoalkanes. ^f Isolated by g.l.c. (10 m SE30, 92 °C). ^g B.p. 96 °C at 779 mmHg; δ_F +9.38 (s), δ_H (ext. C₆H₆) -1.73 [q; (CF₃)₂NOCH₂, ³J_{HH} 6 Hz], -2.95 and -3.25 (AB portion of an ABX₃ system; CH₂), -5.46 [d; (CF₃)₂NOCH₂CH₃, ³J_{HH} 6 Hz], -2.95 and -3.25 (AB portion of an ABX₃ system; CH₃), -5.46 [d; (CF₃)₂NOCH₂CH₃, ³J_{HH} 6 Hz]; *m/e* 240 (top mass peak; *M*⁺ - H·, 1), 226 (*M*⁺ - Me·, 3), 198 [(CF₃)₂NOCHOH⁺, 14], 196 [(CF₃)₂NOCHMe⁺, 52], 150^e [(CF₂=N(OH)CF₃)⁺, 16], 73 (MeCH=OEt⁺, 87), 72 (CH₂=CHOEt⁺, 17), 69 (CF₃⁺, 78), 45 (MeCH=OH⁺, 100), 43 (C₂H₃O⁺, 75), and 29 (C₂H₅⁺, 76%). ^h B.p. 139-140 °C at 764 mmHg; δ_F +7.50 [s; (CF₃)₂NOCH₂] and +8.51 [s; (CF₃)₂NOCH₂], δ_H (ext. SiMe₄ in CCl₄) +0.91 (t, Me, ³J_{HH} = ³J_{HHB} = 7 Hz), +3.43 to +3.80 [overlapping AB sections of ABX₃ (OCH₂CH₃) and ABX (CH₂CHO) systems], and +4.83 [t; (CF₃)₂NOCHO, ³J_{HH} = ³J_{HHB} = 5 Hz]; *m/e* 363 (top mass peak; *M*⁺ - Et·, 12), 240 [*M*⁺ - (CF₃)₂NO·, 43], 226 [(CF₃)₂NOCH=OEt⁺, 23], 212 [(CF₃)₂NOCH₂CHOH⁺, 66], 198 [(CF₃)₂NOCHOH⁺, 60], 150^e [(CF₂=N(OH)CF₃)⁺, 20], 45 (MeCH=OH⁺, 16), and 43 (C₂H₃O⁺, 21%). ⁱ Identified spectroscopically (¹H n.m.r. and g.l.c.-m.s.) by examination of a -23 °C trap fraction also containing (CF₃)₂NOCHMeOEt as [(CF₃)₂NOCHMe]₂O: δ_H (ext. C₆H₆) -1.23 (q) and -5.20 (d, ³J_{HH} 5 Hz); *m/e* 240 [*M*⁺ - (CF₃)₂NO·, 17], 212 (CF₃NOCHMeO⁺, 11), 198 [(CF₃)₂NOCHOH⁺, 13], 196 [(CF₃)₂NOCHMe⁺, 99], 150^e [(CF₂=N(OH)CF₃)⁺, 26], 69 (CF₃⁺, 55), 45 (CH₃CH=OH⁺, 88), 44 [C₂H₄O⁺, 91], and 43 (C₂H₃O⁺, 100%). ^j Isolated from the yellowish-red involatile product by g.l.c. (6 m PEGA, 155 °C). ^k B.p. 175-176 °C at 764 mmHg; δ_F +9.25 (s), δ_H (int. SiMe₄) +5.32 (s; CH₃) and +7.0 (m; C₆H₅); *m/e* 275 (*M*⁺, 26), 107 (PhOCH₂⁺, 100), 77 (C₆H₅⁺, 85), 69 (CF₃⁺, 18), and 65 (C₅H₅⁺, 22%). ^l Present in the yellowish-red liquid referred to in footnote j, and containing unidentified carbonyl compounds (λ_{max} 5.80 and 5.85 μm) and (CF₃)₂N-derivatives [δ_F +21.5 (s) and +21.7 (s)]. ^m Isolated by precise distillation; b.p. 119.5 °C at 758 mmHg; δ_F +8.4 [s; (CF₃)₂NOCH₂], -10.1 (m; CF₂), and -78.0 (dt; CHF, ²J_{HF} 48, ³J_{FF} 11 Hz), δ_H (ext. SiMe₄) +5.17 (s; CH₂) and +5.80 (dt; CHF, ³J_{HF} 4 Hz); *m/e* 182 [top mass peak; (CF₃)₂NOCH₂⁺, 93], 147 (CHF³⁵ClCF₂OCH₂⁺, 61), 117 (CHF³⁶ClCF₂⁺, 87), and 69 (CF₃⁺, 100%). ⁿ Isolated by g.l.c. (4 m PEGA, 60 °C). ^o δ_F +10.2 (m) and +9.7 (m) [two non-equivalent CF₃ groups of (CF₃)₂NOCFCl], +0.2 (vbr q; CFCI), and -13.5 (dd; CF₂), δ_H (ext. SiMe₄) +3.40 (s); *m/e* 296 [top mass peak; *M*⁺ - F·, 6], 280 [*M*⁺ (³⁵Cl) - ³⁵Cl·, 48], 168 [(CF₃)₂NO⁺, 3], 147 (MeOCF₂CF³⁵Cl⁺, 79), 81 (MeOCF₂⁺, 100), and 69 (CF₃⁺, 96). ^p Detected by i.r. spectroscopy and g.l.c. but not estimated. ^q Isolated by g.l.c. (2 m PEGA, 90 °C). ^r A liquid, λ_{max} (film) 5.59 (C=O str.) μm, δ_H (ext. C₆H₆) -3.05 (s), and *m/e* 258 [top mass peak; *M*⁺ - ³⁵Cl·, 24], 234 [(CF₃)₂NOCFCl⁺, 15], 125 (MeOCOCF³⁵Cl⁺, 63), 69 (CF₃⁺, 81), and 59 (MeOCO⁺, 100%). ^s Correct ³⁵Cl : ³⁷Cl ratios were observed for ions containing chlorine.

abstraction by an electrophilic chlorine atom stemming from the polar effect⁷ of the CF₂ group follows the order CHFCl > CH₃,⁸ strongly resists attack by bis-

trifluoromethyl nitroxide at room temperature; and even at 50 °C it takes 6 days for a ca. 2 : 1 molar [nitroxide (R·) : ether] purple mixture of reactants to become

colourless. The products under the latter conditions, in Pyrex, are $\text{RCH}_2\text{OCF}_2\text{CHFCl}$ (5) (67%), $\text{MeOCF}_2\text{-CRFCl}$ (6) (9.5%), RH (94%), $\text{MeOCF}_2\text{CHFCl}$ (23% recovery), and small amounts of $\text{RCH}_2\text{OCOCHFCl}$ (7), MeOCOCRfCl (8), and MeOCOCHFCl (9). Formation of the esters (7)–(9) is ascribed to slow hydrolysis of the difluoromethylene groups * in the corresponding ethers [(5), (6), and $\text{MeOCF}_2\text{CHFCl}$ respectively] at the walls of the reaction vessel [possibly with assistance from $(\text{CF}_3)_2\text{NOH}$]: † they are produced in higher yields when the $\text{MeOCF}_2\text{CHFCl}-(\text{CF}_3)_2\text{NO}\cdot$ reaction is carried out in Pyrex at a higher temperature (70 °C) but appear to be absent from material prepared using a carefully dried stainless-steel reaction vessel. Acid-induced (H_2SO_4) hydrolysis of a mixture of the ethers $\text{RCH}_2\text{OCF}_2\text{CHFCl}$ (5) and $\text{Me}_3\text{OCF}_2\text{CRfCl}$ (6) at 80–90 °C in the presence of powdered glass does yield the corresponding esters $\text{RCH}_2\text{OCOCHFCl}$ (7) and MeOCOCRfCl (8) [$\text{R} = (\text{CF}_3)_2\text{NO}$], and a pure sample of the former product (7) was obtained by using only bistrifluoromethylamino-oxymethyl 2-chloro-1,1,2-trifluoroethyl ether (5) as starting material. The isomeric ester (8) is best prepared by treating methyl chlorofluoroacetate with bistrifluoromethyl nitroxide.

EXPERIMENTAL

Reactions of Bistrifluoromethyl Nitroxide with Ethers and with Methyl Chlorofluoroacetate. ‡—The nitroxide (synthesised from commercial trifluoroacetic acid¹²) was condensed, *in vacuo*, onto the frozen substrate contained in a cold (–196 °C) thick-walled Pyrex ampoule. After the ampoule had been sealed (neck fused), it was placed in a steel guard and allowed to warm to room temperature; in the case of reactions involving 2-chloro-1,1,2-trifluoroethyl methyl ether, it was then heated in a thermostatically controlled tube furnace. The progress of the reaction was followed by occasional inspection of the ampoule (the operator wore stout gauntlets and a polycarbonate face-

* Acid hydrolysis of $\alpha\alpha$ -difluoro-ethers is a classical reaction in the organofluorine field (see ref. 9).

† $\alpha\alpha$ -Difluoro-ethers (including $\text{MeOCF}_2\text{CHFCl}$) are known to react with hot glass to give the corresponding esters and silicon tetrafluoride in high yields; the reactions are autocatalytic, and the addition of small amounts of concentrated sulphuric acid eliminates the prolonged induction periods involved.¹⁰

‡ 2-Chloro-1,1,2-trifluoroethyl methyl ether and hence the corresponding ester were prepared from commercial chlorotrifluoroethylene [$\text{CF}_2=\text{CFCl} + \text{NaOMe}-\text{MeOH} \rightarrow \text{CHFClCF}_2\text{-OMe} \rightarrow$ (with 96% H_2SO_4) $\text{CHFClCO}_2\text{Me}$] by the application of procedures¹¹ used to synthesise the analogous ethyl compounds.

and-neck shield) to note the diminution in the intensity of the purple colour caused by consumption of the nitroxide. Volatile product was transferred to a vacuum system and examined by standard techniques {trap-to-trap fractional condensation at 1–2 mmHg, followed by analysis of trap contents [i.r., g.l.c., and molecular weight determination (Regnault's method)], and, if necessary, final purification of products by g.l.c.}; material too involatile for transfer was examined by g.l.c. Results are listed in the Table.

Hydrolysis of Bistrifluoromethylamino-oxymethyl 2-Chloro-1,1,2-trifluoroethyl Ether.—A mixture of the ether (3.04 g, 10.4 mmol), concentrated sulphuric acid (2 drops), and powdered Pyrex (1.6 g) was sealed in an evacuated Pyrex ampoule (60 cm³) and heated at 80–90 °C for 3 days, to give silicon tetrafluoride and an involatile 5-component (by g.l.c.) liquid. A sample of the major component of the liquid was isolated by g.l.c. (4 m APL, 50 °C) and found to be *bistrifluoromethylamino-oxymethyl chlorofluoroacetate* (Found: C, 20.8; H, 1.3; F, 45.4; N, 4.5. $\text{C}_5\text{H}_3\text{ClF}_7\text{NO}_3$ requires C, 20.4; H, 1.0; F, 45.3; N, 4.8%), λ_{max} (film) 5.57 (C=O str.) μm , δ_{H} (external C_6H_6 as reference) –0.41 (d; CHF, $^2J_{\text{HF}}$ 55 Hz) and –1.10 (s; CH_2) p.p.m., and *m/e* 258 [top mass peak; M^{++} (^{35}Cl)– $^{35}\text{Cl}^+$, 0.1%], 182 [$(\text{CF}_3)_2\text{NOCH}_2^+$, 95%], 125 ($\text{CHF}^{35}\text{ClCO}_2\text{CH}_2^+$, 30%), 95 ($\text{CHF}^{35}\text{ClCO}^+$, 13%), 69 (CF_3^+ , 100%), and 67 ($\text{CHF}^{35}\text{Cl}^+$, 80%) (correct isotopic abundances were observed).

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