Nitroxide Chemistry. Part 18.[1] Reaction of Bistrifluoromethyl Nitroxide with Some Ethers

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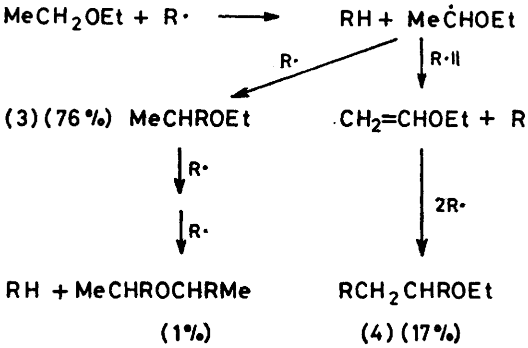
Treatment of the methyl ethers MeOX (X = Me, Ph) with a stoicheiometric amount of bistrifluoromethyl nitroxide [$(CF_3)_2NO\cdot$ = R·] at room temperature converts them efficiently into their bistrifluoromethylamino-oxymethyl counterparts, RCH_2OX; the bis-derivative $(RCH_2)_2O$ is a minor by-product in the case of dimethyl ether (X = Me). Multiple hydrogen-abstraction increases in importance with diethyl ether as substrate, the expected products RCHMeOEt and $(RCHMe)_2O$ being accompanied by a bis-derivative ($RCH_2CHROEt$) arguably produced *via* the αβ-dehydrogenation $2R\cdot + Et_2O \longrightarrow 2RH + CH_2{=}CHOEt$. The halogeno-ether $MeOCF_2CHFCl$ reacts slowly with the nitroxide at 50 °C to yield a 7 : 1 mixture of the derivatives RCH_2OCF_2CHFCl and $RCFClCF_2OMe$, hydrolysis of which gives the esters $RCH_2OCOCHFCl$ and $RCFClCO_2Me$, respectively. The latter ester is best obtained *via* treatment of methyl chlorofluoroacetate with bistrifluoromethyl nitroxide.

Continuing interest in nitroxide chemistry, coupled with the publication recently of information concerning the lethargic hydrogen-abstraction reaction which occurs between benzoyl t-butyl nitroxide and diethyl ether at room temperature,[2,†] prompts us to report work carried out in the early 1970s on the action of bistrifluoromethyl nitroxide on the ethers Me_2O, Et_2O, PhOMe, and $CHFClCF_2OMe$.[3]

As indicated earlier in a communication concerning organosilane substrates (including methoxy-compounds[4,‡]), bistrifluoromethyl nitroxide attacks dimethyl ether at room temperature to yield a mixture of mono- and bis(bistrifluoromethylamino-oxy)-derivatives, *viz.* $(CF_3)_2NOCH_2OMe$ (1) and $(CF_3)_2NOCH_2OCH_2ON(CF_3)_2$ (2); reaction between the ether and 2 molar equivalents of the nitroxide is complete after 15 h and provides, virtually quantitatively, *NN*-bistrifluoromethylhydroxylamine and a 19 : 1 mixture of products (1) and (2). The preference shown by the nitroxide for attack at the methyl group of the primary product {$R\cdot + (1) \longrightarrow RH + RCH_2OCH_2\cdot \longrightarrow$ (with R·) (2; $R = [CF_3]_2NO$)} rather than the methylene was predictable since the bistrifluoromethylamino-oxy-group deactivates an α-hydrogen [$(CF_3)_2NOC$*H*],[4-6] a phenomenon discussed previously[6] in terms of a polar transition state $[(CF_3)_2N\overset{\delta-}{O}{-}{-}{-}H{-}{-}{-}\overset{\delta+}{C}\lessdot]\cdot$.§

Anisole, like dimethyl ether, reacts sedately with bistrifluoromethyl nitroxide [2 $(CF_3)_2NO\cdot$: 1 PhOMe] at room temperature, virtually complete consumption of the radical occurring during 24 h with formation of the mono-bistrifluoromethylamino-oxy-derivative $PhOCH_2ON(CF_3)_2$ in 93% yield.

Not unexpectedly, diethyl ether is much more susceptible to attack by bistrifluoromethyl nitroxide than its dimethyl analogue: complete consumption of the radical occurs when a *ca.* 2 : 1 (R· : Et_2O) mixture of reactants is allowed to warm from −196 °C to 20 °C then kept in the dark for 30 min. The products and the proposed mechanistic pathways involved are shown in the Scheme; only the source of the second most abundant product (4) can be classed as contentious, and the proposal advanced ‖ is based on knowledge of (*i*) the αβ-dehydrogenation $2(CF_3)_2NO\cdot + Me_3CH \longrightarrow 2(CF_3)_2NOH + Me_2C{=}CH_2$;[5] (*ii*) the parallelism between the molar ratios of αβ-di- to mono-substituted products in alkane–$(CF_3)_2NO\cdot$ reactions and k_d/k_c values for the alkyl radicals involved;[5] (*iii*) the retarding influence of a bistrifluoromethylamino-oxy-group on abstraction of β-hydrogen [$(CF_3)_2NOCC$*H*, as in (3)] by bistrifluoromethyl nitroxide;[5] and (*iv*) the ease with which the nitroxide saturates alkenes.[5]



$R\cdot = (CF_3)_2NO\cdot$

Scheme

The fluorinated analogue of dimethyl ether CH_3OCF_2CHFCl, in which deactivation of hydrogen towards

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† During 11 days at room temperature the nitroxide, dissolved in a vast excess of diethyl ether, was observed to become completely converted into a mixture of $PhCON(OH)Bu^t$ and $PhCONBu^tOCHMeOEt$ (isolated in 85 and 92% yield, respectively).

‡ The following reactions were reported: 1 $(CF_3)_2NO\cdot$ + 1 $(MeO)_4Si \longrightarrow$ (after 4 h at room temp.) $(CF_3)_2NOCH_2OSi(OMe)_3$ (73%) + $[(CF_3)_2NOCH_2O]_2Si(OMe)_2$ (27%); 1 $(CF_3)_2NO\cdot$ + 1 $(MeO)_3SiMe \longrightarrow$ (1 h, room temp.) $(CF_3)_2NOCH_2OSiMe(OMe)_2$ (95%).

§ Note that no attempt was made in any of the reactions involving ethers to determine the effect on reaction rate of possible association between the substrates or transition states and the hydroxylamine $(CF_3)_2NOH$ being produced.

‖ 'Mixed disproportionation '[5] involving bistrifluoromethyl nitroxide has also been proposed to account for the formation of αβ-bis(bistrifluoromethylamino-oxy)-derivatives in hydrogen-abstraction reactions between the nitroxide and halogenoalkanes,[1] cycloalkanes (R. E. Banks, A. K. Brown, and R. N. Haszeldine, in preparation), and ethylbenzene.[6]

Hydrogen-abstraction reactions of bistrifluoromethyl nitroxide

Substrate (g, mmol)	$(CF_3)_2NO\cdot$ (g, mmol)	Reaction period and temp. (°C) (ampoule size, cm^3)	Products[a] [$R = (CF_3)_2NO$] (g, mmol, %)	Elemental analyses Found (required) (%)
Me_2O (0.46, 10.0)	3.36, 20.0	15 h, 20 (200)	RCH_2OMe (2.02, 9.50, 95)[b,c]	C, 22.3; H, 2.6; N, 6.4 (C, 22.5; H, 2.3; N, 6.6)
			$(RCH_2)_2O$ (0.21, 0.55, 5.5)[b d]	C, 19.0; H, 1.1; N, 7.7 (C, 18.9; H, 1.05; N, 7.4)
			RH (1.54, 9.10, 92)	
			Me_2O $RON(CF_3)_2$ unidentified } traces	
Et_2O (0.76, 10.25)	3.29, 19.6	30 min, 20 (300)	MeCHROEt (1.59, 6.60, 76)[f,g]	C, 29.8; H, 3.4; N, 5.7 (C, 29.9; H, 3.7; N, 5.8)
			$RCH_2CHROEt$ (0.60, 1.46, 17)[f,h]	C, 23.6; H, 2.0; N, 6.9 (C, 23.6; H, 2.0; N, 6.9)
			$(MeCHR)_2O$ (0.05, 0.12, 1)[i]	
			RH (1.68, 9.94, 102)	
			Et_2O (0.12, 1.62, 16)	
			unidentified (0.04 g)	
PhOMe (1.08, 10.0)	3.30, 19.6	24 h, 20 (300)	$PhOCH_2R$ (2.17, 7.89, 93)[j,k]	C, 39.6; H, 2.7; N, 5.4 (C, 39.3; H, 2.5; N, 5.1)
			RH (1.55, 9.18, 94)	
			PhOMe (0.16, 1.48, 15)	
			$R\cdot$ $(CF_3)_2NH$ $CF_3N{=}CF_2$ } traces	
			unidentified (0.44 g)[l]	
$CHFClCF_2OMe$ (6.96, 46.9)	14.46, 86.07	6 d, 50 (300)	RCH_2OCF_2CHFCl (9.10, 28.8, 67)[m]	C, 19.2; H, 1.1; N, 4.4 (C, 19.0; H, 0.95; N, 4.4)
			$RCFClCF_2OMe$ (1.29, 4.09, 9.5)[n,o]	C, 19.3; H, 1.1; N, 4.5 (C, 19.0; H, 0.95; N, 4.4)
			$CHFClCF_2OMe$ (1.63, 11.0, 23)	
			RH (6.81, 40.3, 94)	
			$R\cdot$ (traces)	
			$RCFClCO_2Me$ $RCH_2OCOCHFCl$ $CHFClCO_2Me$ unidentified } [p]	
$CHFClCO_2Me$ (3.00, 23.7)	9.04, 53.8	27 d, 20 (300)	$RCFClCO_2Me$[q,r] (4.17, 14.2, 60)	C, 21.5; H, 1.3; N, 4.4 (C, 20.4; H, 1.0; N, 4.8)
			RH $CHFClCO_2Me$ $R\cdot$ unidentified } [p]	

[a] B.p.s were determined by Siwoloboff's method; ^{19}F n.m.r. chemical shift values (p.p.m.) refer to external CF_3CO_2H (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. C_6H_6) -1.92 (s; CH_2), and -3.20 (s; CH_3); *m/e* 213 ($M^{+\cdot}$, <1), 212 ($M^{+\cdot} - H\cdot$, 3), 182 [$(CF_3)_2NOCH_2^+$, 15], 94 ($CF_2{=}NOCH_2^+$, 7), 69 (CF_3^+, 24), 45 ($MeOCH_2^+$, 100), and 15 (Me^+, 22%). [d] B.p. 127—128 °C at 740 mmHg; δ_F (30% soln. in CCl_4) $+10.20$ (s), δ_H (ext. C_6H_6) -1.41; *m/e* 212 [top mass peak; $(CF_3)_2NOCH_2OCH_2^+$, 31], 182 [$(CF_3)_2NOCH_2^+$, 100], 150[e] {[$CF_2{=}N(OH)CF_3]^+$, 2}, 94 ($CF_2{=}NOCH_2^+$, 24), and 69 (CF_3^+, 49%). [e] This peak (assignment tentative) features prominently in the mass spectra of numerous bistrifluoromethylamino-oxyalkanes.[5] [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. C_6H_6) -1.73 [q; $(CF_3)_2NOCH$, $^3J_{HH}$ 6 Hz], -2.95 and -3.25 (AB portion of an ABX_3 system; CH_2), -5.46 [d; $(CF_3)_2NOCHCH_3$], and -5.66 (t, $OCH_AH_BCH_3$, $^3J_{HHA} = {}^3J_{HHB} = 7$ Hz); *m/e* 240 (top mass peak; $M^{+\cdot} - H\cdot$, 1), 226 ($M^{+\cdot} - Me\cdot$, 3), 198 [$(CF_3)_2NOCHOH^+$, 14], 196 [$(CF_3)_2NOCHMe^+$,52], 150[e] {[$CF_2{=}N(OH)CF_3]^+$, 16}, 73 ($MeCH{=}OEt^+$, 87), 72 ($CH_2{=}CHOEt^+$, 17), 69 (CF_3^+, 78), 45 ($MeCH{=}OH^+$, 100), 43 ($C_2H_3O^+$, 75), and 29 ($C_2H_5^+$, 76%). [h] B.p. 139—140 °C at 764 mmHg; δ_F $+7.50$ [s; $(CF_3)_2NOCH_2$] and $+8.51$ [s; $(CF_3)_2NOCH$], δ_H (ext. $SiMe_4$ in CCl_4) $+0.91$ (t, Me, $^3J_{HHA} = {}^3J_{HHB} = 7$ Hz), $+3.43$ to $+3.80$ [overlapping AB sections of ABX_3 (OCH_2CH_3) and ABX (CH_2CHO) systems], and $+4.83$ [t; $(CF_3)_2NOCHO$, $^3J_{HHA} = {}^3J_{HHB} = 5$ Hz]; *m/e* 363 (top mass peak; $M^{+\cdot} - Et\cdot$, 12), 240 [$M^{+\cdot} - (CF_3)_2NO\cdot$, 43], 226 [$(CF_3)_2NOCH{=}OEt^+$, 23], 212 [$(CF_3)_2NOCH_2CHOH^+$, 66], 198 [$(CF_3)_2NOCHOH^+$, 60], 150[e] {[$CF_2{=}N(OH)CF_3]^+$, 20}, 45 ($MeCH{=}OH^+$, 16), and 43 ($C_2H_3O^+$, 21%). [i] Identified spectroscopically (^1H n.m.r. and g.l.c.–m.s.) by examination of a -23 °C trap fraction also containing $(CF_3)_2NOCHMeOEt$ as $[(CF_3)_2NOCHMe]_2O$: δ_H (ext. C_6H_6) -1.23 (q) and -5.20 (d, $^3J_{HH}$ 5 Hz); *m/e* 240 [$M^{+\cdot} - (CF_3)_2NO\cdot$, 17], 212 ($CF_3NOCHMeO^+$, 11), 198 [$(CF_3)_2NOCHOH^+$, 13], 196 [$(CF_3)_2NOCHMe^+$, 99], 150[e] {[$CF_2{=}N(OH)CF_3]^+$, 26}, 69 ($CF_3^+$, 55), 45 ($CH_3CH{=}OH^+$, 88), 44 [$C_2H_4O^+$, 91), and 43 ($C_2H_3O^+$, 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. $SiMe_4$) $+5.32$ (s; CH_2) and $+7.0$ (m; C_6H_5); *m/e* 275 ($M^{+\cdot}$, 26), 107 ($PhOCH_2^+$, 100), 77 ($C_6H_5^+$, 85), 69 (CF_3^+, 18), and 65 ($C_5H_5^+$, 22%). [l] Present in the yellowish-red liquid referred to in footnote *j*, and containing unidentified carbonyl compounds ($\lambda_{max.}$ 5.80 and 5.85 μm) and $(CF_3)_2N$-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; $(CF_3)_2NOCH_2$], -10.1 (m; CF_2), and -78.0 (dt; CHF, $^2J_{HF}$ 48, $^3J_{FF}$ 11 Hz), δ_H (ext. $SiMe_4$) $+5.17$ (s; CH_2) and $+5.80$ (dt; CHF, $^3J_{HF}$ 4 Hz); *m/e*[s] 182 [top mass peak; $(CF_3)_2NOCH_2^+$, 93], 147 ($CHF^{35}ClCF_2OCH_2^+$, 61), 117 ($CHF^{35}ClCF_2^+$, 87), and 69 (CF_3^+, 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 CF_3 groups of $(CF_3)_2NOCFCl$], $+0.2$ (vbr q; CFCl), and -13.5 (dd; CF_2), δ_H (ext. $SiMe_4$) $+3.40$ (s); *m/e*[s] 296 [top mass peak; $M^{+\cdot}$ (^{35}Cl) $-$ F$\cdot$, 6], 280 [$M^{+\cdot}$ (^{35}Cl) $-$ $^{35}Cl\cdot$, 48], 168 [$(CF_3)_2NO^+$, 3], 147 ($MeOCF_2CF^{35}Cl^+$, 79), 81 ($MeOCF_2^+$, 100), and 69 (CF_3^+, 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, $\lambda_{max.}$ (film) 5.59 (C=O str.) μm, δ_H (ext. C_6H_6) -3.05 (s), and *m/e*[s] 258 [top mass peak; $M^{+\cdot}$ (^{35}Cl) $-$ $^{35}Cl\cdot$, 24], 234 [$(CF_3)_2NOCFCl^+$, 15], 125 ($MeOCOCF^{35}Cl^+$, 63), 69 (CF_3^+, 81), and 59 ($MeOCO^+$, 100%). [s] Correct ^{35}Cl : ^{37}Cl ratios were observed for ions containing chlorine.

abstraction by an electrophilic chlorine atom stemming from the polar effect[7] of the CF_2 group follows the order $\mathrm{C}H\mathrm{FCl} > \mathrm{C}H_3$,[8] strongly resists attack by bistrifluoromethyl nitroxide at room temperature; and even at 50 °C it takes 6 days for a *ca.* 2 : 1 molar [nitroxide ($R\cdot$) : ether] purple mixture of reactants to become colourless. The products under the latter conditions, in Pyrex, are RCH_2OCF_2CHFCl (5) (67%), $MeOCF_2CRFCl$ (6) (9.5%), RH (94%), $MeOCF_2CHFCl$ (23% recovery), and small amounts of $RCH_2OCOCHFCl$ (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 $MeOCF_2CHFCl$ respectively] at the walls of the reaction vessel [possibly with assistance from $(CF_3)_2NOH$]: † they are produced in higher yields when the $MeOCF_2CHFCl$–$(CF_3)_2NO\cdot$ 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 RCH_2OCF_2CHFCl (5) and Me_3OCF_2CRFCl (6) at 80—90 °C in the presence of powdered glass does yield the corresponding esters $RCH_2OCOCHFCl$ (7) and MeOCOCRFCl (8) [R = $(CF_3)_2NO$], 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 acid [12]) 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-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 cm^3) 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. $C_5H_3ClF_7NO_3$ requires C, 20.4; H, 1.0; F, 45.3; N, 4.8%), $\lambda_{max.}$ (film) 5.57 (C=O str.) μm, δ_H (external C_6H_6 as reference) −0.41 (d; C*H*F, $^2J_{HF}$ 55 Hz) and −1.10 (s; C*H*$_2$) p.p.m., and *m/e* 258 [top mass peak; $M^{+\cdot}$ (^{35}Cl)− $^{35}Cl\cdot$, 0.1%], 182 [$(CF_3)_2NOCH_2^+$, 95%], 125 ($CHF^{35}ClCO_2CH_2^+$, 30%), 95 ($CHF^{35}ClCO^+$, 13%), 69 (CF_3^+, 100%), and 67 ($CHF^{35}Cl^+$, 80%) (correct isotopic abundancies were observed).

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

† αα-Difluoro-ethers (including $MeOCF_2CHFCl$) 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 [$CF_2{=}CFCl + NaOMe{-}MeOH \longrightarrow CHFClCF_2OMe \longrightarrow$ (with 96% H_2SO_4) $CHFClCO_2Me$] by the application of procedures [11] used to synthesise the analogous ethyl compounds.

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