Three New Methods for Generation of Bis(polyfluoroalkyl) Nitroxides; Reactions of Nitrite Salts with Polyfluorodiacyl Peroxides, Polyfluoroalkyl Iodides, and Polyfluoroalkylsulphonyl Bromides

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Three new reactions of nitrites with polyfluorodiacyl peroxides (**2**), polyfluoroalkyl iodides (**3**), or polyfluoroalkylsulphonyl bromides (**4**) have been found to produce bis(polyfluoroalkyl) nitroxides (**1**), and their possible mechanistic paths are discussed.

Bis(trifluoromethyl) nitroxide (**1a**), one of the most reactive nitroxides, has been subjected to intensive investigations related to its structure,[1] reactivity in hydrogen-abstraction, halogen-displacement, addition, and substitution reactions[2—4] since its first preparation by oxidation of bis(trifluoromethyl)hydroxylamine.[5] Very recently, we have developed a novel method for the generation of not only (**1a**) but also a series of its analogues (**1b**—**g**) by making use of the electron transfer reactions (SET) between (**2**) and carbanions derived from secondary nitroalkanes.[6,7] We now report three new

Table 1. E.s.r. parameters for the nitroxides (**1**) generated in the reactions of nitrites ($NaNO_2$, $AgNO_2$) with (**2**), (**3**), and (**4**) in $CClF_2$–CCl_2F at 20 ± 2 °C.[a,b]

R_F group in (**1**)	g	From (**2**) + $M^+NO_2^-$ a_N	From (**2**) + $M^+NO_2^-$ a^β_F	From (**2**) + $M^+NO_2^-$ a^γ_F	From (**3**) + $M^+NO_2^-$ a_N	From (**3**) + $M^+NO_2^-$ a^β_F	From (**3**) + $M^+NO_2^-$ a^γ_F
a; CF_3	2.0066				9.35	8.35	
b; C_2F_5	2.0069				8.86	12.13	1.02
c; n-C_3F_7	2.0070	8.77	9.96	1.22	8.80	9.99	1.20
d; n-C_7F_{15}	2.0070				8.75	9.74	1.17
e; HCF_2CF_2	2.0067				9.76	14.40	
f; $H(CF_2)_4$	2.0069				8.94	9.91	1.14
g; $H(CF_2)_6$	2.0069				8.61	9.75	1.16
h; $ClCF_2CF_2$	2.0069	8.65	10.87	0.89			
i; $Cl(CF_2)_4$[c]	2.0072	8.77	9.77	1.22			
j; $Cl(CF_2)_6$[c]	2.0070	8.75	9.67	1.18			
k; $FO_2S(CF_2)_2O(CF_2)_4$	2.0069	8.54	10.22	1.10			

[a] Couplings are in G, ±0.05 to 0.1 G (1 G = 10^{-4} T). [b] The spectra have been satisfactorily simulated using the Varian E-935 software program no. 929970–11. [c] (**1i**) and (**1j**) could be similarly generated in the reactions of $Cl(CF_2)_4SO_2Br$ (**4i**) and $Cl(CF_2)_6SO_2Br$ (**4j**) with $NaNO_2$ respectively.

methods for generating these nitroxides using the reactions of nitrites (*e.g.*, $NaNO_2$, $AgNO_2$) with (**2**), (**3**), and (**4**) in $CClF_2$–CCl_2F at 20 ± 2 °C.

$$\left.\begin{array}{ll} & \underset{\textbf{(2)}}{(R_FCOO)_2} \\ \text{or} & \underset{\textbf{(3)}}{R_FI} \\ \text{or} & \underset{\textbf{(4)}}{R_FSO_2Br} \end{array}\right\} + M^+NO_2^- \longrightarrow \underset{\textbf{(1)}}{R_FN(O)R_F}$$

In a typical experiment, 0.30 ml of a $CClF_2$–CCl_2F solution (~0.1 M) of (**2**) or (**4**) was quickly shaken with an excess of finely powdered nitrite salt ($NaNO_2$ or $AgNO_2$) in a degassed e.s.r. tube; rapid development of a blue colour indicated the presence of polyfluoronitrosoalkane, R_FNO (**10**), and a well resolved e.s.r. spectrum could be recorded a few minutes after shaking. The g factor, a_N, a^β_F and a^γ_F values thus obtained coincide with those previously reported for the bis(polyfluoroalkyl) nitroxides.[2,7] The same procedure is applicable to the iodides (**3**), if the sample tube is u.v. irradiated. The e.s.r. parameters of the nitroxides (**1**) thus generated are listed in Table 1. The spectra of three representative nitroxides (**1c**, **1e**, and **1i**) generated by the three different methods, are shown in Figure 1.

Speculative mechanistic paths are proposed in Scheme 1, in which $R_F^\bullet$ (**5**), $R_FONO^{\bullet -}$ (**6**), R_FONO (**8**), R_FNO (**10**), and NO are key intermediates. Equations (1) to (4) represent initiation steps in which the polyfluoroakyl radicals (**5**) are generated. Some contribution from the unimolecular decomposition of the peroxides (**2**) at 20 °C is expected, since the rate constant at 30 °C is known to be about $8.5 \times 10^{-5}\,s^{-1}$.[8] On the basis of our previous work,[9] however, it is very likely that electron transfer reactions, *i.e.*, equation (3), and maybe also equation (4), are the more important initiation reactions for starting substrates (**2**) and (**4**). This proposition, equation (3), is strongly supported by the isolation of almost stoicheiometric amounts of R_FCOONa. Combinations of carbon-centred radicals with anions, equation (5), are well-known steps, *e.g.*,

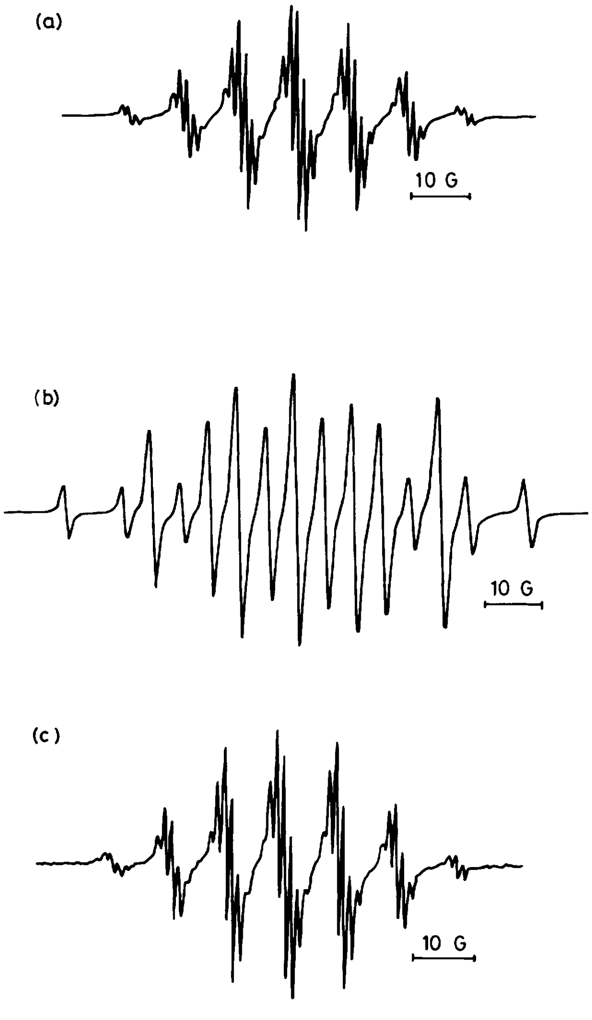

Figure 1. E.s.r. spectra of three representative nitroxides (a) (**1c**), (b) (**1e**), and (c) (**1i**) generated by the reactions of $M^+NO_2^-$ with (**2c**), (**3e**), and (**4i**), respectively.

$$(3) \xrightarrow{\text{u.v.}} \underset{(5)}{R_F^\bullet} + I^\bullet \qquad (1)$$

$$(2) \xrightarrow{\text{Heat}} 2\,(5) + 2\,CO_2 \qquad (2)$$

$$(2) + M^+NO_2^- \xrightarrow{\text{SET}} [(R_FCO_2)_2^{\bullet -}, M^+\dot{N}O_2] \rightarrow \rightarrow (5) + CO_2 + R_FCO_2M + NO_2 \qquad (3)$$

$$(4) + M^+NO_2^- \xrightarrow{\text{SET}} [(R_FSO_2Br)^{\bullet -}, M^+\dot{N}O_2] \rightarrow \rightarrow (5) + SO_2 + MBr + NO_2 \qquad (4)$$

$$(5) + NO_2^- \longrightarrow \underset{(6)}{R_FONO^{\bullet -}} \text{ or } \underset{(7)}{R_FNO_2^{\bullet -}} \qquad (5)$$

$$(7) \longrightarrow (5) + NO_2^- \qquad (6)$$

$$(6) \text{ or } (7) \xrightarrow{-e} \underset{(8)}{R_FONO} \text{ or } \underset{(9)}{R_FNO_2} \qquad (7)$$

$$(9) + (6) \longrightarrow (8) + (7) \qquad (8)$$

$$(5) + NO_2 \longrightarrow (8) \text{ or } (9) \qquad (9)$$

$$(8) + (5) \xrightarrow[\text{steps}]{\text{1 or 2}} \underset{(10)}{R_FNO} + R_FO^\bullet \qquad (10)$$

$$(8) \longrightarrow NO + R_FO^\bullet \qquad (11)$$

$$(5) + NO \longrightarrow (10) \qquad (12)$$

$$(5) + (10) \longrightarrow (1) \qquad (13)$$

Scheme 1

in $S_{RN}1$ reactions.[10] The ability of the $-NO_2$ to act as a leaving group of a radical anion, equation (6), has been documented previously.[11] Equation (7) depicts the oxidation of radical anions (**6**) or (**7**) to products (**8**) or (**9**) by trace oxygen or other electron acceptors, as exemplified by equation (8) which takes R_FNO_2 (**9**) as an acceptor.† Notably, equation (8) is also one of the three reactions [equations (7), (8), and (9)] which generate the key intermediate (**8**). Possibly, the nitrite (**8**) could be attacked by $R_F^\bullet$ (**5**) to give the other key intermediate R_FNO (**10**) directly, equation (10), or this polyfluoroalkyl nitrite might undergo homolysis to yield NO and $R_FO^\bullet$,[12] followed by combination of NO and $R_F^\bullet$ to yield R_FNO (**10**) [equations (11) and (12)]. Finally, equation (13) ends our mechanism with the formation of the e.s.r.-observed products (**1**).

Received, 21st April 1986; Com. 525

References

1 C. Chatgilialoglu, V. Walastesta, and K. U. Ingold, *J. Phys. Chem.*, 1980, **84**, 3597.

2 R. E. Banks, R. N. Haszeldine, and B. Justin, *J. Chem. Soc. C*, 1971, 2777; R. E. Banks, D. R. Choudhury, and R. N. Haszeldine, *J. Chem. Soc., Perkin Trans. 1*, 1973, **1**, 1092.

3 R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc. C*, 1966, 901.

4 S. P. Makarov, M. A. Englin, A. F. Videiko, V. A. Tobolin, and S. S. Dubov, *Dokl. Akad. Nauk. SSSR, Ser. Khim.*, 1966, **168**, 344; *Chem. Abstr.*, 1966, **65**, 8742a.

5 W. D. Blackley and R. R. Rinhard, *J. Am. Chem. Soc.*, 1965, **87**, 802; S. P. Markarov, A. Ya. Yakubovich, S. S. Dubov, and A. N. Medvedev, *Dokl. Akad. Nauk. SSSR*, 1965, **160**, 1319.

6 Cheng-Xue Zhao, Yan-ling Qu, Xi-Kui Jiang, and Xian-Ming Jin, *Acta Chimica Sinica*, 1985, **43**, 1184.

7 Cheng-Xue Zhao, Xi-Kui Jiang, Guo-Fei Chen, Yan-Ling Qu, Xian-Shan Wang, and Jian-Ying Lu, *J. Am. Chem. Soc.*, 1986, **108**, 3132.

8 Cheng-Xue Zhao, Ren-Mo Zhou, He-Qi Pan, Xiang-Shan Jin, Yan-Ling Qu, Cheng-Jiu Wu, and Xi-Kui Jiang, *J. Org. Chem.*, 1982, **47**, 2009.

9 Cheng-Xue Zhao, E.-T. Gamil, and C. Walling, *J. Org. Chem.*, 1983, **48**, 4908; Cheng-Xue Zhao, Xi-Kui Jiang, and Ji-Yue Zhang, *J. Fluorine Chem.*, 1985, **27**, 401; Xiang-Shan Jin, Tian-Fei Xu, Cheng-Xue Zhao, and Xi-Kui Jiang, *Acta Chimica Sinica* (*Engl. Ed.*), 1985, 155; Cheng-Xue Zhao, Xiang-Shan Jin, Xi-Kui Jiang, Mao-Qing Zhou, and Jun-Fa Wei, *Acta Chimica Sinica*, 1986, **44**, in the press.

10 R. A. Rossi and R. H. de Rossi, Aromatic Substitution by the $S_{RN}1$ Mechanism, Am. Chem. Soc. Monograph 178, Washington, D.C., 1983.

11 D. D. Tanner, E. V. Blackburn, and G. E. Diaz, *J. Am. Chem. Soc.*, 1981, **103**, 1557.

12 L. Batt, R. T. Milne, and R. D. McCulloch, *Int. J. Chem. Kinet.*, 1977, **9**, 567.

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† In the reaction of (**3**) with $NaNO_2$ in $CClF_2$–CCl_2F at 16 °C, small amounts of R_FNO_2 (**9**) were indicated by i.r. peaks for stretching vibrations of the NO_2 group, *i.e.*, $\nu_{\text{sym.}}$ 1365 cm^{-1} and $\nu_{\text{asym.}}$ 1610 cm^{-1}.