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THE CHEMISTRY OF DIACYL PEROXIDES IX.

AN ESR STUDY OF THE REDUCTION OF POLYFLUORODIACYL PEROXIDES BY COPPER (O) IN THE PRESENCE OF 2-NITRO-2-NITROSOPROPANE : THE GENERATION OF POLYFLUOROALKYL NITROALKYL NITROXIDES

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SUMMARY

Polyfluoroalkyl radicals generated by one-electron reduction of polyfluorodiacyl peroxides by copper (O) were trapped by 2-nitro-2-nitrosopropane to yield polyfluoroalkyl nitroalkyl nitroxides, $R_FN(O)CMe_2NO_2$.

INTRODUCTION

Some new fluorinated nitroxides, i.e.,polyfluoroalkyl nitroalkyl nitroxides **1** and bis(polyfluoroalkyl) nitroxides **2**, were generated in the electron-transfer oxidation of the carbanions derived from secondary nitroalkanes by polyfluorodiacyl peroxides **3** in F-113 (CCl_2F-$CClF_2$) solution [1]. For characterization of the spectra of nitroxides **1**, we resorted to the method of generating the same species by different reactions. Rather unexpectedly, in experimental attempts to generate **1** by trapping the $R_F\cdot$ radicals derived from the thermal decomposition of the peroxides **3** with 2-nitro-2-nitrosopropane **4** in F-113 solutions at room temperature, none of the nitroxides **1** , but well resolved ESR spectra of bis-

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(polyfluoroalkyl)nitroxides **2** were observed [2]. Product analysis showed that the main reaction was the rapid oxidation of **4** by **3** to 2,2-dinitropropane(yield, ~60 %). The present work reports successful attempts to make the nitroxides **1** by the copper powder induced reductive decomposition of **3** in the presence of **4** under similar conditions.

RESULTS AND DISCUSSION

A F-113 solution of peroxide **3** (0.1M, 0.2ml) was added into a degassed ESR tube containing reddish-brown activated copper powder and 0.2 ml (0.1M) of a blue solution of **4** in the same solvent. The tube was shaken vigorously for about 2 min. at a constant temperature (ranges from 0 to 20 °C). Well resolved ESR spectra of nitroxides **1** were recorded.Some representative spectra of nitroxides **1** and **2** plus Cu^{2+} are shown in Fig.1. The ESR parameters of **1** are given in Table 1. The assignment of nitroxides **1** is based on the following evidence: (1) The a_N values and g factors of the spectra coincide with those reported for nitroxides $R_FN(O)CMe_2NO_2$ generated in the reactions between **3** and the carbanions derived from nitroalkanes [1a]; (2) The dependancy of the a_N values on the nature of the polyfluoroalkyl groups shows a consistent trend. In other words, if the electron-attracting power of the R_F groups are CF_3 < secondary R_F < tertiary R_F [3,4] ,then the decreasing order of a_N values (CF_3 > C_2F_5 > $\underline{n}$-C_3F_7 and $\underline{n}$-C_7F_{15} ; HCF_2CF_2 > $HCF_2(CF_2)_3$ ≳ $HCF_2(CF_2)_5$ nicely bears out the notion that in addition to geometric factors the polar effect may play a role in affecting the a_N values [5]. Notably, ω-hydrogen atoms in HCF_2CF_2 and $HCF_2(CF_2)_3$ groups significantly reduce their electron-attracting power and hence increase a_N values of the corresponding nitroxides, **1e** and **1f** . Interestingly, the effect is a long range interaction which is still felt four carbon atoms away from the nitrogen atom in nitroxide **1f** .

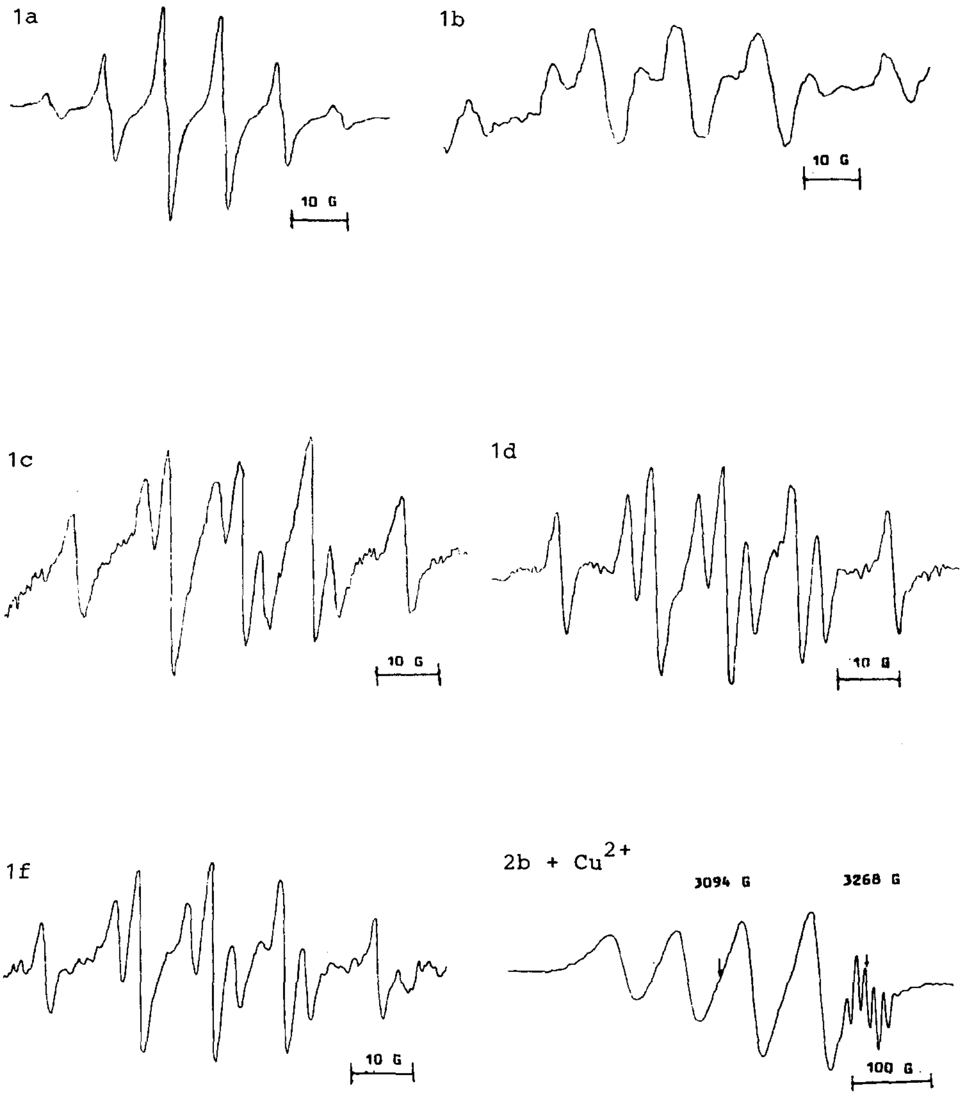


Fig. 1. ESR spectra of some representative polyfluoroalkyl 2-nitropropyl nitroxides, $R_FN(O)CMe_2NO_2$, **1**

1a , **1b** , **1c** , **1d** , **1f** , **2b** + Cu^{2+}

TABLE 1

ESR parameters of polyfluoroalkyl nitroalkyl nitroxides **1** generated from the reduction of polyfluorodiacyl peroxides **3** by copper(0) in the presence of 2-nitro-2-nitrosopropane **4** in F-113 solution(Couplings are in Gauss, ± 0.05 to 0.10 Gauss)

$R_FN(O)CMe_2NO_2$ (1)

	R_F	g	a_N	a^{β}_F	a^{γ}_F	t °C
a	CF_3	2.0065	10.83	10.83		19.0
b	C_2F_5	2.0066	10.55	15.75	0.94	19.0
c	$\underline{n}$-C_3F_7	2.0066	10.50	13.77		19.5
d	$\underline{n}$-C_7F_{15}	2.0066	10.50	13.96		20.0
e	HCF_2CF_2	2.0063	11.00	16.35		20.5
f	$HCF_2(CF_2)_3$	2.0065	10.67	13.98		5.0
g	$HCF_2(CF_2)_5$	2.0065	10.41	14.08		19.5

TABLE 2

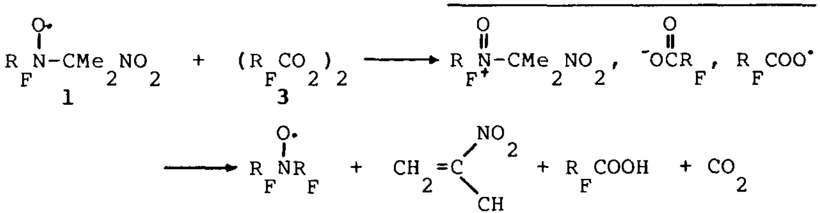
Bis(polyfluoroalkyl) nitroxides **2** generated from the reduction of **3** (excess) by copper(0) in the presence of **4** in F-113 solution at 20+2 °C(Couplings are in Gauss, + 0.05 to 0.10 Gauss)

$R_FN(O)R_F$ (2)

	R_F	g	a_N	a^{β}_F	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	$\underline{n}$-C_3F_7	2.0070	8.77	9.96	1.22
d	$\underline{n}$-C_7F_{15}	2.0070	8.75	9.74	1.17
e	HCF_2CF_2	2.0067	9.76	14.41	
f	$HCF_2(CF_2)_3$	2.0069	8.94	9.91	1.14
g	$HCF_2(CF_2)_5$	2.0069	8.61	9.75	1.16

When an excess of peroxides **3** was used (molar ratio **3**:**4**:Cu= 2 or 3:1:1), it was found that the signals of 1 diminished quickly and that for nitroxides **2** grew simultaneously and finally became predominant. The ESR parameters thus obtained for **2** are the same as the reported data [1a, 2, 6] and are given in Table 2 . Consequently, either **1** or **2** can be selectively generated simply by varying the molar ratio of the reactants.

Predominance in the formation of nitroxides **2** in the presence of excess of 3 might be related to the following possibilities:
(A) Formation of unsymmetrical nitroxides **1** would need significant amounts of **4**, but excess of the peroxides **3** would oxidize and thus consume **4** , and thus favor the formation of the symmetrical nitroxides **2** through other paths involving R_F , NO and fluorine- and nitrogen-containing intermediates [2].)
(B) Peroxides **3** would destroy nitroxides 1 by one-electron oxidation. The oxidation products, oxoammonium salts, would decompose subsequently and also end up as nitroxides 2 (Scheme I);



$$R_F\overset{O^\bullet}{\overset{|}{N}}\text{-}CMe_2NO_2\;(\mathbf{1}) + (R_FCO_2)_2\;(\mathbf{3}) \longrightarrow \overline{R_F\overset{O}{\overset{\|}{\overset{+}{N}}}\text{-}CMe_2NO_2,\ {}^-O\overset{O}{\overset{\|}{C}}R_F,\ R_FCOO^\bullet} \longrightarrow R_F\overset{O^\bullet}{\overset{|}{N}}R_F + CH_2{=}C(NO_2)CH_3 + R_FCOOH + CO_2$$

Scheme I

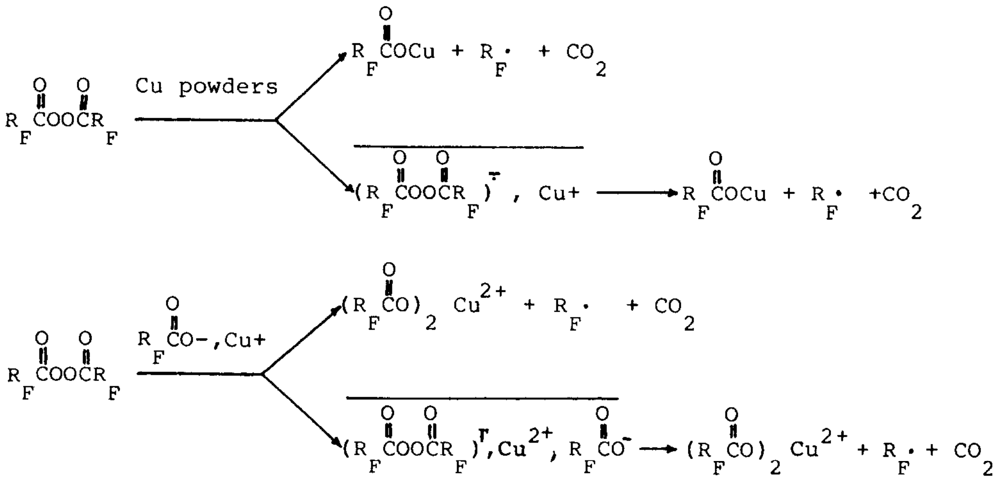
(C) Excess of **3** provided a source of R_F radicals through thermal decomposition ($k_1 = 8.5 * 10^{-5}\ S^{-1}$, $t_{1/2} = 137$ min. at 30°C) [7]. The $R_F^\bullet$ thus produced would eventually replace the 2-nitropropyl groups in **1** and yield **2** :

$$\mathbf{1} \xrightarrow{R_F^\bullet} R_FN{=}O + {}^\bullet CMe_2NO_2$$

$$R_FN{=}O + R_F\cdot \longrightarrow \mathbf{2}$$

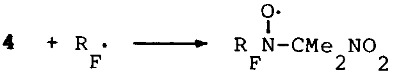
$$2\ \dot{C}Me_2NO_2 \longrightarrow Me_2(NO_2)C\text{-}CMe_2(NO_2)$$

The following observations made after mixing the reactants in an ESR tube are relevant to the electron-transfer nature of the studied reactions: (A) The blue solution turned green immediately; and the strong ESR signal of Cu^{2+} ($I=3/2$) was observed as a quartet(with splitting constant ~ 78 Gauss) at the central magnetic field, 3094 Gauss; (B) The reddish-brown copper powders disappeared and white solids [$Cu(OCOR_F)_2$ by elementary analysis] precipitated; (C) There was an evolution of carbon dioxide during the reaction. These redox reactions would generate $R_F\cdot$ radicals either directly on the surface of the activated copper powders or through the fast fragmentation of the peroxide radical anions, $(R_FCO_2)_2^{\overline{\cdot}}$, initially formed as shown in Scheme II.



Scheme II

Since activated copper is a more powerful reducing agent than the nitroso compound **4** , it would react with the peroxides first thus large amount of R_F radicals would be formed within a short period of time. In other words, copper could protect **4** from being oxidized by **3** and therefore **4** could serve as an efficient spin trap of the R_F radicals:



$$\mathbf{4} + R_F\cdot \longrightarrow R_F\overset{O\cdot}{N}\text{-}CMe_2NO_2 \qquad \mathbf{1}$$

EXPERIMENTAL

Polyfluorodiacyl peroxides [7] and 2-nitro-2-nitrosopropane [2] were prepared as described previously. Powdered copper was activated by vigorous stirring in hydrochloric acid (38%) for 1 hr, washing with acetone (A. R.) and drying under vacuum. The brownish-red activated copper powder was sealed in glass tubes under vacuum. F-113 was purified by conventional methods.

ESR spectra were recorded on a Varian E-112 X-band spectrometer with 100 KH_Z modulation. Temperature variation was achieved with a Varian E-257 variable temperature accessory. Spectral simulations were performed by using Varian E-935 software program, No 929970-11.

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