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EPR STUDIES OF POLYFLUOROALKYL t-BUTYL NITROXIDES

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SUMMARY

A number of poly- or perfluoroalkyl t-butyl nitroxides $R_FN(O^\bullet)tBu$ have been generated by a new method which makes use of the electron-transfer initiated reaction between polyfluoroalkyl iodides and various electron donors, i.e., MNO_2, CH_2NO_2Na, $MeCHNO_2Na$, Me_2CNO_2Na and $Na_2S_2O_4$, in the presence of 2-methyl-2-nitrosopropane. Substituent effects on the hyperfine coupling constants a_N and a_F^β values are discussed.

INTRODUCTION

The chemistry of polyfluorinated nitroxides $R_FN(O^\bullet)R$ (1-R) and $R_FN(O^\bullet)-R_F$(2) has been investigated by many workers [1] and very recently reviewed [2]. The present work reports yet another electron-transfer (ET) initiated reaction for the generation of nine fluoroalkyl t-butyl nitroxides $R_FN(O^\bullet)t\text{-}Bu$ (1-tBu). This new method involves the interaction between poly- or perfluoroalkyl iodides R_FI and five different donors, namely, MNO_2, CH_2NO_2Na, $MeCHNO_2Na$, Me_2CNO_2Na and $Na_2S_2O_4$, in the presence of 2-methyl-2-nitrosopropane (t-BuNO). Seven other nitroxides 1-R have been prepared by known reactions (eq 2 to eq 4) [1a,3]. Substituent effects on the hyperfine coupling constant a_N and a_F^β of these nitroxides are discussed.

EXPERIMENTAL

Materials:

Di-tert-butyl nitroxide (Kodak), tBuNO (Aldrich), $ClCF_2CF_2I$, $ICF_2CF_2OCF_2CF_2SO_2F$,$I(CF_2CF_2)_2OCF_2CF_2SO_2F$ and $i\text{-}C_3F_7I$ were kindly supplied by Dr. Wi-Qing Hu and Mr. Ke-Qiang Hu. The fluorinated diacyl peroxides, CH_2NO_2Na, $MeCHNO_2Na$, Me_2CNO_2Na were prepared and $CF_2ClCFCl_2$(F113) was purified as previously reported [4].

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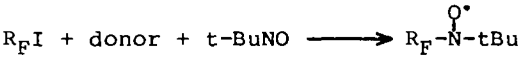
EPR spectra were recorded on a Varian E-112 X-band spectrometer with 100 KHz modulation. Temperature variation was achieved with a Varian E-257 variable temperature accessory. The temperature was measured with a Ni-Cr/Ni-Al thermocouple.

Samples were prepared in EPR tubes by adding a blue solution of t-BuNO in F113 to the fluoroalkyl iodide and a donor at room tempera in the dark. The tube was quickly shaken and placed in the cavity of the spectrometer, the tube was adjusted to the desired temperature, the EPR spectra of the sample was then recorded. Typical spectra thus obtained are shown in Fig.1. Photolysis of fluoroalkyl iodide with t-BuNO was performed in the EPR cavity using a ILC Technology Inc. Model PS-150-8 apparatus.

Reactions of fluorinated diacyl peroxide with di-tert-butyl nitroxide were carried out according to previously described procedure [3].

RESULTS AND DISCUSSION

Sixteen poly- or perfluoroalkyl t-butyl nitroxides, i.e., $R_FN(O^\bullet)tBu$ or 1-tBu, have been generated by reactions shown by equations (1) to (4); their EPR parameters are summarized in Table 1. in which eight new compounds are asterisked. Equation (1) describes a new method for the generation of nitroxides 1-tBu-c,-f,-g,-h,-j,-k,-l, and -o .



$$R_FI + \text{donor} + t\text{-BuNO} \longrightarrow R_F\text{-}\overset{O^\bullet}{N}\text{-tBu} \qquad (1)$$

1-tBu

1-tBu: a,b,c,... to p, for various R_F groups as indicated in Table 1

$$(R_FCOO)_2 + t\text{-BuNO} \longrightarrow 1\text{-tBu} \qquad (2)$$

$$R_FI + t\text{-BuNO} \xrightarrow{h\nu} 1\text{-tBu} \qquad (3)$$

$$(R_FCOO)_2 + t\text{-Bu}_2NO \longrightarrow 1\text{-tBu} \qquad (4)$$

The spectra of fourteen nitroxides 1-tBu-b,-c,... to -o show a characteristic triplet of triplets due to the coupling of the nitrogen atom and two equivalent fluorine atoms. Identity of the

TABLE 1

EPR Parameters (G) of Polyfluoroalkyl t-Butyl Nitroxides (1-tBu)

1-tBu-z z =	R_F	T C ±2 C	a_N ±0.05 G	a_F ±0.05 G	g ±0.0004	method eq
a	CF_3	19	11.65	12.77		4
b	$F-C_2F_4$†	19	11.30	22.70		4
c	$Cl-C_2F_4$	19	11.41	20.78	2.0060	1,3
d	$H-C_2F_4$†	19	12.10	21.90		4
e	$CF_3C_2F_4$†	19	11.45	18.83		1,3
f	$FSO_2C_2F_4OCF_2CF_2$*	19	11.38	22.50		2
g	$F-(CF_2)_4$*	24	11.54	19.98	2.0066	1,3
h	$Cl-(CF_2)_4$*	24	11.43	20.13	2.0064	1,3
i	$H-(CF_2)_4$*	25	12.17	19.39		4
j	$FSO_2C_2F_4O(CF_2)_4$*	25	11.39	20.69		1,3
k	$F-(CF_2)_6$*	24	11.52	19.68	2.0065	1,3
l	$Cl-(CF_2)_6$*	24	11.43	19.05		1,3
m	$H-(CF_2)_6$	24	11.61	19.35		4
n	$CF_3-(CF_2)_6$	24	11.37	19.33		2
o	$Cl-(CF_2)_8$*	24	11.49	19.50	2.0065	1,3
p	$(CF_3)_2CF$	26	11.26	2.48	2.0063	1,3

† Similar EPR has been reported in ref.[3]. * New compounds

spectra of $CF_3N(O^\bullet)tBu$ (1-tBu-a) and $(CF_3)_2CFN(O^\bullet)tBu$ (1-tBu-p) with those reported by Klabunde [1a] confirms the structures of the fluorinated nitroxides generated by the reactions shown by equations (1) to (4).

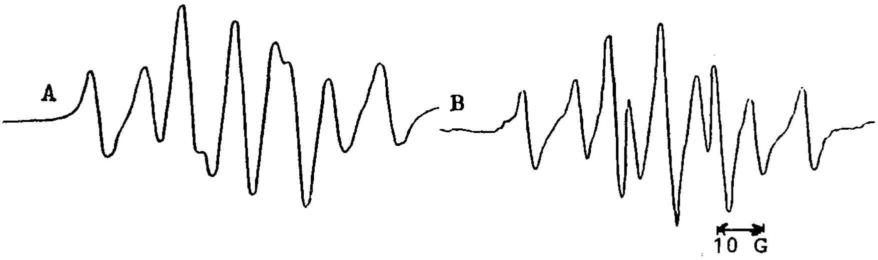


Fig.1. EPR spectra of (A) $F(CF_2)_6N(O^\bullet)tBu$ formed from $n(C_6F_{13})I$ and $NaNO_2$, (B) $Cl(CF_2)_6N(O^\bullet)tBu$ formed from $Cl(CF_2)_6I$ and $Na_2S_2O_4$, both in the presence of t-BuNO.

Reaction 1 is believed to be initiated by one electron transfer [2]. Immediate fragmentation of the intermediate radical anion $R_FI^{\cdot -}$ generates the radical $R_F^{\cdot}$ and trapping of $R_F^{\cdot}$ by tBuNO leads to the formation of poly- or perfluoroalkyl tert-butyl nitroxides 1-tBu.

TABLE 2

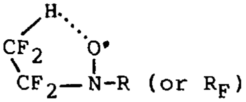
EPR parameters of symmetrical and unsymmetrical polyfluoroalkyl alkyl nitroxides with a β-Y substituent

	$YCF_2CF_2N(O^{\cdot})tBu$ (β-1-tBu)		$YCF_2CF_2N(O^{\cdot})$ tAm* (β-1-tAm)		$YCF_2CF_2N(O^{\cdot})CF_2CF_2Y$* ($\beta$-2)		
Y	a_N(G)	a_F^{β}(G)	a_N(G)	a_F^{β}(G)	a_N(G)	a_F^{β}(G)	a_F^{γ}(G)
H	12.10	21.90	11.93	22.12	9.76	14.40	/
CF_3	11.45	18.83	11.33	20.00	8.80	9.99	1.20
Cl	11.41	20.78	/	/	8.65	10.87	0.89
F	11.30	22.70	11.18	23.64	8.86	12.13	1.02

Couplings are in G, ±0.05 to 0.1 G, at 20±2°C

*taken from ref. [8,9].

Examination of the EPR parameters of 1-tBu and $Y-CF_2CF_2N(O^{\cdot})-CF_2CF_2-Y$($\beta$-2) listed in Table 1 and Table 2 shows that for the four $Y-CF_2CF_2N(O^{\cdot})tBu$ nitroxides designated as β-1-tBu with Y = H, Cl, F and CF_3, the order of decreasing a_N values, i.e., H(12.10 G) $>$ CF_3(11.45 G), Cl(11.41 G) $>$ F(11.30 G) seems to parallel an order of increasing σ_I values (parenthesized) [5], i.e., H(0.0) $<$ CF_3(0.45), Cl(0.46) $<$ F(0.50) or σ_x values [6], i.e., H(0.0) $<$ CF_3(0.02) $<$ Cl(0.16) $<$ F(0.70). However, for symmetrical β-2 nitroxides [7] the order of decreasing a_N values i.e., H(9.76 G) $>$ F(8.86 G) $>$ CF_3(8.80 G) $>$ Cl(8.65G) does not correlate with σ_I and σ_x values. These contrasting results might be a reflection of subtle differences in interactions between various types of electronic (polar) and steric (including conformational) effects [10]. For example, symmetry in the symmetrical nitroxides β-2 may reduce the relative importance of polar effects. Furthermore, there is the possibility that the β-substituents (β-Y) in 1-tBu might be very close to the oxygen atom and this interaction might perturb the usual field and inductive effects. On the other hand, this perturbation might be affected (reduced ?) by bulky t-butyl or t-amyl groups [9] in unsymmetrical nitroxides, such as β-1-tBu and β-1-Am. The subtle and complicated nature of various types of interactions is similarly reflected in the a_F^{β} values, i.e., sometimes a_F^β values run parallel to a_N values, e.g., for Y-C_6H_4-C(O)N(O•)$(CF_2)_6$H [2], Y-CF_2CF_2N(O•)CMe_2NO [11], Y-CF_2CF_2N(O•)Ph [1c], and sometimes they do not, e.g., for Y-CF_2CF_2N(O•)tBu of the present work, Y-CF_2CF_2N(O•)tAm (Table 2) and Y-CF_2CF_2N(O•)CMe_2C(O)-Me [1c]. Certainly, the observed substituent effect of ω-Y on the a_N and a_F^β values in long-chain nitroxides(1-tBu-f,-g,... to -o) is even more complicated, and no speculation on its rationalization will be attempted. Finally, it should be pointed out that in addition to inductive/field effects, the effect of intramolecular hydrogen-bonding as shown in structure 3 could also enhance the a_N values [8,9]. Notably, our data show that even when there are four CF_2 groups (1-tBu-i) between Y and the nitroxide group, the a_N value is still large if compared with those with six CF_2 groups (1-tBu-m).



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