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# GENERATION OF $^{15}N$ LABELLED BIS(POLYFLUOROALKYL) NITROXIDES AND THEIR HYDROGEN-ABSTRACTION REACTIONS WITH ALKANES, ALKYLBENZENES AND ALDEHYDES

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## SUMMARY

Blue solutions containing $^{15}N$ labelled bis(polyfluoroalkyl) nitroxides and spin traps, polyfluoronitrosoalkanes, were conveniently made from the reactions of $Na^{15}NO_2$ with polyfluorocompounds, $(R_FCO_2)$ $R_FI$ and $R_FSO_2Br$ in F113. It has been found that the nitroxides effected fast H-abstraction from alkanes, alkylbenzenes, aldehydes and the radicals derived from the substrates were in turn effectively trapped by $R_F{}^{15}NO$ to give $^{15}N$ labelled spin adducts detectable by ESR. The bigger $a_N(15_N)$ values as well as much simpler splittings of both the nitroxides and the spin adducts have made the kinetic studies of the H-abstraction and other radical reactions quite feasible.

## INTRODUCTION

Bis(trifluoromethyl) nitroxide (1a), one of the most reactive nitroxides, first prepared by the oxidation of the corresponding hydroxylamine in 1965, has since been intensively studied in the respects of its structure,[1] reactivity in hydrogen-abstraction, halogen-displacement, addition and substitution reactions [2-4]. Very recently, a series of its analogues have been successfully

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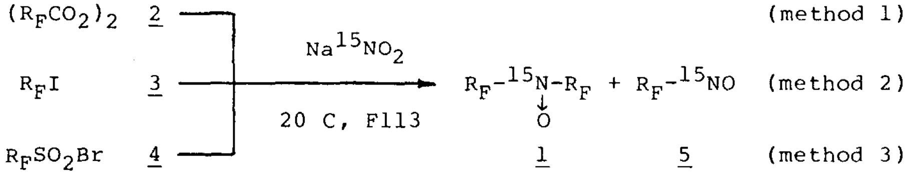
generated in our laboratory by a number of different methods, viz, the novel electron transfer reactions between polyfluorodiacyl peroxides 2 and the carbanions derived from nitroalkanes,[5] the reactions of the same peroxides 2 with pseudonitrole, 2-nitro-2-nitrosopropane,[6] etc. However, the most convenient and effective method used in our laboratory has been the reactions of the metal nitrites ($M^+NO_2^-$, M=Ag or Na) with the titled fluorine-compounds 2, 3 or 4 [7].

In the present paper, we report the ESR characterization of the $^{15}N$ labelled nitroxides 1 and some examples of their applications in the studies of H-abstraction from alkanes, alkylbenzenes and aldehydes by ESR.

## RESULTS AND DISCUSSION

At room temperature (20±2°C) in F113 ($CClF_2$-$CCl_2F$), 2, 3, or 4 reacted quickly with $Na^{15}NO_2$ to give blue solutions containing spin traps, $R_F{}^{15}NO$ 5 and the stable but reactive nitroxides 1



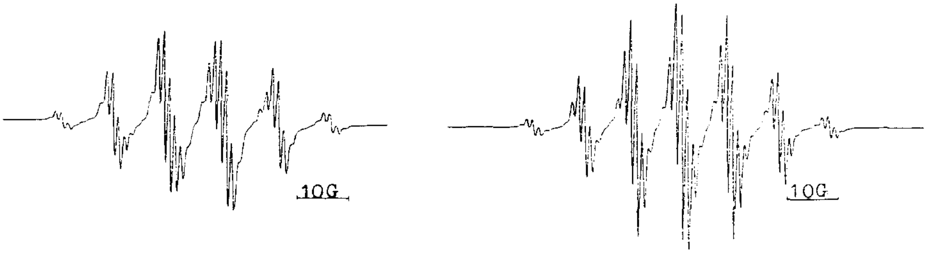
The ESR parameters of nitroxides 1 and their $^{14}N$ isotopomers are given in Table 1 . The ESR spectra of some representative nitroxides 1 ($^{15}N$ and $^{14}N$ isotopomers) are shown in Figure 1 . By comparison of data given in Table 1, we find: 1. For a specific $R_F$ group and at the same temperature (± 2°C), $^{15}N$ and $^{14}N$ isotopomers have the same g factors, $a_F^{\beta}$ and $a_F^{\gamma}$ values; 2. $a_N$ values of $^{15}N$ nitroxides are about 40% higher than those of $^{14}N$ nitroxides($a_N(15_N)/a_N(14_N) \simeq 1.40$), which is in accord with the ratio of the nuclear magnetons of the two nuclei, $^{15}N$ and $^{14}N$, ( $\left|\frac{\gamma 15_N}{\gamma 14_N}\right| = \left|\frac{-0.27107}{+0.19324}\right| = 1.4028$) [8]; 3. The dependency of the $a_N(15_N)$ values on the nature of the $R_F$ groups shows the same trend as previously reported for their $^{14}N$ isotopomers[5]. If the

TABLE 1

ESR parameters of $^{15}N$ labelled bis(polyfluoroalkyl) nitroxides generated in the reactions of $Na^{15}NO_2$ with polyfluorodiacyl peroxides, polyfluoroalkyl iodides and polyfluorosulfonyl bromides at 20 ± 2 °C

| $R_F$ | g | $^{15}N$ (1) | | | $^{14}N$ * | | | synth. method |
|---|---|---|---|---|---|---|---|---|
| | | $a_N$(G) | $a_F^{\beta}$(G) | $a_F^{\gamma}$(G) | $a_N$(G) | $a_F^{\beta}$(G) | $a_F^{\gamma}$(G) | |
| a $CF_3$ | 2.0069 | 13.12 | 8.28 | | 9.35 | 8.35 | | 1 |
| b $C_2F_5$ | 2.0071 | 12.13 | 12.13 | 1.03 | 8.86 | 12.13 | 1.02 | 1 |
| c $n-C_3F_7$ | 2.0070 | 12.16 | 9.96 | 1.22 | 8.80 | 9.99 | 1.20 | 1 |
| d $n-C_7F_{15}$ | 2.0072 | 12.38 | 9.69 | 1.12 | 8.75 | 9.74 | 1.17 | 1 |
| e $H(CF_2)_2$ | 2.0068 | 13.62 | 14.38 | | 9.76 | 14.40 | | 1 |
| f $H(CF_2)_4$ | 2.0071 | 12.62 | 9.98 | 1.14 | 8.94 | 9.91 | 1.14 | 1 |
| g $H(CF_2)_6$ | 2.0071 | 12.05 | 9.81 | 1.16 | 8.61 | 9.75 | 1.16 | 1 |
| h $Cl(CF_2)_2$ | 2.0069 | 12.41 | 10.87 | 0.92 | 8.65 | 10.87 | 0.89 | 2 |
| i $Cl(CF_2)_4$ | 2.0071 | 12.47 | 9.88 | 1.19 | 8.77 | 9.77 | 1.22 | 2,3 |
| j $Cl(CF_2)_6$ | 2.0072 | 12.45 | 9.67 | 1.15 | 8.75 | 9.67 | 1.18 | 2,3 |
| k $FO_2S(CF_2)_2O(CF_2)_6$ | 2.0071 | 12.22 | 10.22 | 1.10 | 8.54 | 10.22 | 1.10 | 2 |

* See Reference [7].

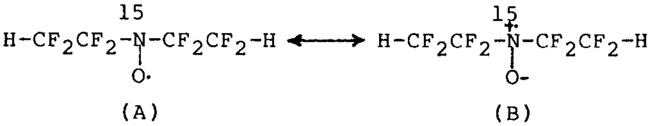


1f

1f' $^{14}N$ isotopomer

Fig. 1. ESR spectrum of 1f generated in the reaction of $Na^{15}NO_2$ with $(H(CF_2)_4CO_2)_2$ in F113 at 20 ± 2 °C.

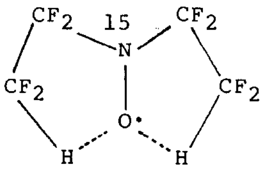
electron-attracting power of the $R_F$ groups is $CF_3$ < secondary $R_F$ < tertiary $R_F$ [9,10], then the decreasing order of the $a_N(15_N)$ values ($CF_3 > C_2F_5$, $n\text{-}C_3F_7$ and $n\text{-}C_7F_{15}$) nicely confirms the notion that, in addition to geometric factors, polar effects may play a major role in affecting the $a_N$ values [11] which should be proportional to the spin densities on $^{15}N$ atoms in the nitroxides derived from different $R_F$ groups, i.e., $F\text{-}CF_2CF_2$ < $Cl\text{-}CF_2CF_2$ < $H\text{-}CF_2CF_2$ . The replacement of a strongly electron-withdrawing F atom in the $C_2F_5$ group by a less electron-withdrawing Cl atom,should not lead to considerable steric effects, so that the significant increase in $a_N$ values (0.21 G for $a_N(^{14}N)$ and 0.30 G for $a_N(^{15}N)$) indicates the importance of polar factors in affecting the spin densities on $^{15}N$ atoms. More interestingly, in comparison with the $C_2F_5$ substituted nitroxide, the $H\text{-}CF_2CF_2$ substituted nitroxide has much higher $a_N$ values, i.e., 0.90 G for $a_N(^{14}N)$ and 1.49 G for $a_N(^{15}N)$. This fact is very likely a reflection of the reduced electron-withdrawing ability of the $H\text{-}CF_2CF_2\text{-}$ group. Any reduction of the electron-withdrawing ability of alkyl groups in nitroxides would enhance the interaction of nitrogen atom with the free electron and thus favour spin delocalization on the N atom as shown by the canonical structure B:



$$H{-}CF_2CF_2{-}\underset{\displaystyle O\cdot}{\overset{15}{N}}{-}CF_2CF_2{-}H \longleftrightarrow H{-}CF_2CF_2{-}\underset{\displaystyle O^-}{\overset{15}{\overset{+}{N}}}{-}CF_2CF_2{-}H$$

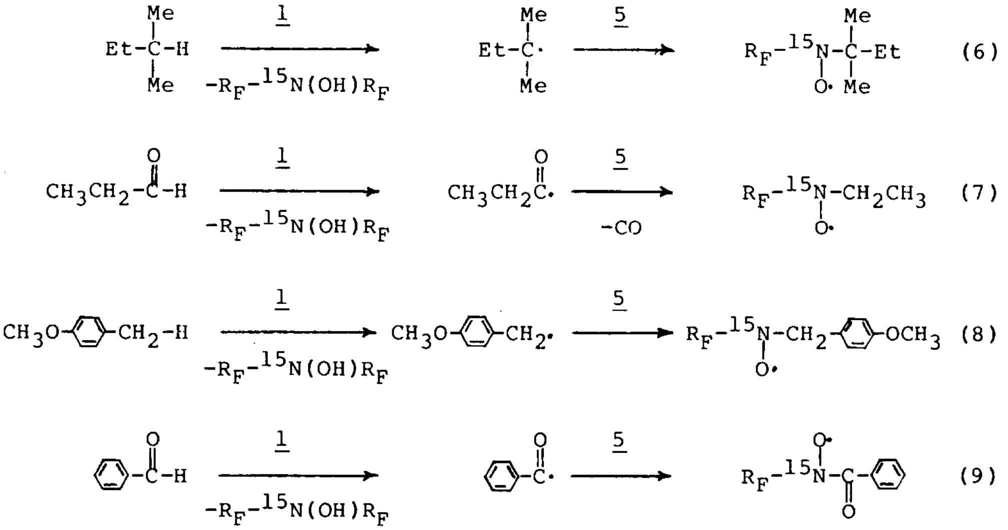
(A) (B)

However, there might be other causes for the unusually large $a_N$ value of 1e.For instance,we suggest that the combination of the acidity and location of the ω -H atoms may lead to the formation of a 5-membered intramolecular H-bond with the lone pair on oxygen. Such hydrogen-bonding would favour the structure B or the delocalization of spin onto the nitrogen and thus increase the $a_N$ value. Obviously, as the chain lengthens, the ω -H or ω-Cl-substitution effects will be reduced.



1e

Our technique has essentially provided a general method for making solutions containing $^{15}N$ labelled nitroxides 1 and spin traps 5 . When the very reactive attacking radicals 1 abstracted hydrogen atoms from alkanes, alkylbenzenes and aldehydes, the derived radical intermediates and/or their radical fragments were immediately captured by the traps 5 and usually very stable nitroxides were formed and eventually observed by ESR. The succession of spin trapping step to the radical attacking step (H-abstraction here), the simplicity and the breadth of the ESR spectra of both the attacking nitroxides and the spin adducts have enabled us to use these working solutions to study many important radical processes kinetically by ESR by monitoring the disappearance of the attacking radicals 1 and the formation of the spin adducts. Several examples are given in Scheme 1 to show the applications of this technique in H-abstraction reactions[12]. The ESR spectra of some $^{15}N$ labelle nitroxides are shown in Figure 2 and their ESR parameters are presented in Table 2.

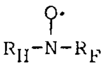


Scheme 1

Systematic studies are now being conducted of H-abstraction, addition and substitution reactions of these reactive nitroxides with a variety of substrates.

TABLE 2

ESR parameters[1] of $^{15}N$ nitroxides (6 - 9)[2] and their $^{14}N$ isotopomers (10 - 13)[3]



$R_H-\overset{O\cdot}{N}-R_F$

| Substrate | $R_H$ in spin adduct | Spin adduct | ESR parameters |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  | g | $a_N$ | $a_F^{\beta}$ | $a_F^{\gamma}$ | $a_H^{\beta}$ | T°C |
| $i-C_5H_{11}-H$ | $i-C_5H_{11}-$ | 6 | 2.0061 | 16.20 | 20.92 |  |  | 20 |
|  |  | 10 | 2.0060 | 11.62 | 20.89 |  |  | 20 |
| $C_2H_5\overset{O}{\overset{\|}{C}}-H$ | $C_2H_5-$ | 7 | 2.0062 | 15.74 | 15.80 | 1.62 | 8.93 | 14 |
|  |  | 11 | 2.0061 | 11.24 | 15.74 | 1.62 | 8.93 | 13 |
| $p-MeOC_6H_4CH_2-H$ | $p-MeOC_6H_4CH_2-$ | 8 | 2.0062 | 15.62 | 15.60 | 1.49 | 6.94 | 11 |
|  |  | 12 | 2.0062 | 11.16 | 15.48 | 1.51 | 6.92 | 11 |
| $C_6H_5\overset{O}{\overset{\|}{C}}-H$ | $C_6H_5\overset{O}{\overset{\|}{C}}-$ | 9 | 2.0066 | 10.24 | 8.76 | 0.76 |  | 20 |
|  |  | 13 | 2.0065 | 7.31 | 8.76 | 0.77 |  | 19 |

[1] Coupling constants are in Gauss (± 0.05 Gauss).

[2] Spin adducts 6 - 8 were derived from $H(CF_2)_4NO$, whereas 9 was derived from $H(CF_2)_6NO$.

[3] Spin adducts were generated in the reactions of $(R_F{}^{14}N(O)R_F + R_F{}^{14}NO)$ and the same substrates.

## EXPERIMENTAL

Sodium nitrite ($Na^{15}NO_2$) was 98.5% pure based on $^{15}N$ content. Peroxides 2 were synthesized as reported previously [11]. The iodides 3 were distilled before use and kept in the dark. Sulfonyl bromides 4 were synthesized according to the literature [13]. The other solvents were purifi according to the standard procedures [14].

In a typical experiment, 0.2~0.3 ml of a F113 solution (~0.1M) of 2 or 4 was quickly shaken with an excess of finely powdered nitrite salt ($Na^{15}NO_2$) in a degassed ESR tube. Then, 0.02~0.03 ml of substrate was added to the tube. In a few minutes, a well resolved ESR spectrum was

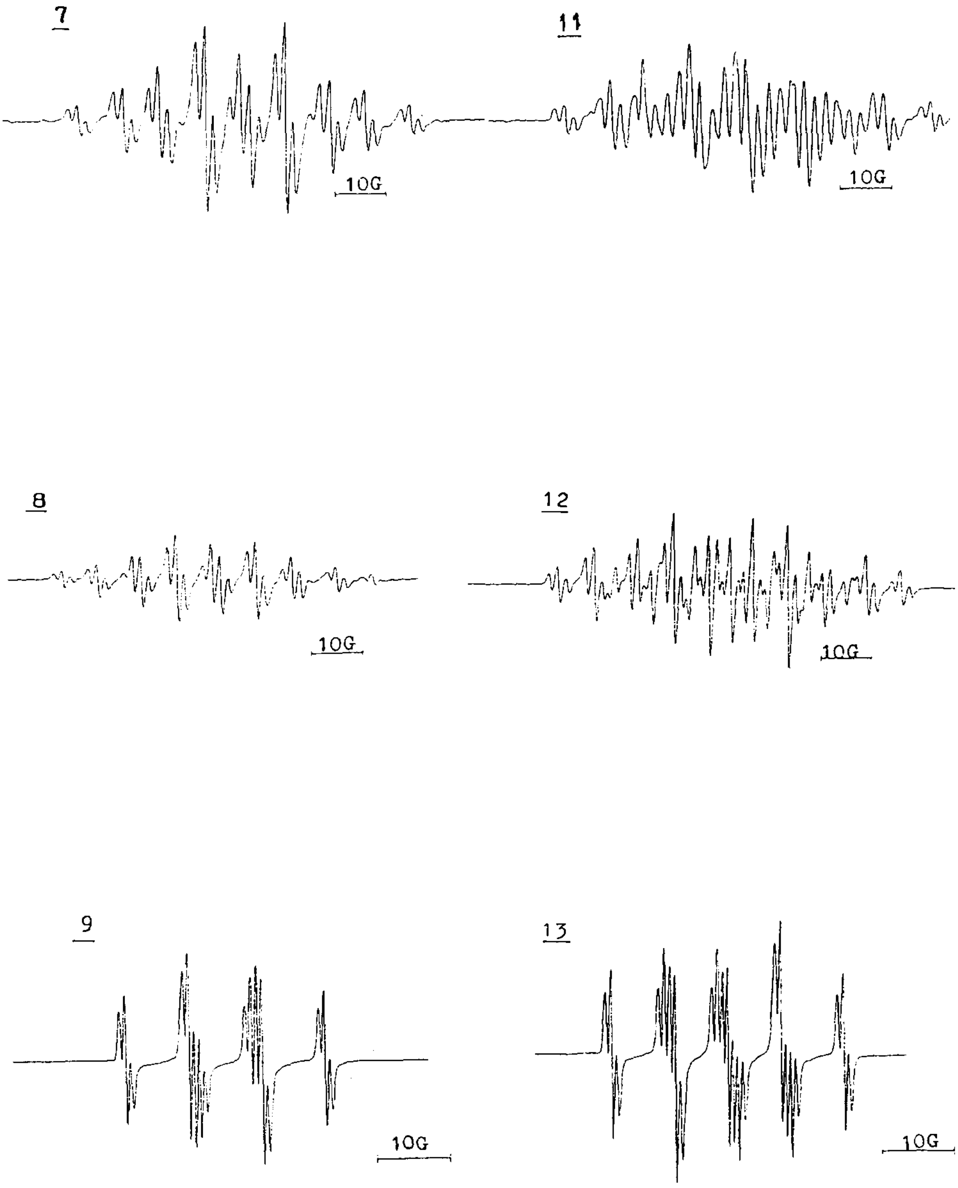


Fig. 2. ESR spectra of $^{15}N$ nitroxides (7 - 9) and their $^{14}N$ isotopomers (11 - 13).

recorded on a Varian E-112 X-band spectrometer with 100 KHz magnetic field modulation.

Spectral simulations were performed by using Varian E 935 softwa program, NO 929970-11.

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