neutral trans diphosphene HP=PH. For the $\sigma$ configuration (Figure 2b) the highest MO's are the $\sigma_{PP}$ and the orbitals obtained by the mixing of the two symmetrical ($n^A_+, n^B_+$) or the two unsymmetrical ($n^A_-, n^B_-$) phosphorus "lone-pair" combinations.

For the two configurations, the SOMO (Figure 2) is not of the right symmetry to mix with the subjacent filled MO. However, as in the case of the diphosphine cation radical, a strong interaction is expected to occur between the $n_-$ orbital ($\pi$ configuration) or the ($n^A_- + n^B_-$) orbital ($\sigma$ configuration) and the $\sigma_{PP}$. In the two cases the interaction involves two filled orbitals and thus is expected to destabilize the system, while it was stabilizing in the case of $(H_2PPH_2)^{+\cdot}$. However, since the two orbitals involved in the interaction have a lower energy gap and a better overlap for the $\sigma$ configuration than for the $\pi$ configuration, the destabilizing effect is stronger for the former and is expected to favor the $\pi$ configuration.

Finally, it may be noted in passing that the anion radicals $(TsiP{=}PTsi)^{-\cdot}$ and[4] $(ArP{=}PAr)^{-\cdot}$ are the first reported molecules for which the electronic structure involves a three-electron P-P $\pi$-bond.

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(11) Lee, J. G.; Cowley, A. H.; Boggs, J. G. *Inorg. Chim. Acta* **1983**, *77*, L61-L62.

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# Novel Technique for the Generation of Bis(polyfluoroalkyl) and Polyfluoroalkyl Nitroalkyl Nitroxides. ESR Verification of Mechanistic Propositions for the Reactions between Polyfluorodiacyl Peroxides and Carbanions Derived from Secondary Nitroalkanes†

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Polyfluoroalkyl akyl nitroxide radicals have been investigated by Klabunde,[1] Konaka and Terabe,[2] Tabata and co-workers,[3] Kochi,[4] and others. Rather surpisingly, only one nitroxide of the bis(perfluoroalkyl) type, i.e., bis(trifluoromethyl) nitroxide, has been studied in detail.[5-7] Now, we wish to communicate a novel and general method for the generation of bis(polyfluoroalkyl) nitroxides **9** as well as polyfluoroalkyl nitroalkyl nitroxides **10** by making use of the spontaneous electron-transfer-initiated reactions between polyfluorodiacyl peroxides **1** and carbanions derived from nitroalkanes **2**. Product studies of these novel reactions accord with a mechanism which reckons in an initial electron transfer from the carbanion **2** to the peroxide **1** (cf. Scheme I).[8] It also speculates that one of the major products, an aldehyde or ketone **6**, comes from the fragmentation of an unstable intermediate, **5**. Another key unstable intermediate is believed to be the acyl nitrite **7**. Decarboxylation of **7** should lead directly to the in situ for-

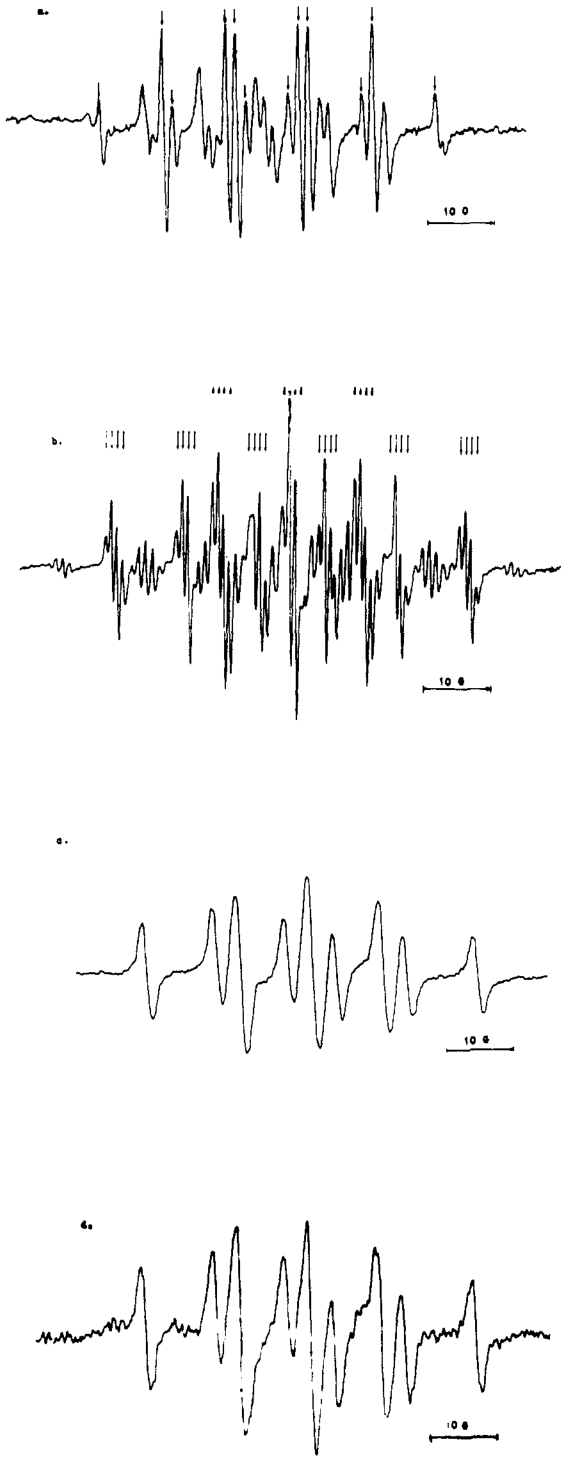

**Figure 1.** Some representative ESR spectra of nitroxides **9** and **10** obtained in $CClF_2CCl_2F$ at 20 °C. (a) mixture of $CF_3N(O)CF_3$ (**9a**) and $CF_3N(O)CMe_2NO_2$ (**10a**, represented by ↓), from **1a** + **2a**; (b) mixture of $C_2F_5N(O)C_2F_5$ (**9b**) and $C_2F_5N(O)CMe_2NO_2$ (**10b**, ↓), from **1b** + **2a**; (c) $n$-$C_7F_{15}N(O)CMe_2NO_2$ (**10d**) from **1d** + **2a**; (d) **10d** from **1d** + 2-nitroso-2-nitropropane + $Cu^0$.

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† Dedicated to Professor Cheves Walling on the occasion of his 70th birthday.

(1) Klabunde, K. J. *J. Am. Chem. Soc.* **1970**, *92*, 2427.

(2) Terabe, S.; Konaka, R. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 825.

(3) Katsumura, Y.; Ishigure, K.; Tabata, Y. *J. Am. Chem. Soc.* **1979**, *83*, 3152.

(4) Chen, K. S.; Krusic, P. J.; Meakin, P.; Kochi, J. K. *J. Phy. Chem.* **1974**, *78*, 2014.

(5) (a) Ang, H. G. *J. Chem. Soc., Chem. Commun.* **1968**, 1320. (b) Emeleus, H. J.; Shreeve, J. M.; Spaziante, P. M. *J. Chem. Soc. A* **1969**, 431. (c) Banks, R. E.; Haszeldine, R. N.; Stevenson, M. J. *J. Chem. Soc. C* **1966**, 901. Booth, B. L.; Browne, R. F.; Haszeldine, R. N.; Verley, J. S. *J. Fluorine Chem.* **1984**, *24*, 485 and references cited therein.

(6) Makarof, S. P.; Videiko, A. F.; Tobolin, V. A.; Englin, M. A. *Zh. Obschch. Khim.* **1967**, *37*, 1528.

(7) Chatgilialoglu, C.; Walastesta, V.; Ingold, K. U. *J. Phys. Chem.* **1980**, *84*, 3597.

(8) Zhao, C.-X.; Qu, Y.-L.; Jiang, X.-K.; Jin, X.-M. *Acta Chim. Sin.* **1985**, *43*, 1184.

0002-7863/86/1508-3132$01.50/0

**Table I.** Parameters for Bis(polyfluoroalkyl) Nitroxides **9**[a] Generated by SET Reactions between **1** and **2** in $CClF_2$–$CCl_2F$ at 20 ± 2 °C

| $R_F$ of $(R_FCO_2)_2$ | **2a**, $R^1 = R^2 = CH_3$ | | | | **2b**, $R^1 = CH_3$, $R^2 = C_2H_5$ | | | **2c**, $R^1 + R^2 =$ $-(CH_2)_4-$ | | | **2d**, $R^1 = CH_3$, $R^2 =$ $CH_3OC(O)CH_2CH_2$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $g$ | $a_N$ | $a_F^\beta$ | $a_F^\gamma$ | $a_N$ | $a_F^\beta$ | $a_F^\gamma$ | $a_N$ | $a_F^\beta$ | $a_F^\gamma$ | $a_N$ | $a_F^\beta$ | $a_F^\gamma$ |
| $CF_3$ | 2.0066 | 9.35[b] | 8.35[b] | | | c | | 9.4 | 8.3 | | 9.4 | 8.3 | |
| $C_2F_5$ | 2.0069 | 8.86 | 12.13 | 1.02 | 8.83 | 12.13 | 1.02 | | c | | 8.83 | 12.12 | 0.99 |
| $n$-$C_3F_7$ | 2.0070 | 8.77 | 9.96 | 1.22 | 8.80 | 9.99 | 1.20 | 8.79 | 9.94 | 1.19 | 8.72 | 9.97 | 1.19 |
| $n$-$C_7F_{15}$ | 2.0070 | 8.75 | 9.74 | 1.17 | 8.75 | 9.72 | 1.17 | 8.72 | 9.82 | 1.15 | 8.70 | 9.80 | 1.15 |
| $H(CF_2)_4$ | 2.0069 | 8.94 | 9.91 | 1.14 | 8.94 | 9.91 | 1.14 | 8.86 | 9.96 | 1.14 | | c | |
| $H(CF_2)_6$ | 2.0069 | 8.61 | 9.75 | 1.16 | 8.71 | 9.83 | 1.19 | | c | | 8.66 | 9.78 | 1.14 |

[a] Couplings are in gauss. [b] $a_N$ = 9.4 G, $a_F$ = 8.3 G, from ref 7. [c] Well-resolved spectra could not be obtained.

**Table II.** Parameters for Some Representative Fluoroalkyl Nitroalkyl Nitroxides **10**[a] Generated by Two Different Methods in $CClF_2$–$CCl_2F$ at 20 ± 2 °C, $R_FN(O)CMe_2(NO_2)$

| $R_F$ in $(R_FCO_2)_2$ | **1** + **2a** | | | | **1** + $Me_2C(NO_2)NO$ + $Cu^0$ | | |
|---|---|---|---|---|---|---|---|
| | $g$ | $a_N$ | $a_F^\beta$ | $a_F^\gamma$ | $a_N$ | $a_F^\beta$ | $a_F^\gamma$ |
| $CF_3$ | 2.0065 | 10.85 | 9.32 | | 10.83 | 10.83[d] | |
| $C_2F_5$ | 2.0066 | 10.50[b] | 15.76[b] | 0.88 | 10.55 | 15.75 | 0.94 |
| $n$-$C_3F_7$ | 2.0066 | 10.37[c] | 13.45[c] | | 10.36 | 13.83 | |
| $n$-$C_7F_{15}$ | 2.0066 | 10.55 | 13.87 | | 10.50 | 13.96 | |
| $H(CF_2)_4$ | 2.0065 | 10.64 | 13.47 | | 10.68[c] | 13.53[c] | |
| $H(CF_2)_6$ | 2.0066 | 10.44 | 14.01 | | 10.41 | 14.08 | |

[a] Couplings are in gauss. [b] Solvent, isopentane. [c] At 5 °C. [d] Well-resolved spectrum could not be obtained.

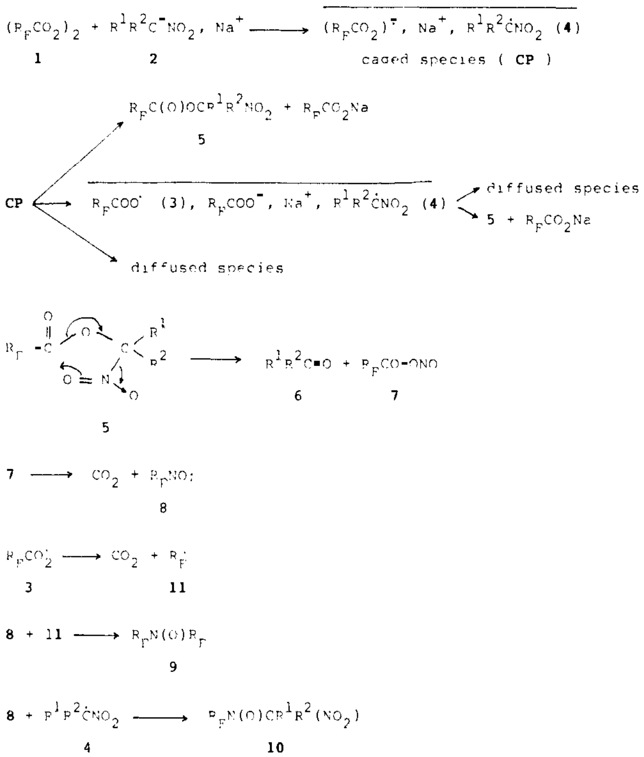
mation of an effective spin-trapping agent, the polyfluoronitrosoalkane **8**. Finally, trapping of the radicals **11** and **4** by **8** yields the nitroxide products **9** and **10**. This mechanistic proposition is now confirmed by the ESR study described below.

In a typical experiment, dry powdered sodium salt of a nitroalkane **2** was quickly mixed in a degassed ESR tube with 0.5 mL of a 0.2 M solution of a fluorinated diacyl peroxide **1** in $CClF_2$–$CCl_2F$. The ESR spectrum was then immediately recorded at 20 ± 2 °C by a Varian E-112 spectrometer. If an excess of peroxide (e.g., molar ratio of **1**:**2** = 2:1) was employed, the radicals recorded were mainly **9** accompanied by small amounts of **10**. Presumably, under these conditions, relatively large amounts of $R_F$ radicals (**11**) formed from the induced decomposition of the peroxide could be easily trapped by $R_FNO$ (**8**).

If a reversed ratio of the reactants was used, signals of **10** would become the predominant component of the spectra. This could be partly a consequence of oxidations by trace $O_2$ of amino oxyanions, $R_F[CR^1R^2(NO_2)]N-O^-$, formed from nucleophilic attacks of excess carbanions of **2** on **8**.[9] Hfsc values from 20 spectra for symmetric nitroxides are shown in Table I, and hfsc values from six representative spectra of 24 unsymmetric nitroxides are shown in Table II.[10] The assignment of the symmetric nitroxides **9a–f** is based on the following: (1) The spectrum of the only previously known bis(perfluoroalkyl)nitroxide **9a** coincides with reported values.[7] (2) For each of the six peroxides, similar $a_N$, $a_F^\beta$, and $a_F^\gamma$ values are obtained no matter which one of the four donors is used. (3) The dependency of the $a_N$ values on the nature of the perfluoroalkyl groups shows a consistent trend. In other words, if the electronattracting power of the $R_F$ groups are $CF_3$ < secondary $R_F$ < tertiary $R_F$,[11,12] then the decreasing order of the $a_N$ values ($CF_3 > C_2F_5 > n$-$C_3F_7$ and $n$-$C_7F_{15}$) nicely bears out the notion that in addition to geometric factors the polar effect may play a major role in affecting the $a_N$ values.[7] Similarly, the $g$ factors of the symmetrical nitroxides are also consistent with the fact that they become larger when the nitroxides are substituted by more electronegative groups.

For the characterization of the spectra of the unsymmetrical nitroxides **10**, we further resorted to the method of generating the same species by a different reaction. Namely, in a copper-catalyzed decomposition of all the six peroxides **1**,[13] the so-generated polyfluoroalkyl radicals were trapped by 2-nitroso-2-nitropropane in the same solvent and at the same temperature to yield the same nitroxides **10**, as shown in Table II. Therefore, the structures of the unsymmetrical nitroxides **10** have also been unequivocally established.

**Scheme I**



Most of nitroxides **9** and **10** decay rather quickly in the reaction mixture. With a molar ratio of **1**:**2** = 1:1 the yields of **9** and **10** as determined at 20 °C by external reference (DPPH) technique were 0.03% and 0.02%, respectively, about 10–20 min after mixing in an ESR tube. However, nitroxides **9** and **10** could be separated when the reaction mixture was flash-chromatographed on a silica gel column; **9** and **10** in thus separated F-113 solutions were characterized by UV and IR and were found to have lifetimes of several days at room temperature in the dark.

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(9) Forrester, A. R.; Hepburn, S. P. *J. Chem. Soc. C* **1971**, 701.

(10) The spectra have been satisfactorily simulated using the Varian E-935 software program No. 929970-11.

(11) Chen, C.-y.; Jiang, H.-k. (Jiang, X.-K.); Chen, B.-q.; Liang, M.-L. *Sci. Sin.* (*Engl. Ed.*) **1966**, *15*, 498.

(12) Sheppard, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 2410.

(13) Zhao, C.-X.; Chen, G.-F.; Wang, X.-S.; Jiang, X.-K., unpublished results.