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Preliminary Note

Electron paramagnetic resonance spectroscopic monitoring of the reactions of t-butyl perfluoroalkyl nitroxides with alcohols

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Abstract

Electron paramagnetic resonance spectroscopic monitoring of the reactions of various alcohols with a mixture of perfluoroalkyl nitroxides ($R_F = CF_3$, n-C_3F_7, etc.) and a spin trap (Bu^tNO) in F113 ($CFCl_2CF_2Cl$) solutions have been found to provide a novel and informative technique for studying H-abstraction and subsequent radical reactions.

Di-t-alkyl nitroxides possess an unpaired electron which is divided almost equally between the nitroxyl N and O atom ($\rho_N \simeq 0.46$, $\rho_O \simeq 0.54$) [1]. Because of their strongly electron-withdrawing R_F groups, however, perfluoroalkyl t-butyl nitroxides [2] possess a much bigger spin density on the O atom ($\rho_O \simeq 0.66$) [3] and are thus more reactive than their hydrocarbon analogs. However, we could find no report about their reactions in the literature.

By making use of the electron-transfer reactions of *O*-benzoyl-*N*-t-butylhydroxylamine with $(R_FCO_2)_2$ ($R_F = CF_3$, C_2F_5, n-C_3F_7, n-C_7F_{15}, $H(CF_2)_{2,4,6,\text{ etc.}}$) in F113 ($CFCl_2CF_2Cl$) solutions at room temperature we could prepare blue solutions containing a spin trap (Bu^tNO) and the pure R_F-nitroxides at higher concentrations. The mechanism is proposed as follows [4]:

$$Bu^tNHOCOPh + (R_FCO_2)_2 \xrightarrow[\text{F113, r.t.}]{\text{SET}} \overline{Bu^t\overset{+\bullet}{N}HOCOPh, (R_FCO_2)_2^{\bar{\bullet}}} \xrightarrow{-R_FCO_2H}$$

$$\overline{Bu^t\dot{N}O \,\vdots\, COP, R_F \,\vdots\, COO^\bullet} \xrightarrow[-CO_2]{-Ph\overset{\bullet}{C}=O} Bu^tN(O^\bullet)R_F$$

A small amount of the blue 'magic' solution was dropped into an EPR tube containing the alcohol (occasionally plus solvent). After shaking the tube was inserted into the EPR cavity. The signal of the R_F-nitroxide generated

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diminished with decoloration of the blue in the mixture, and at the same time new nitroxide(s) were detected. The reactions of various kinds of alcohols have been monitored. We present some examples, for demonstration, in Table 1.

Both R_F-nitroxides reacted readily with the alcohols. However, depending on the structure of the alcohols and the solvent systems employed, quite different nitroxides were observed. Their structures have been established unequivocally through interpretation of their well-resolved spectra (see Fig. 1).

By varying the substrate structure and the solvent, it was possible to trace the course of every individual step involved in the process back to the very first step, which is H-abstraction by the nitroxyl oxygen at the α-carbon of the alcohol. The possible mechanisms forming the tabulated nitroxides are listed as follows:

Reaction 1

$$CF_3N(O^{\cdot})Bu^t\ (I) + PhCH_2OH \longrightarrow CF_3N(OH)Bu^t\ (IH) + Ph\dot{C}HOH$$
$$I + Ph\dot{C}HOH \longrightarrow IH + PhCHO$$
$$I + PhCHO \longrightarrow IH + Ph\dot{C}{=}O$$
$$Ph\dot{C}{=}O + Bu^tNO \longrightarrow PhCON(O^{\cdot})Bu^t$$

Reaction 2 (in $HOCH_2CH_2OH$)

$$I + HOCH_2CH_2OH \longrightarrow IH + HOCH_2\dot{C}HOH$$
$$HOCH_2\dot{C}HOH + Bu^tNO \longrightarrow HOCH_2CH(OH)N(O^{\cdot})Bu^t$$

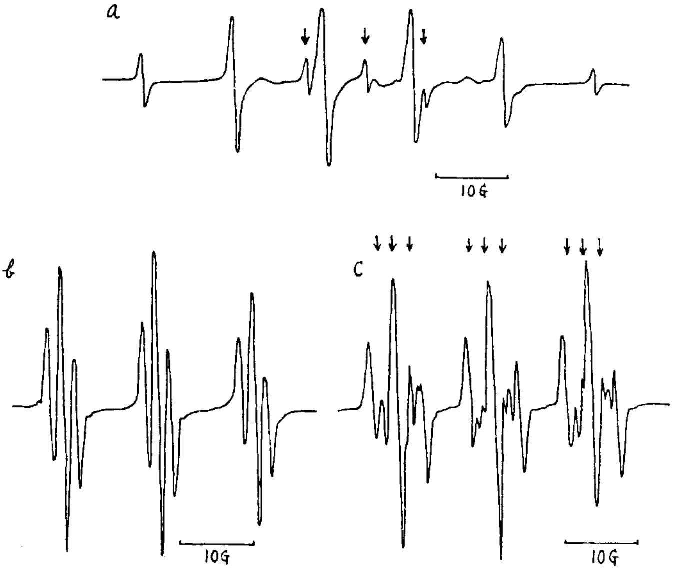
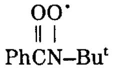
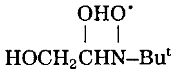
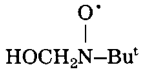
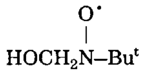


Fig. 1. (a) $PhCON(O^{\cdot})Bu^t$ (minor, ↓) + $CF_3N(O^{\cdot})Bu^t$ (major) in Reaction 1. (b) $HOCH_2N(O^{\cdot})Bu^t$ in Reaction 4. (c) $HOCH_2N(O^{\cdot})Bu^t$ (↓) + $HCOCH_2OCH_2CH_2N(O^{\cdot})Bu^t$ in Reaction 3.

TABLE 1

Nitroxides generated in the reactions of R_F-nitroxides with alcohols at 25 °C

Reaction No.	R_F in $R_FN(O^{\bullet})Bu^t$	ROH + solvent	Nitroxide(s) generated (±0.05 G)				Comments
			Structure(s)	a_N	a_H	g	
1	CF_3	$PhCH_2OH$	 $\mathrm{Ph\overset{\overset{O}{\Vert}}{C}\overset{\overset{O^{\bullet}}{|}}{N}\text{–}Bu^t}$	8.05			slow
2	CF_3	$HOCH_2CH_2OH$	 $\mathrm{HOCH_2\overset{\overset{O}{|}}{C}\overset{H}{H}\overset{\overset{O^{\bullet}}{|}}{N}\text{–}Bu^t}$	14.67	1.64	2.0054	fast
3	CF_3	$HOCH_2CH_2OH$ + dioxan	 $\mathrm{HOCH_2\overset{\overset{O^{\bullet}}{|}}{N}\text{–}Bu^t}$	13.39	1.72		after standing overnight
			 $\mathrm{H\overset{\overset{O}{\Vert}}{C}CH_2OCH_2CH_2\overset{\overset{O^{\bullet}}{|}}{N}BBu^t}$	13.39	3.68		
4	$n\text{-}C_3F_7$	$HOCH_2CH_2OH$ + F113	 $\mathrm{HOCH_2\overset{\overset{O^{\bullet}}{|}}{N}\text{–}Bu^t}$	13.37	1.74	2.0059	fast

Reaction 3 ($\mathrm{HOCH_2CH_2OH}$ in dioxan)

$$3\mathrm{I} + \mathrm{HOCH_2CH_2OH} \longrightarrow \longrightarrow \longrightarrow 3\mathrm{IH} + \mathrm{HOCH_2\dot{C}{=}O}$$
$$\mathrm{HOCH_2\dot{C}{=}O} \longrightarrow \mathrm{HOCH_2^{\bullet}} + \mathrm{CO}$$
$$\mathrm{HOCH_2^{\bullet}} + \mathrm{Bu^tNO} \longrightarrow \mathrm{HOCH_2N(O^{\bullet})Bu^t}$$
$$\mathrm{I} + \text{dioxan} \longrightarrow \mathrm{IH} + \mathrm{HCOCH_2CH_2OCH_2^{\bullet}}$$
$$\mathrm{HCOCH_2CH_2OCH_2^{\bullet}} + \mathrm{Bu^tNO} \longrightarrow \mathrm{HCOCH_2CH_2OCH_2N(O^{\bullet})Bu^t}$$

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