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Reaction of Bis(heptafluorobutyryl) Peroxide with Carbanions and a Thiolate Anion

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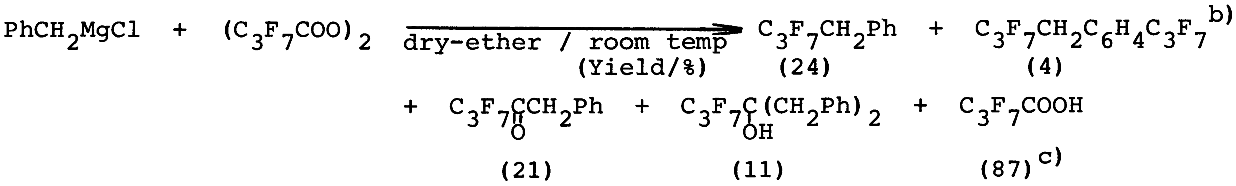
In the reaction of bis(heptafluorobutyryl) peroxide with carbanions and a thiolate anion, two types of reactions were observed; one is an electron transfer reaction to give perfluoropropylated compounds and the other is a nucleophilic substitution.

The decomposition of diacyl peroxides ($(RCO_2)_2$) is usually initiated by homolytic cleavage of the O-O bond with a low bond energy. On the other hand, the diacyl peroxides also react as electrophiles in the presence of an electron donor.[1] It is known that the energy level of the O-O antibonding orbital of the peroxide is lowered when Rs are electron-withdrawing groups.[2] Peroxides substituted with strongly electronegative perfluoroalkyl groups are expected to have a significantly decreased O-O antibonding energy level. This consideration prompted us to investigate the reaction of bis(heptafluorobutyryl) peroxide 1 with various nucleophilic substrates.

The peroxide 1 was prepared from heptafluorobutyryl chloride and hydrogen peroxide in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) according to the literature.[3] The peroxide 1 was used as a solution in Freon-113.

At first, we investigated the reaction of the peroxide 1 with Grignard reagents. A solution of the peroxide 1 in Freon-113 was added to a solution of benzylmagnesium chloride, which was prepared from benzyl chloride and magnesium turnings in ether under nitrogen. After the reaction was completed, the mixture was decomposed by aqueous ammonium chloride and the ether layer was washed with water and dried over magnesium sulfate. The products were identified by GC-MS, ^{1}H-, ^{13}C-NMR, and IR. The results are shown in Scheme 1.



$$\mathrm{PhCH_2MgCl} + \mathrm{(C_3F_7COO)_2} \xrightarrow[\substack{\text{dry-ether / room temp}\\ \text{(Yield/\%)}}]{} \underset{(24)}{\mathrm{C_3F_7CH_2Ph}} + \underset{(4)}{\mathrm{C_3F_7CH_2C_6H_4C_3F_7}^{b)}}$$

$$+ \underset{(21)}{\mathrm{C_3F_7\underset{\underset{O}{\|}}{C}CH_2Ph}} + \underset{(11)}{\mathrm{C_3F_7\underset{OH}{C}(CH_2Ph)_2}} + \underset{(87)^{c)}}{\mathrm{C_3F_7COOH}}$$

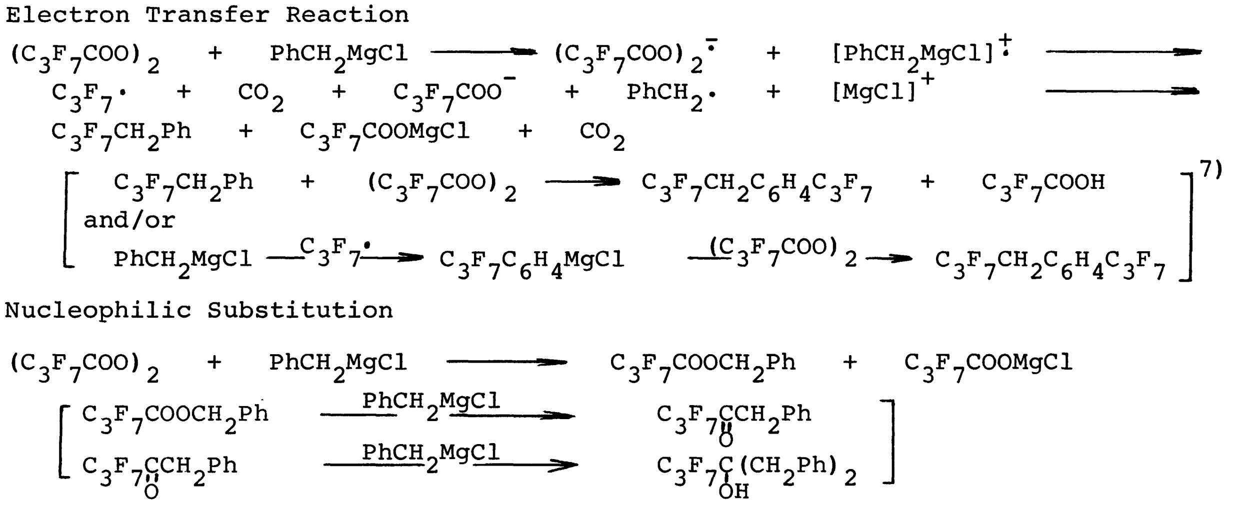
a) Yields were determined by GC and calculated based on 1.

b) Structure was estimated from only MS data due to the low yield. Orientation of fluoropropylation of the ring was unknown.

c) The acid was isolated and determined as the pyridinium salt.

Scheme 1.

Although the thermal decomposition of the peroxide 1 is known to proceed homolytically to generate perfluoropropyl radicals,3,4) the formation of $C_3F_7CH_2Ph$ cannot be explained by the reaction of perfluoropropyl radical and benzylmagnesium chloride, which should give mainly aromatic ring substituted products. We propose the electron transfer mechanism from benzylmagnesium chloride to the peroxide to give the radical anion of the peroxide and the radical cation of the benzylmagnesium chloride. The radical anion decomposes to a perfluoropropyl radical and a perfluorobutyrate anion, and the radical cation gives a benzyl radical; the recombination of benzyl and perfluoropropyl radicals in a solvent cage gives $C_3F_7CH_2Ph$. The ketone or the alcohol shown in Scheme 1 should be formed by the reaction of an ester ($C_3F_7COOCH_2Ph$) and benzylmagnesium chloride. Since the decarboxylation of $C_3F_7COO\cdot$ easily occurs,4) the ester should be formed by a nucleophilic substitution on the O-O bond of the peroxide but not by a recombination of a benzyl radical and a $C_3F_7COO\cdot$ radical.6) The plausible mechanism is shown in Scheme 2.



Electron Transfer Reaction

$$(C_3F_7COO)_2 + PhCH_2MgCl \longrightarrow (C_3F_7COO)_2^{\bar{\cdot}} + [PhCH_2MgCl]^{+\cdot} \longrightarrow$$
$$C_3F_7\cdot + CO_2 + C_3F_7COO^- + PhCH_2\cdot + [MgCl]^+ \longrightarrow$$
$$C_3F_7CH_2Ph + C_3F_7COOMgCl + CO_2$$

$$\left[\begin{array}{l} C_3F_7CH_2Ph + (C_3F_7COO)_2 \longrightarrow C_3F_7CH_2C_6H_4C_3F_7 + C_3F_7COOH \\ \text{and/or} \\ PhCH_2MgCl \xrightarrow{C_3F_7\cdot} C_3F_7C_6H_4MgCl \xrightarrow{(C_3F_7COO)_2} C_3F_7CH_2C_6H_4C_3F_7 \end{array}\right]^{7)}$$

Nucleophilic Substitution

$$(C_3F_7COO)_2 + PhCH_2MgCl \longrightarrow C_3F_7COOCH_2Ph + C_3F_7COOMgCl$$

$$\left[\begin{array}{lcl} C_3F_7COOCH_2Ph & \xrightarrow{PhCH_2MgCl} & C_3F_7\underset{O}{\underset{\|}{C}}CH_2Ph \\ C_3F_7\underset{O}{\underset{\|}{C}}CH_2Ph & \xrightarrow{PhCH_2MgCl} & C_3F_7\underset{OH}{\underset{|}{C}}(CH_2Ph)_2 \end{array}\right]$$

Scheme 2.

The electron transfer reaction is very interesting. Owing to the high electronegativity of the perfluoroalkyl group, reactions involving a perfluoroalkyl group as a cationic intermediate are very limited.8) However, in the electron transfer reaction shown in Scheme 2, the perfluoroalkyl group was introduced to the nucleophile superficially as a cation.

The reaction of the peroxide 1 with several organometallic compounds was also investigated and the results are summarized in Table 1.

As a metal, lithium and mercury were chosen; lithium has less electronegativity and mercury has higher electronegativity compared to magnesium. In both benzylmagnesiums or benzylmercuries, the nucleophilic substitution took place in preference to the electron transfer reaction. The nucleophilicity of benzyllithium is so high that benzyllithium reacted with Freon-113.

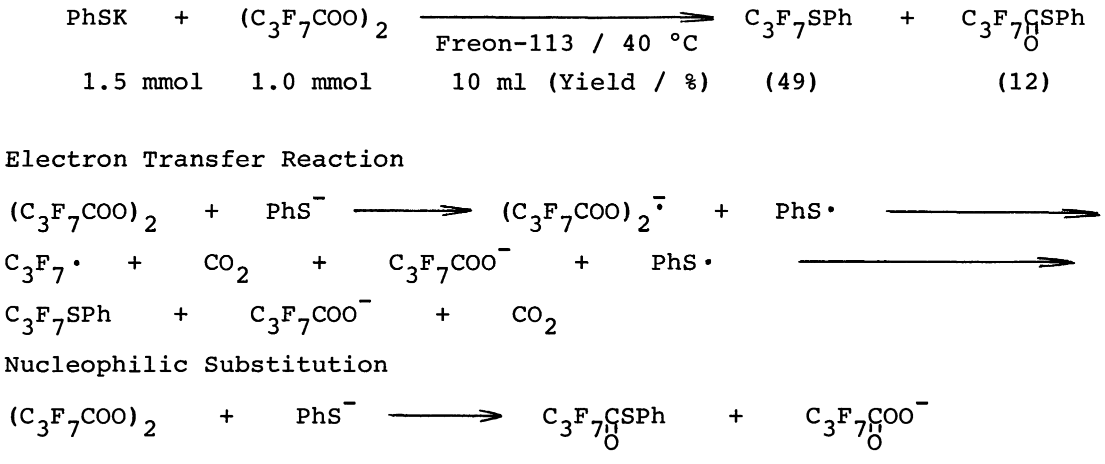
The thiolate anion is known to be a soft base in the sense of Hard and Soft

Table 1. Reactions of Nucleophiles with $(C_3F_7COO)_2$ 1

Substrate (Molar ratio of Substrate to 1)	Solvent	Products (Yield / %)[a] Rf = C_3F_7			
		$RfCH_2Ph$	$RfCH_2C_6H_4C_3F_7$	$Rf(CO)CH_2Ph$	$Rf(OH)C(CH_2Ph)_2$
$PhCH_2MgCl$ (5.0)	Et_2O - Freon-113	(24)	(4)	(21)	(11)
$PhCH_2MgBr$ (5.0)	Et_2O - Freon-113	(21)		(45)	(12)
$(PhCH_2)_2Hg$ (1.0)	Freon-113	(12)		$RfCOOCH_2Ph$ (81)	
$PhCH_2HgCl$ (1.0)	Freon-113	(4)	(8)	(42)	Recovered $PhCH_2HgCl$ (19)
$PhCH_2Li$ (1.5)	Et_2O - Freon-113	(<1)		($PhCH_2Cl$, $PhCH_2CCl{=}CF_2$)	

a) Yields were determined by GC based on 1.

Acids and Bases (HSAB) theory[9)] and should release an electron more readily than carbanions. So in the reaction of a thiolate anion with 1, the electron transfer reaction is expected to take place in preference to the nucleophilic substitution. The reaction of 1 with potassium thiophenoxide was investigated. Potassium thiophenoxide was added to a solution of 1 in Freon-113, and the mixture was degassed and kept at 40 °C for 5 h. The products and the proposed mechanism for the formation of the products are shown in Scheme 3. In this case perfluoropropylated compounds were obtained in 50% yields. The reaction of the thiolate anion with the peroxide 1 seems to be a good synthetic way to introduce a perfluoroalkyl group on the sulfur atom.



$$\underset{1.5\ \text{mmol}}{PhSK} + \underset{1.0\ \text{mmol}}{(C_3F_7COO)_2} \xrightarrow[\text{Freon-113 / 40 °C}]{} \underset{(49)}{C_3F_7SPh} + \underset{(12)}{C_3F_7\underset{\underset{O}{\|}}{C}SPh}$$

10 ml (Yield / %)

Electron Transfer Reaction

$$(C_3F_7COO)_2 + PhS^- \longrightarrow (C_3F_7COO)_2^{\cdot -} + PhS\cdot \longrightarrow$$

$$C_3F_7\cdot + CO_2 + C_3F_7COO^- + PhS\cdot \longrightarrow$$

$$C_3F_7SPh + C_3F_7COO^- + CO_2$$

Nucleophilic Substitution

$$(C_3F_7COO)_2 + PhS^- \longrightarrow C_3F_7\underset{\underset{O}{\|}}{C}SPh + C_3F_7\underset{\underset{O}{\|}}{C}OO^-$$

(Yields were determined by GC based on 1.)

Scheme 3.

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