CHEMISTRY LETTERS, pp. 755-758, 1985.

HEPTAFLUOROPROPYLATION OF ELECTRON-RICH OLEFINS WITH BIS(HEPTAFLUOROBUTYRYL) PEROXIDE

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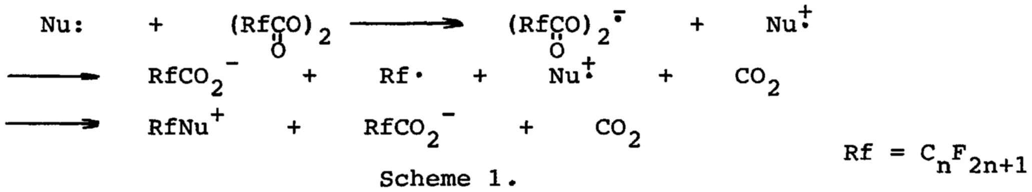
Bis(heptafluorobutyryl) peroxide reacted with electron-rich olefins to give the adducts of $C_3F_7CO_2$ and C_3F_7 groups in good yields. The peroxide should be the useful reagent for the introduction of heptafluoropropyl moiety into olefins.

The introduction of perfluoroalkyl groups has been the subject of much research in organofluorine chemistry, since the usual methods for alkylation can not be applied to perfluoroalkylation. Especially, the development of the reagents for cationic perfluoroalkylation should be important, because owing to the high electronegativity of perfluoroalkyl group, reactions involving a perfluoroalkyl cation as an intermediate are very limited.[1)] We have been studying the decomposition of perfluoroalkanoyl peroxide (Rf(CO)OO(CO)Rf) and found that the peroxide suffered a facile decomposition induced by the attack of nucleophile.[2,3)] High reactivity of this peroxide may be attributed to the low energy level of the O-O antibonding due to the high electroneganivity of perfluoroalkyl group.[4)] This suggests the possibility of the electrophilic perfluoroalkylation using perfluoroalkanoyl peroxide via one-electron transfer as shown in Scheme 1.



$$\begin{aligned}
&\mathrm{Nu{:}} + (\mathrm{Rf}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{O})_2 \longrightarrow (\mathrm{Rf}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{O})_2^{\overset{\bullet}{-}} + \mathrm{Nu}^{\overset{+}{\bullet}}\\
&\longrightarrow \mathrm{RfCO_2^-} + \mathrm{Rf\cdot} + \mathrm{Nu}^{\overset{+}{\bullet}} + \mathrm{CO_2}\\
&\longrightarrow \mathrm{RfNu^+} + \mathrm{RfCO_2^-} + \mathrm{CO_2} \qquad \mathrm{Rf} = \mathrm{C_nF_{2n+1}}
\end{aligned}$$

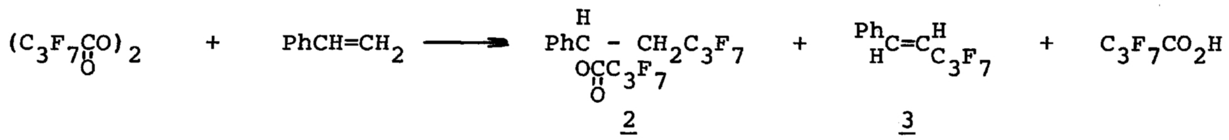
Scheme 1.

In this communication, we wish to report introduction of heptafluoropropyl group to olefins using bis(heptafluorobutyryl) peroxide ($C_3F_7(CO)OO(CO)C_3F_7$ $\underline{1}$).

The peroxide $\underline{1}$ was prepared from heptafluorobutyryl chloride and hydrogen peroxide in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) according to the literature.[5)] The solution of $\underline{1}$ in Freon-113 was used without further purification and the concentration of the peroxide was determined by iodometry.

The reaction of $\underline{1}$ and styrene was shown as a typical example. One and half mol of styrene per mol of $\underline{1}$ was added to a solution of $\underline{1}$ in Freon-113 and the mixture was degassed by a freeze-thaw cycle, sealed in an ampoule and kept at

40 °C for 3 h. As shown in Scheme 2, the adduct (2) of $C_3F_7CO_2$ and C_3F_7 groups to styrene, and the substituted compound (3) of C_3F_7 to β-carbon of styrene were obtained.



$$(C_3F_7\underset{\underset{O}{\|}}{C}O)_2 \quad + \quad PhCH{=}CH_2 \longrightarrow \underset{\underset{\underset{O}{\|}}{OCC_3F_7}}{\overset{H}{PhC}} - CH_2C_3F_7 \quad + \quad {}^{Ph}_{H}C{=}C^{H}_{C_3F_7} \quad + \quad C_3F_7CO_2H$$

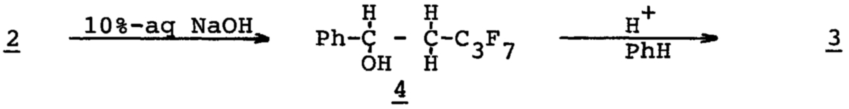
2 3

2; ^{1}H-NMR ($CDCl_3$) δ 7.38 (m; 5H), 6.35 (d,d J = 9.6, 3.6 Hz; 1H), 2.10-3.19 (m; 2H), ^{13}C-NMR ($CDCl_3$) δ 157.1, 136.5, 129.9, 129.3, 126.4, 73.4, 37.1 (t J_{CCF}= 21.2 Hz), IR $\nu_{C=O}$= 1790, ν_{CF_3}= 1360, ν_{CF_2}= 1230 cm^{-1}, MS 486 (M^+), Exact MS; 486.0269 (calcd. for $C_{15}H_8F_{14}O_2$ 486.0238).

3; ^{1}H-NMR ($CDCl_3$) δ 7.4 (m; 5H), 7.07 (d J = 16 Hz; 1H), 6.18 (d,t J_H= 16 Hz, J_F= 22 Hz; 1H), ^{13}C-NMR ($CDCl_3$) δ 139.7 (t J_{CCCF}= 9.2 Hz), 133.5, 130.1, 128.1, 127.6, 114.1 (t J_{CCF}= 23.8 Hz), IR ν_{CF_3}= 1360, ν_{CF_2}= 1230 cm^{-1}, MS 272 (M^+).

Scheme 2.

The hydrolysis of 2 under basic conditions gave alcohol 4. The alcohol was also converted into olefin 3 by refluxing in benzene in the presence of p-toluenesulfonic acid.



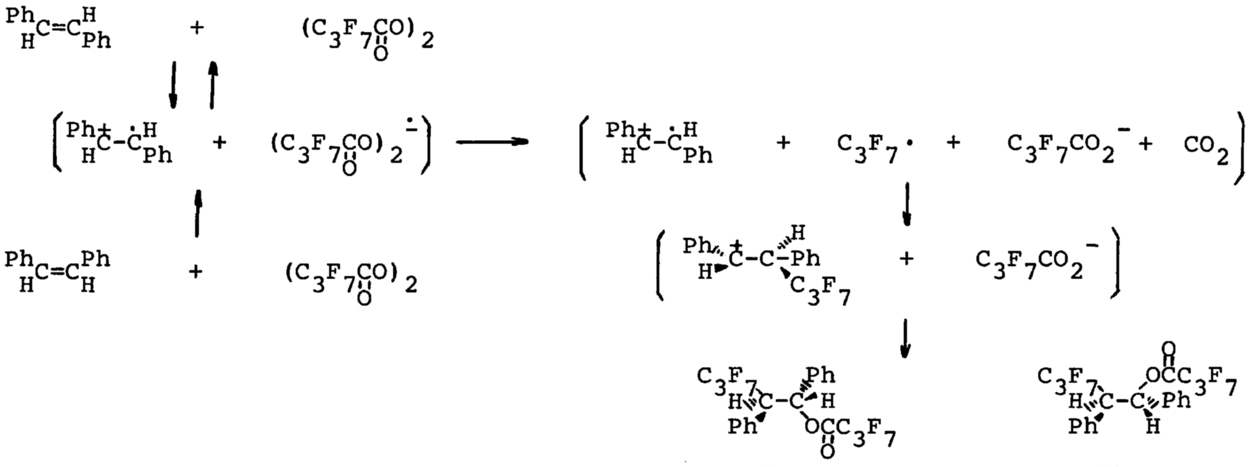
$$2 \xrightarrow{10\%\text{-aq NaOH}} Ph-\underset{OH}{\overset{H}{C}} - \underset{H}{\overset{H}{C}}-C_3F_7 \xrightarrow[PhH]{H^+} 3$$

4

Thus, this method is useful for introduction of perfluoroalkyl group into β-position of styrene.$^{6)}$ The OH group in alcohol 4 should be converted into other important functional groups. So the alcohol 4 may have high potential as an important intermediate in organic synthetic chemistry.

In order to examine the stereochemistry of addition of 1 to olefin, the reactions of 1 with E and Z stilbene were carried out. As the adducts, a mixture of two isomers 5a and 5b in almost same molar ratio was obtained in the reaction with either E- or Z-stilbene (Scheme 3). In the reaction of 1 with Z-stilbene, the recovered unchanged stilbene was found to be isomerized to E form. In order to explain these results, we propose the mechanism as shown in Scheme 3. The reaction is induced by one-electron transfer from stilbene to 1; the common stilbene radical cation is produced from both E and Z isomers. This electron-transfer process is reversible to form thermally stable E-stilbene and 1. The cation, which was produced by coupling with stilbene radical cation and C_3F_7 radical, has planar configuration to give the two adducts 5a and 5b in equal amount.

In the reaction of α-methylstyrene and ethyl vinyl ether with 1, the adducts were obtained in good yields, too. These results were summarized in Table 1. However, reactions of 1 with 1-octene, cyclohexene, or methyl acrylate gave no adducts but considerable amounts of polymeric compounds. This suggests that in the reaction of 1 with electron-deficient olefins, one-electron transfer from olefins to 1 was difficult and usual free radical decomposition of 1 proceeded.

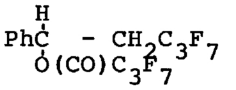
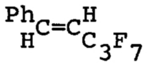
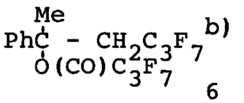
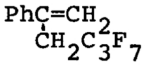
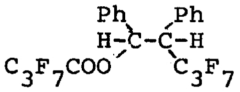


5a 5b

5a,b; ^{1}H-NMR (CDCl$_3$) δ 7.23-7.12 (m; 5H), 4,47-3.47 (m; 2H), ^{13}C-NMR δ 78.1 and 76.2 (-$\underline{C}$-O(CO)-), 53.3 and 52.6 (-$\underline{C}$-C$_3$F$_7$, J$_{CCF}$= 19.5 Hz), IR $\nu_{C=O}$= 1780, ν_{CF_3} = 1340, ν_{CF_2} = 1220 cm^{-1}, MS 562 (M$^+$). The ratio of 5a/5b = 1.06 from E and 0.98 from Z.

Scheme 3.

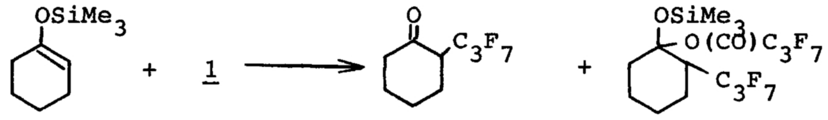
Table 1. The Reaction of 1 and Olefins

Olefin	Products (Yield/%)[a]			
PhCH=CH$_2$	 $\overset{H}{PhC}$ - CH$_2$C$_3$F$_7$ O(CO)C$_3$F$_7$	(89)	 $^{Ph}_{H}$C=C$^{H}_{C_3F_7}$	(7)
PhCMe=CH$_2$	 $\overset{Me}{PhC}$ - CH$_2$C$_3$F$_7$[b)] O(CO)C$_3$F$_7$ 6	(77)	 PhC=CH$_2$ CH$_2$C$_3$F$_7$ 7	(21)
PhCH=CHPh	 5a + 5b		PhCH=C(C$_3$F$_7$)Ph (E and Z)	
(E)	(59)		(18)	
(Z)	(58)		(18)	
H$_2$C=CHOEt	C$_3$F$_7$CH$_2$-CH(OEt)OOCC$_3$F$_7$[c)]	(95)		

a) Determined by GC. b) 6 is thermally unstable and changed to olefin 7 during the distillation; 7; ^{1}H-NMR (CDCl$_3$) δ 7.30 (m; 5H), 5.58 (s; 1H), 5.32 (s; 1H), 3.20 (t J$_{CF_2}$ = 18 Hz; 2H), ^{13}C-NMR (CDCl$_3$) δ 140.4, 137.1, 128.4, 127.9, 126.0, 120.4, 36.1 (t J$_{CCF}$=21.9 Hz), IR ν_{CF_3} = 1350, ν_{CF_2} = 1220 cm^{-1}, MS 286 (M$^+$), Exact MS 286.0566 (calcd. for C$_{12}$H$_9$F$_7$ 286.0540).

c) ^{1}H-NMR (CDCl$_3$) δ 6.30 (t J = 6.0 Hz; 1H), 3.60 (q J = 7.0 Hz; 2H), 2.65 (t,d J$_F$= 18.0, J$_H$= 6.0 Hz; 2H), 1.28 (t J = 7.0 Hz; 3H), ^{13}C-NMR (CDCl$_3$) δ 158.0 (t J$_{CCF}$= 28.3 Hz), 97.2, 67.1, 36.2 (t J$_{CCF}$=20.0 Hz), 14.7, IR $\nu_{C=O}$= 1780, ν_{CF_3} = 1350 cm^{-1} .

Silyl enol ether should be good electron-donor and expected to react with 1 via one-electron transfer. In the reaction of trimethylsilyloxy cyclohexene with 1, two products 8 and 9 were obtained; the adduct 9 could be converted into 8. This means that 1 may be used as a good α-perfluoropropylation reagent of carbonyl compounds.[7)]



8 (27%) 9 (48%)

8; ^{1}H-NMR ($CDCl_3$) δ 3.1 (-C$\underline{H}$-CF_2-, m; 1H), ^{13}C-NMR ($CDCl_3$) δ 203.0, 51.8 (J_{CCF}= 18.3 Hz), 42.6, 27.5, 27.2, 23.5, IR $\nu_{C=O}$= 1720 cm^{-1}.

Scheme 4.

This work was in part supported by Grant-in-Aid for Scientific Research from Ministry of Education, Science, and Culture.

References

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(Received March 25, 1985)