Journal of Fluorine Chemistry, *48* (1990) 145–147

Received: October 4, 1989; accepted January 20, 1990

PRELIMINARY NOTE

A Novel Nucleophilic Polyfluoroalkylating Agent R_fI-$P(NEt_2)_3$

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SUMMARY

In the presence of tris(diethylamino)phosphine polyfluoroalkyl iodides reacted with various aroyl chlorides to give the corresponding aryl polyfluoroalkyl ketones.

Nigumi et al. reported that treatment of perfluoroalkyl iodides with an electron rich phosphine, i.e. tris(dialkylamino)-phosphine($P(NR_2)_3$), gave dialkylaminoperfluoroalkylphosphines ($(R_2N)_2PR_f$)[1]. Recently, Ruppert and Bürger et al. reported that, in the presence of tris(dialkylamino)phosphine, trifluoromethyl bromide reacted with electropositive elements E, e.g. R_3Si-, R_2B-, to give CF_3E[2,3].

We now report R_fI-$P(NEt_2)_3$ as a novel nucleophilic polyfluoroalkylating agent for aroyl chlorides.

In the presence of tris(diethylamino)phosphine, polyfluoroalkyl iodides reacted with aroyl chlorides in refluxing methylene chloride to give aryl polyfluoroalkyl ketones in moderate yield. The results were summarized in the Table.

$$R_fI + ArCOCl + P(NEt_2)_3 \longrightarrow ArCOR_f$$

0022-1139/90/$3.50

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TABLE

The reaction of polyfluoroalkyl iodides with tris(diethylamino) phosphine and aroyl chlorides[a]

ArCOCl	R_fI	t(h)	Yield(%)[b]
p-ClC_6H_4COCl	$CF_3(CF_2)_5I$	6	41
2,4-$Cl_2C_6H_3COCl$	$CF_3(CF_2)_7I$	6	36
p-ClC_6H_4COCl	$Cl(CF_2)_4I$	3.5	42
C_6H_5COCl	"	6	43
2,4-$Cl_2C_6H_3COCl$	"	4	43
p-ClC_6H_4COCl	$Cl(CF_2)_6I$	5	41
p-BrC_6H_4COCl	"	7	40
o-ClC_6H_4COCl	"	6.5	32
C_6H_5COCl	"	6	41
2,4-$Cl_2C_6H_3COCl$	"	6.5	40

[a] All reactions were carried out at 45°C in methylene chloride.

[b] Isolated yields based on the starting ArCOCl.

The first step of such reaction is considered as a nucleophilic attack of phosphine on the positive iodine atom. In the presence of electrophiles, i.e. aroyl chloride, further nucleophilic attack of the anionic polyfluoroalkyl group on the carbonyl group leads to the formation of a ketone rather than diethylaminopolyfluoroalkyl phosphine[1].

$$\begin{tikzcd}
(Et_2N)_3P\cdots IR_f \arrow[r] & {[\,(Et_2N)_3PI^+R_f^-\,]} \arrow[d, "ArCOCl"] \\
 & ArCOR_f + (Et_2N)_3PICl
\end{tikzcd}$$

Typical procedure: To a mixture of 3g(8.3 mmol) of ω-chlorooctafluorobutyl iodide and 525mg(3 mmol) of p-chlorobenzoyl chloride in dry CH_2Cl_2(10 ml), was added 885mg(3 mmol) of tris-(diethylamino)phosphine within 5 min. The mixture was then refuxed at 45°C for 3.5h. After usual workup, 470 mg of p-chlorophenyl ω-chlorooctafluorobutyl ketone was isolated by column chromatography in a 42% yield. Anal. for $C_{11}H_4Cl_2F_8O$: Calcd, C,35.23, H,1.07, Cl,18.91, F, 40.53; Found, C,34.86, H,0.91, Cl,18.72, F,41.16. IR(film) 1710, 1590, 1490, 1400, 1200-1150, 820 cm^{-1}; ^1H-NMR(CCl_4): 7.26(d, J=9Hz, 2H), 7.81(d, J=9Hz, 2H); ^{19}F-NMR(CCl_4): -8.2(s,2F), +36.6(S, 2F), +42.8(S, 2F), +44.0(s,2F); MSm/z: 375(M^+), 377(M^++2), 311, 140, 111, 75. Elemental analyses and spectra of other products were all in accordance with their structure.

Further work on this nucleophilic polyfluoroalkylating agent is in progress.

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