CHEMISTRY LETTERS, pp. 1337-1338, 1981.

PERFLUOROALKYLTIN(IV) HALIDES : A NOVEL PERFLUOROALKYLATING AGENT FOR CARBONYL COMPOUNDS

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Perfluoroalkyltin(IV) halides (R_fSnX_2I) were prepared in situ by the oxidative addition of perfluoroalkyl iodides to tin(II) halide in N,N-dimethylformamide. Aldehydes and ketones readily reacted with R_fSnCl_2I giving perfluoroalkylcarbinols in the N,N-dimethylformamide-pyridine system. R_fSnF_2I, however, did not undergo the reactions with these carbonyl compounds.

The introduction of a perfluoroalkyl group into organic molecules is one of the most attractive procedures in the field of organic fluorine chemistry. Reported synthetic reagents for the perfluoroalkylation include so far (1) perfluoroalkylmagnesium compounds, which, however, readily decompose into perfluoroalkenes and magnesium halides,[1] (2) heptafluoro-1-methylethylzinc iodide, which is useful to prepare heptafluoro-1-methylethyl aryl ketones,[2] and (3) perfluoroalkylcopper compounds[3-5] which are useful for the introduction of a perfluoroalkyl group into an aromatic ring. However, it is not easy to handle these perfluoroalkyl metallic compounds and their low reactivity reduces their synthetic utilities.

Recently, Mukaiyama et al.[6] and Tagliavini et al.[7] have reported the synthetic utility of tin(IV) halides which were prepared by the oxidative addition of allyl halides to tin(II) halides. In our continuing studies of the reactivities of perfluoroalkylmetal halides,[2,3] we have found that it is possible to introduce a perfluoroalkyl group into carbonyl compounds by the reaction with a perfluoroalkyltin(IV) dihaloiodide (1).

$$R_fI + SnX_2 \xrightarrow[r.t.]{DMF} \underset{\sim}{1}\ R_fSnX_2I \qquad (X = F, Cl;\ R_f = CF_3, (CF_3)_2CF, CF_3(CF_2)_5, \text{etc.})$$

The compound 1 could not be isolated in a pure form in spite of various attempts. The presence of these compounds in an N,N-dimethylformamide solution, however, was evident from their ^{19}F nmr spectrum. The ^{19}F nmr spectrum of CF_3SnCl_2I in the solution showed only one singlet signal at δ -67.0 ppm and that of CF_3SnF_2I showed two singlet signals at δ -65.0 and -25.5 ppm in the ratio 3 : 2 upfield from external CF_3CO_2H standard, respectively.

Further, we found out that the presence of pyridine promoted the nucleophilic reaction of 1 (X = Cl) with aldehydes and ketones, affording perfluoroalkylated carbinols in good yields. When 1 (X = F) was employed in the above reaction, however, the yields of the corresponding carbinols were poor.

The reaction should proceed as follows. Pyridine[8] probably accelerates the releasing of a perfluoroalkyl anion by coordinating on the tin atom of 1.

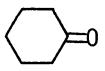
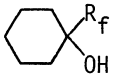
$$R_fSnCl_2I \xrightarrow{Pyr.} [\ R_fSnCl_2I(Pyr)_n\ ] \xrightarrow{RC(O)R'} R_f\text{-}\overset{R}{\underset{R'}{C}}\text{-O-}SnCl_2I(Pyr)_n \xrightarrow{H^+} R_f\text{-}\overset{R}{\underset{R'}{C}}\text{-OH}$$

1 (X = Cl) 2

Heptafluoro-1-methylethylphenylcarbinol. Into a mixture of $SnCl_2$ (3.8 g, 20 mmol) and N,N-dimethylformamide (20 ml), heptafluoro-1-methylethyl iodide (6.2 g, 21 mmol) was slowly added at room temperature. To this solution, benzaldehyde (2.1 g, 20 mmol) in pyridine (5 ml) was added and after 5 h of stirring, the reaction mixture was poured into 10% hydrochloric acid. The precipitates were removed by filtration, and an oily material in the filtrate was extracted with diethyl ether. The ethereal solution was washed with 5% aqueous sodium hydrogencarbonate and water. After removing the solvent, distillation gave heptafluoro-1-methylethylphenylcarbinol in a yield of 86% (4.5 g), bp 120 - 123 °C/104 mmHg. The ^{19}F nmr spectrum in $CDCl_3$ shows resonances at δ -6.6, 3.5, and 104.0 in the ratio 3 : 3 : 1. The last one, assigned to the $\underline{CF}(CF_3)_2$, was an overlapping doublet of quartets split by $\underline{CH}Ph$ (J_{F-CH} = 12.5 Hz) and $\underline{CF}_3$ (J_{F-CF_3} = 7.5 Hz). The ^1H nmr shows resonances at δ 4.05 (O$\underline{H}$), 5.30 (C$\underline{H}$) and 7.50 (Ar$\underline{H}$). Anal. Calcd.[3] for $C_{10}H_7OF_7$: C, 43.39; H, 2.56%. Found: C, 43.40; H, 2.56%.

Reactions with other substrates were carried out in a similar manner (Table 1).

Table 1 Perfluoroalkylation of carbonyl compounds

Reactants		Conditions		Product	Yield	B.p.
Carbonyl Compound	R_fI	Temp (°C)	Time (h)		(%)	(°C/mmHg)
PhCH=O	CF_3I	r.t.	24	$PhCH(OH)R_f$	18	92-95/26
"	$n\text{-}C_3F_7I$	"	12	"	72	86-88/15
"	$i\text{-}C_3F_7I$	"	5	"	86	120-123/104
"	$n\text{-}C_6F_{13}I$	"	24	"	66	86-88/18
$p\text{-}MeC_6H_4CH=O$	$i\text{-}C_3F_7I$	"	5	$p\text{-}MeC_6H_4CH(OH)R_f$	82	105-107/87
$n\text{-}C_4H_9CH=O$	CF_3I	"	24	$n\text{-}C_4H_9CH(OH)R_f$	21	71-73/130
"	$n\text{-}C_3F_7I$	"	12	"	68	96-97/137
$n\text{-}C_5H_{11}CH=O$	$i\text{-}C_3F_7I$	"	5	$n\text{-}C_5H_{11}CH(OH)R_f$	67	90-91/112
	$n\text{-}C_3F_7I$	70	10		57	90-93/50
PhC(O)Me	$i\text{-}C_3F_7I$	70	10	$PhC(OH)(Me)R_f$	37	115-118/58
EtC(O)Me	"	70	15	$EtC(OH)(Me)R_f$	46	80-83/135

References

1) R. C. Chambers, W. K. R. Musgrave, and J. Savory, J. Chem. Soc., 1962, 1993.
2) A. Sekiya and N. Ishikawa, Chem. Lett., 1977, 81 and references cited therein.
3) N. Ishikawa and M. Ochiai, Nippon Kagaku Kaishi, 1973, 2351.
4) V. C. R. McLoughlin and J. Throwers, Tetrahedron, 25, 5921 (1969).
5) Y. Kobayashi and I. Kumadaki, Tetrahedron Lett., 1969, 4095.
6) T. Mukaiyama, T. Harada, and S. Shoda, Chem. Lett., 1980, 1507; 1981, 621, 723.
7) A. Gambaro, V. Peruzzo, G. Plazzogna, and G. Tagliavini, J. Organomet. Chem., 197, 45 (1980).
8) When other bases, e.g., triethylamine, N,N-dimethylaniline, N-methylpiperidine, were used in the above reaction, no formation of carbinol was observed.

(Received June 29, 1981)