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PRELIMINARY NOTE

THE EFFECT OF LEWIS ACIDS ON THE THALLATION OF POLYFLUOROARENES

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The marked deactivation of polyfluoroarenes towards electrophilic attack [1] is exemplified by their resistance to thallation by thallic trifluoroacetate in trifluoroacetic acid [2, 3]. However, many of these compounds can be metallated by the powerful thallating agent thallic trifluoromethanesulphonate in trifluoroacetic acid [2, 3]. Nevertheless, there are still problems with the least reactive polyfluoroarenes. For example, 1,2,3,5-tetrafluoro-4-nitrobenzene is only thallated in trace amounts [3], substitution of pentafluorobenzene requires a long reaction time [3], and, somewhat surprisingly, 4,4'-dihydrooctafluorobiphenyl is unaffected by thallic trifluoromethanesulphonate in trifluoroacetic acid (this work). We now report that Lewis acids facilitate thallation of polyfluoroaromatic compounds.

The products of the thallation reactions (below),

$$RH + TlX_3 \rightarrow RTlX_2 + HX \qquad (1)$$

$$(X = CF_3CO_2, CF_3SO_3, \text{ or } FSO_3)$$

were identified by conversion into the corresponding polyfluoroaryl iodides on reaction with aqueous sodium iodide,

$$RTlX_2 + 2I^- \rightarrow RI + TlI + 2X^- \qquad (2)$$

$$(X = CF_3CO_2, CF_3SO_3, \text{ or } FSO_3)$$

a reaction characteristic of monoarylthallium(III) compounds [4].

The effect of Lewis acids was first established with the relatively reactive [3] polyfluoroarene, 2,3,5,6-tetrafluoroanisole. No thallation was observed when the compound was treated with an equimolar amount of thallic trifluoroacetate in 1,2-dichloroethane for 1.5 days at room temperature. However, addition of boron trifluoride etherate to the reaction mixture [2 mole $BF_3.OEt_2$/mole of $Tl(O_2CCF_3)_3$] for the same reaction time gave, after cleavage with iodide ions, a 48% yield of 2,3,5,6-tetrafluoro-4-iodoanisole [reactions (1) and (2); R = *p*-$MeOC_6F_4$, X = CF_3CO_2]. This method could not be extended to other polyfluoroarenes (e.g. C_6F_5H or *p*-MeC_6F_4H), and boron trifluoride etherate had no significant effect on thallation in trifluoroacetic acid. By contrast, antimony pentafluoride caused enhanced thallation of 1,2,3,5-tetrafluorobenzene in both trifluoroacetic acid and trifluoromethanesulphonic acid [reaction (1); R = *m*-HC_6F_4, X = CF_3CO_2 or CF_3SO_3] (Table 1). In the latter medium, the Lewis acid had more effect on the yield of dithallated arene *m*-$[(CF_3SO_3)_2Tl]_2C_6F_4$ (as indicated by the yield of *m*-$I_2C_6F_4$) than on the yield of *m*-$HC_6F_4Tl(O_3SCF_3)_2$.

TABLE 1

The effect of antimony pentafluoride on the thallation of 1,2,3,5-tetrafluorobenzene with thallic trifluoroacetate [a]

Acid	SbF_5 (mmol)	Polyfluoro-(iodo)arene	Yield (%)
CF_3CO_2H	0	*m*-HC_6F_4I	13
CF_3CO_2H	30	*m*-HC_6F_4I	26
CF_3SO_3H	0	*m*-HC_6F_4I	44
		m-$I_2C_6F_4$	2
CF_3SO_3H	30	*m*-HC_6F_4I	51
		m-$I_2C_6F_4$	8

[a] All reactions between $Tl(O_2CCF_3)_3$ (15 mmol), *m*-$H_2C_6F_4$ (5 mmol), and 10 ml of acid for 3 h at 80°C in sealed Carius tubes.

Dithallation of monocyclic arenes is difficult to achieve [5], since the electron-withdrawing character [6] of the first thallium substituent causes deactivation towards further substitution.

By using antimony pentafluoride in a fluorosulphuric acid medium, a further increase in the yield of dithallated 1,2,3,5-tetrafluorobenzene was obtained (Table 2), hence this procedure was adopted for subsequent reactions. Thus, monothallation and dithallation of the unreactive 4,4'-dihydrooctafluorobiphenyl and significant thallation of the highly unreactive 1,2,3,5-tetrafluoro-4-nitrobenzene were achieved, whilst the reaction time for extensive thallation of pentafluorobenzene was substantially reduced from the reported value [3] (Table 2).

TABLE 2

Thallation of polyfluoroarenes in fluorosulphuric acid
(Reactions at 80^o were carried out in sealed Carius tubes)

Polyfluoroarene (5 mmol)	Other Reagents	Temp. (^oC)	Time (h)	Polyfluoro-(iodo)arene	Yield (%)
m-$H_2C_6F_4$	A	80	3	m-HC_6F_4I	50
				m-$I_2C_6F_4$	18
4,4'-$H_2C_{12}F_8$	A	25	12	4-H,4'-$IC_{12}F_8$	53
	A	80	24	4-H,4'-$IC_{12}F_8$	52
				4,4'-$I_2C_{12}F_8$	24
m-$HC_6F_4NO_2$	A	80	24	m-$IC_6F_4NO_2$	11
C_6F_5H	B	80	3	C_6F_5I	90

A $Tl(O_2CCF_3)_3$ (15 mmol), FSO_3H (10 ml), and SbF_5 (30 mmol)

B $Tl(O_2CCF_3)_3$ (10 mmol), FSO_3H (5 ml), and SbF_5 (20 mmol)

The polyfluoro(iodo)arenes (Tables 1 and 2) were identified by ^1H and ^{19}F n.m.r. spectroscopy, and their yields were determined by n.m.r. methods. New products were isolated by preparative gas liquid chromatography, and were additionally characterized by microanalysis and mass spectrometry.

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