

PRELIMINARY NOTE

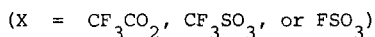
THE EFFECT OF LEWIS ACIDS ON THE THALLATION OF POLYFLUOROARENES

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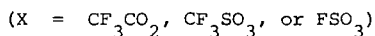
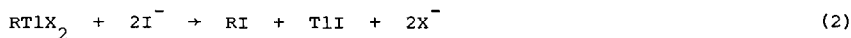
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The marked deactivation of polyfluoroarenes towards electrophilic attack [1] is exemplified by their resistance to thallation by thallic trifluoroacetate in trifluoroacetic acid [2, 3]. However, many of these compounds can be metallated by the powerful 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),



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



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 $\text{BF}_3 \cdot \text{OEt}_2$ /mole of $\text{Tl}(\text{O}_2\text{CCF}_3)_3$] 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); $\text{R} = \text{p-MeOC}_6\text{F}_4$, $\text{X} = \text{CF}_3\text{CO}_2$]. This method could not be extended to other polyfluoroarenes (e.g. $\text{C}_6\text{F}_5\text{H}$ or $\text{p-MeC}_6\text{F}_4\text{H}$), 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); $\text{R} = \text{m-HC}_6\text{F}_4$, $\text{X} = \text{CF}_3\text{CO}_2$ or CF_3SO_3] (Table 1). In the latter medium, the Lewis acid had more effect on the yield of dithallated arene $\text{m-}[(\text{CF}_3\text{SO}_3)_2\text{Tl}]_2\text{C}_6\text{F}_4$ (as indicated by the yield of $\text{m-I}_2\text{C}_6\text{F}_4$) than on the yield of $\text{m-HC}_6\text{F}_4\text{Tl}(\text{O}_3\text{SCF}_3)_2$.

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 (%)
$\text{CF}_3\text{CO}_2\text{H}$	0	$\text{m-HC}_6\text{F}_4\text{I}$	13
$\text{CF}_3\text{CO}_2\text{H}$	30	$\text{m-HC}_6\text{F}_4\text{I}$	26
$\text{CF}_3\text{SO}_3\text{H}$	0	$\text{m-HC}_6\text{F}_4\text{I}$	44
		$\text{m-I}_2\text{C}_6\text{F}_4$	2
$\text{CF}_3\text{SO}_3\text{H}$	30	$\text{m-HC}_6\text{F}_4\text{I}$	51
		$\text{m-I}_2\text{C}_6\text{F}_4$	8

^a All reactions between $\text{Tl}(\text{O}_2\text{CCF}_3)_3$ (15 mmol), $\text{m-H}_2\text{C}_6\text{F}_4$ (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° were carried out in sealed Carius tubes)

Polyfluoroarene (5 mmol)	Other Reagents	Temp. (°C)	Time (h)	Polyfluoro- (iodo)arene	Yield (%)
$\underline{m}\text{-H}_2\text{C}_6\text{F}_4$	A	80	3	$\underline{m}\text{-HC}_6\text{F}_4\text{I}$	50
				$\underline{m}\text{-I}_2\text{C}_6\text{F}_4$	18
4,4'- $\text{H}_2\text{C}_{12}\text{F}_8$	A	25	12	4-H,4'- IC_{12}F_8	53
	A	80	24	4-H,4'- IC_{12}F_8	52
				4,4'- $\text{I}_2\text{C}_{12}\text{F}_8$	24
$\underline{m}\text{-HC}_6\text{F}_4\text{NO}_2$	A	80	24	$\underline{m}\text{-IC}_6\text{F}_4\text{NO}_2$	11
$\text{C}_6\text{F}_5\text{H}$	B	80	3	$\text{C}_6\text{F}_5\text{I}$	90

A $\text{Ti}(\text{O}_2\text{CCF}_3)_3$ (15 mmol), FSO_3H (10 ml), and SbF_5 (30 mmol)

B $\text{Ti}(\text{O}_2\text{CCF}_3)_3$ (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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