

Preliminary communication

A NOVEL DESULPHINATION PATH TO TRIS(POLYFLUOROPHENYL)-
 THALLIUM(III) COMPOUNDS

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Summary

Tris(polyfluorophenyl)thallium(III) compounds, R_3Tl ($R = C_6F_5$, $p\text{-}HC_6F_4$, or $o\text{-}HC_6F_4$) have been prepared by reaction between the corresponding bromobis(polyfluorophenyl)thallium(III) derivatives and barium or thallos polyfluorobenzenesulphinates in pyridine.

There are problems with all reported routes to tris(polyfluorophenyl)-thallium(III) compounds. The Grignard preparation of tris(pentafluorophenyl)-thallium is difficult to reproduce, and involves separation of the air-sensitive $(C_6F_5)_3Tl$ from $(C_6F_5)_2TlBr$ [1]. The recently reported symmetrization [2] and decarboxylation [3] syntheses of tris(polyfluorophenyl)thallium(III) compounds are limited to derivatives with two fluorines ortho to thallium, e.g. tris(2,3,4,5-tetrafluorophenyl)thallium(III) cannot be obtained by either method. We now report that tris(polyfluorophenyl)thallium(III) compounds, including $(o\text{-}HC_6F_4)_3Tl$, can be formed by sulphur dioxide elimination reactions. Few other Group 3B organometallics, viz. some acetatobis(polyfluorophenyl)thallium(III) compounds [4], and some mono- and di-mesitylthallium(III) compounds [5] have been obtained by this method.

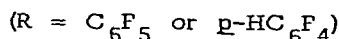
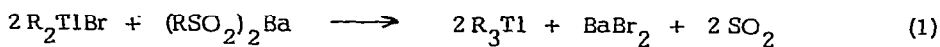
Reaction of bromobis(polyfluorophenyl)thallium(III) compounds, R_2TlBr ($R = C_6F_5$, $p\text{-}HC_6F_4$, or $o\text{-}HC_6F_4$), with either the corresponding barium or thallos polyfluorobenzenesulphinates, $(RSO_2)_2Ba$ ($R = C_6F_5$ or $p\text{-}HC_6F_4$)

TABLE 1
The Formation of Tris (polyfluorophenyl)thallium (III) Compounds by Sulphur Dioxide Elimination Reactions

Reactants	C ₅ H ₅ N ml	Reaction Time (min.)	Product	% Yield	
				a	b
(C ₆ F ₅) ₂ TlBr 0.49 mmol	(C ₆ F ₅ SO ₂) ₂ Ba 0.33 mmol	10	(C ₆ F ₅) ₃ Tl	66	(38)
(p-HC ₆ F ₄) ₂ TlBr 0.57 mmol	(p-HC ₆ F ₄ SO ₂) ₂ Ba 0.29 mmol	10	(p-HC ₆ F ₄) ₃ Tl	68	(38) ^c
(o-HC ₆ F ₄) ₂ TlBr 3.1 mmol	(p-HC ₆ F ₄ SO ₂) ₂ Ba 1.7 mmol	30	(p-HC ₆ F ₄) ₃ Tl	68	(60)
(o-HC ₆ F ₄) ₂ TlBr 0.74 mmol	(o-HC ₆ F ₄ SO ₂) ₂ Tl 0.49 mmol	10	(o-HC ₆ F ₄) ₃ Tl	34	(9) ^d

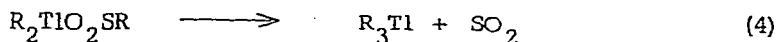
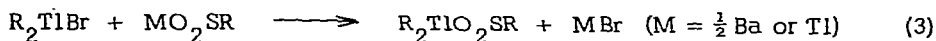
^a Determined from the ¹⁹F n.m.r. spectra of the reaction mixtures, on the assumption that no polyfluorophenyl groups were lost from the reaction mixture. ^b Yields of recrystallized R₃Tl(diox) complexes, obtained as described in the text. ^c Sulphur dioxide (58%) was obtained in a similar experiment. ^d Crude (o-HC₆F₄)₃Tl(diox), 24% yield; Tl₂SO₄ (c. 50%) also formed.

or $\underline{\text{O}}\text{-HC}_6\text{F}_4\text{SO}_2\text{Tl}$, in boiling dry pyridine under nitrogen gave the corresponding tris (polyfluorophenyl)thallium(III) compounds (Table 1).

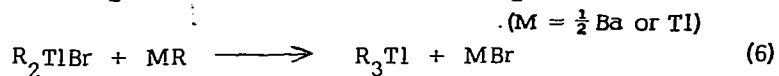
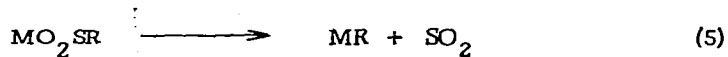


The products were identified in the resulting reaction mixtures by their ^{19}F n.m.r. spectra, and in particular by the thallium-fluorine coupling constants, which were significantly less than those of the corresponding R_2TlBr derivatives. After filtering the reaction mixtures, the compounds were isolated as crude pyridine complexes contaminated with R_2TlBr derivatives. Sublimation and crystallization of the sublimates from 1,4-dioxan (diox) gave the corresponding pure 1,4-dioxantris (polyfluorophenyl)thallium(III) complexes, $\text{R}_3\text{Tl}(\text{diox})$. These had spectroscopic properties and melting points in agreement with reported data ($\text{R} = \text{C}_6\text{F}_5$ or $\underline{\text{O}}\text{-HC}_6\text{F}_4$) [2, 3, 6], whilst the new complex $(\underline{\text{O}}\text{-HC}_6\text{F}_4)_3\text{Tl}(\text{diox})$, m.p. 238° (dec.), was obtained analytically pure with a satisfactory ^{19}F n.m.r. spectrum. The formation of thallos sulphate (Table 1) during the preparation of $(\underline{\text{O}}\text{-HC}_6\text{F}_4)_3\text{Tl}$ arises from thermal decomposition of the thallos sulphinate. Use of longer reaction times in reaction (1) ($\text{R} = \text{C}_6\text{F}_5$) and reaction (2) gave the tris (polyfluorophenyl)thallium(III) pyridinates as unsublimable gúues, and the same problem was encountered with the latter reaction unless an excess of $(\underline{\text{O}}\text{-HC}_6\text{F}_4)_2\text{TlBr}$ was used.

Detection of sulphur dioxide in good yield from a representative reaction eliminated the possibility that the tris (polyfluorophenyl)thallium(III) compounds were formed by rearrangement of bis (polyfluorophenyl)thallium(III) species. It is likely that reactions (1) and (2) proceed via formation (3) and desulphination (4) of bis (polyfluorophenyl)sulphinatothallium(III) complexes, even though these intermediates could not be isolated.



The alternative path (5) and (6) can be ruled out, since thallos 2,3,4,5-tetrafluorobenzenesulphinate does not decompose by (5), and thermal decomposition of the barium sulphinates proceeds too slowly to be a step in reaction (1).



Acknowledgement

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References

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