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## PRELIMINARY NOTE

### New Decarboxylation Syntheses of Polyfluorophenylorganometallic Compounds

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Syntheses of organometallic compounds by thermal decarboxylation reactions are currently limited to derivatives of Group 2B [1,2], Group 1B [3], nickel [4], tin [1,5], lead [1,6], and arsenic [1]. Applications to fluorocarbon compounds have been important in development of the method and are known [1-4,6] for all the above elements except tin. We now report decarboxylation syntheses of tris(pentafluorophenyl)thallium (the first successful application to a Group 3B derivative\*), some fluorocarbon tin compounds, and pentafluorophenyltriphenylgermanium (the first use of an elimination reaction in the formation of a germanium-carbon bond).

Thermal decomposition of pentafluorobenzoatobis(pentafluorophenyl)thallium(III) [8] at ca. 280-300<sup>o</sup> under nitrogen (1 atm.) for 1 hr. gave tris(pentafluorophenyl)thallium, whilst several polyfluorophenyltin compounds (Table 1) were prepared by decomposition of the appropriate polyfluorobenzoates in boiling pyridine for 1-10 hr., and pentafluorophenyltriphenylgermanium was obtained by 'in situ' formation and decomposition (3 hr.) of pentafluorobenzoatotriphenylgermanium(IV) in the same solvent. Details of the reactions are given in Table 1.

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\*Decarboxylation of thallic carboxylates under mass spectrometric conditions has been observed, but is caused by electron impact and has no preparative consequences [7].

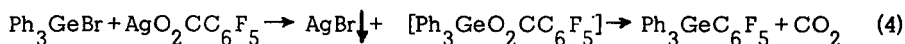
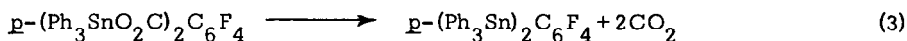
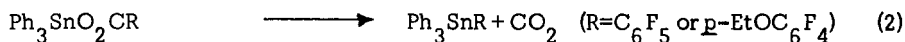
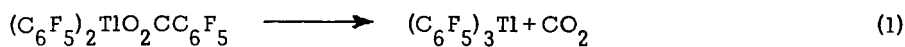
TABLE 1  
Syntheses of Polyfluorophenyl-thallium, -tin, and -germanium  
Compounds by Decarboxylation Reactions

Reactant	Product	Yield (%)	m.p. (°)	lit. m.p.	[Ref.]
$(C_6F_5)_2TiO_2CC_6F_5$	$(C_6F_5)_3Ti$ .diox	40	258 - 263	260 - 265	[ 9]
$Ph_3SnO_2CC_6F_5 \cdot H_2O$ <sup>b</sup>	$Ph_3SnC_6F_5$	65	84 - 85	86	[10]
$Ph_3SnO_2C-p-EtOC_6F_4 \cdot H_2O$ <sup>b</sup>	$Ph_3Sn-p-EtOC_6F_4$	47	63	<u>d</u>	
$p-(Ph_3SnO_2)_2C_6F_4 \cdot H_2O$ <sup>b</sup>	$p-(Ph_3Sn)_2C_6F_4$	81	236	<u>d</u>	
	+ $p-HC_6F_4SnPh_3$	15	90 - 93	<u>d</u>	
$Ph_3GeBr + AgO_2CC_6F_5$	$Ph_3GeC_6F_5$	25	116 - 117	114 - 116	[10]

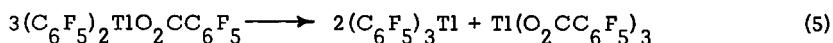
<sup>a</sup> From treatment of the product with 1,4-dioxan. Infrared, NMR, and mass spectra in agreement with those of an authentic sample prepared by the reported method [9].

<sup>b</sup> Prepared from triphenyltin hydroxide and the appropriate acid in methanol, and obtained analytically pure.

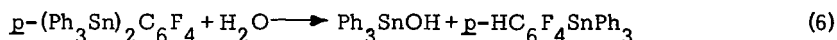
<sup>c</sup> Satisfactory analyses obtained. <sup>d</sup> New compound. <sup>e</sup> Identified by NMR and mass spectrometry.



Detection of a near quantitative yield of carbon dioxide in reaction (1) precluded the possibility that the organothallium compound was formed by rearrangement (5).



Tri(pentafluorophenyl)thallium was conveniently isolated as the air-stable [9] complex  $(\text{C}_6\text{F}_5)_3\text{Tl}$ .diox (diox = 1,4-dioxan) by dissolution of the crude product in dioxan, evaporation to dryness, and washing the complex with petrol to remove perfluoropolyphenyls. In other cases [reactions (2) - (4)], the compounds were isolated by preparative t.l.c. (eluted with acetone/petrol) of the residue obtained on evaporation of the pyridine. Triphenyl-2,3,5,6-tetrafluorophenyltin, obtained in low yield (Table 1) on chromatography of the crude product from (3), may be formed by slight hydrolysis (6) of the major product  $\text{p}-(\text{Ph}_3\text{Sn})_2\text{C}_6\text{F}_4$  on the t.l.c. plates.



These results indicate considerably increased potential for decarboxylation reactions in organometallic synthesis. Extensions to other derivatives of thallium, germanium, and tin are being investigated.

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