

SHORT COMMUNICATION

The preparation of some aryltrialkyl- and tetraaryl-stannanes

We have prepared for kinetic studies¹ a series of ArylSn(Alkyl)_3 and $m\text{-CF}_3\text{C}_6\text{H}_4\text{Sn(Aryl)}_3$ compounds by treating a trialkyl- or triaryl-tin halide with the appropriate Grignard or organolithium reagent. We have also made the compound $p\text{-Me}_3\text{SnC}_6\text{H}_4\text{NMe}_3^+\text{I}^-$.

Experimental

Preparations involving Grignard reagents. In a typical preparation, chlorotrimethylstannane (20 g, 0.10 mole) was added at 0° to the Grignard reagent prepared from *p*-bromochlorobenzene (21.0 g, 0.11 mole) in ether (50 ml). The mixture was refluxed for 2 h, then cooled and treated with saturated aqueous ammonium chloride. The ethereal layer was separated, washed, dried (Na_2SO_4), and fractionated to give (*p*-chlorophenyl)trimethylstannane (58%), b.p. $87^\circ/3.5$ mm, n_D^{25} 1.5489 (lit.² b.p. $82\text{--}5^\circ/\text{ca. } 2$ mm, n_D^{25} 1.5487). Physical properties of new compounds prepared by this method are listed in Table 1.

TABLE I

NEW $\text{XC}_6\text{H}_4\text{MR}_3$, $\text{X}_2\text{C}_6\text{H}_3\text{MR}_3$, OR $\text{X}_3\text{C}_6\text{H}_2\text{MR}_3$ COMPOUNDS MADE FROM GRIGNARD REAGENTS

X_n	$B.p. (^{\circ}C/mm)$	n_D^{25}	Yield (%)	$Found (\%)$		$Required (\%)$	
	or $m.p. (^{\circ}C)$			C	H	C	H
$MR_3 = SnMe_3$							
<i>m</i> -Br	63/0.3	1.5672	37	33.9	4.0	33.8	4.1
<i>o</i> -OMe	70/1.2	1.5369	55	44.7	6.0	44.3	6.0
<i>m</i> -OMe	61/0.4	1.5389	78	44.4	5.9	44.3	6.0
<i>p</i> -SMe	85/0.4	1.5832	73	41.9	5.6	41.9	5.6
<i>o</i> -CF ₃	67/3.6	1.4920	65	39.1	4.2	38.9	4.2
<i>m</i> -CF ₃	53/1.4	1.4790	91	38.8	4.3	38.9	4.2
<i>o</i> -Me	90/7	1.5379	48	46.8	6.6	47.1	6.3
<i>p</i> -tert-Bu	74 ^a		92	52.6	7.5	52.6	7.5
2,3-Me ₂	78/0.8	1.5419	32	49.2	6.8	49.1	6.7
2,4-Me ₂	84/2.5	1.5363	56	49.4	6.8	49.1	6.7
2,4,6-Me ₃	29–30 ^a		47	50.8	7.3	50.9	7.1
3,5-(CF ₃) ₂	81–82/8.5	1.4445	68	35.2	3.5	35.1	3.2
$MR_3 = SnEt_3$							
<i>m</i> -CF ₃	63/0.3	1.4869	71	44.3	5.5	44.5	5.5
$MR_3 = SnPh_3$							
<i>m</i> -CF ₃	110 ^a		70	60.5	3.9	60.6	3.9
$MR_3 = Sn(p\text{-tolyl})_3$							
<i>m</i> -CF ₃	133–134 ^a		76	62.8	4.9	62.6	4.7

^a Recrystallised from ethanol.

Preparations involving organolithium reagents. (*m*-Chlorophenyl)trimethylsilane (20 g, 0.11 mole) was added during 1.5 h, to butyllithium, prepared from *n*-butyl bromide (17.8 g, 0.13 mole) and lithium (1.7 g, 0.25 g-atom) in tetrahydrofuran (20 ml), and cooled in an ice-salt bath. The mixture was stirred for 24 h at room temperature then treated with chlorotrimethylstannane (20 g, 0.10 mole) and refluxed for 8 h. Addition of saturated aqueous ammonium chloride followed by separation, drying (Na_2SO_4), and fractionation of the tetrahydrofuran layer gave [*m*-(trimethylsilyl)-phenyl]trimethylstannane (57%), b.p. $87^\circ/1.5$ mm, n_D^{25} 1.5171. (Found: C, 46.4; H, 7.0. $\text{C}_{12}\text{H}_{22}\text{SiSn}$ calcd.: C, 46.0; H, 7.1%.)

By the same method, but using the appropriate aryl bromide and trialkyltin chloride, with ether as solvent and shorter reflux times, were prepared: 3-(trimethylstannyl)biphenyl (76%), b.p. $107^\circ/0.2$ mm, n_D^{25} 1.5960 (Found: C, 56.8; H, 5.7. $\text{C}_{15}\text{H}_{18}\text{Sn}$ calcd.: C, 56.8; H, 5.7%); phenyltriisopropylstannane (42%), b.p. $82^\circ/0.3$ mm, n_D^{25} 1.5303 (Found: C, 56.6; H, 8.0. $\text{C}_{15}\text{H}_{27}\text{Sn}$ calcd.: C, 55.3; H, 8.4%); and [*p*-(dimethylamino)phenyl]trimethylstannane (37%), b.p. $97^\circ/0.85$ mm, m.p. 38° (from ethanol) (lit.² b.p. $102\text{--}104^\circ/6$ mm, m.p. $40\text{--}41^\circ$).

(3,5-Dibromophenyl)trimethylstannane. An ethereal solution of butyllithium (0.08 mole) was added to a stirred solution of sym-tribromobenzene (25 g, 0.077 mole) in ether (800 ml) at 25° . After one minute, bromotrimethylstannane (19.5 g, 0.082 mole) was added, and the reaction mixture was refluxed for a short period. Working up in the usual way followed by fractional distillation gave hexamethyldistannoxane (2.87 g) b.p. $25^\circ/1.2$ mm, *n*-butyltrimethylstannane (0.95 g) b.p. $51^\circ/1.4$ mm and a small quantity of sym-tribromobenzene b.p. $104^\circ/1.5$ mm, followed by a colourless liquid, b.p. $105\text{--}9^\circ/1.5$ mm, which was carefully refractionated to give (3,5-dibromophenyl)-trimethylstannane (7 g, 32%), b.p. $109^\circ/1.5$ mm, n_D^{25} 1.6000. (Found: C, 27.0; H, 3.1. $\text{C}_9\text{H}_9\text{Br}_2\text{Sn}$ calcd.: C, 27.1; H, 3.0%.)

[*p*-(Trimethylstannyl)phenyl]trimethylammonium iodide. A solution of [*p*-(dimethylamino)phenyl]trimethylstannane (14.2 g, 0.05 mole) and methyl iodide (22.5 g, 0.15 mole) in ethanol (250 ml) was kept in the dark at room temperature for three days. The solvent and remaining methyl iodide were evaporated off, and the residue was twice recrystallised from benzene to give the compound *p*- $\text{Me}_3\text{SnC}_6\text{H}_4\text{-NMe}_3^+\text{I}^-$ (19.6 g, 92%), m.p. $186\text{--}187^\circ$ (dec.). (Found: C, 34.2; H, 5.2; N, 3.23. $\text{C}_{12}\text{H}_{22}\text{N}\text{Sn}$ calcd.: C, 33.8; H, 5.2; N, 3.29%.)

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