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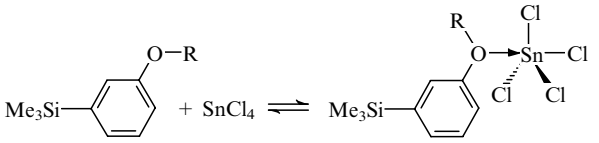
Synthesis of substituted 2- and (4-alkoxyphenyl)trichlorostannanes. A novel method of preparative cleavage of the Si–C bond

Igor M. Lazarev,*[a] Gennadii V. Dolgushin,[a] Valentin P. Feshin[b] and Mikhail G. Voronkov[a]

[a] *Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation. Fax: +7 3952 35 6046; e-mail: root@irioch.irkutsk.su*
[b] *Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences, 614000 Perm, Russian Federation.*

The reaction of *ortho*- and *para*-(alkoxyaryl)trimethylsilanes with tin tetrachloride proceeds under mild conditions with cleavage of the Si–C bond and formation of the corresponding stannanes.

Earlier we have reported[1] that the interaction of *meta*-(alkoxyaryl)trimethylsilanes with $SnCl_4$ leads to the formation of donor–acceptor complexes:



R = Me, Et

The trigonal-bipyramidal structure of these complexes was confirmed by ^{35}Cl NQR spectra.[1] During our investigations of tin tetrachloride complex formation with different ligands we unexpectedly found a new method of cleavage of the Si–C(Ar) bond.

The purpose of this work is to search for a preparative route to organotin compounds from various trimethylsilyl derivatives.

Cleavage of the Si–C bond has been investigated in terms of the reaction mechanism and by the preparative synthesis of different classes of compounds, both organic[2] and organometallic compounds being the target products. Among the latter, compounds of mercury,[3] gallium,[4] palladium,[5] zirconium and hafnium[6] have been obtained.

In studying the complex formation of tin tetrachloride with *ortho*- and *para*-isomers of (alkoxyaryl)trimethylsilanes we could not isolate the above complexes.

Instead, we found a tin tetrachloride-induced cleavage of the Si–C bond in the initial compounds, leading to the corresponding (alkoxyaryl)trichlorostannanes:†

†*General method of synthesis.* To (alkoxyaryl)trimethylsilanes an equimolar amount of tin tetrachloride was added. The mixture was heated to boiling and refluxed for a few hours (Table 1). During this time the boiling temperature of the reaction mixture dropped from 100–135 to 72–93 °C. After cooling the reaction mixture, the products formed were isolated by recrystallization from hexane (*ortho*-isomers) or distillation (*para*-isomers). The reaction conditions and physicochemical data of the compounds are presented in Tables 1 and 2.

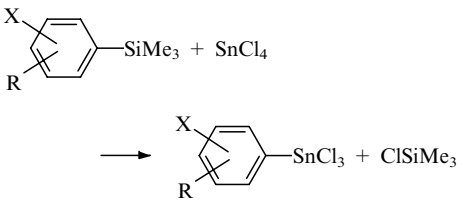
Table 1 Reaction time, yield and physicochemical properties of (alkoxyaryl)trichlorostannanes.

Compound	Reaction time/ h	Yield (%)	Mp/°C (bp/mmHg)	Found (Calc.) (%)			
				C	H	Cl	Sn
1	6.0	78	95–97	25.4 (25.31)	2.1 (2.12)	32.2 (32.02)	35.8 (35.73)
2	5.0	68	94–96	27.7 (27.75)	2.6 (2.62)	30.5 (30.72)	34.4 (34.28)
3	4.0	87	122–124	27.8 (27.75)	2.6 (2.62)	30.8 (30.72)	34.3 (34.28)
4	0.2	91	66 (dif.)	26.6 (26.53)	2.4 (2.50)	29.5 (29.36)	32.7 (32.77)
5	4.5	45	67–69	30.3 (30.01)	3.2 (3.08)	29.5 (29.52)	32.5 (32.95)
6	4.5	40	(120–122/1)	25.7 (25.31)	2.45 (2.12)	32.3 (32.02)	35.1 (35.73)
7	4.0	32	(135–138/1)	27.9 (27.75)	2.5 (2.62)	30.1 (30.72)	34.7 (34.28)

Table 2 Chemical shifts in the ^{1}H, ^{13}C and ^{119}Sn NMR spectra of (alkoxyaryl)stannanes.[a]

Compound	^{1}H δ(ppm)	^{13}C δ(ppm)				^{119}Sn
	OCH_3	OCH_3	$COCH_3$	$CSnCl_3$	Other atoms	δ(ppm)
1	3.93	56.67	160.90	125.36	111.54, 123.30, 134.51, 135.11	−75.14
2	4.19[b]	65.44[b]	160.25	125.90	14.30, 111.87, 123.14, 134.57, 135.00	−75.32
3	3.90	56.77	158.89	125.09	111.38, 133.11, 134.52, 135.65	−75.10
4	3.91	56.29	162.79	111.65	104.88, 136.52	−91.22
5	3.93	62.08	158.03	130.29	17.04, 20.64, 129.83, 131.59, 136.17, 138.33	−81.90
6	3.79	55.36	163.34	126.39	115.99, 135.43	

[a] The spectra were run at room temperature for 10% solutions of compounds in deuteriochloroform on a JEOL FX 90Q spectrometer. The chemical shifts values are presented relative to tetramethylsilane (^{1}H, ^{13}C) and tetramethylstannane (^{119}Sn). [b] OCH_2 group signals. Methyl group protons signal = 1.48 ppm.



1 X = 2-OMe, R = H
2 X = 2-OEt, R = H
3 X = 2-OMe, R = 5-Me
4 X,R = 2,6-$(OMe)_2$
5 X = 2-OMe, R = 3,5-Me_2
6 X = 4-OMe, R = H
7 X = 4-OEt, R = H

The reaction previously discovered by us for *ortho*-(alkoxyaryl)trimethylsilanes is also suitable for *para*-isomers.[7]

This reaction proceeds by boiling a mixture of the initial compounds. The reaction products are slightly-coloured crystals (*ortho*-isomers) and liquid compounds (*para*-isomers) with a faint specific smell.

The simplicity of the procedure and the high yield of products permit this reaction to be used as a preparative method for the obtention of previously inaccessible *ortho*- and *para*-isomers of (alkoxyaryl)trichlorostannanes. The composition and structure of the synthesized compounds **1**–**7** were confirmed by elemental analysis and ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy.

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