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Reaction of 1-Iodoalkynes with Tin Metal: A New Approach to the Sn–C_{sp} Bond Formation

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Abstract—Tin iodoalkynylides were synthesized by the reaction of 1-iodoalkynes with tin metal. The scope of the reaction and the composition of the resulting mixtures were studied. The formation of tin iodoalkynylides was confirmed by counter synthesis via the reaction of disproportionation of tetra(phenylethynyl)tin with tin tetraiodide. The compounds synthesized were characterized by means of ^{119}Sn NMR spectroscopy.

Keywords: tin iodoalkynylides, tin tetraalkynylides, iodoalkynes

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Alkynyl tin are widely used in organic synthesis as reactants for the synthesis of alkenes [1] and conjugated unsaturated compounds [2], as well as for construction of carbo- and heterocycles [3, 4], including biologically active substances [5]. The Stille reaction involving tin alkynylides is a reliable tool for construction of compounds with molecules of high complexity [6] and self-assembling acetylene moieties [7]. Alkynyl tin containing four acetylene moieties are suitable as atom-economic reactants in the synthesis of aryl acetylenes [8] and acetylenic ketones [9–11]. Widespread use of alkynyl tin prompts the search for new synthetic routes to these compounds, as discussed in a number of recent publications [12–14].

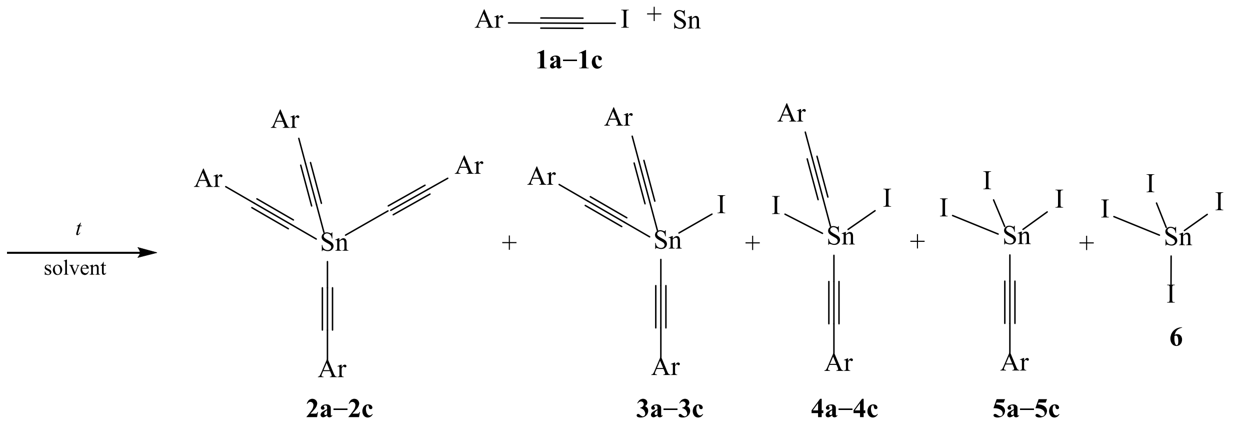
Direct synthesis of organotin compounds was the subject of numerous studies [15–19], but there is no information yet on the possibility of the Sn–C_{sp} bond formation by this method.

We presumed that 1-iodoalkynes may be reactive toward tin metal. Indeed, heating (iodoethynyl)benzene **1a** in aromatic solvents at 130–140°C with tin metal chips (0.2–0.5 mm fraction) led to dissolution of the latter and development of a color of the reaction mixture. According to the ^{119}Sn NMR spectroscopic data, the reaction gave a mixture of tetra(phenylethynyl)tin **2a**, tin iodoalkynylides with different degrees of substitution **3a–5a,** and tin tetraiodide **6** (Scheme 1). The composition of the product mixture was dependent on the solvent used, which is attributable to the difference in the solubility of SnI_4, affecting the equilibrium between the tin iodoalkynylides being formed.

At the same time, the reaction proceeded very slowly and required ca. 150 h for completion. Its acceleration was achieved through the use of tin alloy containing 1.5% zinc, which allowed decreasing the reaction time to 8 h. More active proceeding of the reaction was observed when commercially available finely divided tin powder (particle size 10 μm) was used, whereby the reaction temperature was reduced to 100°C. We studied the effect of the solvent on the reaction time and on the composition of the resulting product mixtures (Table 1). The progress of the reaction was monitored by GC/MS via following the consumption of (iodoethynyl)benzene **1a** with the use of hexadecane as an internal standard. The reaction proceeded most rapidly in polar solvents such as 1,4-dioxane and 1,2-dimethoxyethane, with increases in the concentrations of the reactants from 25 to 40% accelerating the reaction only insignificantly. In all the cases an induction period was observed, after which the main interaction proceeded for ~1 h. The products mixture changed most significantly by using toluene due to low solubility of SnI_4 in it. This caused a shift in the equilibrium between compounds **2a**–**5a**, resulting in the lack of the SnI_4 signal in the ^{119}Sn NMR spectrum.

The reaction of 1-iodoalkynes containing substituents in the benzene ring proceeded in a similar manner. For example, 1-(iodoethynyl)-4-chlorobenzene **1b** fully reacted with tin metal in 1,4-dioxane at 100°C within 4 h

Scheme 1.



Ar = Ph (**a**), 4-Cl-C_6H_4 (**b**), 4-Me-C_6H_4 (**c**).

to give the reaction products in the **2b** : **3b** : **4b** : **5b** : **6** = 5 : 35 : 33 : 23 : 4 ratio. 1-(Iodoethynyl)-4-methylbenzene **1c** turned out to be more reactive; its complete consumption within 2 h led to formation of the reaction products in the **2c** : **3c** : **4c** : **5c** : **6**=3 : 22 : 38 : 33 : 4 ratio. Table 2 presents the ^{119}Sn NMR chemical shifts, recorded for compounds **2–5, 6** in various solvents.

The counter synthesis of tin iodoalkynylides by the reaction of disproportionation of tetra(phenylethynyl)tin **2a** with tin tetraiodide **6** in 1,4-dioxane (Scheme 2) gave a mixture dominated by certain products depending on the ratio of the reactants (Fig. 1).

The reaction proceeded similarly to the reaction of disproportionation of tin tetraalkynylides with tin tetrachloride [20]. It should be noted that the total shielding constant of the substituents in $(ArC{\equiv}C)_nSnI_{4-n}$ exponentially varies with n. The linear relationship ln (δ)–n thus observed allows predicting the ^{119}Sn NMR chemical shifts for this type of organotin compounds. A similar relationship was reported for $(RC{\equiv}C)_nSnI_{4-n}$ at n = 1–4 in [20].

Thus, we have demonstrated the possibility of preparing tin iodoalkynylides by both direct synthesis and disproportionation reaction.

EXPERIMENTAL

We used tin powder with particle size of 10 μm, available from Aldrich, and tetra(phenylethynyl)tin obtained by the technique from [14]. (Iodoethynyl)-benzene **1a**, 1-(iodoethynyl)-4-chlorobenzene **1b**, and 1-(iodoethynyl)-4-methylbenzene **1c** were synthesized by the procedure similar to that described in [21].

Scheme 2.

$$(Ph{-}C{\equiv}C)_4Sn + SnI_4 \rightleftarrows (Ph{-}C{\equiv}C)_nSnI_{4-n}$$

n = 1–3.

Table 1. Influence of various conditions on the time of the reaction of compound **1a** with tin metal and on the composition of the resulting mixture

Run no.	Solvent	t, °C	Reaction time, h[a]	Content,%				
				2a	**3a**	**4a**	**5a**	**6**
1	1,4-Dioxane	100	3	3	34	35	23	6
2	1,4-Dioxane[b]	100	2.5	3	32	35	23	7
3	Toluene	100	>20	–	–	–	–	–
4	Toluene	120	6	21	39	28	12	0
5	1,2-Dichloroethane	100	5	6	23	33	30	8
6	1,2-Dimethoxyethane	100	3	4	29	33	28	6
7	1,2-Dimethoxyethane[b]	100	2	5	28	31	29	7

[a] Reaction time indicates the time until compound **1a** was completely consumed.

[b] The concentrations of the reactants were increased from 25 to 40%.

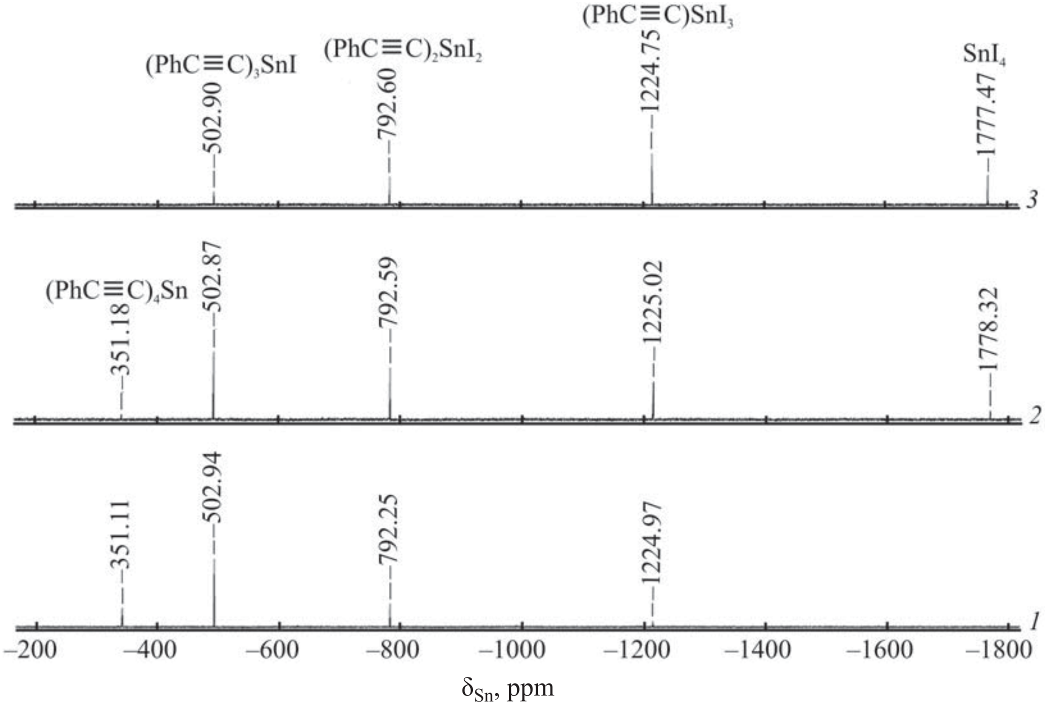


Fig. 1. ^{119}Sn NMR spectra of the reaction mixture of tetra(phenylethynyl)tin with tin tetraiodide in 1,4-dioxane at (*1*) 3 : 1, (*2*) 1 : 1, and (*3*) 1 : 3 ratio of the reactants.

^{119}Sn NMR spectra were recorded on a JEOL ECA400 spectrometer. The reaction progress was monitored by gas chromatography-mass spectrometry using a Shimadzu GC-2010 instrument with a Shimadzu QP-2010 mass-selective detector : Supelco 28064U column, 30 m, temperature-programmed heating from 60 to 260°C at a rate of 30°C/min.

1-(Iodoethynyl)-4-chlorobenzene (1b). A mixture of 310 mg (2.3 mmol) of 4-chlorophenylacetylene, 7 mL of anhydrous acetone, 570 mg (2.53 mmol) of *N*-iodosuccinimide, and 34 mg (0.2 mmol) of silver nitrate was stirred at room temperature for 2 h. Thereupon, 20 mL of hexane and 15 mL of water were added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with diethyl ether–hexane (1 : 1) mixture (2×10 mL). The combined organic layers were dried over magnesium sulfate and then evaporated. The residue was chromatographed (eluent—hexane–ethyl acetate, 90 : 10, with 1% triethylamine addition). Yield 555 mg (92%), light yellow crystals. Mass spectrum (EI, 70 eV), m/z (I_{rel}, %) : 264 (17) $[M]^+$, 262 (100), 135 (23), 100 (16), 99 (84), 98 (12), 74 (77), 50 (18).

The spectral data correspond to those published in [22].

1-(Iodoethynyl)-4-methylbenzene (1c) was obtained in a similar manner from 0.32 mL (2.5 mmol) of 4-methylphenylacetylene, 7 mL of anhydrous acetone,

Table 2. Chemical shifts in the ^{119}Sn NMR spectra of $(\mathrm{ArC{\equiv}C})_n\mathrm{SnI}_{4-n}$ in various solvents

Run no.	Reactant	Solvent	δ_{Sn}, ppm				
			$n = 4$	$n = 3$	$n = 2$	$n = 1$	$n = 0$
1	**1a**	1,4-Dioxane	–351.2	–502.9	–792.6	–1225.0	–1777.5
2	**1a**	1,2-Dimethoxyethane	–337.6	–489.3	–767.5	–1204.3	–1789.8
3	**1a**	1,2-Dichloroethane	–335.3	–473.2	–739.9	–1169.4	–1744.6
4	**1a**	Toluene	–332.0	–472.9	–743.5	–1177.5	–
5	**1b**	1,4-Dioxane	–355.3	–508.8	–797.7	–1225.3	–1777.5
6	**1c**	1,4-Dioxane	–352.4	–503.9	–793.1	–1225.2	–1777.3

620 mg (2.75 mmol) of *N*-iodosuccinimide, and 34 mg (0.2 mmol) of silver nitrate. Yield 546 mg (90%), yellow liquid. Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %) : 242 (83) $[M]^+$, 115 (100), 114 (17), 89 (23), 74 (10), 65 (11), 63 (21), 62 (12).

The spectral data correspond to those published in [22].

Reaction of (iodoethynyl)benzene 1a with tin. A mixture of 55 mg (0.463 mmol) of tin metal, 191.5 mg (0.84 mmol) of (iodoethynyl)benzene, 600 μL of dehydrated solvent (300 μL at increased concentrations of the reactants), and 5 μL of hexadecane as an internal standard were heated under stirring, with samples taken after 20, 40, 60, 90, and 120 min and further every hour until (iodoethynyl)benzene was completely consumed.

The reactions of 1-(iodoethynyl)-4-chlorobenzene **1b** and 1-(iodoethynyl)-4-methylbenzene **1c** with tin were carried out in a similar manner.

Disproportionation of tetra(phenylethynyl)tin 2a with tin tetraiodide 6. To a mixture of tetra(phenylethynyl)tin **2a** with tin tetraiodide **6,** taken in molar ratios of 3 : 1, 1 : 1, and 1 : 3, 1 mL of 1,4-dioxane was added. The resulting mixture was heated at 100°C with stirring for 3 h. The composition of the reaction mixture was analyzed by ^{119}Sn NMR spectroscopy.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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