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> LETTERS TO THE EDITOR

## Reaction of Tetra(phenylethynyl)tin with Aromatic Aldehydes: A New One-Pot Method for The Synthesis of α-Acetylene Ketones

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**Abstract**—The reaction of tetra(phenylethynyl)tin with aromatic aldehydes in the presence of  $ZnCl_2$  afforded  $\alpha$ -acetylene ketones in a yield of 77–98%.

Keywords: α-acetylene ketones, tin acetylenides, Lewis acid

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 $\alpha$ -Acetylene ketones are sufficiently reactive compounds widely used as substrates in the construction of various carbo- and heterocyclic compounds, like polyfunctional pyrroles [1], chromones [2, 3], indenones [4], quinolones [5], benzodiazepines [6], spirocycles [7], etc.

One of the general methods of the preparation of  $\alpha$ -acetylene ketones involves the reaction of metal acetylides with aldehydes, followed by oxidation of propargyl alcohols [2, 5, 8–11].

Trialkylstannylacetylenes are inert with respect to many functional groups, therefore they are actively used as alkynylating reagents in the construction of complex organic structures, including cross-coupling reactions [12, 13]. We have previously developed effective methods for the preparation of tin tetraacetylides from 1-alkynes and tin tetrachloride [14, 15] or tin tetra(N,N-dialkylcarbamates) [16]. It was expectable that the resulting tetraalkynylstannanes (RC=C)<sub>4</sub>Sn will have several advantages over trialkylstannylacetylenes Alk<sub>3</sub>Sn-C=C-R, due to atom-efficiency and lesser toxicity. To date, the properties of tin tetraacetylides have been studied insufficiently and their application in organic synthesis is limited to several reactions with organometallic [17] or organoboron compounds [18].

Recently we showed the possibility of using tetraalkynylstannanes ( $RC\equiv C$ )<sub>4</sub>Sn in the Stille crosscoupling reaction with aryl halides [19]. It should be noted that all four alkynyl moieties are involved into this process, i. e., the reaction has a high *E*-factor, and produced relatively low toxic inorganic tin(IV) halides as a by-product.

In continuation of our research, here we studied the reactivity of tin tetraalkynides with respect to aromatic aldehydes. Thus, it was found that the reaction of tetra-(phenylethynyl)tin 1 with aromatic aldehydes 2a-2c occurred only in the presence of ZnCl<sub>2</sub> at 60°C. Contrary to the expectations,  $\alpha$ -acetylene ketones 4a-4c were obtained as the main products instead of propargyl alcohols 3.

The reaction mechanism presumably includes the Oppenauer oxidation stage similar to the oxidative addition of alkynes to aldehydes in the presence of indium bromide [20]. The tin alkoxides formed in the first stage are rapidly oxidized by Oppenauer reaction with the second aldehyde molecule to form ketone **4** and the corresponding alcohol.

## Scheme 1.



Toluene was the best solvent for the process, while in ether solvents only trace amounts of the reaction product **4a** were detected (see the table). Target  $\alpha$ -acetylene ketones **4a–4c** were readily isolated by column chromatography eluting with toluene. The structure of the obtained compounds was confirmed by <sup>1</sup>H, <sup>13</sup>C NMR, IR spectroscopy, and chromatographymass spectrometry. The structure of the previously unknown 1- (2,3-dihydro-1,4-benzodioxin-6-yl)-3-phenylprop-2-yn-1-one **4c** was additionally confirmed by X-ray diffraction (XRD) analysis (see the figure and Scheme 1).

In summary, tetra(phenylethynyl)tin reacted with aromatic aldehydes in the presence of zinc chloride to form acetylene ketones. The suggested reaction mechanism involves the Oppenauer oxidation of intermediates. The advantage of the new method is a high atom-economy, availability of reagents, one-stage process, and no toxic waste.

Tetra(phenylethynyl)tin was prepared according to the procedure [14]. Aromatic aldehydes were purchased from Aldrich.

1,3-Diphenylprop-2-yn-1-one (4a). A mixture of anhydrous ZnCl<sub>2</sub> (10.4 mg, 0.076 mmol), toluene (0.8 mL), tetra(phenylethynyl)tin (100 mg, 0.191 mmol), and freshly distilled benzaldehyde (155 µL, 1.53 mmol) was stirred at 60°C for 5 h. The reaction mixture was treated with 1 M HCl solution. The reaction product was extracted with chloroform and purified by column chromatography (eluent toluene). Yield 154 mg (97%), pale yellow liquid. IR spectrum, v, cm<sup>-1</sup>: 3099, 3082, 3059, 3034, 2199 (C=C), 1642 (C=O), 1597, 1582. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 7.39–7.53 m (5H, ArH), 7.60–7.69 m (3H, ArH), 8.22 d (2H, ArH, J = 7.3 Hz). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 86.8, 93.1, 120.1, 128.6, 128.7, 129.5, 130.8, 133.0, 134.1, 136.8, 177.9. Mass spectrum (EI, 70 eV), m/z ( $I_{rel}$ , %):  $206(52)[M]^+$ , 178(88), 152(11), 129(100), 101(14), 89 (11), 77 (26), 76 (21), 75 (33), 51 (35).

**3-Phenyl-1-(4-fluorophenyl)prop-2-yn-1-one (4b)** was prepared similarly from tetra(phenylethynyl)tin (100 mg, 0.191 mmol) and 4-fluorobenzaldehyde (164  $\mu$ L, 1.53 mmol). The reaction product was isolated by column chromatography, eluent toluene. Yield 168 mg (98%), yellow liquid. IR spectrum, v, cm<sup>-1</sup>:

Run no.	Aldehyde	1:2	Solvent	Time, h	Yield, % <sup>a</sup>
1	2a	1:4	1,4-Dioxane	24	4
2	2a	1:4	Toluene	5	50
3 <sup>b</sup>	2a	1:4	Toluene	5	0
4	2a	1:8	Toluene	5	97
5	26	1:8	Toluene	1	98
6	2в	1:8	Toluene	5	77

Effect of the reaction conditions on the yield of compound 4

<sup>a</sup> Yield was calculated relative to tetra(phenylethynyl)tin. <sup>b</sup> In the absence of ZnCl<sub>2</sub>.



Crystal structure of 1-(2,3-dihydro-1,4-benzodioxin-6-yl)-3-phenylprop-2-yn-1-one 4c.

3074, 3065 (C–H), 2199 (C=C), 1643 (C=O), 1608, 1595. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 7.02–7.15 m (2H), 7.29–7.42 m (3H), 7.53–7.61 m (2H), 8.11–8.20 m (2H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 86.7, 93.5, 116.0 d (*J* = 21.9 Hz), 120.0, 128.7, 131.0, 132.3 d (*J* = 9.7 Hz), 133.1, 133.5 d (*J* = 3.2 Hz), 166.4 d (*J* = 256.9 Hz), 176.4.

1-(2,3-Dihydro-1,4-benzodioxin-6-yl)-3-phenyl-nprop-2-yn-1-one (4c) was prepared similarly from tetra(phenylethynyl)tin (64.4 mg, 0.123 mmol) and 2.3dihydro-1,4-benzodioxin-6-carbaldehyde (161.9 mg, 0.986 mmol). The reaction product was isolated by column chromatography, eluent toluene. Yield 100 mg (77%), pale yellow crystals, mp 98.5-99.7°C (hexanechloroform). IR spectrum (KBr), v, cm<sup>-1</sup>: 3065 ( $C_{sp}^{2}$ -H), 2986, 2938, 2922, 2891, 2876 (C<sub>sp</sub>3-H), 2203 (C≡C), 1626 (C=O), 1601, 1584. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 4.28–4.30 m (2H, OCH<sub>2</sub>), 4.32–4.34 m (2H, OCH<sub>2</sub>), 6.95 d (1H, ArH, J = 8.2 Hz), 7.38– 7.48 m (3H, ArH), 7.64-7.66 m (2H, ArH), 7.74-7.77 m (2H, ArH). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 64.2, 64.9, 87.0, 92.4, 111.5, 119.0, 120.4, 124.0, 128.7, 130.7, 131.1, 133.1, 143.5, 149.2, 176.6. Mass spectrum (EI, 70 eV), m/z ( $I_{rel}$ , %): 264 (100)  $[M]^+$ , 236 (53), 180 (49), 152 (50), 129 (65), 126 (15), 101 (11), 75 (18), 51 (23).

Crystals of compound 4c were obtained by recrystallization from hexane-chloroform mixture (8:2). Monoclinic crystals, C<sub>17</sub>H<sub>12</sub>O<sub>3</sub>, M 264.27, space group  $P2_1/c$  (no. 14); the unit cell parameters at 100 K are as follows: a 12.6774(2), b 11.4801(2), c 18.9403(3) Å, β 108.896(2)°, V 2607.97(8) Å<sup>3</sup>, Z 8,  $d_{calc}$  1.346 g/cm<sup>3</sup>,  $\mu(CuK_{\alpha})$  0.751 mm<sup>-1</sup>. The unit cell parameters and intensity of 49562 reflections  $(7.37^{\circ} \le 2\theta \le 148.63^{\circ})$ (5431 independent reflections,  $R_{int}$  0.0658) were measured on an Agilent Super Nova Dual (Cu at zero) Atlas S2 diffractometer. The final divergence factors areas follows:  $R_1$  0.0746 for 5431 independent reflections with  $I > 2\sigma(I)$  and  $wR_2$  0.2357 for all reflections. Structure was solved and refined by the least squares method using Olex2 program package [21] and ShelXT and ShelXL software [22]. Crystallographic data including atomic coordinate tables, temperature factors, tables of bond lengths and bond angles were deposited at the Cambridge Structural Data Centre (CCDC 1535382). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL ECA400 instrument in a CDCl<sub>3</sub> solution using tetramethylsilane as reference. IR spectra were registered on an Infralum FT-02 (Lumex) spectrometer. The reaction progress was monitored by chromatography-mass spectrometry using a Shimadzu GC-2010 instrument equipped with a Shimadzu QP-2010 mass-selective detector (Supelko

28064U column, 30 m, heating from 60 to 260°C at a rate of 30 deg/min). Melting points were measured in open capillaries on a Stuart SMP30 instrument.

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