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Stereospecific synthesis of functional alkenylsilanes via silastannation of but-3-ynoic acid

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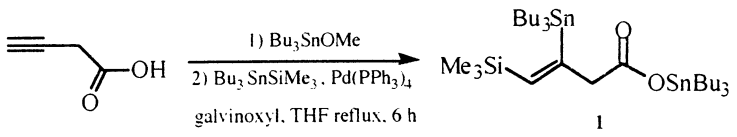
Abstract

Tributylstannyl-(*Z*)-3-tributylstannyl-4-trimethylsilylbut-3-enoate is prepared by the stereospecific addition of (tributylstannyl)-trimethylsilane on the but-3-ynoic acid. Some of the potentialities of this synthon are established through cross-coupling and reverse cross-coupling reactions.

Keywords: alkenylsilane; coupling reactions; palladium catalyst; carboxylic acids.

Alkenylsilanes have been shown to be versatile intermediates in organic synthesis.[1] Various methods are available for their preparation.[2] Among them, the catalytic cross-coupling reaction of organic halides using disilanes as a silicon source has proven to be a versatile method for synthesizing regio- and stereodefined organosilanes.[3,4] Furthermore, the reactions of silylstannanes or organodisilanes with alkynes have been mostly achieved by the catalysis of palladium phosphine complexes[5,6] and recently Sweeney[7] reported the reaction of (tributylstannyl)–trimethylsilane with a propynoate derivative, which unfortunately gave a 1:1 mixture of unseparable acrylate derivatives (the addition of the tributylstannyl group on the triple bond occurred at both sites). We report herein the stereospecific addition of (tributylstannyl)–trimethylsilane on the tributylstannyl ester of but-3-ynoic acid.



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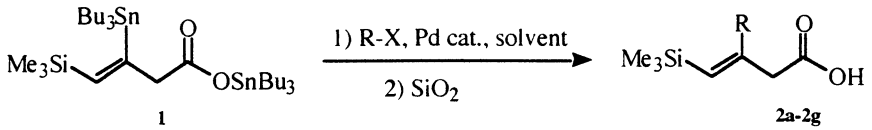
Optimization of the experimental conditions and protection of the acidic function with a tributylstannyl group (with no protection, no reaction was obtained),[8] yielded tributylstannyl-(*Z*)-3-tributylstannyl-4-trimethylsilylbut-3-enoate **1** as the sole product (80% yield after purification).

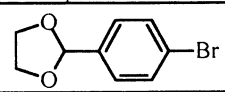
The reactivity of this new compound **1** was then studied using Stille coupling reactions with various organic halides under catalysis with palladium(II) complexes.[9]



1 **2a-2g**

The results are reported in Table 1. The substitution reaction appears to have a general character only if the alkenyl and aryl halides have an electron-withdrawing group in its structure. The temporary protection of the carboxylic acid function is removed at room temperature by stirring with silica gel.[10]

Table 1

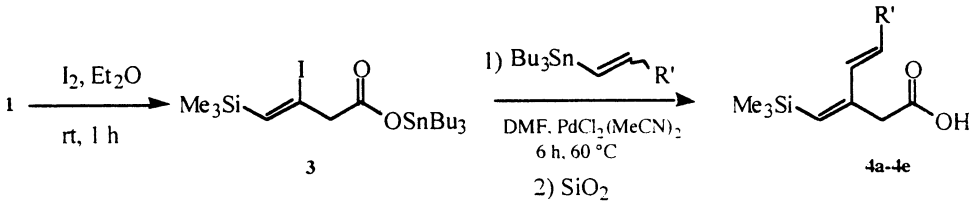
Entry	R-X	Experimental conditions	N°	Yield[a] (%)
1	Ph-I	A	**2a**	0
2	*o*-NO_2-Ph-I	A	**2b**	68
3	*p*-OHC-Ph-Br	A	**2c**	50
4	*m*-CF_3-Ph-Br	A	**2d**	57
5	*p*-F-Ph-Br	A	**2e**	59
6		B	**2f**	65
7		C	**2g**	63

A = toluene, $Pd(PPh_3)_4$, 100 °C, 12 h; B = dioxane, $PdCl_2(MeCN)_2$, 70 °C, 8 h;
C = DMF, $PdCl_2(MeCN)_2$, 50 °C, 8 h; [a] yield after purification

In order to extend the potential of compound **1**, reverse cross-coupling reactions were investigated.[11] Iododestannylation of **1** afforded the tributylstannyl-(*Z*)-3-iodo-4-trimethylsilyl-but-3-enoate **3** with a nearly quantitative yield without isomerization of the double bond and iodine treatment did not affect the tributylstannylcarboxylate function. Using a similar procedure, **3** was cross-coupled with vinyltin reagents affording dienylsilanes **4** in fair yields (Table 2).[12]

In summary, we investigated a general route to stereospecific alkenyl- or dienylsilanes via silastannation of but-3-ynoic acid; the silastannation of other acetylenic acids is currently being studied in our laboratory.

Table 2
Stille reaction of **3** with organotin reagents



Entry	R′	Dienylsilane	Yield[a] (%)
1	H	**4a**	71
2	Me_3Si	**4b**	56
3	CH_2–$CH(OEt)_2$	**4c**	65[b]
4	$SnBu_3$	**4d**	60
5	n-C_5H_{11}	**4e**	64[b]

[a] Yield after purification.
[b] Only the *E* isomer of the vinyltin reacted.

Acknowledgements

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10. *Typical procedure*: Preparation of compound **2d**. 129 mg (0.5 mmol) of dichloro-bis(acetonitrile)palladium(II) were added to a DMF solution (15 mL) of **1** (7.36 g, 10 mmol) and 1-bromo-3-trifluoromethylbenzene (2.48 g, 11 mmol), in a 50 mL flask. The mixture was stirred for 6 h at 60°C, then hydrolyzed with 25 mL of a 1 M solution of potassium fluoride in 25 mL of acetone to precipitate the tributyltin bromide formed. After strong stirring for 2 h, the reaction mixture was filtered, washed with a 0.1N HCl solution and extracted with diethyl ether. After the usual work-up, the crude (*Z*)-4-trimethylsilyl-3-(*m*-trifluoromethylphenyl)but-3-enoic acid **2d** was purified by crystallization (petroleum ether/diethyl ether: 95/5). Mp: 134°C. IR (KBr): 2965, 2900, 1676, 1603, 1438, 1333, 1214, 845. ^{1}H NMR δ ppm (200 MHz, $CDCl_3$): −0.17 (9H, s), 3.46 (2H, s) 5.89 (1H, s), 7.40–7.54 (4H, m), 11.2 (1H, bs). ^{13}C NMR δ ppm (50 MHz, $CDCl_3$): 0.2, 48, 125 (1C, q, $^{3}J_{C-F}=4$ Hz), 126 (1C, q, $^{3}J_{C-F}=4$ Hz), 129, 131, 132 (1C, q, $^{2}J_{C-F}=32$ Hz), 133 (1C, q, $^{1}J_{C-F}=272$ Hz), 136.1, 143.7, 149, 178. MS (70 eV): $m/z=302$ (M^+, 62), 166 (100).
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12. (*Z*)-3-(Trimethylsilylmethylene)-5-trimethylsilylpent-4-enoic acid **4b**: IR: 2980, 2940, 2880, 2860, 1720, 1650, 1560, 1260, 850, 800. ^{1}H NMR δ ppm (200 MHz, $CDCl_3$): 0.07 (9H, s), 0.14 (9H, s), 3.29 (2H, s), 5.72 (1H, s), 5.96 (1H, d, $J=19$ Hz), 6.80 (1H, d, $J=19$ Hz), 9.50 (1H, bs). ^{13}C NMR δ ppm (50 MHz, $CDCl_3$): −1.64 (3C), 0.22 (3C), 42, 131, 136.2, 136.7, 143.7, 178.2. MS (70 eV): $m/z=256$ (M^+, 4), 75 (17), 73 (100), 45 (12).