DOI: 10.1002/adsc.200900828

α- and β-Stannyl Trifluoromethylbutenoates: Regioselective Preparation and Use in Copper(I)-Catalyzed Allylation and Propargylation Reactions

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Received: November 28, 2009; Published online: April 7, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900828.

Abstract: The palladium-free hydrostannylation of ethyl 4,4,4-trifluorobutynoate **1** with tributyltin hydride at room temperature is highly regio- and stereoselective, providing good yields of β-trifluoromethyl (*Z*)-α- or (*Z*)-β-stannylacrylates **2**. Vinylstannanes **2** undergo a copper(I)-catalyzed coupling reactions with allylic or propargylic bromides leading selectively to good yields of the corresponding allylated or propargylated products without allylic or allenic transposition.

Keywords: allylation; copper(I)-catalyzed cross coupling; ethyl trifluorobutynoate; propargylation; regioselective hydrostannylation

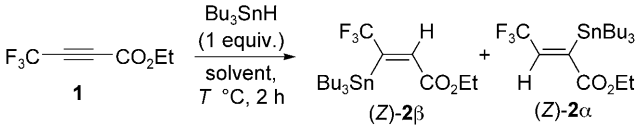
Organic compounds containing one or more fluorine atoms have received increasing attention in medicinal, agricultural and material sciences.[1] They often confer significant changes in their chemical and physical properties. The introduction of a fluorine or perfluoroalkyl group into organic compounds often dramatically changes their structure, stability, reactivity and biological activity.[2] The development of a simple method to obtain perfluoroalkylated building blocks for their subsequent utilization in the synthesis of R_f-containing compounds is therefore essential to organofluorine chemistry.[3,4]

Perfluoroalkylated vinylmetals constitute an important class of these building blocks. Perfluoroalkylated vinylmetals have been demonstrated in which lithium,[5] magnesium,[6] zinc,[7] silver[8] and palladium[9] species were prepared and alkylated with electrophiles specific to the carbon attached to the metal. Vinylstannanes bearing a perfluoroalkyl group also opened the way for the preparation of these types of compounds.[10] In this context, the preparation of new vinyltin reagents bearing perfluorylalkyl group and another functionalities is highly desirable.

However, to the best of our knowledge, no free palladium-catalyzed hydrostannylation of **1** has yet been described. We recently reported the preparation of (*Z*)-ethyl 3-perfluoroalkyl-3-magnesiated crotonates from (*Z*)-ethyl 3-perfluoroalkyl-3-iodoenoates by an iodine-magnesium exchange reaction with isopropylmagnesium bromide.[11] These new reagents reacted with a wide range of electrophiles, leading to polyfunctional products bearing a fluoroalkyl group.[12] As a continuation of our previous research on methods for preparing various derivatives bearing the trifluoromethyl group, we report here the first highly regioselective free-metal hydrostannylation of ethyl 4,4,4-trifluorobutynoate **1**[13] without any additive, followed by copper(I)-catalyzed allylation and propargylation.

We investigated the hydrostannation of **1** to prepare α or β-stannylvinyl esters **2**. We initially focused on the selection of an efficient solvent and a suitable temperature for a highly regio- and stereoselective hydrostannylation reaction of alkynoate **1** with *n*-Bu_3SnH (Scheme 1 and Table 1). A number of solvents were tested and the results are summarized in Table 1.

As shown in Table 1, the hydrostannation of **1** was very dependent on the choice of solvent. Thus, using ether, dichloromethane or toluene as solvents, a mixture of α- and β-regioisomers was obtained (entries 3,



Scheme 1. Hydrostannation of ethyl 4,4,4-trifluorobutynoate **1**.

Table 1. Hydrostannation of ethyl 4,4,4-trifluorobutynoate **1** in various solvents and temperatures.

Entry	Solvent	*T* [°C]	α/β	(*Z*)-β/ (*E*)-β	(*Z*)-α/ (*E*)-α	Yield [%][a]
1	hexane	−40	>5/95	75/25	–	97
2	hexane	20	>5/95	75/25	–	98
3	Et_2O	20	30/70	100/0	100/0	98
4	DCM	20	80/20	100/0	100/0	97
5	CH_3CN	20	95/5	–	85/15	99
6	MeOH	−40	100/0	–	85/15	96
7	MeOH	20	95/5	–	85/15	97
8	toluene	20	40/60	100/0	100/0	96

[a] Combined yield of α- and β-regioisomers related to Bu_3SnH.

4 and 8, Table 1). Very interestingly, the hydrostannation of **1** in hexane provided the β-stannylated product with high regioselectivity (>95%) and excellent yield (>97%) (entries 1 and 2, Table 1).

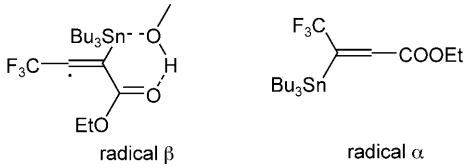
The observed stereoselectivity was in favour of the (*Z*)-isomer (*Z*-**2**β/*E*-**2**β=75/25). Surprisingly, total α-regioselectivity of the hydrostannylation of **1** at −40 °C was observed in MeOH, providing α-tributylstannylacrylate **2**α as the sole regioisomer in a nearly quantitative yield (entry 6, Table 1). In this case, the stereoselectivity was also largely in favour of the (*Z*)-isomer (*Z*-**2**α/*E*-**2**α=85/15). Temperature had no significant effect on the regioselectivity. Similarly, the reaction of **1** with *n*-Bu_3SnH in acetonitrile selectively afforded the corresponding (*Z*)-**2**α product, together with a small amount of β-isomer (<5%) (entry 5, Table 1). It should be noted that in all cases, hydrostannylation of **1** by Bu_3SnH was performed without using a radical initiator or a transition metal catalyst.

These results suggest that the ratio of α:β adducts depends very strongly of the nature of the solvent. The regioselectivity of vinylstannanes **2** was deduced without ambiguity from NMR data, especially from the chemical shifts and $J_{H,F}$ coupling patterns. The *Z* stereochemistry of **2**α and **2**β was assigned taking into account that the $^3J_{Sn,H}$ coupling constant observed in the ^1H NMR spectra was over 70 Hz, which indicates the existence of *trans* H–C–C–Sn linkages in these compounds.[14] Moreover, an iododestannylation reaction of **2**β provided the corresponding vinyl iodide with the *Z* configuration in which the ^1H NMR values of this vinyl iodide are in full agreement with the spectral values reported in the literature.[15]

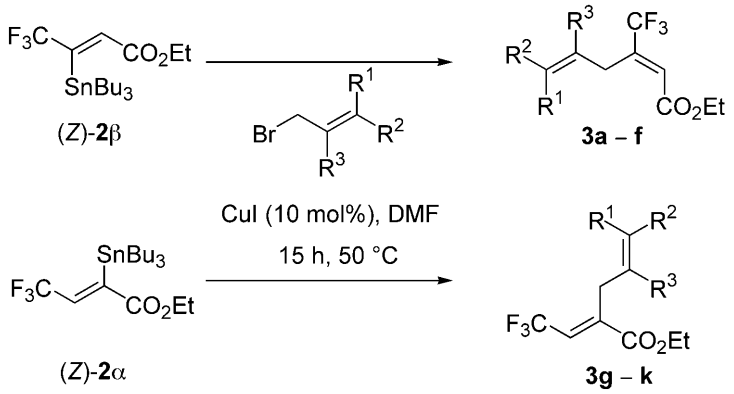
The mechanism and the solvent effects observed are not very clear at this time. Nevertheless, some of our unpublished experimental results have proved that the alkyne **1**, bearing two electron-withdrawing groups, exhibits unusual reactivity. An ionic mechanism cannot explain the regioselectivity observed in methanol. Furthermore, if we compare the addition of Bu_3SnH to ethyl propiolate the opposite regioisomer should be observed, as for the alkynyl triflones described by Fuchs et al.[16] Ethyl trifluorobutynoate **1** spontaneously reacted with tetrahydrofuran through a radical mechanism and without a radical initiator to provide the THF adduct. In fact, the extremely electron-deficient *sp*-hybridized alkyne moiety engenders efficient trapping of all radical intermediates. Indeed, we believe that small amounts of dioxygen certainly serve to initiate the process. Nevertheless, attempts conducted in a controlled atmosphere (glove box) and in the dark led to identical results. The stability of the two radicals possibly explains the regioselectivity of the reaction.

Theoretical calculations are currently being tested in order to propose a realistic mechanism describing the solvent effect. Our preliminary results indicate that in the presence of methanol there would be a hydrogen bond with the carbonyl of ester of **1** (2 kcal/mol more stable). The addition of a tributylstannyl radical to this complex would thus provide two radicals in the α- and β-positions (Scheme 2). We found that the radical in the β-position was more stable that the radical in the α-position by 3–4 kcal mol^{-1}. In hexane and in the absence of methanol, the radical in the α-position is more stable than the radical in the β-position (1.9 kcal/mol).

Attention was next directed to the reactivity of the vinyltin reagents **2** using a known coupling reaction procedure. Although Stille reported that $Pd(PPh_3)_4$ alone catalyzed the coupling reaction of vinylstannanes and allyl bromides,[17] no coupling reaction between **2** and allyl bromides was observed using these experimental procedures. In contrast, on the basis of transmetallation from the organotin compound to the organocopper intermediate,[10a,18] we investigated a palladium-free cross-coupling of vinylstannane **2**β with allyl bromide in the presence of a catalytic amount of CuI (10 mol%). A very clean reaction was



Scheme 2. Molecular structures of expected intermediates.



Scheme 3. Copper(I)-catalyzed allylation reaction.

observed and good yield of the desired product was obtained. It was discovered that the reaction was complete within 15 h using 10 mol% of CuI at 50 °C (Scheme 3). The use of CuBr instead of CuI provided similar results. To investigate the scope of the copper-allylated reaction, a variety of allyl bromides were tested to react with (*Z*)-**2**α and (*Z*)-**2**β, and the results are summarized in Table 2.

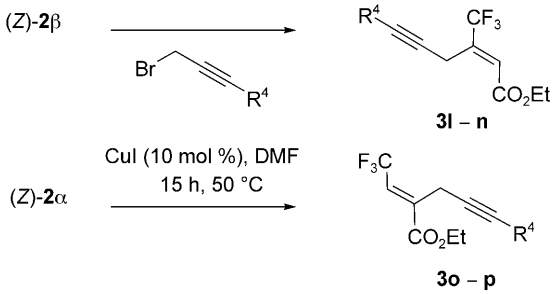
Vinyltin reagents (*Z*)-**2**α and (*Z*)-**2**β reacted smoothly in the presence of a catalytic amount of a copper(I) salt with a range of allylic bromides, leading to the expected allylated products **3a–k** with excellent yields. Interestingly, we found that the use of an equimolar amount of copper salt led to moderate yields of coupling products (< 60%). No coupling reaction was observed in the absence of Cu(I) catalyst, and the starting material was integrally recovered. Equally, no homocoupling product (dienes) was observed under the conditions employed.[18d]

In the case of **3a–k**, the coupling reaction occurred with retention of configuration of the C(2)=C(3) double bonds of **2** and the starting allyl bromides. These results indicated that the presumed intermediate copper reagent formed after catalytic transmetallation of vinyltin reagents with copper iodide was configurationally stable and reacted stereoselectively with allylic bromides substrates. The (*Z*)-**2**α- and (*Z*)-**2**β-derivatives were allowed to react with crotyl bromide under similar conditions, and the reaction produced a cross-coupled product without allylic transposition, and the configuration of the starting reagent was conserved (entries 4 and 10, Table 2). Interestingly, geranyl bromide also reacted with (*Z*)-**2**α and (*Z*)-**2**β affording the expected trifluorotrienes **3f** and **3k** in good yields and with retention of the olefinic configurations (entries 6 and 11, Table 2), thus providing a new, efficient entry to this important class of compounds.

To investigate the scope and limitations of the copper-catalyzed reaction, attention was next directed to the copper (I)-catalyzed propargylation reaction of **2** under the same conditions as described above. Indeed, compounds (*Z*)-**2**α and (*Z*)-**2**β underwent reaction with propargyl bromides to provide the 2 or 3-propargylated products **3l–p** with reasonable to good yields and with a clean *E* configuration of the double bond, demonstrating again that the copper(I) catalyst coupling reaction occurred with retention of configuration (Scheme 4 and Table 2, entries 12–16) and no homocoupling or allenic product was detected.

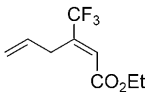
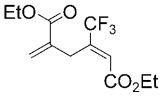
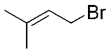
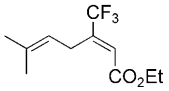
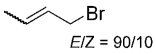
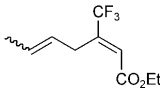
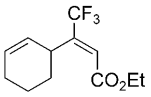
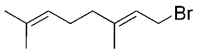
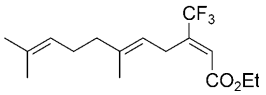
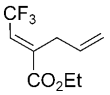
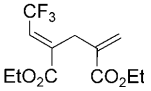
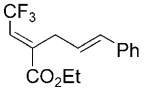
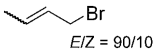
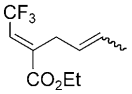
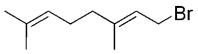
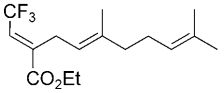
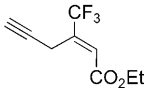
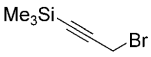
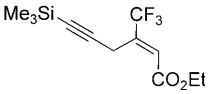
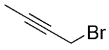
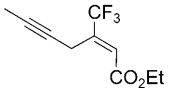
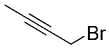
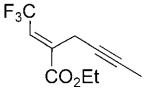
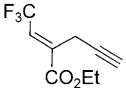
Propargyl bromides substituted in the terminal position were used, and they reacted well with (*Z*)-**2**β and (*Z*)-**2**α, providing the expected products **3m–o** (entries 13–15, Table 2). The presence of a trimethylsilyl group as substituent in the terminal alkyne was well tolerated (entry 13, Table 2).

To the best of our knowledge, there is no report in the literature on the reactions of vinyltin reagents with propargyl halides. A plausible mechanism is proposed for the copper(I)-catalyzed coupling reaction and would proceed as follows. Copper(I) iodide would transmetallate the vinyltin reagent (*Z*)-**2**,[10a,17] leading to a vinylcopper species, which then would react with allylic or propargylic bromide to generate a copper(III) intermediate. Finally, *via* a reductive elimination step, the expected diene or enyne **3** would be obtained giving the Cu(I) active species.



Scheme 4. Copper(I)-catalyzed propargylation of (*Z*)-**2**α and (*Z*)-**2**β.

Table 2. Copper (I)-catalyzed allylation and propargylation of (*Z*)-**2**α and (*Z*)-**2**β.

Entry	**2**	Allyl/Propargyl Bromides	Product **3**		Yield [%]
1	(*Z*)-**2**β			**3a**	92
2	(*Z*)-**2**β			**3b**	91
3	(*Z*)-**2**β			**3c**	68
4	(*Z*)-**2**β			**3d**	75[a]
5	(*Z*)-**2**β			**3e**	66
6	(*Z*)-**2**β			**3f**	77
7	(*Z*)-**2**α			**3g**	70
8	(*Z*)-**2**α			**3h**	84
9	(*Z*)-**2**α			**3i**	58
10	(*Z*)-**2**α			**3j**	74[b]
11	(*Z*)-**2**α			**3k**	73
12	(*Z*)-**2**β			**3l**	55[c]
13	(*Z*)-**2**β			**3m**	65
14	(*Z*)-**2**β			**3n**	62
15	(*Z*)-**2**α			**3o**	78
16	(*Z*)-**2**α			**3p**	67

[a] (*E*)-**5**/(*Z*)-**5** = 90/10.
[b] (*E*)-**4**/(*Z*)-**4** = 90/10.
[c] 20 mol% of CuI were used.

In summary, we have investigated the transition metal-free catalyzed hydrostannylation of ethyl 4,4,4-trifluorobut-2-ynoate. The hydrostannylation took place smoothly in the absence of additive, providing regioselectively high yields of the corresponding α- or β-stannylated alkenoates depending on the nature of the solvent used. These new reagents readily undergo copper(I)-catalyzed coupling reactions with allylic and propargylic bromides to provide good yields of the corresponding allyl- or propargylacrylate esters bearing a β-trifluoromethyl group. This method provided a new efficient entry to this important class of compounds. Investigations into the synthesis of new acrylic esters containing a trifluoromethyl group using other electrophiles are currently in progress

Experimental Section

General Procedure for the Synthesis of Stannylvinyl Esters 2α, β

n-Bu_3SnH (790 mg, 2.71 mmol) was slowly added to a solution of ethyl 4,4,4-trifluorobutynoate (500 mg, 3.01 mmol) in 20 mL of solvent, at room temperature. The mixture was stirred for 2 h and the solvent was then evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether as an eluent, and products (*Z*)-**2**α, β were isolated as colourless oils.

(*Z*)-Ethyl 4,4,4-trifluoro-2-tributylstannyl-but-2-enoate (2α): 82% isolated yield; colourless oil; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 6.85$ (q, $J_{H,F} = 7.6$ Hz, $J_{Sn,H} = 72$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 1.60–0.80 (m, 30H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 171.1$, 151.7, (q, $J_{C,F} = 6.7$ Hz), 134.8 (q, $J_{C,F} = 34.6$ Hz), 123.0 (q, $J_{C,F} = 271.0$ Hz), 61.4, 28.7 ($^2J_{Sn,C} = 20.0$ Hz), 27.1 ($^3J_{Sn,C} = 64.3$ Hz), 14.2, 13.5, 11.7 ($^1J_{Sn,C} = 357$–348 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): $\delta = -62.4$; ^{119}Sn NMR ($CDCl_3$, 149 MHz): $\delta = -26.2$; IR (neat): $\nu = 2958$, 2924, 2873, 2856, 1716, 1465, 1278, 1231, 1145 cm^{-1}; MS (EI): *m/z* (%) = 401 ($M^+ - 57$, 100), 253 (38), 177 (38), 101 (43), 57 (42); HR-MS (EI): *m/z* = 458.1460, calcd. for $C_{18}H_{33}F_3O_2Sn$ (M^+): 458.1455.

(*Z*)-Ethyl 4,4,4-trifluoro-3-tributylstannylbut-2-enoate (2β): 70% isolated yield; colourless oil; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 6.93$ (q, $J_{H,F} = 2.3$ Hz, $J_{Sn,H} = 73.0$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.60–0.85 (m, 30H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 166.6$, 156.7 (q, $J_{C,F} = 34.5$ Hz), 134.3 (q, $J_{C,F} = 9.5$ Hz), 126.6 (q, $J_{C,F} = 272.9$ Hz), 61.4, 28.9 ($^2J_{Sn,C} = 19.6$ Hz), 27.3 ($^3J_{Sn,C} = 65$ Hz), 14.1, 13.6, 11.8 ($^1J_{Sn,C} = 368$–355 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): $\delta = -62.0$; ^{119}Sn NMR ($CDCl_3$, 149 MHz): $\delta = -33.0$; IR (neat): $\nu = 2958$, 2923, 2873, 2855, 1720 cm^{-1}; MS (EI): *m/z* (%) = 401 ($M^+ - 57$, 100), 235 (38), 179 (53), 129 (29), 57 (34); HR-MS (EI): *m/z* = 458.1459, calcd. for $C_{18}H_{33}F_3O_2Sn$ (M^+): 458.1455

General Procedure for the Cross-Coupling Allylations and Propargylations

A solution of allyl bromide or propargyl bromide (2 mmol) in DMF (2 mL) was added to a mixture of (*Z*)-ethyl 4,4,4-trifluoro-3-tributylstannylbut-2-enoate (2 mmol) and CuI (10 mol%) in DMF (8 mL), and the resulting suspension was stirred for 3 h at 50 °C. Ethyl acetate (10 mL) and 1 M aqueous KF (5 mL) were added, and the reaction mixture was stirred for two more hours. The mixture was then extracted three times with ether, and the combined organic layers were washed with saturated aqueous NH_4Cl and brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography, using petroleum ether/diethyl ether (100:0 to 98:2) as eluent.

(*E*)-Ethyl 3-trifluoromethyl-6-methylhepta-2,5-dienoate (3c): 68% isolated yield; colourless oil; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 6.31$ (s, 1H), 5.09 (t, $J = 6.3$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 3.42 (d, $J = 7.0$ Hz, 2H), 1.71 (s, 3H), 1.68 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 164.6$, 145.0 (q, $J_{C,F} = 27.8$ Hz), 134.6, 123.3 (q, $J_{C,F} = 273.6$ Hz), 121.9 (q, $J_{C,F} = 6.0$ Hz), 118.7, 60.9, 25.7 (q, $J_{C,F} = 3.6$ Hz), 25.5, 17.7, 14.0; ^{19}F NMR ($CDCl_3$, 376 MHz): $\delta = -68.9$; IR (neat): $\nu = 2983$, 2932, 1730, 1676, 1308, 1203, 1170: MS (EI): *m/z* (%) = 236 (63), 191 (62), 188 (67), 165 (100), 93 (87); HR-MS (EI): *m/z* = 236.1020, calcd. for $C_{11}H_{15}F_3O_2$ (M^+): 236.1024.

(*E*)-Ethyl 3-trifluoromethylhex-2-en-5-ynoate (3l): 63% isolated yield; colourless oil; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 6.42$ (s, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 3.67 (d, $J = 2.6$ Hz, 2H), 2.03 (t, $J = 2.6$ Hz, 1H), 1.33 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 164.0$, 139.8 (q, $J_{C,F} = 29.8$ Hz), 123.8 (q, $J_{C,F} = 5.5$ Hz), 122.7 (q, $J_{C,F} = 273.5$ Hz), 77.9, 69.2, 61.4, 15.8, 14.0; ^{19}F NMR ($CDCl_3$, 470 MHz): $\delta = -68.7$; IR (neat): $\nu = 3314$, 2961, 2928, 2128, 1730, 1677, 1377, 1186 cm^{-1}; MS (EI): *m/z* (%) = 178 (100), 161 (28), 133 (29), 113 (21), 102 (26); HR-MS (EI): *m/z* = 206.0558, calcd. for $C_9H_8F_3O_2$ (M^+): 206.0555.

Acknowledgements

We thank MESR and CNRS for financial support.

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