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Z-Selective Hydrostannylation of Terminal and Internal C−C Triple Bonds Initiated by the Trityl Cation

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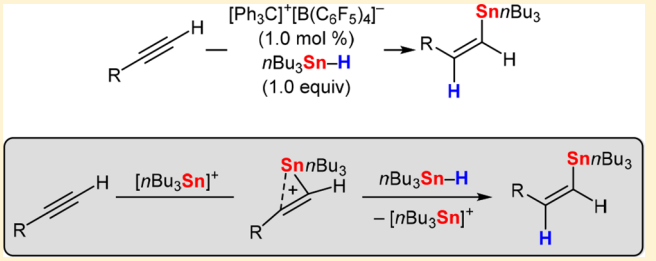
Supporting Information

ABSTRACT: A metal-free method for the *anti*-addition of *n*-Bu_3SnH across terminal and internal alkynes, including related α,β-unsaturated carboxyl compounds, is reported. The reaction is initiated by the trityl salt $[Ph_3C]^+[B(C_6F_5)_4]^-$ and proceeds through β-tin-stabilized vinyl cations. Their reduction by hydride transfer from *n*-Bu_3SnH explains the high *Z*-selectivity in the formation of the vinyl stannanes.



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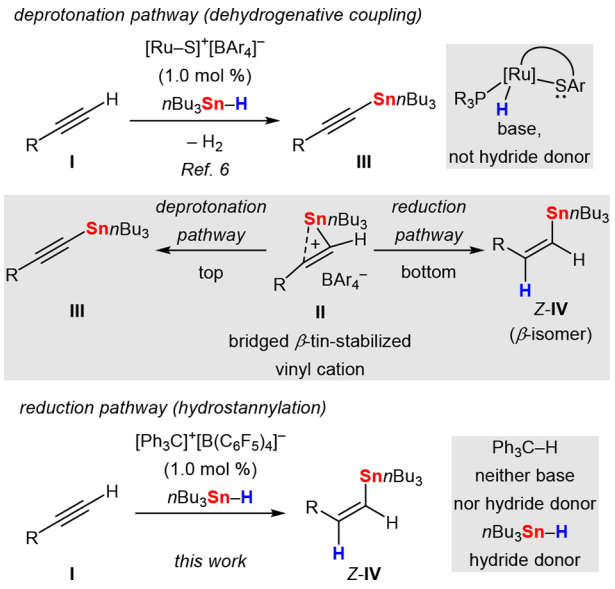
An R_3Sn group attached to an alkene is a versatile linchpin in synthetic chemistry, e.g., in Stille-type cross-coupling reactions.[1] Methods for the stereoselective preparation of these vinyl stannanes have therefore always been in demand. Known procedures are diverse, and a direct way of their formation is by the addition of hydrostannanes R_3SnH across alkynes.[2] These hydrostannylations can be either catalyzed by transition metals[3] or initiated by radical starters,[4] often affording the vinyl stannane with high *E*-selectivity despite their different mechanisms. Conversely, hydrostannylations promoted by Lewis acids arrive at *Z*-configuration of the vinyl stannane.[5]

We recently disclosed a dehydrogenative coupling of various terminal alkynes **I** and *n*-Bu_3SnH catalyzed by tethered Ru−S complexes (**I** → **III**, Scheme 1, top).[6] This transformation proceeds through the intermediacy of bridged β-tin-stabilized vinyl cations[7] **II** (gray box, Scheme 1, middle). Intermediates **II** emerge from **I** and the stannylium-ion-like tin electrophile $[n\text{-}Bu_3Sn{-}S]^+$ that, in turn, is generated by cooperative Sn−H bond activation at the Ru−S bond.[8] The chemoselectivity of the reaction is determined at the stage of **II**: deprotonation **II** → **III** (left) versus hydride reduction **II** → **IV** (right). The neutral Ru−H formed is not sufficiently hydridic,[9] but the sulfur atom is able to abstract the proton from **II**, resulting in the formation of alkynyl stannane **III** (Scheme 1, top). In the light of this insight, we imagined that the chemoselectivity could be reversed in the absence of this internal Brønsted base, thereby forcing *n*-Bu_3SnH into the role of the hydride source[4c] and at the same time regenerating the tin electrophile for the next formation of **II** from **I**. The trityl cation could fulfill this purpose as it is typically employed for the generation of stannylium ions by hydride abstraction,[10] and the resulting triphenylmethane would not participate further in reaction. Consequently, the trityl cation could initiate the hydrostannylation of alkynes (**I** → **IV**, Scheme 1, bottom). Herein, we report the *Z*-selective hydrostannylation of a broad range of terminal and internal alkynes involving cationic intermediates.[11]

Scheme 1. Competing Reaction Pathways: Dehydrogenative Stannylation versus Hydrostannylation [Ar = 3,5-$(CF_3)_2C_6H_3$ or C_6F_5]



Initial experiments using the readily available trityl salt $[Ph_3C]^+[B(C_6F_5)_4]^-$ as initiator for the hydrostannylation of phenyl acetylene (**1a**) furnished desired vinyl stannane *Z*-**2a** in complex mixtures. A systematic screening of reaction conditions revealed a dramatic influence of the solvent and reaction time on the outcome (Table 1). Reactions performed in CH_2Cl_2 largely yielded *E*-**2a** and substantial amounts *n*-Bu_4Sn; however, *Z*-to-*E* isomerization and decomposition occurred at prolonged reaction times (entries 1−3). ^1H and

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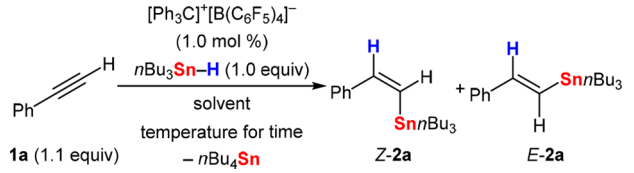
Table 1. Reaction Optimization: The Crucial Role of Solvent and Reaction Time[a]



entry	solvent	T (°C)	t	Z-**2**/E-**2**/n-Bu_4Sn[b]
1	CH_2Cl_2	RT	5 min	15:51:34
2	CH_2Cl_2	RT	1 h	0:54:46
3	CH_2Cl_2	RT	20 h	0:52:47
4	PhH	RT	1 h	0:1:99
5	PhF	RT	1 h	0:42:58
6	PhCl	RT	1 h	6:38:56
7	*n*-pentane	RT	5 min	95:0:5
8	*n*-pentane	RT	1 h	89:0:11
9	*n*-pentane	RT	48 h	0:47:53
10	*n*-pentane	0	24 h	>95:0:<5

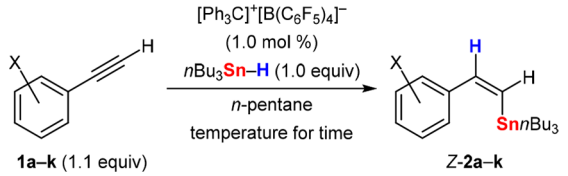
[a]All reactions were performed according to general procedure 1 or 2 (see the Supporting Information for details). [b]Ratios were estimated by $^{119}Sn\{^1H\}$ NMR analysis. Full conversion of n-Bu_3SnH was observed in all reactions.

^{119}Sn NMR analysis showed full conversion of n-Bu_3SnH after 5 min, and the 15% of Z-**2a** present after this short reaction time then quickly disappeared. The same trend was seen in aromatic solvents such as benzene, fluorobenzene, and chlorobenzene (entries 4–6). This situation changed drastically with the use of *n*-pentane as solvent: Almost exclusive formation of Z-**2a** was observed at short reaction times, and isomerization to E-**2a** along with generation of n-Bu_4Sn was slowed down (entries 7–9). Lowering the reaction temperature to 0 °C gave Z-**2a** as the only product (entry 10).

Having identified the optimized setup, we explored the scope for phenyl acetylene derivatives (**1a–k** → Z-**2a–k**, Table 2). Regardless of the electronic property of the aryl group in **1a–i**, almost all vinyl stannanes Z-**2a–i** were formed with high control of the double bond geometry and in good to excellent yields (entries 1–9). To secure high diastereoselectivities, the hydrostannylation of electron-deficient **1b–e** had to be run at 0 °C rather than RT (entries 2–5; see Table 2, footnote e). Importantly, the formation of n-Bu_4Sn was suppressed at that temperature. Electron-rich **1f** with an MeO group converted smoothly into Z-**2f**, whereas Me_2N-substituted **1g** did not afford Z-**2g** even at 60 °C (entries 6 and 7). Steric hindrance was tolerated as verified for the three isomeric tolyl-substituted acetylenes (**1i–k** → Z-**2i–k**, entries 9–11).

Next, we turned our attention to alkyl-substituted terminal alkynes (**1l–p** → Z-**2l–p**, Table 3). Depending on the R group, we observed the formation of alkynyl stannane **3** as the product of dehydrogenative coupling. Linear hex-1-yne (**1l**) gave only low conversion at RT but a higher reaction temperature only led to a complex mixture (entry 1). In turn, benzyl- and cyclopropyl-substituted **1m** and **1n** both formed vinyl stannanes Z-**2m** and Z-**2n** chemoselectively (entries 2 and 3). In contrast, cyclopentyl-substituted **1o** reacted to an almost equimolar mixture of Z-**2o** and **3o**, and that ratio could not be improved at lower temperatures due to insufficient conversion (entry 4). The same applied to another branched substrate, cyclohexyl-substituted **1p**, although the effect was less pronounced (entry 5). It seems that branching

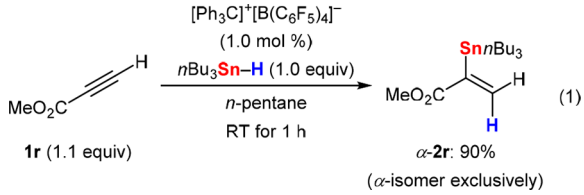
Table 2. Hydrostannylation of Phenyl Acetylene Derivatives Initiated by the Trityl Cation[a]



entry	alkyne **1**	T (°C)	t (h)	Z/E[b]	yield of **2** (%)[c]
1	**1a** (X = H)	0	24	>95:5	96 (**2a**)[d]
2	**1b** (X = 4-F)	0	2	92:8[e]	79 (**2b**)
3	**1c** (X = 4-CF_3)	0	2	88:12	74 (**2c**)
4	**1d** (X = 4-Cl)	0	2	89:11	77 (**2d**)[d]
5	**1e** (X = 4-Br)	0	2	87:13	74 (**2e**)[d]
6	**1f** (X = 4-OMe)	RT	1	>95:5	86 (**2f**)
7	**1g** (X = 4-NMe_2)	60[f]	24		(**2g**)[g]
8	**1h** (X = 4-Ph)	0	2	>95:5	78 (**2h**)
9	**1i** (X = 4-Me)	0	2	>95:5	78 (**2i**)
10	**1j** (X = 3-Me)	RT	1	91:9	95 (**2j**)[d]
11	**1k** (X = 2-Me)	0	2	>95:5[h]	82 (**2k**)

[a]All reactions were performed according to general procedure 1 or 2 (see the Supporting Information for details). [b]Ratios were determined by ^1H NMR analysis. [c]Isolated yield after filtration over a plug of basic Al_2O_3. [d]Along with trace amounts of n-Bu_4Sn. [e]E/Z = 75:25 at RT for 1 h. [f]Reaction performed in *n*-hexane instead of *n*-pentane. [g]Only low conversion of n-Bu_3SnH was observed. [h]E/Z = 80:20 at RT for 1 h.

in the propargylic position hampers the hydride transfer from n-Bu_3SnH to the β-tin-stabilized vinyl cation, turning proton release or even protonation of n-Bu_3SnH into a viable alternative. Triisopropylsilyl-protected propargylic alcohol **1q** was afflicted with the same problem (entry 6). In addition to that, there was no regiocontrol, and Z-**2q** and α-**2q** (not shown) formed in almost equimolar ratio. Propiolic acid methyl ester reacted cleanly but with opposite regioselectivity (**1r** → α-**2r**):



Application of the standard protocol to internal alkynes and related α,β-unsaturated carboxyl compounds[12] was largely satisfactory (Figure 1). No reaction was found for tolan despite full conversion of n-Bu_3SnH but this merely led to the formation of n-Bu_4Sn (not shown). However, the hydrostannylation of 1-phenylprop-1-yne (**1s**) yielded corresponding vinyl stannane Z-**2s** diastereoselectively and with excellent regioselectivity. An internal aliphatic alkyne was far less reactive; **1t** transformed slowly into Z-**2t**, barely reaching 50% conversion after 24 h at 60 °C. Silylated alkynes such as **1u** generally resulted in complex reaction mixtures. Alkynones **1v** and **1w** afforded Z-**2v** and Z-**2w** with superb control of the alkene geometry.

To conclude, we have introduced here a straightforward method for the Z-selective preparation of vinyl stannanes by alkyne hydrostannylation. The reaction is simply initiated by catalytic amounts of the trityl cation, that is by its hydride abstraction from the hydrostannane to formally generate a stannylium ion. The hydrostannane adds *anti* across the C–C

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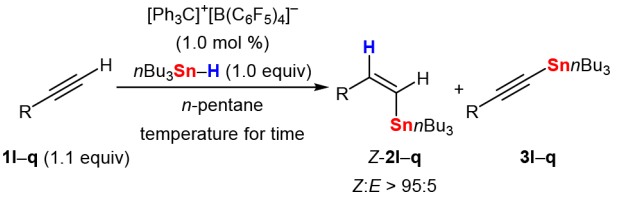
Table 3. Hydrostannylation of Alkyl-Substituted Terminal Alkynes Initiated by the Trityl Cation[a]



entry	alkyne **1**	T (°C)	t (h)	Z-**2**/**3**[b]	yield of **2** (%)[c]
1	**1l** (R = *n*-Bu)	60[d,e]	24		(**2l**)[f]
2	**1m** (R = Bn)	0	1/2	>95:5	76 (**2m**)
3	**1n** (R = *c*Prop)	RT	1	>95:5	96 (**2n**)
4	**1o** (R = *c*Pent)	RT[d]	18	55:45	83 (**2o**+**3o**)
5	**1p** (R = Cy)	RT	24	91:9	96 (**2p**+**3p**)
6	**1q** (R = CH_2OTIPS)	RT	24	97:3	51 (**2q**+**3q**)[g]

[a]All reactions were performed according to general procedure 1 or 2 (see the Supporting Information for details). [b]Ratios were estimated by $^{119}Sn\{^1H\}$ NMR analysis. [c]Isolated yields after filtration over a plug of basic Al_2O_3. [d]Only low conversion of *n*-Bu_3SnH was observed at 0 °C and RT, respectively. [e]Reaction performed in *n*-hexane instead of *n*-pentane. [f]Complex mixture was observed. [g]Combined yield of Z-**2q** (24%) and α-isomer α-**2q** (27%); the ratio of these regioisomers was nearly 1:1 prior to their separation by flash chromatography on silica gel.

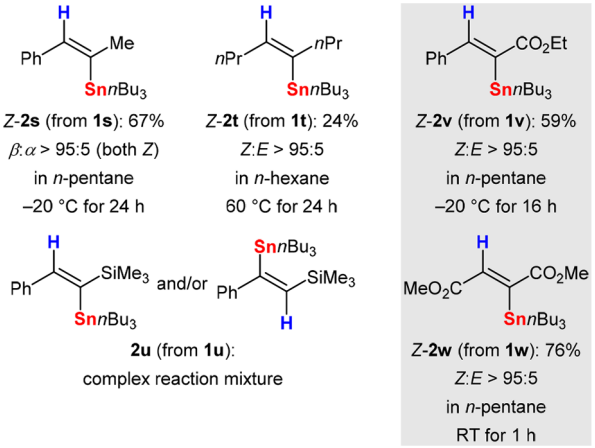


Figure 1. Vinyl stannanes prepared by hydrostannylation of representative internal C−C triple bonds.

triple bond by a mechanism that involves a bridged β-tin-stabilized vinyl cation as an intermediate. Its sterically controlled hydride reduction by the hydrostannane affords the vinyl stannane with Z-configuration and regenerates the tin electrophile.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00409.

Experimental details, characterization, and ^1H, ^{13}C, ^{19}F, ^{29}Si, and ^{119}Sn NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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