Lewis Acid Catalysed *trans*-Hydrostannylation of Acetylenes

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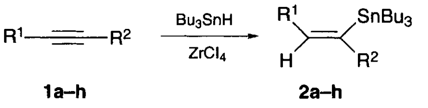
A Lewis acid such as $ZrCl_4$ or $HfCl_4$ catalyses the hydrostannylation of acetylenes **1** to produce the *trans*-hydrostannylation products **2** regio- and stereo-selectively.

It is well known that the hydrostannylation[1] of acetylenes is induced by either radical initiators[2] or transition metal catalysts.[3] The radical induced procedure often gives a mixture of the *trans*- and *cis*-hydrostannylation products, since the isomerization of the alkenyltin products occurs in the presence of tin radicals.[4],† The transition metal catalysed reaction proceeds *via* the *cis*-hydrostannylation pathway.[3] We report that the hydrostannylation process is catalysed dramatically by Lewis acids such as $ZrCl_4$ or $HfCl_4$, and that the $ZrCl_4$ catalysed procedure yields the *trans*-hydrostannylation product regio- and stereo-selectively (Scheme 1).

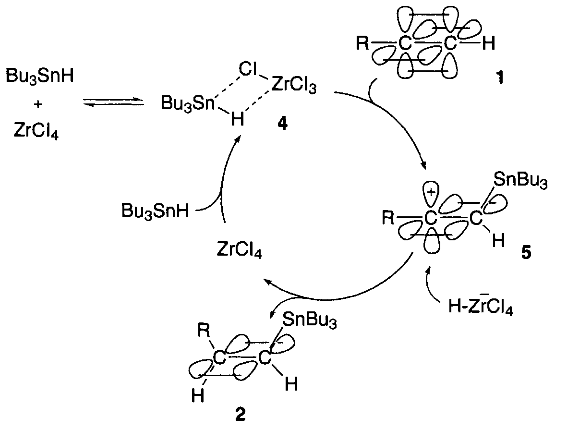
The results are summarized in Table 1. The reaction of oct-1-yne **1a** with Bu_3SnH in the presence of 1.1 equiv. of $ZrCl_4$ in toluene gave the *trans*-hydrostannylation product **2a** (*Z*-vinylstannane) regio- and stereo-selectively in 30% yield (entry 1).‡ Although the yield of **2a** was low, the stereoisomer **3a** (*E*-vinylstannane) was not detected in the ^1H NMR spectra of the reaction products. The chemical yield was enhanced to 76% by using 0.2 equivalents of $ZrCl_4$ (entry 2), and the use of hexane as solvent gave an 89% yield (entry 3). It should be noted that $ZrCl_4$ is not soluble in toluene and hexane at 0 °C and therefore the reaction is carried out as a heterogeneous system. The use of THF and CH_2Cl_2 as solvent, which dissolve the catalyst more effectively than the non-polar solvents, gave lower stereoselectivity and chemical yield. $HfCl_4$ was also an efficient catalyst for the *trans*-hydrostannylation (entry 4), but the reaction time using $HfCl_4$ was slightly longer than that using $ZrCl_4$. The use of a typical Lewis acid of group 14, $AlCl_3$, as a catalyst afforded a 60:40 mixture of **2a** and **3a** in 53% yield.

We examined the $ZrCl_4$ catalysed hydrostannylation of several other alkynes. The reaction of phenylacetylene **1b** gave **2b** in 73% yield along with trace amounts of **3b** (entry 5), whereas the addition to *p*-tolylacetylene **1c** afforded stereoselectively **2c** in 84% yield while the stereoisomer **3c** was not detected (entry 6). The reaction of 5-(*tert*-butyldimethylsilyloxy)pent-1-yne **1d** gave **2d** stereoselectively in high yield (entry 7). On the other hand, the addition to 5-benzyloxypent-1-yne **1e** did not take place and the starting material was recovered quantitatively (entry 8). A Lewis acid can coordinate more easily to a BnO group than to a sterically demanding Bu^tMe_2SiO group. It seems that $ZrCl_4$ coordinates to the BnO group of **1e**, instead of acting as a catalyst for the hydrostannylation. The $ZrCl_4$-catalysed hydrostannylation of 1-chlorooct-1-yne **1f** gave **2f** stereo- and regio-selectively in moderate yield (entry 9). The reaction of dodec-6-yne **1g** and diphenylacetylene **1h** also proceeded smoothly, although the use of stoichiometric amounts of $ZrCl_4$ gave better results.

Preparation of **2d** from **1d** is representative. To a suspension of $ZrCl_4$ (47 mg, 0.2 mmol) in toluene (0.5 ml) was added **1d** (0.24 ml, 1.0 mmol) at 0 °C under an Ar atmosphere. The mixture was stirred for 5 min, and then Bu_3SnH (0.42 ml, 1.5 mmol) was added. The mixture was stirred for 1 h at 0 °C and Et_3N (0.07 ml, 0.5 mmol) was added. The mixture was allowed to warm to room temperature, and stirring was continued for 5 min. Hexane was added and the mixture was filtered through



Scheme 1



Scheme 2

Table 1 Lewis acid catalysed hydrostannylation of acetylenes with Bu_3SnH^a

		1				*trans* : *cis*-hydrostannylation products^c
Entry	Lewis acid (equiv.)	R^1	R^2		Yield (%)^b	**2**:**3**
1	$ZrCl_4$ (1.1)	$Me(CH_2)_5$	H	(**1a**)	30	>95:5
2	$ZrCl_4$ (0.2)	$Me(CH_2)_5$	H	(**1a**)	76	>95:5
3^d	$ZrCl_4$ (0.2)	$Me(CH_2)_5$	H	(**1a**)	89	>95:5
4	$HfCl_4$ (0.2)	$Me(CH_2)_5$	H	(**1a**)	86	>95:5
5	$ZrCl_4$ (0.2)	Ph	H	(**1b**)	73	95:5
6	$ZrCl_4$ (0.2)	*p*-MeC_6H_4	H	(**1c**)	84	>95:5
7	$ZrCl_4$ (0.2)	$Bu^tMe_2SiO(CH_2)_3$	H	(**1d**)	87	>95:5
8	$ZrCl_4$ (0.2)	$BnO(CH_2)_3$	H	(**1e**)	0^e	—
9	$ZrCl_4$ (0.2)	$Me(CH_2)_5$	Cl	(**1f**)	47	>95:5
10	$ZrCl_4$ (1.0)	$Me(CH_2)_4$	$Me(CH_2)_4$	(**1g**)	56	>95:5
11	$ZrCl_4$ (1.0)	Ph	Ph	(**1h**)	33^f	>95:5

[a] Reactions were conducted in toluene at 0 °C under Ar unless otherwise noted. [b] Determined by ^1H NMR spectra of the reaction products using *p*-xylene as an internal standard. [c] Determined by 270 MHz ^1H NMR spectra. The stereoisomers **3** were not detected. The ratio, >95:5, came from the limit of detection for the stereoisomer. [d] Hexane was used as a solvent. [e] The starting material **1e** was recovered quantitatively. [f] *trans*-Stilbene was obtained in 46% yield in addition to a 33% yield of **2h**.

celite to remove solid material. Removal of the solvents under reduced pressure gave an oily material. The ^{1}H NMR spectra indicated that **2d** was produced in 87% yield.

A plausible mechanism for the $ZrCl_4$ catalysed *trans*-hydrostannylation is shown in Scheme 2,§ although it is highly speculative. Presumably, there would be a rapid equilibrium between Bu_3SnH and $ZrCl_4$, and the reactive species **4**. It is most probable that the hydrostannylation of **1** with **4** proceeds through **5** to give **2** and $ZrCl_4$. Although further investigation is needed to establish the mechanism of this $ZrCl_4$ catalysed reaction, the procedure is synthetically useful since the (*Z*)-alkenyltributylstannanes **2** are not readily available.

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Footnotes

† The sonochemical hydrostannylation produces the *trans*-hydrostannylation product stereoselectively [ref. 2(*c*)].

‡ The by-product oct-1-ene was produced.

§ In $AlCl_3$ catalysed hydrosilylation reactions of alkenes, a similar silyl hydride–$AlCl_3$ complex was suggested (ref. 5).

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