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Syntheses and Synthetic Applications of Stannylated Allylic Alcohols

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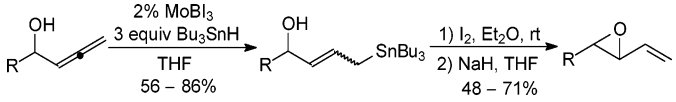


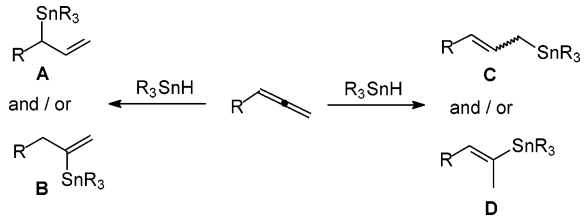
Allenyl carbinols undergo regioselective hydrostannation in the presence of $MoBl_3$, a catalyst originally developed for the hydrostannation of alkynes, giving rise to allyl stannanes. These allyl stannanes can easily be converted into useful synthetic building blocks such as allyl iodides or vinyl epoxides.

Introduction

During recent years functionalized allenes became rather important as synthetic intermediates for the synthesis of complex molecules.[1] For example, carbon−carbon and carbon−heteroatom bond formations are of major interest, triggering the development of preparative useful methods, such as additions[2] or palladium-catalyzed transformations.[3] In addition to cyclizations,[4] especially transition-metal-catalyzed hydrometalations such as hydroborations,[5] hydrozirconations,[6] or hydrostannations[7] became very popular, giving rise to allylic or vinylic organometallics depending of the regioselectivity in the addition step. As illustrated for hydrostannations (Scheme 1), in principle four different products (**A**−**D**) can be expected, and the product distribution depends on the reaction conditions used.

Both the allyl as well as the vinyl stannanes are important intermediates that can be used for, e.g., allylation reactions[8] or Stille couplings.[9] Oshima et al. were the first to report about hydrostannations of allenes in the presence of $Pd(PPh_3)_4$.[10] Allyl stannanes **C** were obtained preferentially, which was explained

SCHEME 1. Possible Reaction Products of Allene Hydrostannations



by a regioselective stannylpalladation transferring the stannyl groups to the terminal position of the allene. Mitchell et al. investigated systematically the influence of substituents and heteroatoms on the regio- and stereoselectivity of these hydrostannations.[11] They also obtained preferentially the terminal allyl stannanes (>85% rs), but in general mixtures of (*E*/*Z*)-isomers were obtained. Similar is the situation in the hydrostannation of alkoxy allenes, as reported by Goré et al.[12] These authors also used $Mo(CO)_6$ as a catalyst and observed a higher

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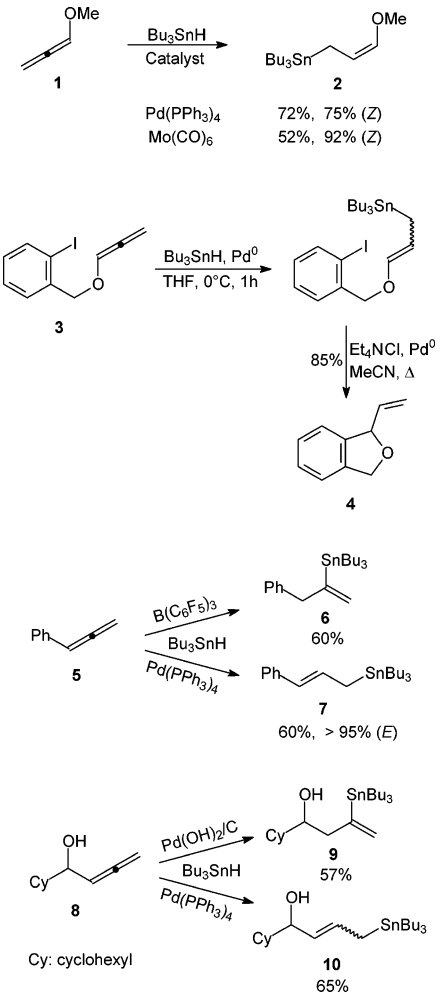
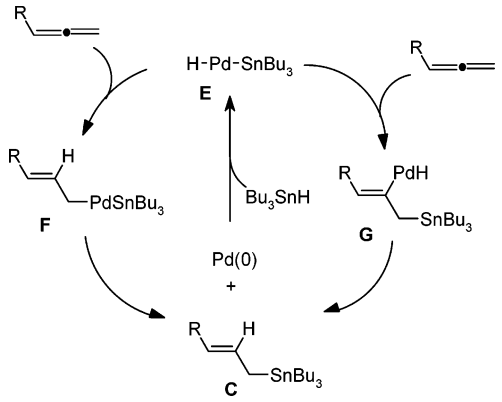
SCHEME 2. Hydrostannations of Allenes



Z-selectivity in the reaction of **1** (Scheme 2), although the molybdenum catalyst proved to be less reactive.

Grigg et al. combined elegantly the regioselective hydrostannation with a cyclization, both reactions catalyzed by Pd^0.[13] This straightforward protocol allows the synthesis of five- to seven-membered heterocycles such as **4**, starting from allene **3**. In 1997 Yamamoto et al. compared the Pd^0-catalyzed hydrostannation of allenes such as **5** with the Lewis acid catalyzed versions.[14] As reported previously, the Pd variant provided preferentially the allyl stannanes **7**,[7] whereas in the presence of $B(C_6F_5)_3$ the corresponding vinyl stannanes **6** were obtained. This was explained by different reaction mechanisms. It is postulated that in the Lewis acid catalyzed mechanism the $B(C_6F_5)_3$ adds to the internal double bond, followed by a hydride transfer onto the zwitterionic intermediate and transmetalation B versus Sn. On the other hand, the palladium-catalyzed version starts with an oxidative addition of the tin hydride to Pd^0 (Scheme 3), giving rise to the highly reactive palladium hydride species **E**. This intermediate can undergo either hydropalladation on the allene, providing allylpalladium species **F**, or palladostannylation yielding **G**. Both intermediates can form the allyl stannane **C** via reductive eliminations. Alkyl-substituted allenes again gave mixtures of the isomeric (*E*/*Z*)-allyl stannanes.

SCHEME 3. Mechanism of Pd-Catalyzed Hydrostannations of Allenes



Surprisingly very high (*E*)-selectivities were obtained for aryl-substituted allenes such as **5**. This was explained by a kinetic reaction control, especially because the isomeric ratio did not depend on the reaction temperature.

Lautens et al. were able to show that vinyl stannanes can also be obtained under palladium catalysis, for example, if Pd-$(OH)_2$/C is used as catalyst (Scheme 2).[15] Under these conditions several allenes, allenylamines, and allenols such as **8** were converted into the corresponding vinyl stannanes (**9**). Again, $Pd(PPh_3)_4$ provided the expected allyl stannane **10** in comparable yield as a 1:1 (*E*/*Z*) mixture.

Besides palladium catalysts, other metal complexes can be used for hydrostannations, such as rhodium[16] or molybdenum.[17] Guibe et al. described the application of $MoBr(allyl)(CO)_2(CH_3CN)_2$ for hydrostannations of propargylic alcohols, unfortunately without significant regioselectivity. The catalytically active species probably is Mo^0, formed in situ via reduction of the Mo-complex with the tin hydride. On the basis of this first report on molybdenum catalysis, we developed a new catalyst, $Mo(CO)_3(CN\mathit{t}Bu)_3$ ($MoBl_3$),[18] which allows highly regioselective hydrostannations of various types of alkynes.[19] As reported previously in a communication, this catalyst also allows regioselective hydrostannations of allenols.[20] Herein, we report details and applications of this reaction.

Results and Discussion

A well-established method for the synthesis of terminal allenes is found in the Crabbé homologization of terminal alkynols,[21] which were easily obtained via a Grignard reaction (Scheme 4). The propargylic alcohols **11** were reacted with

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SCHEME 4. Syntheses of Allenols

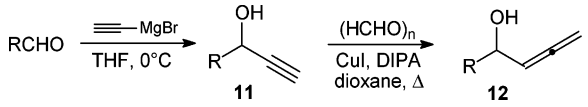
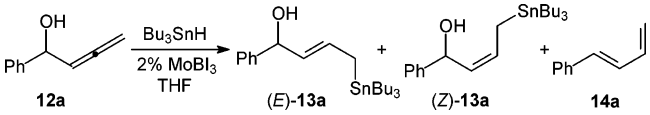


TABLE 1. Synthesis of Allenols

entry	R		yield, %		
1	Ph	**11a**	90	**12a**	60
2	4-MePh	**11b**	84	**12b**	69
3	2-MeOPh	**11c**	91	**12c**	58
4	2,4,6-$(MeO)_3$Ph	**11d**	56	**12d**	63
5	2-BrPh	**11e**	74	**12e**	66
6	4-ClPh	**11f**	90	**12f**	26
7	2,6-Cl_2Ph	**11g**	77	**12g**	34
8	2-NO_2Ph	**11h**	92	**12h**	56
9	4-NO_2Ph	**11i**	86	**12i**	20
10	$PhCH_2$	**11k**	67	**12k**	59
11	$(CH_3)_2CHCH_2$	**11l**	67	**12l**	40[a]
12	3-Cyclohexenyl	**11m**	71	**12m**	68

[a] THF was used as solvent.

SCHEME 5. Hydrostannation of Allenols



paraformaldehyde in the presence of DIPA and a Cu(I) catalyst, giving rise to the required allenols. We applied this protocol to various substituted aromatic (Table 1, entries 1−9) and a few aliphatic aldehydes (entries 10−12). We used strong electron-donating and -withdrawing groups on the aromatic ring to find out if there is an electronic influence of these substituents on the selectivity and the product distribution of the hydrostannation. The substrates prepared and the yields are summarized in Table 1.

In the hydrostannations of alkynes we obtained best results with 3 equiv od Bu_3SnH in refluxing THF.[19] To determine if this is also true with allenes, we investigated the influence of the reaction conditions, especially on the yield and selectivity, with allenol **12a** (Scheme 5). The ratio of the (*E*/*Z*)-stereoisomers was determined by NMR. In general, 2 mol % $MoBl_3$ was used and hydroquinone was added to suppress radical hydrostannation. The results obtained are summarized in Table 2. If the reaction conditions for alkyne hydrostannations were used (3 equiv of Bu_3SnH, refluxing THF), the isomeric allyl stannanes **13a** were obtained in good yield (entry 1). Interestingly, a third product **14a** was formed, obviously by elimination. This is not surprising, because α-metalated alcohols and derivatives thereof undergo elimination toward alkenes, and herein we have an analogous situation. To suppress this side reaction, we lowered the reaction temperature to room temperature, and indeed no elimination was observed under these milder conditions (entry 2). The yield was slightly higher and the (*E*/*Z*)-selectivity was not affected significantly; however, it is worth to mention that the terminal double bond was attacked exclusively. Further decreasing of the temperature to 0 °C resulted in a dramatic loss of yield, but the reaction still worked

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TABLE 2. Optimization of the Reaction Conditions

entry	temp (°C)	equiv of Bu_3SnH	time	yield (%)	ratio (*E*)-**13a** : (*Z*)-**13a** : **14a**
1	55	3	10 h	68	3 : 4 : 1
2	rt	3	18 h	71	2 : 3 : -
3	0	3	18 h	23	2 : 3 : -
4	rt	4	18 h	60	2 : 3 : -[b]
5	rt	3[a]	3 d	61	3 : 2 : -[b]
6	rt	1.1[a]	3 d	34	3 : 1 : -[b]
7	55	1.1[a]	12 h	58	2 : 1 : -[b]

[a] 1 M in THF; slow addition of the tin hydride (0.1 equiv/h). [b] Traces of diene **14a** detected

SCHEME 6. Hydrostannations of Various Allenols 12

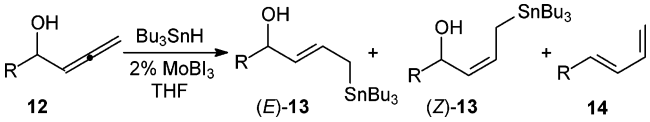
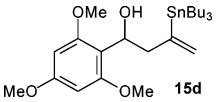


TABLE 3. Hydrostannations of Various Allenols 12

entry	allene	R	time (h)	temp (°C)	yield (%)	ratio (*E*)-**13** : (*Z*)-**13** : **14**
1	**12a**	Ph	18	rt	71	2 : 3 : -
2	**12b**	4-MePh	18	rt	78	10 : 10 : 1
3	**12c**	2-MeOPh	18	rt	62	2 : 5 : 1
4	**12d**	2,4,6-$(MeO)_3$Ph	18	rt	56[a]	6 : 4 : 1
5	**12d**	2,4,6-$(MeO)_3$Ph	4	55	60[b]	- : 1 : 2
6	**12e**	2-BrPh	18	rt	86	4 : 3 : -
7	**12f**	4-ClPh	4	55	68	1 : 1 : -
8	**12g**	2,6-Cl_2Ph	4	55	74	1 : 2 : -
9	**12h**	2-NO_2Ph	4	55	76	1 : 1 : -[c]
10	**12i**	4-NO_2Ph	18	rt	84	4 : 3 : -[c]
11	**12k**	$PhCH_2$	18	rt	68	1 : 2 : -
12	**12k**	$PhCH_2$	18	55	79	2 : 3 : -
13	**12l**	$(CH_3)_2CHCH_2$	18	rt	49	3 : 5 : -
14	**12l**	$(CH_3)_2CHCH_2$	18	55	63	3 : 5 : -
15	**12m**	3-Cyclohexenyl	18	rt	57	2 : 3 : -
16	**12m**	3-Cyclohexenyl	18	55	75	2 : 3 : -

[a] 35% (rel.) vinyl stannane **15d** formed. [b] 25% (rel.) vinyl stannane **15d** formed. [c] Traces of diene **14** formed.



(entry 3). It seems that allenols are significantly more reactive than alkynols, which show nearly no reaction at room temperature. Increasing the amount of Bu_3SnH does not result in a better yield (entry 4); the same is true if the tin hydride is added slowly via a syringe pump (entry 5). Here, also traces of elimination product were observed. Reducing the amount of tin hydride to 1.1 equiv in the slow addition mode provided a low yield even after days (entry 6). Interestingly, for the first time a significant selectivity for the (*E*)-isomer was observed. Increasing the reaction temperature to 55 °C provided a higher yield in a less selective reaction (entry 7).

The best results were obtained if 3 equiv Bu_3SnH was added at once and if the reactions were carried out between room temperature and refluxing THF. Therefore, we used these reaction conditions for the hydrostannation of the other allenols (Scheme 6, Table 3). The yields obtained with the aromatic allenols were generally good, especially for those substrates with electron-withdrawing substituents (**12e**−**i**, entries 6−10). Interestingly, electron-donating groups are obviously less suitable. Not only are the obtained yields lower, but the selectivity is

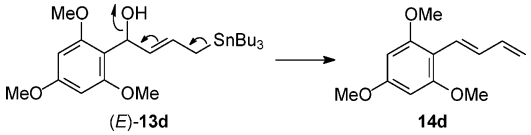
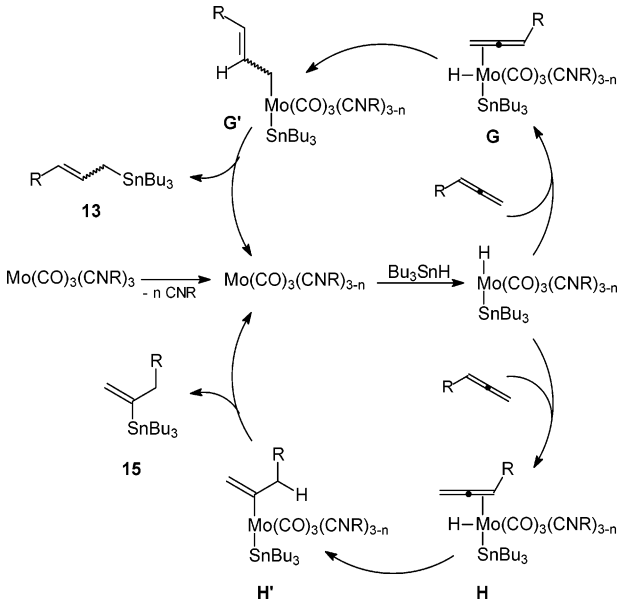


FIGURE 1. Elimination of stannylated allyl alcohols **13**.

SCHEME 7. Proposed Mechanism for the Molybdenum-Catalyzed Hydrostannation of Allenes

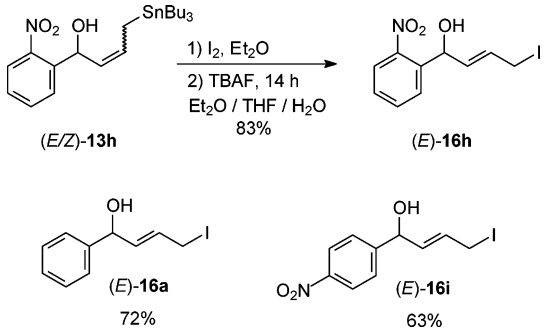


worse and side reactions such as eliminations become more relevant. This is clearly indicated by going from the initial substrate **12a** to the more and more electron-rich derivatives **12d** (entries 1−5). At higher temperatures the elimination product **14d** becomes the major product. Surprisingly, at 55 °C only the (*Z*)-configured allyl stannane **13d** could be isolated, whereas at room temperature this isomer is the minor one. The (*E*)-isomer seems to be the one undergoing elimination preferentially. This assumption is in good agreement with the product ratio (*Z*)-**13d**/**14d** obtained, and the elimination seems to be limited to substrates that can stabilize a carbenium ion in the allylic position (Figure 1).

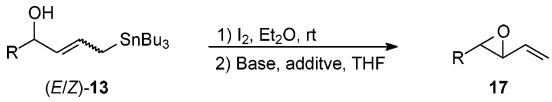
Compound **12d** is an interesting substrate, because it is the only one that reacted relatively unselectively. Here, significant amounts (up to 35%) of vinyl stannane **15d** were isolated, a regioisomer, which was not formed with all of the other substrates. Aliphatic substrates (**11k**−**m**) are less reactive compared to the aromatic ones, but the yields could be increased at higher temperatures without the formation of side products (entries 11−16).

The high selectivity toward the allyl stannanes **13** can be explained by the following mechanistic rational (Scheme 7): Probably in the first step some isonitrile ligands dissociate from the molybdenum, opening free coordination sites for the oxidative addition of the tin hydride and coordination of the allene. With respect to the sterically high demanding molybdenum complex, coordination to the less hindered terminal double bond is reasonable, giving rise to intermediate **G**. Subsequent hydrometalation should provide intermediate **G′**, with the molybdenum fragment added to the less sterically hindered position. The allyl stannanes **13** were formed from this intermediate via reductive elimination. The (*E*/*Z*)-isomers

SCHEME 8. Allyl Iodides 16 via Metal−Halogen Exchange



SCHEME 9. Conversion of Allyl Stannanes 13 into Vinyl Epoxides 17



result from coordination of the molybdenum to the two diastereotopic faces of the terminal double bond. The lower regioselectivity obtained in the hydrostannation of **11d** might have its explanation by an increased electron density of the internal double bond. Therefore this double bond might be a better ligand for the molybdenum favoring the formation of complex **H**, which then undergoes hydrometalation to **H′** and reductive elimination to **15d**. In this case obviously electronic and steric effects keep the balance, providing a mixture of both regioisomers.

Probably this mechanism is different from the one proposed for the hydrostannation of alkynes, which seems to start with a transfer of the stannyl group and a subsequent hydrogen transfer in the reductive elimination step, but both possible mechanisms were also discussed for palladium-catalyzed hydrostannations.[7] Therefore, it is reasonable that the situation with the molybdenum complexes is similar.

We focused our investigations on the allenols because we were interested to convert the allyl stannanes obtained into other synthetically useful intermediates such as vinyl epoxides. Therefore, we subjected the isomeric mixture (*E*/*Z*)-**13h** to a halogen metal exchange (Scheme 8). Although the isomeric mixture was used, the corresponding allyl iodide (*E*)-**16h** was obtained as a single isomer in high yield. Under these conditions only the thermodynamically most stable product is formed. The metal halogen exchange occurs nearly immediately, but the subsequent isomerization to the thermodynamic (*E*)-iodide takes about 20−30 min. This isomerization can easily be monitored by TLC. By this protocol we could also obtain the iodides **16a** and **16i** in reasonably good yield.

Unfortunately, these highly reactive iodides are rather unstable. The results shown are the best obtained; other iodides decompose during workup. Removal of the solvent even at room temperature resulted in a deiodination, and the compounds could not be stored for a longer time. Therefore, we tried to convert the iodides **16** directly without separation into vinyl epoxides. Deprotonation of the hydroxy functionality should provide epoxides **17** via intramolecular S_N2' reaction.

With allyl stannane **13k** we investigated the influence of the base on this two-step vinyl epoxide formation (Scheme 9, Table 4). The best results were obtained with NaH. The *trans* epoxide **17k** was obtained in 69% over both steps. To probe the influence of the counterion, we also performed the reaction in the presence

TABLE 4. Conversion of Allyl Stannanes 13 into Vinyl Epoxides 17

				yield (%)	
entry	stannane	R	base	*trans*-**17**	*cis*-**17**
1	**13k**	Bn	NaH	69	
2	**13k**	Bn	NaH, 15-C-5	72	
3	**13k**	Bn	KO*t*Bu	29	
4	**13k**	Bn	KO*t*Bu, 18-C-6	33	
5	**13k**	Bn	DBU	5	
6	**13b**	4-MePh	NaH	31	17
7	**13c**	2-MeOPh	NaH	45	21
8	**13e**	2-BrPh	NaH	52	19
9	**13i**	4-NO_2Ph	NaH	52	

of crown ether (15-C-5), although without significant changes. Other bases such as KO*t*Bu and DBU were definitely less suitable, but independent of the base used, the *trans* epoxide was formed exclusively.

Therefore, we used NaH for our further investigations and the synthesis of four more vinyl epoxides (Table 4).[22] The yields obtained were in the range of 48−71%. The nitro derivate **13i** also gave the *trans* epoxide **17i** exclusively (entry 4), whereas the other derivatives gave mixtures of the *trans*/*cis* isomers (entries 1−3), as determined by NMR spectroscopy.

In conclusion, we have shown that the molybdenum-catalyzed hydrostannation of allenols is an interesting synthetic tool for the regioselective synthesis of hydroxylated allyl stannanes, which can be converted into useful synthetic intermediates such as allyl iodides or vinyl epoxides. Further investigations concerning synthetic applications are currently in progress.

Experimental Section

General Remarks. All reactions were carried out in oven-dried glassware (100 °C) under argon. All solvents were dried before use. THF was distilled from $LiAlH_4$ and stored over molecular sieves. The products were purified by flash chromatography on silica gel. Mixtures of EtOAc and hexanes were generally used as eluents, and 1% NEt_3 was added for the purification of the stannanes. TLC was performed with commercially precoated Polygram SIL-G/UV 254 plates. Visualization was accomplished with UV light and $KMnO_4$ solution. Melting points are uncorrected. Selected signals in the NMR spectra for the minor isomers are extracted from the spectra of the isomeric mixture. Elemental analyses were carried out at the Department of Chemistry, University of Saarbrücken.

General Procedure for Hydrostannations of Allenols. In a Schlenk tube, $Mo(CO)_3(CN\textit{t}Bu)_3$ (4.3 mg, 0.01 mmol, 2 mol %) and hydroquinone (3 mg) were dissolved in THF (1 mL) under argon. The corresponding allenol (0.5 mmol) in THF (1 mL) was added at room temperature, and the reaction mixture was either kept at this temperature or refluxed for 15 min. Bu_3SnH (0.46 mL, 1.5 mmol, 3 equiv) was added either at once or slowly as a 0.1 M solution in THF via syringe pump (see Tables 2 and 3). The reaction mixture was stirred at the given temperature until all allene was consumed, as determined by TLC. The solvent was evaporated in vacuo, and the crude product was purified by flash chromatography. In general, a mixture of hexane/EtOAc/NEt_3 (98:1:1) was used as eluent.

(*E*/*Z*)-1-Phenyl-4-tributylstannylbut-2-en-1-ol (13a). According to the general procedure for hydrostannations **13a** was obtained from allenol **12a** (198 mg, 1.50 mmol) as a colorless liquid (463 mg, 1.06 mmol, 71%) in a 2:3 (*E*/*Z*) mixture. (*Z*)-**13a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82−0.89 (m, 15H), 1.22−1.30 (m, 6H), 1.41−1.47 (m, 6H), 1.74 (m, 2H), 1.77 (d, J = 3.5 Hz, 1H), 5.37 (m, 1H), 5.50 (dd, J = 8.5, 3.5 Hz, 1H), 5.75 (m, 1H), 7.22−7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.4, 11.3, 13.7, 27.3, 29.1, 69.5, 126.1, 126.4, 127.8, 128.4, 132.1, 144.2. (*E*)-**13a** (selected signals): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (dd, J = 7.4, 3.5 Hz, 1H), 5.46 (ddd, J = 37.5, 15.0, 7.4 Hz, 1H), 5.85 (ddt, J = 49.8, 15.0, 8.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.3, 13.6, 14.5, 29.0, 75.6, 126.0, 128.3, 133.0, 144.0; HRMS (CI) calcd for $C_{18}H_{29}O^{120}Sn$ $[M - Bu]^+$ 381.1186, found 381.1213.

(*E*)-4-Iodo-1-phenylbut-2-en-1-ol (16a). A solution of iodine (381 mg, 1.50 mmol) in ether (40 mL) was added to a solution of the allyl stannane (*E*/*Z*)-**13a** (650 mg, 1.45 mmol) in THF (10 mL). The reaction was monitored by TLC, and after 1 h the isomerization was complete. The organic solution was washed with saturated $Na_2S_2O_3$ and stirred overnight with TBAF (600 mg) as an ether/THF/water mixture at room temperature. The layers were separated, and the aqueous layer was extracted twice with ether. The combined organic layers were dried (Na_2SO_4), and the solvent was evaporated in vacuo in the cold. Flash chromatography (Hex/EtOAc (1) 100/0; (2) 80/20) of the crude product provided **16a** (290 mg, 1.06 mmol, 72%) as a rather unstable yellow oil and as a single stereoisomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.00 (d, J = 3.8 Hz, 1H), 3.88 (d, J = 8.2 Hz, 2H), 5.20 (m, 1H), 5.88 (dd, J = 15.3, 6.0 Hz, 1H), 6.04 (ddt, J = 15.3, 8.2, 0.9 Hz, 1H), 7.22−7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.4, 73.8, 126.3, 127.9,128.7, 135.5, 142.3.

General Procedure for the Conversion of Stannylated Allyl Alcohols into Vinyl Epoxides. A solution of iodine (381 mg, 1.50 mmol, 1.05 equiv) in ether (40 mL) was added to a solution of the allyl stannane (*E*/*Z*)-**13** (1.45 mmol) in THF (10 mL). The reaction was monitored by TLC, and after the isomerization was complete, this solution was added to a suspension of NaH (72 mg, 3.0 mmol) in THF (5 mL). After stirring overnight, the organic layer was washed with saturated $Na_2S_2O_3$ and brine and dried (Na_2SO_4), and the solvent was evaporated in vacuo. The crude product was purified by flash chromatography.

***cis*/*trans*-2-(4-Methylphenyl)-3-vinyloxiran (17b).** According to the general procedure for vinyl epoxide formation, **17b** was obtained from stannane **13b** (990 mg, 2.19 mmol), iodine (583 mg, 2.30 mmol), and NaH (106 mg, 4.40 mmol) as a colorless liquid (168 mg, 1.05 mmol, 48%) in a 1:3 *cis*/*trans*-mixture. *trans*-**17b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.24 (s, 3H), 3.34 (dd, J = 7.3, 1.8 Hz, 1H), 3.73 (d, J = 1.8 Hz, 1H), 5.32 (dd, J = 10.4, 0.9 Hz, 1H), 5.50 (dd, J = 17.4, 0.9 Hz, 1H), 5.72 (ddd, J = 17.4, 10.4, 7.3 Hz, 1H), 7.14−7.24 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 60.2, 62.8, 119.4, 125.4, 129.2, 132.2, 135.2, 138.0. *cis*-**17b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.24 (s, 3H), 3.63 (dd, J = 8.2, 4.3 Hz, 1H), 4.20 (d, J = 4.3 Hz, 1H), 5.26 (dd, J = 10.4, 1.8 Hz, 1H), 5.40 (ddd, J = 17.1, 10.4, 8.2 Hz, 1H), 5.53 (dd, J = 17.1, 1.8 Hz, 1H), 7.14−7.24 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 58.8, 59.8, 121.7, 126.3, 128.8, 132.0, 135.9, 137.4; HRMS (CI) calcd for $C_{11}H_{13}O$ $[M + H]^+$ 161.0968, found 161.0967.

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Supporting Information Available: Analytical and detailed NMR spectroscopic data of compounds **13**−**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) These are all examples investigated so far.