JOC Article

Regiocontrol of the Palladium-Catalyzed Tin Hydride Addition to *Z*-Enynols: Remarkable *Z*-Directing Effects

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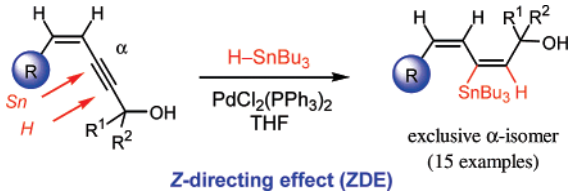

Palladium-catalyzed hydrostannation of substituted *Z*- and *E*-enynols is discussed and compared. The regioselectivity of the H−Sn bond addition was found to be controlled by the geometry of the double bond (*Z*- or *syn*-directing effect) rather than the nature of its substituents. Exclusively α-vinyl stannanes were obtained from *Z*-enynols having various substituents on the double bond regardless of their electronic, steric, or chelating natures.

Introduction

Vinylstannanes are valuable synthetic intermediates for palladium-mediated couplings.[1] As a result of their central importance, considerable effort has been expended toward their synthesis, particularly in the case of trisubstituted vinylstannanes.[2] The addition of tributyltin hydride to unsymmetrical alkynes is a simple and most straightforward route to these vinylmetal intermediates.[3] The main difficulty with this transformation is control of the stereo- and regiochemistry of the alkenylstannane products. Under radical conditions, the addition of the tin hydride to alkynes suffers generally from its low selectivity, affording a mixture of both stereo- and regioisomers.[4] In contrast, palladium-catalyzed hydrostannation of disubstituted alkynes proceeds in a stereoselective manner (*cis*-addition).[5] However, the regiochemistry of this reaction appears to be highly dependent on the alkyne substituents (eq 1). The presence of a bulky substituent on the carbon−carbon triple bond tends to place the Bu_3Sn group on the C_β atom (steric factors).[5a,6] On the contrary, an activating substituent on the carbon−carbon triple bond (e.g., CO_2R, COR, CF_3)[5a,7] or a heteroatom (e.g., S,

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(1) (a) Peyrere, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987. (b) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1 and references therein. (c) Shirakawa, E.; Nakao, Y.; Tsuchimoto, T.; Hiyama, T. *Chem. Commun.* **2002**, 1962.

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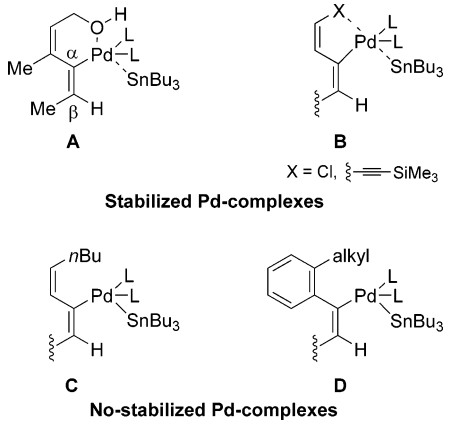
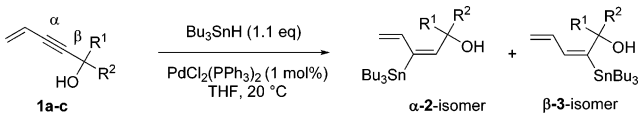
SCHEME 1. Proposed Complexes Leading to Major or Exclusive α-Isomer



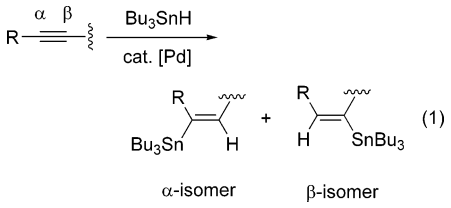
SCHEME 2. Hydrostannation of Enynol 1 as Baseline Regioselectivity Control



a $R^1 = R^2 = H$	(α/β = 19/81)	-[a]	57 %
b $R^1 = H$, $R^2 = Me$	(α/β = 80/20)	61 %	18 %
c $R^1 = R^2 = Me$	(α/β = 86/14)	62 %	12 %

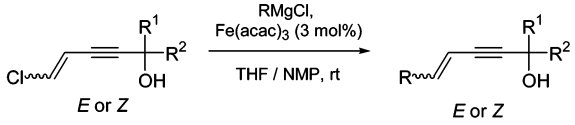
[a] α-**2a** could not be isolated as a pure product

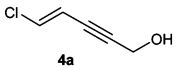
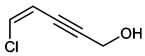
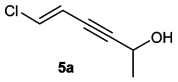
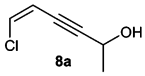
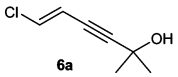
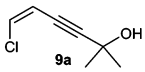
Se, Cl, O, N)[5a,8] delivered the Bu_3Sn group on the C_α atom (electronic factors).



In the cases of enynols, heteroatom-palladium chelation has previously been shown to direct the regiochemistry of palladium-mediated hydrostannation reaction (Scheme 1). Pancrazi suggested a stabilizing complex **A** between palladium and oxygen atom to explain the regioselectivity observed in favor of the α-isomer tin derivatives.[9] This chelation also could account our preliminary results obtained during hydrostannation of *Z*-chloroenynes[10] and *Z*-enediynes[11] (complex **B**) leading to a single α-isomer. We also showed through three examples that, relative to the *E*-enynes, Pd-mediated hydrostannation of *Z*-enynes[10] is highly regioselective for the α-stannanes even when the alkene substituent is nonchelating (e.g., *n*Bu, complex **C**). In addition, we reported that Pd-catalyzed hydrostannation of *ortho*-substituted arylalkyl as well as diaryl alkynes provided probably through complex **D** good to total selectivity for a single regioisomer while no stabilizing effect could occur between palladium and the *ortho* alkyl substituent (e.g., Me, *i*Pr, *ortho*-directing effect (ODE)).[12] Because of the structural similarities of complexes **C** and **D**, we believe that similar factors would be at the origin of this remarkable regioselectivity.

TABLE 1. $Fe(acac)_3$-Catalyzed Cross-Coupling Reactions of Chloroenynols 4a−9a with Alkyl Grignard Reagents



Entry	Chloroenynols	R	R^1/R^2	Yield[a] (%)	enynols
1		nC_4H_9	H/H	64	**4b**
2		cC_6H_{11}	"	73	**4c**
3	 **4a**	C_2H_5	"	60	**4d**
4		*i*Pr	"	52	**4e**
5		*t*Bu	"	30	**4f**
6		nC_4H_9	"	71	**7b**
7		cC_6H_{11}	"	79	**7c**
8	 **7a**	C_2H_5	"	63	**7d**
9		*i*Pr	"	62	**7e**
10		*t*Bu	"	0	**7f**
11	 **5a**	nC_4H_9	H/Me	95	**5b**
12		cC_6H_{11}	"	78	**5c**
13	 **8a**	nC_4H_9	"	71	**8b**
14		cC_6H_{11}	"	68	**8c**
15	 **6a**	nC_4H_9	Me/Me	72	**6b**
16		cC_6H_{11}	"	75	**6c**
17		nC_4H_9	"	66	**9b**
18		cC_6H_{11}	"	90	**9c**
19	 **9a**	C_2H_5	"	60	**9d**
20		*i*Pr	"	55	**9e**

[a] Unoptimized isolated yield.

Palladium-mediated hydrostannations of enynes have not been the subject of systematic investigations exploring the contributions of steric, electronic, and coordinative factors controlling this regioselectivity. Thus, we decided to carefully examine a series of Pd(0)-catalyzed hydrostannation of *E*- and *Z*-enynols variously substituted and to determine how the nature of substituents (alkyl, aryl, chlorine) on the alkene bond impact the regiochemical course of these reactions. The results of this study are now reported.

Results

In order to establish a baseline regioselectivity control, the palladium-catalyzed hydrostannation reaction was first examined with nonsubstituted primary, secondary, and tertiary enynols **1a−c** prepared according to Sonogashira coupling[13] (Scheme 2). The reaction was achieved using Bu_3SnH (1.1 eq)

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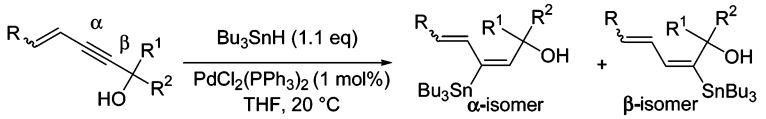
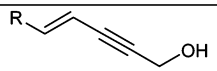
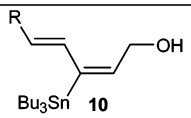
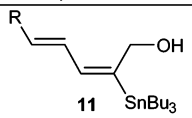
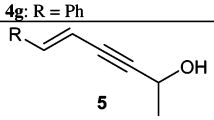
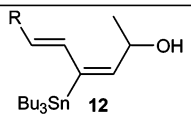
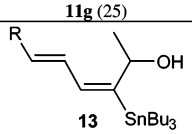
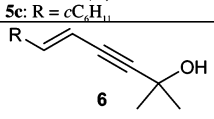
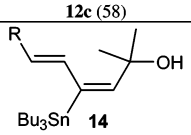
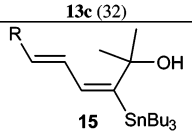
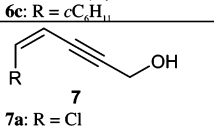
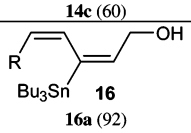
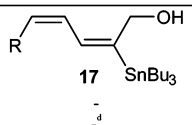
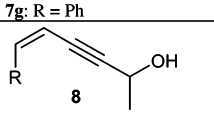
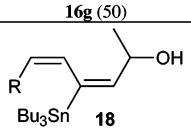
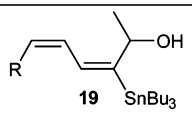
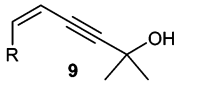
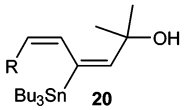
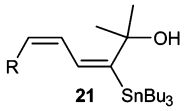
TABLE 2. Hydrostannation Selectivity of *E*- *and Z*-Enynol Series



Entry	Enynol	Ratio[a] α/β	Vinyl stannanes[b] (Isolated yield (%))	
			α-isomer	β-isomer
	 **4**		 **10**	 **11**
1	**4a**: R = Cl	74/26	**10a** (63)	**11a** (22)
2	**4b**: R = nC_4H_9	31/69	**10b** (20)	**11b** (45)
3	**4c**: R = cC_6H_{11}	35/65[c]	**10c** (26)	**11c** (54)
4	**4d**: R = Et	38/62	**10d** (29)	**11d** (48)
5	**4e**: R = *i*-Pr	30/70	-[d]	**11e** (47)
6	**4f**: R = *t*-Bu	32/68	**10f** (19)	**11f** (41)
7	**4g**: R = Ph	20/80	-	**11g** (25)
	 **5**		 **12**	 **13**
8	**5a**: R = Cl	100/0	**12a** (74)	-
9	**5b**: R = nC_4H_9	67/33	**12b** (33)	**13b** (16)
10	**5c**: R = cC_6H_{11}	65/35	**12c** (58)	**13c** (32)
	 **6**		 **14**	 **15**
11	**6a**: R = Cl	100/0	**14a** (94)	-
12	**6b**: R = nC_4H_9	72/28	**14b** (49)	-[d]
13	**6c**: R = cC_6H_{11}	73/27	**14c** (60)	-[d]
	 **7**		 **16**	 **17**
14	**7a**: R = Cl	100/0	**16a** (92)	-
15	**7b**: R = nC_4H_9	91/9	**16b** (83)	-[d]
16	**7c**: R = cC_6H_{11}	96/4[e]	**16c** (93)	-[d]
17	**7d**: R = Et	92/8	**16d** (73)	-[d]
18	**7e**: R = *i*-Pr	95/5	**16e** (85)	-[d]
19	**7g**: R = Ph	100/0	**16g** (50)	-
	 **8**		 **18**	 **19**
20	**8a**: R = Cl	100/0	**18a** (71)	-
21	**8b**: R = nC_4H_9	100/0	**18b** (75)	-
22	**8c**: R = cC_6H_{11}	100/0	**18c** (91)	-
	 **9**		 **20**	 **21**
23	**9a**: R = Cl	100/0	**20a** (89)	-
24	**9b**: R = nC_4H_9	100/0	**20b** (85)	-
25	**9c**: R = cC_6H_{11}	100/0	**20c** (91)	-
26	**9d**: R = Et	100/0	**20d** (67)	-
27	**9e**: R = *i*-Pr	100/0	**20e** (73)	-

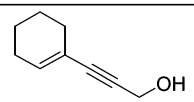
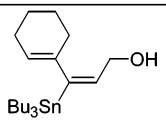
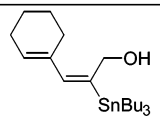
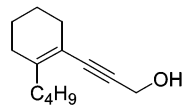
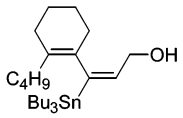
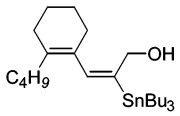
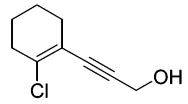
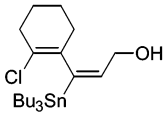
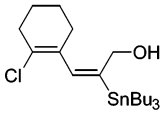
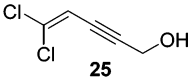
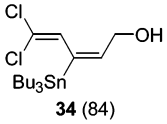
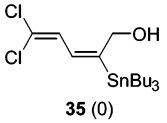
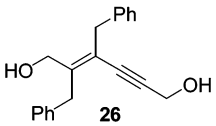
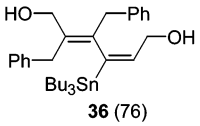
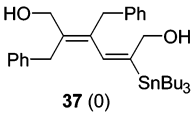
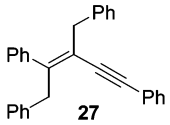
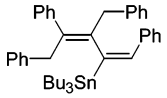
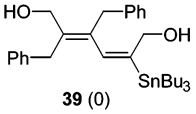
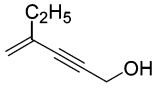
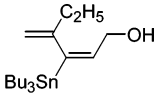
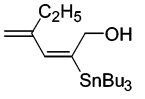
[a] Ratios were determined by ^{1}H NMR spectra on the crude reaction mixture. [b] Exclusive *syn*-addition of tin hydride was observed as evidenced by the vicinal vinylic Sn−H coupling constants in the ^{1}H NMR spectra. [c] When using $HSnPh_3$ as tin source instead of $HSnBu_3$, hydrostannation of **4c** lead to a mixture of α- and *β*-isomers (α/*β* = 44/56) in which only *β*-isomer (**42**) was isolated (54%). [d] *β*-Isomer has not been isolated with a satisfactory purity to be characterized. [e] With $HSnPh_3$ as tin source instead of $HSnBu_3$, hydrostannation of **7c** lead to a single α-isomer **43** in a 66% isolated yield.

in THF at room temperature in the presence of $PdCl_2(PPh_3)_2$ (1 mol %). Primary enynol **1a** afforded mainly the *β*-isomer **3a** (α/*β* 19:81). This regiochemical preference is reversed upon hydrostannation of bulkier propargyl alcohol analogues **1b** and **1c** leading, as expected,[6] principally to α-**2b** and α-**2c** regioisomers, respectively (Scheme 2).

To determine if this regioselectivity is influenced by the geometry of the double bond and the steric hindrance of its substituents, we have prepared a series of various substituted *E*- and *Z*-enynols **4**−**9**. To this end, coupling of primary, secondary, and tertiary propargyl alcohols with *E*- or *Z*-1,2-

(13) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

TABLE 3. Hydrostannation of Various Substituted Enynols 22−27

Entry	Enynol	Ratio[a] α/β	Vinyl stannanes[b] (Isolated yield (%))	
			α-isomer	β-isomer
1	 **22**	8/92	 **28** (2)	 **29** (25)
2	 **23**	90/10	 **30** (35)	 **31** (4)
3	 **24**	100/0	 **32** (80)	 **33** (0)
4	 **25**	100/0	 **34** (84)	 **35** (0)
5	 **26**	100/0	 **36** (76)	 **37** (0)
6	 **27**	100/0	 **38** (95)	 **39** (0)
7	 **28**	73/27	 **40** (51)	 **41** (19)

[a] Ratios were determined by ^{1}H NMR spectra on the crude reaction mixture. [b] Exclusive *syn*-addition of tin hydride was observed as evidenced by the vicinal vinylic Sn−H coupling constants in the ^{1}H NMR spectra.

dichloroethylene under palladium-copper-catalysis afforded the corresponding *E*- and *Z*-chloroenynols **4a**−**6a** and **7a**−**9a**, respectively.[14] Subsequent stereoselective alkylation of the chlorine atom on these free alcohols substrates was achieved with a variety of alkyl Grignard reagents in the presence of a catalytic amount of iron(III) salts as we previously reported (Table 1).[15]

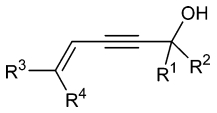
Under these conditions, good to moderate yields of geometrically pure substituted *E*- and *Z*-enynols **4b**−**f, 5b**,**c, 6b**,**c** and **7b**−**e**, **8b**,**c**, **9b**−**e** having various alkyl substituents on the double bond were obtained. Contrary to that of *E*-chloroenynol **4a**, the introduction of a *t*Bu substituent in the *Z*-isomer **7a** failed presumably for steric hindrance considerations (entries 5 and 10).

First, we examined the Pd-catalyzed hydrostannation of primary *E*-enynols **4b**−**f** under the above-described conditions (Table 2). The reaction provides a mixture of isomers **10b**−**f** and **11b**−**f** where the *β*-isomers predominated (α/*β* ∼ 33/67, entries 2−6), probably due to a coordination between Pd and the oxygen atom. We noticed that the presence of alkyl substituents on the double bond whatever their steric hindrance (primary, secondary, or tertiary alkyl) does not affect significantly this α/*β* ratio compared to the nonsubstituted enynol **1a** (baseline control). A similar result was obtained from *E*-enynol **4g** with a phenyl substituent on the double bond (entry 7). However, replacement of the substituents (alkyl or phenyl) by a chlorine atom reverses the α/ *β* ratio, and hydrostannation reaction of chloroenynol **4a** leads mainly to α-isomer **10a**, presumably due to electronic triple bond polarization induced by halide atom (entry 1). Predominant α-regioselectivity (α/*β* ∼ 70/30) was again obtained upon increasing steric bulk at the propargylic position even if the *E*-double bond was substituted by an alkyl group (entries 9, 10, 12, and 13), indicating that the methyl substituents on the propargylic position probably prevent oxygen−palladium chelation. Combination of steric and chlorine atom electronic effects in hindered chloroenynols **5a** and **6a** increased, as expected, the α-selectivity leading to the exclusive formation of **12a** and **14a**, respectively (entries 8 and 11). More interestingly, hydrostannation of

(14) (a) Alami, M.; Gueugnot, S.; Domingues, E.; Linstrumelle, G. *Tetrahedron* **1995**, *51*, 1209. (b) Alami, M.; Ferri, F.; Gaslain, Y. *Tetrahedron Lett.* **1996**, *37*, 57.

(15) Seck, M.; Franck, X.; Hocquemiller, R.; Figadère, B.; Peyrat, J.-F.; Provot, O.; Brion, J.-D.; Alami, M. *Tetrahedron Lett.* **2004**, *45*, 1881.

TABLE 4. ^{13}C NMR Data of C≡C in *Z*- and *E*-Enynols 4−9



				^{13}C shifts[a] (±0.05 ppm)		
entry	enynol	R^1/R^2	R^3/R^4	$\delta_{C\alpha}$	$\delta_{C\beta}$	$\Delta\delta_{C\beta-C\alpha}$
1	**4a**	H/H	Cl/H	80.7	89.8	9.1
2	**7a**	H/H	H/Cl	79.5	95.6	16.1
3	**4b**	H/H	nC$_4$H$_9$/H	84.6	85.6	1.0
4	**7b**	H/H	H/nC$_4$H$_9$	82.6[b]	91.1[b]	8.6
5	**4c**	H/H	cC$_6$H$_{11}$/H	84.8	85.8	1.0
6	**7c**	H/H	H/cC$_6$H$_{11}$	82.6	90.8	8.2
7	**4d**	H/H	Et/H	84.6	85.7	1.1
8	**7d**	H/H	H/Et	82.3	91.3	9.0
9	**4e**	H/H	iPr/H	84.6	85.8	1.2
10	**7e**	H/H	H/iPr	82.3	91.0	8.7
11	**4g**	H/H	Ph/H	84.7	89.4	4.7
12	**7g**	H/H	H/Ph	84.1	93.8	9.7
13	**5a**	H/Me	Cl/H	79.1	93.6	14.5
14	**8a**	H/Me	H/Cl	77.9	99.3	21.4
15	**5b**	H/Me	nC$_4$H$_9$/H	82.9	89.3	6.4
16	**8b**	H/Me	H/nC$_4$H$_9$	80.9	95.0	14.1
17	**5c**	H/Me	cC$_6$H$_{11}$/H	83.0	89.6	6.6
18	**8c**	H/Me	H/cC$_6$H$_{11}$	80.9	94.6	13.7
19	**6a**	Me/Me	Cl/H	77.2	96.4	19.2
20	**9a**	Me/Me	H/Cl	76.1	102.1	26.0
21	**6b**	Me/Me	nC$_4$H$_9$/H	80.9	92.2	11.3
22	**9b**	Me/Me	H/nC$_4$H$_9$	79.0	97.8	18.8
23	**6c**	Me/Me	cC$_6$H$_{11}$/H	81.1	92.4	11.3
24	**9c**	Me/Me	H/cC$_6$H$_{11}$	79.1	97.6	18.5

[a] Shifts are relative to external $CDCl_3$. The assignment of the ^{13}C NMR chemical shifts of the triple bond was established by HMBC and HSQC NMR spectroscopy. [b] No change of the ^{13}C NMR data was observed when adding equimolar of $PdCl_2(PPh_3)_2$ to enynol **7b**.

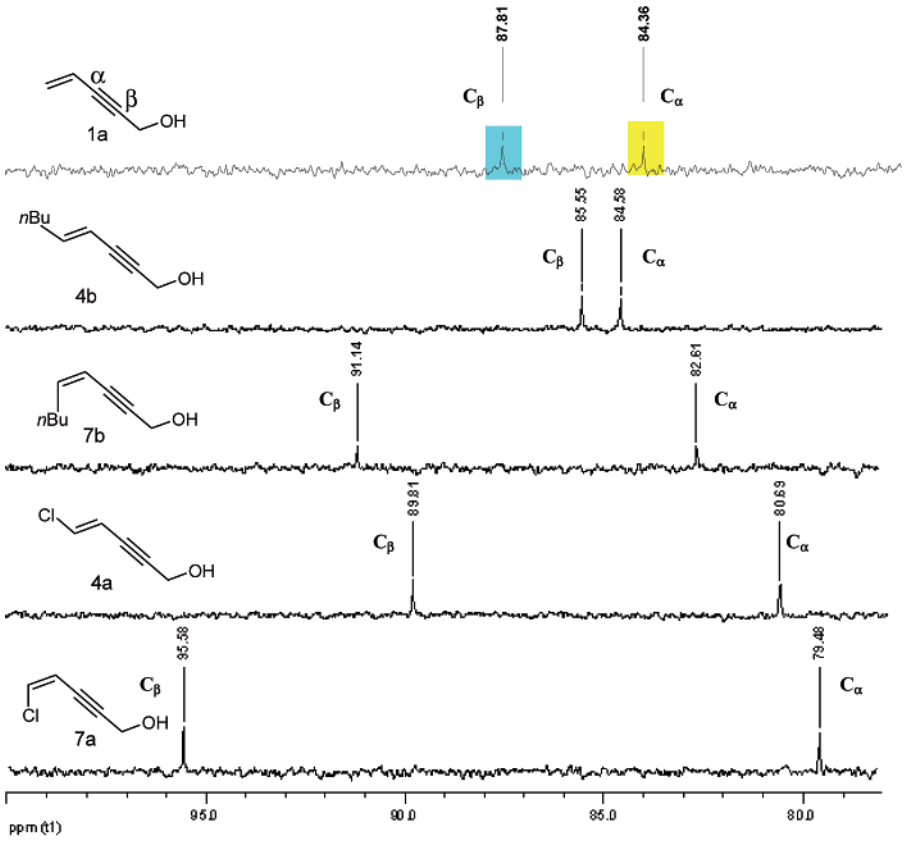
homologous *Z*-enynols **7**−**9** afforded mainly to exclusively the α-regioisomers. Thus, (*Z*)-alkyl primary enynols **7b**−**e** lead to their corresponding α-vinyl stannanes **16b**−**e** together with a small amounts (<10%) of *β*-isomers (entries 15−18). Total selectivity toward the formation of α-isomers was observed for chlorine- and phenyl-substituted *Z*-enynols **7a** and **7g** (entries 14 and 19). Remarkably, *Z*-secondary or tertiary enynols **8** and **9** again exhibited total α-selectivity whatever the nature of the double bond substituent (entries 20−27).

In order to evaluate the controlling factors in the regioselectivity of the tin hydride addition, we have studied the reaction with primary enynols **22**−**27** where the double bond was either tri-, tetra-, or 4,4-disubtituted (Table 3). For chelating considerations, hydrostannation of **22** lead, mainly to *β*-isomer **29** (α/*β* = 8/92, entry 1) whereas enynol **23** with a tetrasubstituted double bond reverses the α/*β* ratio (α/*β* = 90/10, entry 2). When replacing the alkyl substituent on the cyclohexene by a chlorine atom, total α-selectivity was observed (entry 3). As evidence, hydrostannation of *gem*-dichloroenynol **25** gave the unique α-isomer **34** (entry 4).

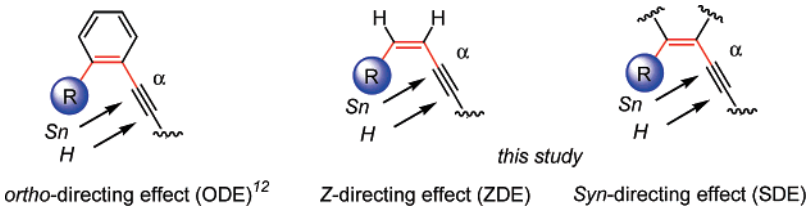
This regioselectivity control has been successfully extended to enynol **26**[16] having a tetrasubstituted double bond and to enyne **27** with no propargylic alcohol function (entries 5 and 6). Interestingly, 4-ethylenynol **28** (entry 7) follows this trend in α-regioselectivity by comparison with hydrostannation of **1a** (baseline control, Scheme 2), indicating that the C-4 substitution may be also an important controlling factor in the regioselectivity of addition.

The excellent regioselectivity of the palladium-catalyzed hydrostannation of *Z*-enynols **7**−**9** compared to their *E*-homologous **4**−**6** could not be only explained by coordination

SCHEME 3. Experimental ^{13}C NMR Data of the Carbon−Carbon Triple Bond in Enynols 1a, 4a,b, and 7a,b



SCHEME 4. R Substituent-Directed Tin Hydride Addition



(alkyl groups induce high selectivity) or by steric effects (hindered alkyl groups are rather in favor of α-isomer).

The factors governing this remarkable regioselectivity would be close to those observed in the hydrostannation of *ortho*-substituted arylalkynes (ODE).[12a,b] We have observed in these later derivatives that *ortho*-substituents induced dramatic variations in ^{13}C NMR data of the triple bond. On the basis of this observation, we decided to carefully examine the C_α and C_β chemical shifts of *E*- and *Z*-enynol derivatives (Table 4).

^{13}C NMR data depicted in Scheme 3 showed a 5.6 ppm downfield shift in the C_β and a 2.0 ppm upfield shift in the C_α of the triple bond for *Z*-alkylenynol **7b** compared to the corresponding *E*-isomer **4b**. Similarly, the signal arising from the C_β atom is 5.8 ppm downfield and the signal from the C_α atom is 1.2 ppm upfield when *E*- and *Z*-chloroenynol **4a** and **7a** were compared, respectively (Scheme 3). As shown in Table 4, a similar situation was also noted when comparing various *E*- and *Z*-enynols having an alkyl or an aryl substituent on the double bond. In all cases studied, we noticed that switching from *E*- to *Z*-enynols isomers increases the difference in the ^{13}C NMR chemical shift of the signals arising from the $\Delta\delta_{C\beta-C\alpha}$ atom from 5.0 to 7.9 ppm (entries 11, 12 and 7, 8). To our knowledge, such observation is unprecedented.

According to these ^{13}C NMR data, it seems that the *Z*-substituent which induced electronic polarization of the triple bond may be one of the factors[17] at the origin of the observed regioselectivity. Although at the moment, we did not succeed in correlating the α/β ratio observed with the triple bond polarization, these results unambiguously support that the presence of a substituent on the *Z*-double bond, whatever its nature, dictates the sense of the regioselectivity (*Z*-directing effect (ZDE)). As depicted in Scheme 4, this trend in α-regioselectivity was also observed with substrates having R groups and alkyne substituents on the same side of the double bond whatever its substitution degrees (*syn*-directing effect (SDE)).

Conclusion

In conclusion, we have succeeded in providing some evidence for the *Z*- or *syn*-directing effect (ZDE or SDE) of the double bond in the palladium-catalyzed tributyltin hydride addition on various substituted enynols. High to excellent α-regioselectivity is observed for *Z*-enynols bearing nonchelating alkyl substituents. Combining either steric effects (secondary and tertiary enynols) with ZDE or SDE leads to exclusive α-isomer as observed with *Z*-arylenynol or *Z*-chloroenynol substrates. Although, ^{13}C NMR data showed a marked electronic polarization of the alkyne bond when *Z*- and *E*-enynols were compared, the exact origin of this *syn*- or *Z*-induced high regioselectivity remains unclear but would be similar to those observed in the *ortho*-substituent regiocontrol concept.[12,18]

This study shows that it is possible to predict the major or exclusive α-isomer formation when a R substituent (regardless of its nature) and the alkyne are on the same side of the double bond. This "ZDE/SDE" demonstrated herein should find many applications for the synthesis of more elaborated unsaturated molecules.

Experimental Section

General Procedure for the Hydrostannation of Enynes.[12b] Tributyltin hydride or triphenyltin hydride (13 mmol) was added dropwise at room temperature to a solution of $PdCl_2(PPh_3)_2$ (0.1 mmol) and enyne (10 mmol) in THF (15 mL). The dark brown reaction mixture was stirred for 30 min, and more tributyltin hydride (2 mmol) was added to the crude mixture to complete the hydrostannation reaction. After stirring for an additional 30 min, the solution was concentrated in vacuo. Purification by flash chromatography on silica gel gave the desirated products.

Hydrostannation of **5b** with tributyltin hydride:

(3*E*,5*E*)-4-Tributylstannanyl-deca-3,5-dien-2-ol 12b (33%); R_f 0.17 (Et_2O/cyclohexane, 10/90, SiO_2); IR (neat): 3330, 2956, 2924, 2871, 2854, 1633, 1463, 1418, 1376, 1340, 1291, 1101, 1069, 955, 862, 768, 742, 688 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$): δ 0.75−0.95 (m, 18H), 1.05 (d, 3H, J = 7.0 Hz), 1.20−1.50 (m, 17H), 1.70−1.90 (m, 2H), 4.65 (m, 1H), 5.30 (m, 2H), 6.40 (d, 1H, J = 6.4 Hz, J_{H-Sn} = 64.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.0 (CH), 142.7 (C), 136.1 (CH), 130.1 (CH), 64.4 (CH), 32.8 (CH_2), 31.7 (CH_2), 29.1 ($3CH_2$), 27.3 ($3CH_2$), 23.4 (CH_3), 22.2 (CH_2), 13.9 (CH_3), 13.7 ($3CH_3$), 10.1 ($3CH_2$); Anal. Calcd for $C_{22}H_{44}OSn$ (443.29): C 59.61, H 10.00, found C 59.61, H 10.11.

(3*E*,5*Z*)-3-Tributylstannanyl-deca-3,5-dien-2-ol 13b (16%); R_f 0.49 (Et_2O/cyclohexane, 10/90, SiO_2); IR (neat): 3420, 2956, 2923, 2871, 2854, 1637, 1576, 1463, 1419, 1340, 1291, 1247, 1181, 1149, 1070, 1049, 964, 940, 865, 768, 742, 665 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.70−0.95 (m, 18H), 1.15 (d, 3H, J = 6.4 Hz), 1.20−1.50 (m, 17H), 2.05 (m, 2H), 4.95 (m, 1H), 5.60 (m, 1H), 5.95 (dd, 1H, J = 10.7 Hz, J = 1.5 Hz, J_{H-Sn} = 64.0 Hz), 6.70 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1 (C), 136.7 (CH), 136.1 (CH), 125.6 (CH), 69.0 (CH), 32.5 (CH_2), 31.5 (CH_2), 29.2 ($3CH_2$), 27.5 ($3CH_2$), 24.2 (CH_3), 22.3 (CH_2), 14.0 (CH_3), 13.7 ($3CH_3$), 10.5 ($3CH_2$);. Anal. Calcd for $C_{22}H_{44}OSn$ (443.29): C 59.61, H 10.00, found C 59.73, H 10.25.

Hydrostannation of **8b** with tributyltin hydride:

(3*E*,5*Z*)-4-Tributylstannanyl-deca-3,5-dien-2-ol 18b (75%); R_f 0.37 (Et_2O/cyclohexane, 10/90, SiO_2); IR (neat): 3315, 2956, 2924, 2872, 2854, 1463, 1417, 1377, 1339, 1291, 1142, 1054, 960, 927, 864, 782, 688, 662 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80−1.00 (m, 18H), 1.15 (d, 3H, J = 6.3 Hz), 1.20−1.65 (m, 15H), 1.95 (m, 2H), 4.50 (quint, 1H, J = 6.4 Hz), 5.25 (m, 1H), 5.60 (m, 1H, J_{H-Sn} = 65.6 Hz), 6.00 (dq, 1H, J = 11.4 Hz, J = 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9 (CH), 142.8 (C), 130.1 (CH), 127.7 (CH), 65.9 (CH), 31.8 (CH_2), 29.0 ($3CH_2$), 28.5 (CH_2), 27.4

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($3CH_2$), 22.6 (CH_2, CH_3), 14.0 (CH_3), 13.7 ($3CH_3$), 9.8 ($3CH_2$); Anal. Calcd for $C_{22}H_{44}OSn$ (443.29): C 59.61, H 10.00, found C 59.52, H 9.97.

Hydrostannation of **4c** with triphenyltin hydride:

(2*E*,4*E*)-5-Cyclohexyl-2-triphenylstannanyl-penta-2,4-dien-1-ol 42 (54%); mp: 133 °C; R_f 0.29 (EtOAc/cyclohexane, 5/95, SiO_2); IR (neat): 3566, 3063, 3014, 2922, 2849, 1636, 1579, 1480, 1447, 1427, 1332, 1301, 1259, 1190, 1074, 1030, 997, 973, 908, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.05−1.45 (m, 6H), 1.65−1.85 (m, 4H), 1.90 (t, 1H, J = 5.3 Hz), 2.10 (m, 1H), 4.70 (m, 2H), 5.70 (dd, 1H, J = 14.7 Hz, J = 7.1 Hz), 6.20−6.45 (m, 2H), 7.35−7.50 (m, 10H), 7.60−7.70 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.6 (C), 143.6 (CH), 140.2 (CH), 139.5 (3C), 137.5 (6CH), 128.8 (3CH), 128.2 (6CH), 123.3 (CH), 63.5 (CH_2), 41.1 (CH), 32.8 ($2CH_2$), 27.0 (CH_2), 26.0 ($2CH_2$); Anal. Calcd for $C_{29}H_{32}OSn$ (515.27): C 67.60, H 6.26, found C 67.44, H 6.20.

Hydrostannation of **7c** with triphenyltin hydride:

(2*E*,4*Z*)-5-Cyclohexyl-3-triphenylstannanyl-penta-2,4-dien-1-ol 43 (66%); R_f 0.55 (Et_2O/cyclohexane, 5/95, SiO_2); IR (neat): 3334, 3064, 2989, 2922, 2849, 1578, 1480, 1447, 1428, 1333, 1301, 1259, 1190, 1074, 1022, 997, 909, 889 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.00−1.30 (m, 6H), 1.40−1.50 (m, 2H), 1.55−1.65 (m, 2H), 1.90 (br s, 1H), 2.15−2.30 (m, 1H), 4.40 (m, 2H), 5.35 (t, 1H, J = 11.1 Hz), 6.20 (m, 2H), 7.40−7.60 (m, 10H), 7.70−7.90 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.1 (CH), 140.4 (C), 139.3 (C), 138.3 (2C), 137.9 (2CH), 137.6 (4CH), 136.7 (CH), 129.2 ($3CH_2$), 128.9 ($2CH_2$), 128.7 ($4CH_2$), 127.1 (CH), 61.5 (CH_2), 37.8 (CH), 32.8 ($2CH_2$), 26.1 (CH_2), 25.9 ($2CH_2$); Anal. Calcd for $C_{29}H_{32}OSn$ (515.27): C 67.60, H 6.26, found C 67.29, H 6.15.

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Supporting Information Available: Experimental details for preparation of starting materials, full characterization data, and copies of ^1H and ^{13}C NMR spectra for all new compounds and enynes. This material is available free of charge via the Internet at http://pubs.acs.org.

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