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Wurtz-Type Reductive Coupling Reaction of Allyl Bromides and Haloorganotins in Cosolvent/$H_2O(NH_4Cl)$/Zn Media as a Route to Allylstannanes and Hexaaryldistannanes

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Twenty-one allylstannanes have been prepared *via* a simple Wurtz-type coupling reaction of allyl bromides and R_3SnX compounds (R = Me, Et, Pr, Bu, Ph; X = Cl, I, OH), Bu_2SnCl_2, and $(Bu_2SnCl)_2O$ in cosolvent/H_2O (NH_4Cl saturated) media under the mediation of zinc powder. Also R_3SnSnR_3 compounds (R = Ph, *p*- and *m*-Tol) have been prepared *via* coupling of triaryltin chlorides. The stereochemical course of the reaction between R_3SnCl and $(C_4H_7)Br$ (C_4H_7 = α-methylallyl, *trans*- and *cis*-crotyl) has been extensively studied. Two distinct reactions are involved in the overall process: (i) the coupling reaction, which gives rise stereoselectively to the sole $R_3SnCH(CH_3)CH{=}CH_2$ (α-isomer), and (ii) the subsequent isomerization of the α-isomer furnishing mixtures of (α, *trans*, *cis*)-isomers. The occurrence of reaction ii depends upon the nature either of the R group or the employed cosolvent. In cyclohexane, the α-isomer is exclusively obtained with R = Bu, while with R = Me, Et, and Pr it is found as a major component in the ternary isomeric mixture. In tetrahydrofuran, 2-propanol, acetonitrile, and pyridine, the isomerization occurs to an extent which depends on the polarity and the coordinating ability of the cosolvent itself. The observed stereoselection has been hypothesized to occur through one-electron transfer from the zinc metal to the $(C_4H_7)Br$ to form stereoselectively an adsorbed $CH_2{=}CHCH(CH_3)Br^{\bullet -}Zn^{\bullet +}$ radical ion which is trapped by the R_3SnCl reactant to form the α-isomer. Similarly, ditin compounds are thought to be formed by interaction of $R_3SnCl^{\bullet -}Zn^{\bullet +}$ radical ions with R_3SnCl molecules.

Introduction

The deliberate use of water as a component either in homogeneous or heterogeneous systems for C–C bond-forming reactions has been receiving increasing attention in the last years and is documented by the considerable work on the subject.[1-10] Among its effects, the use of water or water–cosolvent media, instead of hydrocarbons, increases the reaction rate[1,4] and promotes different stereochemical reaction courses.[7] Owing to the scant presence of waste organic materials or their total absence, water as a component allows in many cases a one-pot procedure and has great environmental advantages.

Organometallic reactants have been examined for the following C–C bond-forming reactions in the presence of water: (i) selective tin and zinc mediated allylations of carbonyl compounds,[2] (ii) preparation of homoallylic alcohols by allylstannation of carbonyl compounds,[3] (iii) aldol reaction of silyl enol ethers with carbonyl compounds,[7] (iv) amino desilylation–cyclization processes promoted by allyltrimethylsilane with iminium salts,[8,9] and (v) aminomethano destannylations of allylstannanes and immonium salts.[10]

So far, these reactions are restricted solely to the use of metal derivatives bearing allyl or allyl-like groups. The particular behavior of these allyl derivatives can be explained by considering their higher reaction rates with appropriate electrophiles, as compared to those in reactions leading to allyl–metal bond cleavage by protonolysis.

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(1) For recent reviews, see: (a) Multzer, J.; Altenbach, H. J.; Braun, M.; Krohn, K.; Reissig, H. U. In *Organic Synthesis Highlights* VCH; Weinheim, Germany, 1991; p 71. (b) Grieco, P. A. *Aldrichim. Acta* **1991**, *24*, 59.

(2) For allylation *via* Barbier reaction, see: (a) Petrier, C.; Luche, J. L. *J. Org. Chem.* **1985**, *50*, 910. (b) Petrier, C.; Einhorn, J.; Luche, J. L. *Tetrahedron Lett.* **1985**, *26*, 1449. (c) Petrier, C.; Dupuy, C.; Luche, J. L. *Tetrahedron Lett.* **1986**, *27*, 3149. (d) Einhorn, J.; Luche, J. L. *J. Organomet. Chem.* **1987**, *322*, 177. (e) Luche, J. L.; Allavena, C. *Tetrahedron Lett.* **1988**, *29*, 5369. (f) Luche, J. L.; Allavena, C.; Petrier, C.; Dupuy, C. *Tetrahedron Lett.* **1988**, *29*, 5373. (g) Nokami, J.; Otera, J.; Sudo, T.; Okawara, R. *Organometallics* **1983**, *2*, 191. (h) Mandai, T.; Nokami, T.; Yoshinoga, Y.; Yano, T.; Otera, J. *J. Org. Chem.* **1984**, *49*, 172.

(3) For C–C bond formation using allyl-, allenyl-, and propargyltin halides, see: (a) Boaretto, A.; Marton, D.; Tagliavini, G.; Gambaro, A. *J. Organomet. Chem.* **1985**, *286*, 9. (b) Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1985**, *297*, 149. (c) Furlani, D.; Marton, D.; Tagliavini, G.; Zordan, M. *J. Organomet. Chem.* **1988**, *341*, 345. (d) Marton, D.; Tagliavini, G.; Vanzan, N. *J. Organomet. Chem.* **1989**, *376*, 269.

(4) For Diels–Alder reactions in water, see: (a) Rideout, D. C.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 7816. (b) Breslow, R.; Maitra, U.; Rideout, D. C. *Tetrahedron Lett.* **1983**, *24*, 1901. (c) Breslow, R.; Maitra, U. *Tetrahedron Lett.* **1984**, *25*, 1239. (d) Breslow, R.; Guo, T. *J. Am. Chem. Soc.* **1988**, *110*, 5613. (e) Grieco, P. A.; Garner, P.; He, Z. *Tetrahedron Lett.* **1983**, *24*, 1897. (f) Braun, R.; Schuster, F.; Sauer, J. *Tetrahedron Lett.* **1986**, *27*, 1285. (g) Grieco, P. A.; Yoshida, K.; Garner, P. *J. Org. Chem.* **1983**, *48*, 3137.

(5) For a Reformatsky-type reaction, see: Mattes, H.; Benezra, C. *Tetrahedron Lett.* **1985**, *26*, 5697.

(6) For synthesis of 5-allyl-substituted γ-lactones, see: Kunz, T.; Reissig, H. U. *Liebigs Ann. Chem.* **1989**, 891.

(7) Lubineau, A.; Meyer, E. *Tetrahedron* **1988**, *44*, 6065.

(8) Larsen, S. D.; Grieco, P. A.; Fobare, W. F. *J. Am. Chem. Soc.* **1986**, *108*, 3512.

(9) Grieco, P. A.; Fobare, W. F. *Tetrahedron Lett.* **1986**, *27*, 5067.

(10) Grieco, P. A.; Bahsas, A. *J. Org. Chem.* **1987**, *52*, 1378.

(11) Tagliavini, G.; Boaretto, A.; Marton, D.; Furlani, D. The Fifth International Conference on the Organometallic and Coordination Chemistry of Ge, Sn, and Pb, Padua, 1986; p 58.

(12) Carofiglio, T.; Marton, D.; Tagliavini, G. *Organometallics* **1992**, *11*, 2961.

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Actually, the kinetic stability of the allyl–tin bond in the presence of water has been extensively proved.[3] The main reaction of allyldibutyltin chloride, in a stirred heterogeneous aqueous system, is the disproportionation to diallyldibutyltin and dibutyltin dichloride,[11] *i.e.*, the formation of a new allyl–tin bond.

On the basis of these findings, we could recently synthesize some allylstannanes *via* a simple and direct procedure.[12] Tributyl- and dibutylallylstannanes have been obtained in a one-pot synthesis in the presence of air and water. A Wurtz-type reductive coupling reaction mediated by zinc powder, as depicted in eq 1, forms the basis of this novel preparative method.

$$n\mathrm{RBr} + \mathrm{Bu}_{4-n}\mathrm{SnCl}_n \xrightarrow[\text{room temp, stirring}]{\mathrm{THF/H_2O(NH_4Cl)/Zn}} \mathrm{Bu}_{4-n}\mathrm{SnR}_n \qquad (1)$$

$$\mathrm{R} = \text{allyl- or allyl-like group; } n = 1, 2$$

For a deeper insight into this methodology, we synthesized mixed allylorganostannanes of the type R_3SnAll and R_2SnAll_2 (R = Me, Et, Pr, Bu, and Ph; All = allyl- or allyl-like group). We turned particular attention to the study of the stereochemical courses in reactions between R_3SnCl substrates and $(C_4H_7)Br$ (C_4H_7 = α-methylallyl, *trans*- and *cis*-crotyl) leading to $R_3Sn(C_4H_7)$, on varying the R group, the organic cosolvent, and the salt. Furthermore, in the course of this research we ascertained the possibility of synthesizing hexaaryldistannanes *via* this same procedure.

Results and Discussion

Preparation of Butylallylstannanes. Reactions between Bu_3SnCl, Bu_2SnCl_2, and $(Bu_2SnCl)_2O$ substrates and various allyl bromides have been performed using a three-phase cosolvent/H_2O(NH_4Cl saturated)/Zn medium. Table 1 summarizes the experimental data and results of the prepared butylallylstannanes **1**–**10**. The reactions are characterized by high exothermicity and are completed in a very short time (10–15 min).

Data of entries 1–5 show that this Wurtz-type coupling reaction can be carried out using as cosolvent dioxane, cyclohexane, and toluene instead of tetrahydrofuran. The yields of the pure isolated products are high (69–87%) for the coupling of allyl bromide with mono- and dibutyltin chlorides (entries 1–6). A lower yield (50%) is observed when Bu_2SnCl_2 is replaced by $(Bu_2SnCl)_2O$ (compare entry 8 with entry 6), or when equimolar amounts of reactants are used (compare entry 7 with entry 6, where a large excess of allyl bromide is involved). It is to be noted that the run of entry 7 is an attempt to prepare in a one-step procedure $Bu_2(CH_2{=}CHCH_2)SnCl$ (**3**), which is known as a powerful allylating agent.[13] In this case, a mixture of the expected compound **3** together with dibutyldiallyltin was recovered.

Data about the preparation of cycloallyltin derivatives **4**–**6**, that is cyclopent-, cyclohex-, and cyclohepten-2-enyltributyltin, are given in entries 9–11, respectively. The yields are here lower, higher however than those of the procedures used so far.[14] In these cases, in addition to the

Table 1. Preparation of Allylstannanes from Butyltin Derivatives in a Cosolvent/$H_2O(NH_4Cl)$/Zn Medium

entry no.	reagent: organotin	reagent: amt, g (mmol)	reagent: organic bromide	reagent: amt, g (mmol)	reagent: Zr[a] amt, g (mmol)	cosolvent	amt of CS[b]/H_2O, mL	product	product amt, g (yield, %)
1	Bu_3SnCl	20 (61.4)	$CH_2{=}CHCH_2Br$	22.3 (184.2)	12.0 (184.2)	THF	50/50	$Bu_3SnCH_2CH{=}CH_2$ (**1**)	14.0 (69)
2	Bu_3SnCl	20 (61.4)	$CH_2{=}CHCH_2Br$	22.3 (184.2)	12.0 (184.2)	dioxane	50/50	**1**	13.2 (65)
3	Bu_3SnCl	20 (61.4)	$CH_2{=}CHCH_2Br$	22.3 (184.2)	12.0 (184.2)	cyclohexane	50/50	**1**	17.7 (87)
4	Bu_3SnCl	20 (61.4)	$CH_2{=}CHCH_2Br$	22.3 (184.2)	12.0 (184.2)	toluene	50/50	**1**	16.1 (79)
5	Bu_2SnCl_2	20 (65.8)	$CH_2{=}CHCH_2Br$	47.8 (394.8)	25.8 (394.8)	THF	100/100	$Eu_2Sn(CH_2CH{=}CH_2)_2$ (**2**)	16.6 (80)
6	Bu_2SnCl_2	30 (98.7)	$CH_2{=}CHCH_2Br$	71.7 (592.4)	38.7 (592.4)	cyclohexane	100/100	**2**	25.2 (81)
7	Bu_2SnCl_2	10 (33.0)	$CH_2{=}CHCH_2Br$	4.4 (36.2)	4.3 (65.8)	THF	100/100	**2** + $Bu_2Sn(CH_2CH{=}CH_2)Cl$ (**3**)[c]	4.4 (42)
8	$[Bu_2SnCl]_2O$	8.3 (15.0)	$CH_2{=}CHCH_2Br$	14.5 (120.0)	7.8 (120.0)	THF	30/50	**2**	4.7 (50)
9	Bu_3SnCl	8.9 (27.2)	$CH_2CH_2CH{=}CHCHBr$	8.0 (54.4)	3.6 (54.4)	THF	25/50	$Bu_3SnCHCH{=}CHCH_2CH_2$ (**4**)	3.9 (40)
10	Bu_3SnCl	10 (30.7)	$CH_2CH_2CH_2CH{=}CHCHBr$	9.9 (61.5)	4.0 (61.5)	THF	25/50	$Bu_3SnCHCH{=}CHCH_2CH_2CH_2$ (**5**)	6.7 (59)
11	Bu_3SnCl	10 (30.7)	$CH_2CH_2CH_2CH_2CH{=}CHCHBr$	10.8 (61.5)	4.0 (61.5)	THF	25/50	$Bu_3SnCHCH{=}CHC_2HCH_2CH_2CH_2$ (**6**)	6.1 (52)
12	Bu_3SnCl	10 (30.7)	$CH_2{=}C(CH_3)CH_2Br$	8.3 (61.5)	4.0 (61.5)	THF	25/50	$Bu_3SnCH_2C(CH_3){=}CH_2$ (**7**)	8.8 (83)
13	Bu_3SnCl	20 (61.4)	$CH_3CH{=}CHCH_2Br$[d]	16.7 (122.8)	8.0 (122.8)	THF	100/100	$Bu_3Sn(C_4H_7)$[e] (**8**)	8.5 (80)
14	Bu_3SnCl	10 (30.7)	$(CH_3)_2C{=}CHCH_2Br$	8.3 (61.5)	4.0 (61.5)	THF	25/50	$Bu_3Sn(C_5H_9)$[f] (**9**)	8.7 (82)
15	Bu_3SnCl	10 (30.7)	$PhCH{=}CHCH_2Br$	12.5 (61.5)	4.0 (61.5)	THF	25/50	$Bu_3SnCH_2CH{=}CHPh$[g] (**10**)	8.1 (67)

[a] Zinc powder, 325 mesh (from Aldrich). [b] CS = cosolvent. [c] In this case a mixture of $Bu_2Sn(CH_2CH{=}CH_2)_2$ (**2**) and $Bu_2Sn(CH_2CH{=}CH_2)Cl$ (**3**) is recovered with a ratio **2**:**3** = 50:50. [d] Crotyl bromide (from Aldrich) consists of a mixture of α-methylallyl (15%) and *trans*- (76)%) and *cis*-crotyl (9%). [e] Isomeric composition of the C_4H_7 group: α:*trans*:*cis* = 70:11:19. [f] Compound **9** is isolated as a mixture of two isomers: 3-methyl-1-buten-3-yltributyltin (**9a**) and 2-methyl-2-butenyltributyltin (**9b**) with a ratio **9a**:**9b** = 40:60. [g] Completely recovered in the *trans* form.

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(13) Tagliavini, G. *Rev. Silicon, Germanium, Tin and Lead Compd.* 1985, *8*, 237.

(14) (a) Ganis, P.; Valle, G.; Tagliavini, G.; Kitching, W.; Penman, K. G.; Jones, M. A. *J. Organomet. Chem.* 1988, *349*, 57. (b) Kitching, W.; Penman, G. P.; Valle, G.; Tagliavini, G.; Ganis, P. *Organometallics* 1989, *8*, 785.

Table 2. Cosolvent Effect on the Stereochemical Course of the Reaction[a]

$$Bu_3SnCl + (C_4H_7)Br \xrightarrow{\text{cosolvent}/H_2O(NH_4Cl)/Zn} Bu_3Sn(C_4H_7)$$

entry no.	cosolvent	$Bu_3Sn(C_4H_7)$ (**8**) yield, %	isomeric composition,[b] % after 15 min[b] **8a**	 **8b**	 **8c**	 isolated mixture[c] **8a**	 **8b**	 **8c**	degree of isomerization	*trans*:*cis* ratio
16	cyclohexane	85	100	0	0	100	0	0	0	
17	toluene	74	78	8	14	80	8	12	0.20	40:60
18	THF	83	75	5	20	70	11	19	0.30	37:63
19	2-propanol	81	46	16	38	45	20	35	0.55	36:64
20	acetonitrile	78	*d*	*d*	*d*	35	26	39	0.65	40:60
21	pyridine	58	8[e]	36[e]	56[e]	10	36	54	0.90	40:60

[a] All of the runs have been performed with the following amount of components: Bu_3SnCl, 10 g (30.7 mmol); $(C_4H_7)Br$, 8.35 g (61.5 mmol); Zn, 4 g (61.5 mmol); cosolvent, 25 mL; H_2O(NH_4Cl saturated), 50 mL. [b] The quoted figures represent the percentages of the three isomers $Bu_3SnCH(CH_3)CH{=}CH_2$ (**8a**), *trans*-$Bu_3SnCH_2CH{=}CHCH_3$ (**8b**), and *cis*-$Bu_3SnCH_2CH{=}CHCH_3$ (**8c**) after 15 min, a time necessary for the completion of the reaction. [c] The quoted figures represent the percentages of the three isomers of the crude product isolated after extraction with *n*-pentane, removing the solvent without any heating. [d] Not determined. [e] In this case the pyridine allows the formation of a nearly homogeneous system. The quoted figures are roughly estimated because of the difficulty of having a neat sample.

reaction leading to the desidered compounds, side reactions occur such as reduction and coupling of the cycloallyl bromides, together with the formation of hexabutyldistannane.

Methyl-substituted allyl bromides (entries 12–14) give rise once more to very good results with yields of the pure isolated products between 80 and 83%. Entries 13 and 14 are of particular interest for the stereochemical course of the reaction since isomeric mixtures of $Bu_3Sn(C_4H_7)$ (**8**) (C_4H_7 stands for α-methylallyl and *trans*- and *cis*-crotyl) and $Bu_3Sn(C_5H_9)$ (**9**) (C_5H_9 stands for α-dimethyl- and γ-dimethylallyl) are recovered, respectively. Product **8** represents a three-component isomeric mixture, the composition of which (α:*trans*:*cis* = 70:11:19) has no relation with that of the starting $(C_4H_7)Br$ (α:*trans*:*cis* = 15:76:9). Similarly, the coupling reaction performed using the sole prenyl bromide leads to an isomeric mixture of $Bu_3Sn(C_5H_9)$ formed of $Bu_3SnC(CH_3)_2CH{=}CH_2$ (α-isomer) and $Bu_3SnCH_2CH{=}C(CH_3)_2$ (γ-isomer), the ratio of which is $\alpha:\gamma$ = 40:60.

These results allow one to affirm that both allyl bromides couple with Bu_3SnCl substrates preferentially at the more substituted carbon atoms,[15] giving rise to a fairly good amount of the corresponding α-allyltin isomers. However, we must point out that the isomeric compositions of the isolated $Bu_3Sn(C_4H_7)$ and $Bu_3Sn(C_5H_9)$ mixtures are greatly influenced by either the adopted workup[12] or the presence in the mixtures themselves of substances capable of favoring isomerization processes,[16–18] which lower the content of the α-isomers[19] (see below).

As for the reaction of Bu_3SnCl and cinnamyl bromide (entry 15), only *trans*-$Bu_3SnCH_2CH{=}CHC_6H_5$ has been isolated with a good yield (ca. 67%). Likely, steric factors or rapid isomerization processes may prevent the formation of the α-phenylallyl isomer.

Cosolvent Effect on the Stereochemical Course of the Coupling of Bu_3SnCl and $(C_4H_7)Br$. The reaction of Bu_3SnCl and (α, *trans*, *cis*)–$(C_4H_7)Br$ (α:*trans*:*cis* = 15:76:9) was examined using various cosolvents, as shown in Table 2 (entries 16–21). In all the runs constant amounts of the components were employed and the progress of reactions was monitored from time to time by analysis of the isomeric ratios of the formed $R_3Sn(C_4H_7)$ mixtures.

Two sets of analytical data are given in Table 2, they refer to the isomeric composition of the product (a) 15 min after the mixing of the reagents and (b) after its isolation. The relevant points to be noted are (i) in all cases, the overall process is very fast, while it does not occur or is very slow if the reaction is performed in THF without the presence of the water–ammonium chloride phase; (ii) in cyclohexane (entry 16) only a clear coupling reaction occurs, yielding stereoselectively the sole α-isomer; (iii) the isomerization of the α-isomer to the *trans*- and *cis*-isomers, as a process subsequent to the coupling reaction, occurs when cyclohexane is replaced by other organic solvents (entries 17–21).

The extent of the isomerization process can be estimated by the degree of isomerization, which is to a large extent influenced by the solvent, in contrast with the isomerization stereochemical course, in which a constant *trans*:*cis* ratio is found (*ca.* 40:60). Isomerization is thought to be a polar reaction taking place in the bulk of the cosolvent, since the *trans*:*cis* ratio (40:60) is here the same as that found when ternary mixtures of (α, *trans*, *cis*)–$Bu_3Sn(C_4H_7)$ undergo isomerization[19] in the presence of Bu_3SnCl[17] or donor substances, as previously reported.[16,20]

The degree of isomerization seems to be related to the polarity and/or the donor ability of the cosolvent, since it increases with the increase of these properties. An additional factor to be considered is the formation of complexes such as $R_3SnCl(CS)_n$ (CS = tetrahydrofuran,

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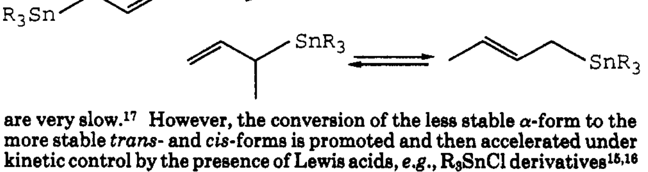
(15) Similarly, crotyl and prenyl bromides always react with carbonyl compounds under the mediation of zinc powder in THF/H_2O(NH_4Cl) at the more substituted carbon.[2a]

(16) Verdone, J. A.; Mangravite, J. A.; Scarpa, N. M.; Kuivila, H. G. *J. Am. Chem. Soc.* **1975**, *97*, 843.

(17) (a) Carofiglio, T.; Marton, D.; Lenzmann, F. *Anal. Chim. Acta* **1993**, *281*, 119. (b) Tagliavini, G.; In *Frontiers of Organogermanium, -tin and -lead Chemistry*; VIIth ICOCC, Riga, 1992; Lukevics, E., Ignatovich, L., Eds.; Riga, 1993, p 181.

(18) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555.

(19) Ternary mixtures of (α, *trans*, *cis*)-$R_3Sn(C_4H_7)$ compounds freshly prepared have a low tendency to isomerize since the interconversion rates of the metallotropic equilibrium:



are very slow.[17] However, the conversion of the less stable α-form to the more stable *trans*- and *cis*-forms is promoted and then accelerated under kinetic control by the presence of Lewis acids, *e.g.*, R_3SnCl derivatives[15,16] in the order of their acidity $Me_3SnCl > Et_3SnCl > Pr_3SnCl > Bu_3SnCl$.

(20) Matarasso-Tchiroukhine, E.; Cadiot, P. *J. Organomet. Chem.* **1976**, *121*, 155.

Table 3. Preparation of $Bu_3SnCH(CH_3)CH{=}CH_2$ (8a) from Bu_3SnCl and $(C_4H_7)Br$[a] in a Cyclohexane/$H_2O(NH_4Cl)$/Zn Medium

entry no.	reagent amt Bu_3SnCl, g (mmol)	 $(C_4H_7)Br$, g (mmol)	 Zn, g (g at)	amt of cyclohexane/H_2O, mL	isolated product	product amt, g (yield, %)
22	8 (24.6)	6.6 (48.9)	3.2 (48.9)	20/40	**8a**	7.2 (84.5)
23	8 (24.6)	6.6 (48.9)	3.2 (48.9)	40/20	**8a**	7.3 (85)
24	20 (61.4)	24.9 (184.4)	12.0 (183.6)	50/100	**8a**	19.0 (90)
25	20 (61.4)	24.9 (184.4)	12.0 (183.6)	50/100	**8a**	19.0 (90)

[a] $(C_4H_7)Br$ is a mixture of three isomers: *trans*-crotyl (76%), *cis*-crotyl (9%), and α-methylallyl bromide (15%).

Table 4. R Group Effect on the Stereochemical Course of the Reaction[a]

$$R_3SnCl + (C_4H_7)Br \xrightarrow{\text{cyclohexane}/H_2O(NH_4Cl)/Zn} R_3Sn(C_4H_7)\ (R = Me, Et, Pr, Bu)$$

entry no.	R_3SnCl R	$R_3Sn(C_4H_7)$ yield, %	$R_3Sn(C_4H_7)$ yield, % α-(C_4H_7)[c]	 *trans*-(C_4H_7)	 *cis*-(C_4H_7)	degree of isomerization,[b] %	*trans*:*cis* ratio
26	Bu	85	100	0	0		
27	Pr	75	85	4	11	0.15	27:73
28	Et	77	49	12	39	0.51	24:76
29	Me	80	27	21	52	0.73	29:71

[a] All of the runs have been performed using the same amount (mmol) of reagents and volume of cosolvent/H_2O(NH_4Cl saturated) as indicated in footnote *a* of Table 2. [b] The degree of isomerization is calculated as [*trans* (%) + *cis* (%)]:100. [c] α-(C_4H_7) = α-methylallyl.

2-propanol, acetonitrile, pyridine). It is to be noted that the maximum degree of isomerization (0.90) is reached in pyridine (entry 21). As a matter of fact, pyridine determines a nearly homogeneous system, in which the activity of Bu_3SnCl is lowered owing to the formation of the $Bu_3SnCl{\cdot}py$ complex.[21] As a consequence, the frozen Bu_3SnCl can be more available—together with the pyridine—as a catalyst for the isomerization process.

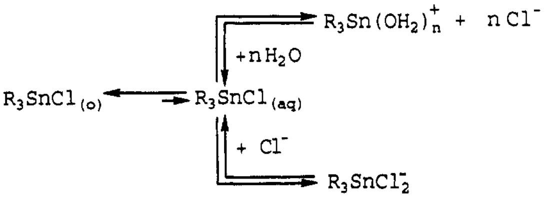
With regard to the preparative aspects of this reaction, interest in the one-pot synthesis of the more unstable[16-20] tributyl (α-methylallyl)tin isomer in cyclohexane is of great interest: as one can see from Table 3, this isomer can be obtained in high yield (85–90%) under a preparative scale from 20 to 60 of Bu_3SnCl.

R Group Effect on the Stereochemical Course of the Coupling of R_3SnCl Compounds (R = Me, Et, Pr) and $(C_4H_7)Br$ in Cyclohexane. Reactions between Pr_3SnCl, Et_3SnCl, and Me_3SnCl with $(C_4H_7)Br$ have been performed using cyclohexane as cosolvent. The results are listed in Table 4 in comparison with the corresponding data obtained with Bu_3SnCl.

These results make evident that the isomerization process depends on the R groups of the R_3SnCl reactant. The degree of isomerization increases in the order $Bu_3SnCl < Pr_3SnCl < Et_3SnCl < Me_3SnCl$, that is in the same order of the increasing ability of the R_3SnCl to solubilize into the water phase. It is to be noted that in all cases, the value of the ratio *trans*:*cis* = 25:75 is the same as that found for the catalytic isomerization ruled by the polar metallotropic exchange.[19]

Therefore, the balance between the coupling reaction to form the α-isomer and the subsequent rapid isomerization of the α-form into the *trans*- and *cis*-forms can be understood by considering the equilibria[22,23] depicted in Scheme 1.

Scheme 1



Likely, when Bu_3SnCl is used, the equilibria are completely displaced to the left; in such a way this reactant would be completely held in the cyclohexane phase, totally involved in the sole coupling reaction. Therefore, no Bu_3SnCl is available for catalyzing the isomerization. When Me_3SnCl is used, a portion of it is surely present in the aqueous phase, because its ability to participate in the equilibria[22] represented in Scheme 1 is greater than that of Bu_3SnCl. This portion cannot participate in the coupling reaction, so that it represents a useful reserve for the subsequent isomerization. This fact occurs, even though to a minor extent, for both Et_3SnCl and Pr_3SnCl, on account of their mutual solubilities in such a heterogeneous system. In addition, the extent of the isomerization processes is also governed by the relative acidity of the R_3SnCl substrates.[19]

Salt Effect on the Coupling of Bu_3SnCl and $(C_4H_7)Br$. The salt effect on the reaction of Bu_3SnCl and $(C_4H_7)Br$ has been studied. The following runs have been performed: (a) in THF/H_2O[$NH{=}C(NH_2)_2{\cdot}HCl$ saturated], (b) in THF/H_2O(LiCl saturated), (c) in H_2O(NH_4Cl saturated), and (d) in H_2O, in comparison with that (e) in THF/H_2O(NH_4Cl saturated).

Due to the saltlike nature of the organotin chloride, no significant difference was expected using guanidinium chloride (run a) and lithium chloride (run b) which, as is well-known, given rise to a salting-in and salting-out effect, respectively. In fact, in all cases, independently of the employed salt, the α-isomer is recovered as the major product inside the ternary isomeric mixtures of Bu_3Sn-

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(21) (a) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459. (b) Beattie, I. R.; McQuillan, G. P. *J. Chem. Soc.* **1963**, 1519.

(22) Janssen, M. J.; Luijten, J. G. A. *Recl. Trav. Chim.* **1963**, *82*, 1008. (b) Tobias, R. S. *Organomet. Chem. Rev.* **1966**, *1*, 93. (c) Tobias, R. S. In *Organometals and Organometalloids. Occurrence and Fate in the Environment*; Brinckman, F. E., Bellama, J. H., Eds.; ACS Symposium Series 82; American Chemical Society: Washington, 1978.

(23) As it is well-known, $R_3SnX_2^-$ anionic complexes are present in concentrated solutions of halide ligands X^-.

(C_4H_7), which have the same composition *α:trans:cis* = 67:11:22; the *trans:cis* ratios are the same (33:67, as an average value), and the degree of isomerization has a constant value around 0.35. Yields only are influenced by the different salts: 59% for run a, 56% for run b, 60% for run c, and 41% for run d, compared with 83% for run e. Ammonium chloride provides the best yield. In this case, the activation process is accelerated,[24] since the zinc particle surface is continuously cleansed of oxides by the acidity of the ammonium salt solution without formation of gels.[25]

Preparation of Triphenylallylstannanes. Table 5 lists data and results of the triphenylallylstannanes (**11**–**21**) prepared by using a three-phase medium THF/$H_2O(NH_4Cl)$/Zn. For the majority of the cases we used Ph_3SnCl and, for some runs, Ph_3SnI and Ph_3SnOH (entries 34, 35, and 39).

Yields of the pure products are fairly good: the system $Ph_3SnCl/CH{\equiv}C{-}CH_2Br$ produces an isomeric mixture of $Ph_3SnCH{=}C{=}CH_2$ (**11a**) and $Ph_3SnCH_2{-}C{\equiv}CH$ (**11b**) isomers with a ratio **11a**:**11b** = 58:42, and a total yield of 74%. Reaction with allyl bromide gives rise to triphenylallyltin with an 80% yield (entry 31). When methyl-substituted allyl bromides are used yields are between 65 and 88% (entries 32–35). Ternary mixtures of (*α*, *trans*, *cis*)-$Ph_3Sn(C_4H_7)$ are isolated (entry 33–35). The system $Ph_3SnCl/(CH_3)_2C{=}CHCH_2Br$ furnishes an isomeric mixture of the two isomers 3-methyl-1-buten-3-yltriphenyltin (**16a**) and 2-methyl-2-butenyltriphenyltin (**16b**) with a ratio **16a**:**16b** = 25:75 (entry 37). Good results are achieved working with cyclopent-, cyclohex-, and cyclohept-2-enyl bromides, as shown in entries 38–40.

As for these systems, we point out that (i) once again the coupling reaction between Ph_3SnCl and $(C_4H_7)Br$ allows the primary formation of the $Ph_3SnCH(CH_3)$-$CH{=}CH_2$ isomer (**14a**),[26] (ii) the rate of the reaction[27] is a little slower than that encountered for the corresponding reactions performed with R_3SnCl reactants, and (iii) a competitive coupling of the Ph_3Sn species to give hexaphenyldistannane takes place in many cases (entries 30, 31, 33, 35, 38, 39). The lowering of the coupling reaction rate makes more competitive the isomerization process. As a consequence, a total *α*-stereoselectivity, as encountered in the case of Bu_3SnCl, seems to be impossible with Ph_3SnCl.[26]

Preparation of Hexaaryldistannanes via Coupling of Triaryltin Derivatives in a THF/$H_2O(NH_4Cl)$/Zn Medium. We have shown that the coupling of Ph_3SnCl and allyl bromides is accompanied by a competitive coupling side reaction at the expense of the organotin chloride itself, leading to hexaphenyldistannane. Therefore the zinc as condensing agent is able, under the adopted experimental conditions, to promote the coupling of the R_3Sn groups. Thus, we could prepare hexaaryldistannanes working in the THF/$H_2O(NH_4Cl)$/Zn medium by using the sole triaryltin derivatives as starting reactants.

Table 5. Preparation of Allenyl- and Allylstannanes from Phenyltin Derivatives in a THF/$H_2O(NH_4Cl)$/Zn Medium

	reagent							
entry no.	organotin	amt, g (mmol)	organic bromide	amt, g (mmol)	Zn amt, g (mmmol)	amt of THF/H_2O, mL	product	product amt, g (yield, %)
30	Ph_3SnCl	7.4 (19.2)	$CH{\equiv}CCH_2Br$	4.6 (38.4)	2.5 (38.4)	150/150	$Ph_3SnC_3H_3$[a,b] (**11**)	5.6 (74)
31	Ph_3SnCl	10.0 (25.9)	$CH_2{=}CHCH_2Br$	6.3 (51.9)	3.4 (51.9)	150/150	$Ph_3SnCH_2CH{=}CH_2$[c] (**12**)	8.1 (80)
32	Ph_3SnCl	5.7 (14.8)	$CH_2{=}C(CH_3)CH_2Br$	4.1 (30.1)	1.9 (30.0)	50/50	$Ph_3SnCH_2C(CH_3){=}CH_2$[d] (**13**)	3.9 (65)
33	Ph_3SnCl	20.0 (51.9)	$CH_3CH{=}CHCH_2Br$[e]	14.0 (103.8)	6.8 (103.8)	250/250	$Ph_3Sn(C_4H_7)$[f,g] (**14**)	15.9 (75)
34	Ph_3SnI	7.0 (14.7)	$CH_3CH{=}CHCH_2Br$[e]	4.0 (29.4)	1.9 (29.4)	50/50	**14**[h]	5.2 (88)
35	Ph_3SnOH	5.5 (15.0)	$CH_3CH{=}CHCH_2Br$[e]	4.1 (30.0)	1.9 (30.0)	60/60	**14**[h,i]	4.3 (70)
36	Ph_3SnCl	5.7 (14.8)	$PhCH{=}CHCH_2Br$	5.8 (29.6)	1.9 (29.6)	50/50	$Ph_3SnCH_2CH{=}CHPh$ (**15**)	3.7 (53)
37	Ph_3SnCl	5.7 (14.8)	$(CH_3)_2C{=}CHCH_2Br$	4.5 (29.6)	1.9 (29.6)	50/50	$Ph_3Sn(C_5H_9)$[j] (**16**)	5.2 (84)
38	Ph_3SnCl	5.7 (14.8)	$CH_2CH_2CH{=}CHCHBr$	4.4 (29.9)	1.9 (29.6)	50/50	$Ph_3SnCHCH{=}CHCH_2CH_2$[k] (**19**)	2.5 (45)
39	Ph_3SnI	5.7 (14.8)	$CH_2CH_2CH_2CH{=}CHCHBr$	3.4 (21.0)	1.4 (21.0)	50/50	$Ph_3SnCHCH{=}CHCH_2CH_2CH_2$[l] (**20**)	4.4 (70)
40	Ph_3SnCl	5.7 (14.8)	$CH_2CH_2CH_2CH_2CH{=}CHCHBr$	5.7 (32.6)	1.9 (29.6)	50/50	$Ph_3SnCHCH{=}CHCH_2CH_2CH_2CH_2$ (**21**)	2.5 (42)

[a] In this case a mixture of $Ph_3SnCH{=}C{=}CH_2$ (**11a**) and $Ph_3SnCH_2C{\equiv}CH$ (**11b**) is recovered with a ratio **11a**:**11b** = 58:42. [b] 0.5 g of $Ph_3SnSnPh_3$ is recovered as a byproduct. [c] Traces of $Ph_3SnSnPh_3$ are present. [d] 0.6 g of $Ph_3SnSnPh_3$ is recovered as byproduct. [e] Crotyl bromide is a mixture of *trans* (76%), *cis* (9%), and *α*-methylallyl (15%) forms. [f] Compound **14** is an isomeric mixture where C_4H_7 = *α*-methylallyl (**14a**), *trans*-crotyl (**14b**), and *cis*-crotyl (**14c**) with a ratio **14a**:**14b**:**14c** = 48:34:18. [g] 1.3 g of $Ph_3SnSnPh_3$ is recovered as a byproduct. [h] The product consists of a mixture of the isomers *α* (**14a**), *trans* (**14b**) and *cis* (**14c**) where **14a** is the major component. [i] 0.76 g is recovered as a byproduct. [j] Compound **16** is isolated as a mixture of two isomers: 3-methyl-1-buten-3-yltriphenylstannane (**16a**) and 3-methyl-2-buten-3-yltriphenylstannane (**16b**) with a ratio **16a**:**16b** = 25:75. [k] 0.9 g of $Ph_3SnSnPh_3$ is recovered as a byproduct. [l] 0.74 g of $Ph_3SnSnPh_3$ is recovered as a byproduct.

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(24) The reaction performed in the presence of LiCl is less exothermic than that performed with NH_4Cl. Guanidinium chloride is able to form complexes with R_3SnCl compounds, similarly as amino compounds do.[21a]

(25) Both LiCl and $HN{=}C(NH_2){\cdot}HCl$ lead to the formation of gels which envelop the zinc particles, reducing their activity.

(26) Ph_3SnCl is insoluble in cyclohexane and soluble in toluene. Two runs, performed using these cosolvents, gave (i) a very poor yield (around 30%), (ii) a high *α*-isomeric stereoconvergence, and (iii) $Ph_3Sn(C_4H_7)$ mixtures having the same composition: *α:trans:cis* = 80:11:9 in cyclohexane and *α:trans:cis* = 83:12:5 in toluene.

(27) Reactions with Ph_3SnCl are completed in about 20 min.

Table 6. Preparation of Some Hexaaryldistannanes from Triaryltin Derivatives in a THF/$H_2O(NH_4Cl)$/Zn Medium

entry no.	organotin	amt, g (mmol)	Zn amt, g (mmol)	amt of THF/H_2O, mL	product	product amt, g (yield, %)
41	Ph_3SnCl	10.0 (25.9)	3.4 (52.0)	100/100	$Ph_3SnSnPh_3$ (**22**)	5.98 (66)
42	Ph_3SnCl	10.0 (25.9)	2.9 (44.3)	150/150	**22**	6.14 (67)
43	Ph_3SnI	4.0 (8.4)	1.0 (15.3)	50/50	**22**	1.76 (60)
44	Ph_3SnOH	5.5 (15.0)	1.5 (22.7)	60/60	**22**	3.46 (66)
45	*p*-Tol_3SnCl	4.0 (7.7)	1.0 (15.3)	25/25	(*p*-Tol)$_3$SnSn(*p*-Tol)$_3$ (**23**)	1.09 (36)
46	*m*-Tol_3SnCl	4.0 (7.7)	1.0 (15.3)	25/25	(*m*-Tol)$_3$SnSn(*m*-Tol)$_3$ (**24**)	0.81 (27)

Table 6 shows that Ph_3SnX substrates (X = Cl, I, OH) allow the preparation of hexaphenyldistannane with good yields varying from 60 to 67%. Coupling reactions performed with *p*-Tol_3SnCl and *m*-Tol_3SnCl (entry 45 and 46) furnish the corresponding hexaaryldistannanes, albeith with very low yields: 36 and 27%, respectively.

Preliminary investigations indicate that this procedure can be generalized to prepare hexaalkyldistannanes, provided that workup is done under nitrogen atmosphere.[28]

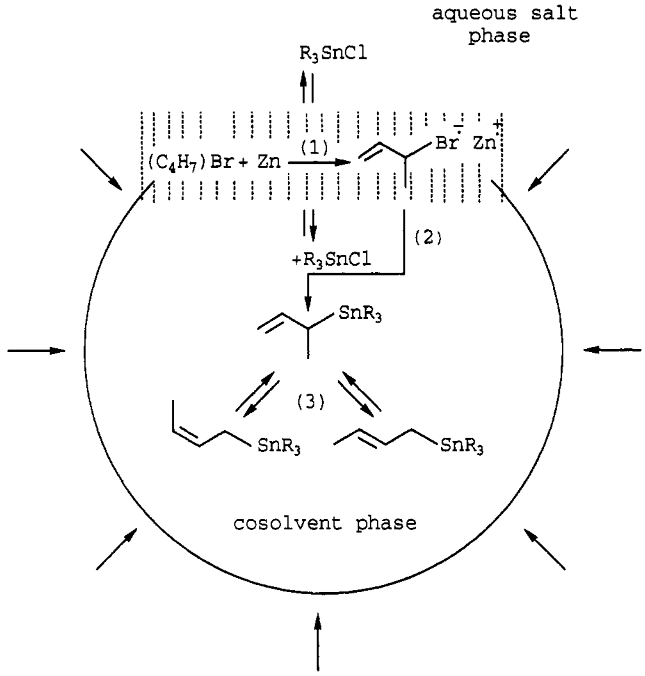
The formation of Sn–Sn bonds through this procedure allows some advantages in comparison with the well-known preparative methods of ditin compounds based on the reaction of the same substrates with sodium in organic solvent or in liquid ammonia or triaryltin lithium with triaryltin halides.[21a]

It is to be noted that the coupling of Ph_3Sn species to give Ph_6Sn_2 has a much slower rate than that of the coupling between Ph_3SnCl and allyl bromides. This simple coupling of the R_3Sn species is highly accelerated using a two-phases cosolvent–water heterogeneous system. On the contrary, Ph_3SnCl does not react with zinc metal if THF alone is used as the medium.[29] Even Bu_3SnCl does not couple under the same conditions, as similarly verified for the coupling of R_3SnCl compounds with $(C_4H_7)Br$.

Conclusive Comments about the Mechanistic Pathways of the Reactions. Zinc powder is not able to couple R_3Sn species, as well as R_3SnCl compounds with allyl bromide, if reactions are performed in tetrahydrofuran alone. Thus, the coupling reaction seems to be highly activated, and consequently accelerated, only when a two-phase cosolvent–water system is used.[30] Under heterogeneous conditions, the zinc particles, mainly located in the boundary surface of the emulsified system, are forced to interact with an appropriate electrophile (either allyl bromide or R_3SnCl compound, which are held in the organic phase) by the high cohesive energy density developed by the water phase.[31]

Three different kinds of coupling reactions can be hypothesized if both allyl bromide and R_3SnCl are considered: (I) the coupling between the allyl bromide and the R_3SnCl compound to form allylstannane, (II) the coupling of the R_3Sn species to form ditin compounds, and (III) the coupling of the allyl groups to form diallyl derivatives. Actually, only couplings I and II occur to a high extent, the overall reaction rate of I being much greater than that of II. Coupling II seems not to interfere with the above processes.[32] Therefore, when both electrophiles are present, the zinc particles do interact with the allyl bromide rather than with the R_3SnCl substrate, which can be competitive in same way only when R = Ph.

Scheme 2



The result obtained working with the system Bu_3SnCl, $(C_4H_7)Br$, and cyclohexane/$H_2O(NH_4Cl)$/Zn allows us to speculate about the mechanistic aspects of this Wurtz-type reaction. The very high reaction rate of this process (its high exothermicity) and its stereoselective course leading completely to the $Bu_3SnCH(CH_3)CH{=}CH_2$ isomer can be thought to arise from a pathway in which "radical" species are present. A polar condensation between Bu_3SnCl and organometallic species, such as $(C_4H_7)ZnBr$, must be rejected, since organozinc compounds are hardly useful as reagents in diastereoselective addition.[18,33] A probable mechanistic pathway of the overall coupling–isomerization process is discussed with the aid of Scheme 2.

We assume that $CH_2{=}CH{-}CH(CH_3)Br^{\bullet-}Zn^{\bullet+}$ radical ions are formed by one-electron transfer mechanism from zinc metal to $(C_4H_7)Br$ (path 1). The transfer, promoted by the high interfacial energy developed by water, occurs

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[28] Coupling of Bu_3SnCl to form Bu_6Sn_2 occurs to a low extent under an air atmosphere, being a very easily oxidized ditin compound.[21a] However, hexabutyldistannane has been isolated (54% yield) by reacting the sole Bu_3SnCl (10 g) in THF/$H_2O(NH_4Cl)$ under a nitrogen atmosphere. The reaction is much slower than that between allyl bromide and Bu_3SnCl.

[29] Des Tombe, F. J. A.; Van der Kerk, G. J. M.; Noltes, J. G. *J. Organomet. Chem.* **1973**, *51*, 173.

[30] The reaction acceleration promoted by two-phase cosolvent–water systems recalls that due to sonification. Trialkyltin halides (R = Me, Bu) give good yields of Me_6Sn_2 (60%) and Bu_6Sn_2 (94%) with lithium wire in THF under sonification. See: Boudjouk, P.; Hee Han, B. *Tetrahedron Lett.* **1981**, *22*, 3813.

[31] Water is thought to have a cohesive energy density of 22 kbars. See ref 7.

[32] In cyclohexane/$H_2O(NH_4Cl)$, zinc powder poorly mediates the coupling of (*α*, *trans*, *cis*)-$(C_4H_7)Br$ (*α*:*trans*:*cis* = 20:76:4) to diallyl derivatives. They are isolated in very low yield (*ca.* 10%) as a six-isomeric mixture with a ratio *α* groups: *trans* + *cis* groups = 38:62.

[33] (a) Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674. (b) Whitesides, G. M.; Nordlander, J. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 2010. (c) Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1. (d) Felkin, H.; Gault, Y.; Roussi, G. *Tetrahedron* **1970**, *26*, 3761.

under kinetic control. Among the several transition states, the more compact will be favored, with the more negative $\Delta V^{\ddagger}$.[34] Namely, the transition state with the branched allyl group will have a volume smaller than those with *cis*- and *trans*-linear groups. The branched radical ion adsorbed on the zinc particle surface will be trapped by the R_3SnX species (path 2) to form the sole $R_3SnCH(CH_3)CH{=}CH_2$ isomer, subjected, in some particle cosolvent, to an isomerization process *via* the metallotropic equilibrium 3, under the mediation of either some unreacted R_3SnX or the cosolvent itself.

Moreover, in the case of the clear Wurtz-type reaction regarding the sole R_3SnCl species, we assume that $R_3SnCl^{\bullet -}Zn^{\bullet +}$ radical ions[35] are produced by one-electron transfer from the metal to the electrophilic R_3SnCl, at a favourable rate, such as to be trapped by other R_3SnCl molecules to form ditin compounds.

The one-electron transfer from the zinc metal to the electrophile is a process dependent upon the acceptor ability of each reactant, so that, among various employed electrophilic reagents, the radical ion actually formed will be the one deriving from the species with higher acceptor ability. According to our results the ability to form radical ions decreases in the order $CH_2{=}CHCH_2Br$ = $CH_3CH{=}CHCH_2Br \gg Bu_3SnCl > Pr_3nCl > Et_3SnCl \geq Me_3SnCl > Ph_3SnCl >>> CH_2{=}CHCH_2Cl$.[36]

Experimental Section

All manipulations were carried out at room temperature, under air atmosphere. Solvents, salts, and zinc powder (325 mesh), commercially available, were used as received.

R_3SnCl compounds (R = Me, Et, Pr, and Bu), commercially available, were distilled under vacuum before use. Bu_2SnCl_2 was recrystallized before use. $[Bu_2SnCl]_2O$ was prepared by hydrolysis of dibutyltin dichloride in a water–acetone medium and then crystallized from an ethanol–water mixture.[37] Ph_3SnCl (Aldrich) and Ph_3SnOH (Ventron, α-Inorganics) were recrystallized before use. Ph_3SnI was prepared by iodinaton of Ph_4Sn[38] or Ph_6Sn_2.[39] Tritolyltin iodides were prepared by iodination of the corresponding tetratolyltins.[21a] All the allyl bromides were distilled before use. 3-Bromo-2-methyl-2-propene[40] and cyclopent-,[41] cyclohex-,[42] and cyclohept-2-enyl bromide[43,44] were prepared according to known literature procedures.

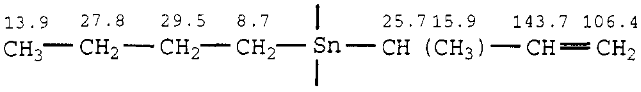
Boiling and melting points as well as the infrared patterns of all prepared compounds were in agreement with the literature data.[3,14,21] However, further characterization was made by means of ^{13}C and ^{119}Sn nuclear magnetic resonance spectrometry using a JEOL FX90Q Fourier Transform NMR spectrometer. Spectra of samples either as $CDCl_3$ solutions or as pure liquids were recorded using Me_4Si and Me_4Sn as internal and external standards, respectively.

Analysis of the isolated isomeric mixtures was based on the integrated intensities of the appropriate ^{13}C NMR signals, as previously described.[17a] Quantitative determinations from ^{13}C NMR spectra were made by using sufficiently long pulse intervals in order to avoid saturation of the nuclear spins (at least 25 s) together with the gated decoupling method[17a,45] in order to suppress the nuclear Overhauser effect (NOE). These determinations were confirmed by data arising from the integrated intensities of the ^{119}Sn NMR signals.[17a] Additional GLC analyses were performed for liquid products using a Perkin-Elmer gas chromatograph Model 8310 equipped with a flame-ionization detector (DB225 polar column, 15 m, 0.25-mm i.d., T_i = 200 °C, T_d = 220 °C, and T_c = 80–220 °C, 10 °C/min rampe rate, nitrogen as carrier gas at 10 psi).

The progress of the reactions was monitored by means of ^{119}Sn NMR or GLC in order to analyze, during the time, the content of R_3SnCl reactant in the system. The complete disappearance of the R_3SnCl signal (or peak), or its standing at a constant value, marked the end of the reactions. In such a way, we have had the possibility to make a rough comparison between the velocities of the various processes here considered.

Preparation of Tri- and Dialkylallylstannanes (Entries 1–29). In a round-bottom two-necked flask (100–300 mL) equipped with a condenser and dropping funnel,[46] the appropriate alkyltin chloride was added to a cosolvent/H_2O(NH_4Cl saturated) mixture together with an excess of zinc powder (quantities are given in Table 1–4). Under magnetic stirring, the appropriate allyl bromide (generally in 1:1 stoichiometric ratio with respect to zinc) was added dropwise at a rate sufficient to maintain a gentle reflux due to the exotermicity of the reaction. The addition lasts about 5 min, a time sufficient to note the disappearance of the zinc powder. The heterogeneous mixture was stirred for a further 30 min. Then, extraction with petroleum ether (40–60 °C) was performed. The separated organic layer was washed with saturated aqueous NaCl and dried over $MgSO_4$. Removal of the solvent left a crude oil, which was distilled under vacuum to afford the pure allyltin compound. Yields, listed in Tables 1–4, have been calculated from the amounts of the pure distilled products.

Entries 22–25 of Table 3 deal with the stereoselective preparation of $Bu_3SnCH(CH_3)CH{=}CH_2$ (**8a**) using cyclohexane as cosolvent. Compound **8a** boils at 105–106 °C/0.5 mmHg. Its ^{119}Sn NMR spectrum shows a sole resonance line at −17.5 ppm.[17a] The ^{13}C NMR chemical shift values are as follows:[17a]



$$\overset{13.9}{CH_3}-\overset{27.8}{CH_2}-\overset{29.5}{CH_2}-\overset{8.7}{CH_2}-\underset{|}{\overset{|}{Sn}}-\overset{25.7}{CH}\,(\overset{15.9}{CH_3})-\overset{143.7}{CH}=\overset{106.4}{CH_2}$$

Preparation of Triphenylallylstannane (Entries 30–40). Apart from the final workup, the mixing procedure was the same as that described above. Also in these cases reactions are highly exothermic. After 1 h from the mixing, the zinc powder residue was removed by filtration. Then, the tetrahydrofuran was removed by means of a rotary evaporator. The slurry formed was first treated with chloroform; then extraction with the same solvent was made. The organic solution was dried over Na_2SO_4; then the solvent was evaporated to leave an oil residue. This was treated with petroleum ether (40–60 °C) or *n*-hexane in order to separate the ditin compound if formed as a byproduct. After separation of this compound, the solvent was evaporated and the oil–solid residue was crystallized using anhydrous ethanol. Yields of the so-obtained allyltriphenylstannanes (see Table 5) refer the to the amount of pure crystallized product.

Preparation of Hexaaryldistannanes (Entries 41–46). Following the same procedure as above described an appropriate amount of triaryltin chloride dissolved in a few milliliters of THF

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[34] Dack, M. R. J. *Chem. Soc. Rev.* **1975**, *4*, 211.

[35] Formation of $Ph_3SnZnCl$ by an oxidative-addition process may be rejected because this complex in THF solution affords exclusively Ph_4Sn upon reaction with Ph_3SnCl together with benzene upon reaction with water present in THF solution. See: Des Tombe, F. J. A.; Van der Kerk, G. J. M.; Noltes, J. G. *J. Org. Chem.* **1968**, *13*, p 9.

[36] Reactions performed with $CH_2{=}CHCH_2Cl$ or other allyl chlorides instead of allyl bromides give rise to bad results.

[37] Alleston, D. L. *J. Chem. Soc., London* **1963**, 5469.

[38] Chambers, R. F. *J. Am. Chem. Soc.* **1926**, *48*, 1054.

[39] Poller, R. C. *J. Organomet. Chem.* **1968**, *11*, 489.

[40] Nichols, P. L. *J. Am. Chem. Soc.* **1946**, *68*, 2022.

[41] Bordwell, F. C.; Kern, R. J. *J. Am. Chem. Soc.* **1955**, *77*, 1141.

[42] McCoy, L. L.; Dauben, H. J., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 4863.

[43] Cope, A. C.; Liss, T. A.; Wood, G. *J. Am. Chem. Soc.* **1957**, *79*, 6287.

[44] Braude, E. A.; Evans, E. A. *J. Chem. Soc., London*, **1954**, 607.

[45] Freeman, R.; Hill, H. D.; Kaptein, R. *J. Magn. Reson.* **1872**, *7*, 327.

[46] In many cases, a flat-bottom flask equipped on the top with a funnel as condenser has been used as the reactor.

was added under stirring to the system THF/H_2O(NH_4Cl)/Zn. Different from the previous cases, the overall reactions had a very low exothermicity. Reactions need 1-1.5 h for their completion. After this time, THF was removed by means of a rotary evaporator. The slurry formed was first treated with chloroform; then extraction with the same solvent was made. The solid residue left after evaporation of the chloroform was recrystallized from anhydrous ethanol to give the ditin compounds.

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