

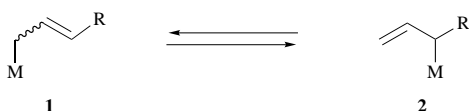
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The photochemical 1,3-stannyl rearrangement of allylic stannanes has been investigated. The photorearrangement of (*E*)-cinnamyl(triphenyl)stannane is not observed in benzene under anaerobic conditions, while the photoinduced 1,3-stannyl migration takes place in the same solvent under aerobic conditions, or in the presence of organic halides or a radical-trapping agent to give a photoequilibrium mixture of the cinnamylstannane and its branched regioisomer, 1-phenylprop-2-enyl(triphenyl)stannane, with the latter predominating. Cinnamyl(trialkyl)stannanes and their homologues also afford the corresponding branched allylstannanes under similar photochemical conditions. These 1,3-stannyl migrations proceed intramolecularly *via* cinnamyl π - π^* excitation in competition with homolytic (cinnamyl)C–Sn bond fission. In contrast, the 1,3-stannyl migration of crotyl- and prenyl-(tributyl)stannanes is not efficient, but their triphenyl or dibutylphenyl derivatives undergo the 1,3-rearrangement *via* excitation of the phenyl group(s) on the tin atom to give a regioisomeric mixture of the starting linear tin compounds and the branched ones with the former predominating.

Introduction

It is well known that most allyl-metal reagents are subjected to more or less rapid 1,3-allylic rearrangement from **2** to thermodynamically more stable **1**.¹ Among allyl-metal reagents the branched allylstannanes **2** (R = Me or Ph, M = SnBu₃) are relatively stable, but they have also been found to undergo some isomerization to the corresponding linear allylstannane **1** at a temperature above ~100 °C in nonpolar solvents or at an ambient temperature in polar solvents.^{2,3} In contrast, interestingly, it has been reported that allylic silanes⁴ and germanes⁵ reversely rearrange from species **1** to isomers **2** under photochemical

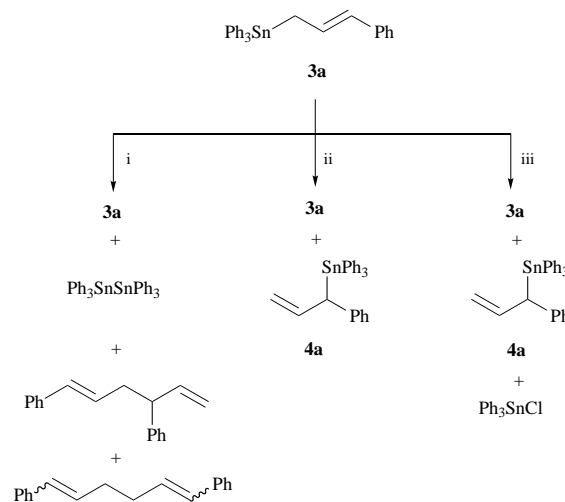


conditions. However, unambiguous evidence for such photochemical rearrangement of allylic stannanes from species **1** to isomers **2** has not been reported.⁶

Recently, we have communicated that cinnamylstannanes **1** (R = Ph, M = SnBu₃ or SnPh₃) isomerize photochemically to the branched regioisomers **2**.⁷ In this paper, we describe in detail the photochemical 1,3-stannyl migration from carbon to carbon in allylstannanes. This novel photorearrangement is observed in a solvent containing organic halides or radical-trapping agents. Some mechanistic features of this photorearrangement are also discussed.

Results and discussion

Although the photochemical 1,3-allylic rearrangement **1** \rightarrow **2** of allylic silanes⁴ and germanes⁵ has been observed in a benzene or hexane solution, the photochemical 1,3-stannyl rearrangement of (*E*)-cinnamyl(triphenyl)stannane **3a** was not observed in these solvents. For example, when irradiation of compound **3a** was carried out in benzene under nitrogen with a 300-W high-pressure mercury arc lamp through saturated aq. CuSO₄ (>320 nm), no 1,3-rearrangement product, 1-phenylprop-2-enyl(triphenyl)stannane **4a**, not obtained but a small amount of hexaphenyldistannane and diphenylhexa-1,5-dienes were produced together with recovery of substrate **3a** (78%) (Scheme 1). The formation of hexaphenyldistannane and



Scheme 1 Conditions: i, $h\nu$ (>320 nm), 1 h, C₆H₆, N₂; ii, $h\nu$ (>320 nm), 1 h, C₆H₆, O₂; iii, $h\nu$ (>320 nm), 1 h, CHCl₃, N₂

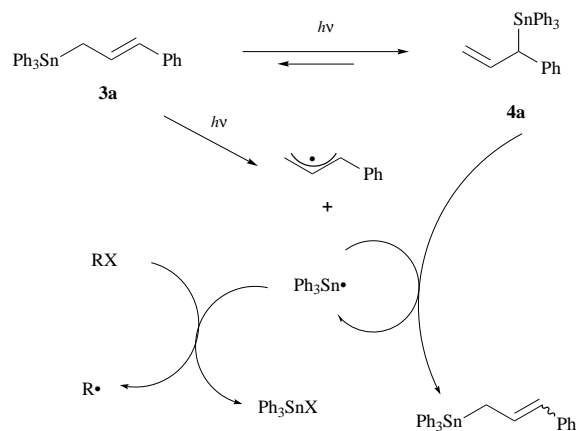
diphenylhexa-1,5-dienes as by-products clearly indicated that the homolytic (cinnamyl)C–Sn bond cleavage⁸ took place partially, because they are the self-coupling products of triphenyltin radical and cinnamyl radical, respectively.

On the other hand, irradiation of compound **3a** in benzene under oxygen gave a mixture of regioisomers **3a** and **4a** (ratio of 1:9) in 50% yield. Thus, the photochemical 1,3-rearrangement from the cinnamylstannane **3a** to the benzylstannane **4a** could be observed in benzene under aerobic conditions. These results suggest that the homolytic (cinnamyl)C–Sn bond cleavage and the 1,3-stannyl migration process occur competitively (Scheme 2). Even though the branched allyltin **4a** was formed under anaerobic conditions, it would be reconverted to the starting linear allyltin **3a** by free-radical chain reaction involving an $S_{\text{H}}2'$ process⁹ between compound **4a** and the triphenyltin radical. Such an $S_{\text{H}}2'$ reaction, however, would be inhibited under aerobic conditions because of the triphenyltin radical reacting rapidly with oxygen.¹⁰ These two competitive processes were also supported by the result from the photolysis in chloroform. Irradiation of compound **3a** in chloroform under anaerobic conditions gave again a regioisomeric mixture of **3a** and **4a** (ratio of 1:13) in 55% yield together with triphenyltin

Table 1 Thermal reactions of compounds **3a** and **4a** in the presence of AIBN^a

Run	Allyltin	Conditions	Ratio of 3a : 4a ^b	Total yield (%)
1	3a	AIBN-C ₆ H ₆ -N ₂	100:0	96
2	4a	AIBN-C ₆ H ₆ -N ₂	100:0	97
3	4a	AIBN-C ₆ H ₆ -O ₂	7:93	91
4	4a	AIBN-CHCl ₃ -N ₂	1:99	73

^a The reactions were carried out under reflux for 6 h in the presence of 10 mol% AIBN under the conditions described in the Table. ^b Ratios were determined by ¹H NMR spectra.

**Scheme 2**

chloride (30%), where the triphenyltin radical could abstract a chlorine atom^{8c-e} from the solvent (Scheme 2).†

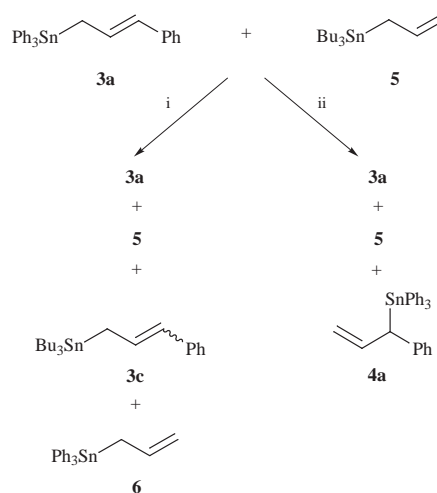
The S_H2' processes were confirmed by the following experiments under free-radical conditions and the results are summarized in Table 1. The linear allyltin **3a** was recovered intact after being refluxed in benzene containing a catalytic amount of 2,2'-azoisobutyronitrile (AIBN) under nitrogen, whereas the branched allyltin **4a** isomerized completely to compound **3a** under the same conditions. However, the allyltin **4a** was recovered without isomerization to the cinnamyltin **3a** when refluxed with AIBN in benzene solution under oxygen or in chloroform solution (runs 3 and 4). Since it is known that tributyltin radical is generated by heating of allyl(tributyl)stannane in the presence of AIBN,^{8d} the results of the present radical reactions clearly indicate that triphenyltin radical converts benzyl isomer **4a** into cinnamyl isomer **3a** but it is trapped efficiently with oxygen¹⁰ or with chloroform^{8c-e} before selectively attacking the sterically less crowded terminal olefinic carbon in compound **4a** rather than the sterically more congested internal one in isomer **3a**. This is a reason why photochemical 1,3-rearrangement of compound **3a** was *not* observed in benzene or hexane under anaerobic conditions, but *was* observed under aerobic conditions or in chloroform solution.

Thus, in order to observe directly the photochemical 1,3-rearrangement of compound **3a** it was found necessary to suppress the S_H2' chain reaction between the 1,3-stannyl-migrated product **4a** and the triphenyltin radical formed by homolytic cleavage of (cinnamyl)C-Sn bond. Therefore, we examined the photolysis of compound **3a** in benzene solution containing various organic halides, from which the halogen atom is known to be readily transferred to trialkyltin radical.^{8c-e,11} The 1,3-rearrangement was again observed under the conditions shown in Table 2. The ratio of products **3a** and **4a** obtained varied from 1:0 to 1:19 depending on the organic halides used as an additive. The amount of **4a** increased with increasing reactivity

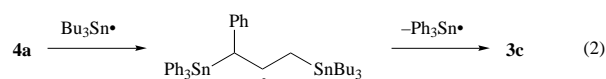
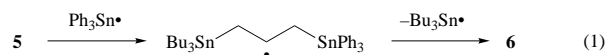
† Cinnamyl radical was also scavenged by dimerization or coupling with chloromethyl radicals to afford small amounts of diphenyl-1,5-hexadienes, 4,4-dichloro-1-phenylbut-1-ene and 3-trichloromethyl-1-phenylprop-1-ene.

of organic halides towards triphenyltin radical; the reactivity increases in the order primary < secondary < tertiary < allyl for different alkyl groups in the alkyl halides, and the ease of abstraction of halogens increases in the order Cl < Br.^{8d,11c,d,12} Unexpectedly, iodoform was not an effective organic halide for the photorearrangement probably due to its absorption of the light (>320 nm; data not shown). Thus, the **4a**:**3a** ratios were very high in benzene solution containing CCl₄, CHCl₃, CH₂Br₂, CH₂=CHCH₂Br or PrⁱBr. Similar ratios were obtained when the branched allyltin **4a** was subjected to photolysis in chloroform or in benzene containing CH₂Br₂ (runs 14,15). Thus, the photo-equilibrium should be attained between compound **3a** and **4a** under these conditions, in which the sterically more crowded compound **4a** was the major product. The 1,3-rearrangement was also observed when compound **3a** was irradiated in benzene containing radical scavengers such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) or galvinoxyl (runs 11,12).

In addition, we further confirmed the photochemical (cinnamyl)C-Sn bond fission in competition with 1,3-stannyl migration by a crossover experiment between compound **3a** and allyltributylstannane **5** (Scheme 3). When an equimolar mixture

**Scheme 3** Conditions: i, *hv* (>320 nm), 1 h, C₆H₆, N₂; ii, *hv* (>320 nm), 1 h, CHCl₃, N₂

of allylstannanes **3a** and **5** in benzene was irradiated (>320 nm) for 1 h under nitrogen, cinnamyl(tributyl)stannane **3c** (15%) and allyltributylstannane **6** (22%) were obtained together with starting tin reagents, **3a** (76%) and **5** (48%). Since compound **5** does not absorb light of longer wavelength than 280 nm, (cinnamyl)C-Sn bond fission of compound **3a** occurred selectively under these conditions to produce the triphenyltin radical, which attacks the terminal olefinic carbon in compound **5** to give the cross-coupling product **6** and tributyltin radical *via* S_H2' reaction [equation (1)]. The resulting tributyltin radical reacts with photorearranged product **4a** from substrate **3a** to afford another cross-coupling product **3c** [equation (2)]. On



the other hand, the cross-coupling reaction was negligible when the photolysis was carried out in chloroform, and 1,3-rearrangement product **4a** (**3a**:**4a** = 6:94) was again observed without any contamination of the cross-coupling products (Scheme 3).

Table 2 Photochemical isomerization of [(*E*)-3-arylbut-2-enyl]tin compounds **3a–d** and **4a**^a

Run	Allyltin	Solvent	Additive	Ratio of 3 : 4 ^b	<i>E</i> : <i>Z</i> ratio of 3 ^b	Total yield (%)
1	3a	Benzene	CH ₂ Br ₂	6:94	40:60	54
2	3a	Benzene	CH ₂ Cl ₂	96:4	82:18	71
3	3a	Benzene	CHCl ₃	14:86	47:53	47
4	3a	Benzene	CCl ₄	5:95	20:80	24
5	3a	Benzene	Bu ⁿ Br	13:87	75:25	59
6	3a	Benzene	Pr ⁱ Br	6:94	27:73	55
7	3a	Benzene	Bu ⁿ Cl	99:1	93:7	80
8	3a	Benzene	Bu ⁿ Cl ^c	95:5	86:14	73
9	3a	Benzene	Allyl bromide	8:92	67:33	57
10	3a	Benzene	Allyl chloride	78:22	81:9	65
11	3a	Benzene	TEMPO ^d	6:94	42:58	64
12	3a	Benzene	Galvinoxyl ^e	64:36	98:2	84
13	3a	Chloroform		7:93	53:47	55
14	4a	Chloroform		10:90	29:71	42
15	4a	Benzene	CH ₂ Br ₂	7:93	38:62	52
16	3b	[² H]Chloroform		1:99		53
17	3c	Benzene	CH ₂ Br ₂	3:97	50:50	58
18	3c	Benzene	TEMPO ^d	7:93	30:70	68
19	3d ^e	Benzene	CH ₂ Br ₂	12:88	38:62	76

^a Irradiation was carried out in a solvent containing 3 equivalents of an additive under nitrogen with a 300-W high-pressure mercury lamp (>320 nm) for 1 h. ^b Ratios were determined by ¹H NMR spectra. ^c Butyl chloride (10 equiv.) was added. ^d TEMPO (1.0 equiv.) was added. ^e Galvinoxyl (0.2 equiv.) was added. ^e Irradiation was carried out with >400 nm light for 40 min.

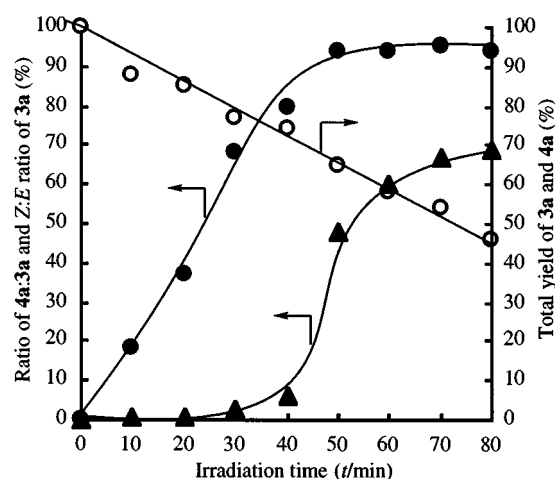
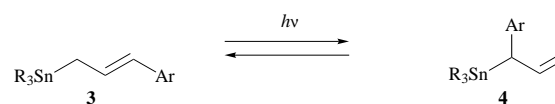


Fig. 1 Photoisomerization of (*E*)-**3a** to **4a** in a nitrogen purged benzene solution in the presence of dibromomethane (3 equiv.) under irradiation with >320 nm light. Ratio of **4a**:**3a** (●); *Z*:*E* ratio of recovered **3a** (▲); total yield of compounds **3a** and **4a** (○).

Next, attention was focused on the *E*:*Z* ratio of compound **3a**. While starting compound **3a** was the *E*-form, the recovered **3a** was a mixture of *E*/*Z*-isomers (Table 2). For example, the *E*:*Z* ratio of recovered substrate **3a** was 1:1.5 after irradiation of a benzene solution of (*E*)-**3a** in the presence of dibromomethane (Table 2, run 1). Then the variation of both the *E*:*Z* ratio of compound **3a** and the ratio of products **3a**:**4a** was followed as a function of irradiation time under the same conditions. The results are shown in Fig. 1, which also includes the total yield of compounds **3a** and **4a**.

Equilibrium of the 1,3-rearrangement between **3a** and **4a** was accomplished after irradiation for 50 min (ratio of compound **3a**:**4a** 1:19). Interestingly, the *Z*-isomer was little observed in recovered compound **3a** until equilibrium was attained, but the amount of *Z*-isomer increased dramatically soon after that and (*Z*)-**3a** became the main geometrical isomer with further continuous irradiation. This phenomenon implies that the photoexcited isomer (*E*)-**3a** rearranges more rapidly to the regioisomer **4a** than to the geometrical isomer (*Z*)-**3a**. Since compound (*Z*)-**3a** could be formed alternatively by the reverse photochemical 1,3-stannyl migration (**4a** → **3a**) (Table 2, runs 14, 15), the proportion of (*Z*)-**3a** increases steeply around the equilibrium state, in which isomer **4a** becomes the main regioisomer. The total yields of isomers **3a** and **4a** decreased

gradually with irradiation time due to C–Sn bond fission of both compounds **3a** and **4a** occurring in parallel with the 1,3-stannyl migration. The photochemical 1,3-stannyl rearrangement was also tested by using allyltin compounds bearing substituents on the tin center or on the allylic framework (Scheme 4). When all the phenyl groups on the tin in compound **3a** were replaced by methyl (in **3b**) or butyl groups (in **3c**), the 1,3-stannyl migration also proceeded under the same photochemical conditions used for compound **3a**, to give a regioisomeric mixture of products **3** and **4** in which compound **4b** or **4c** was obtained as the major regioisomer, respectively (runs 16–18 in Table 2; Scheme 4). Thus, the substituents (R) on



a: R = Ar = Ph; b: R = Me, Ar = Ph;

c: R = Bu, Ar = Ph; d: R = Ph, Ar = pyren-1-yl

Scheme 4

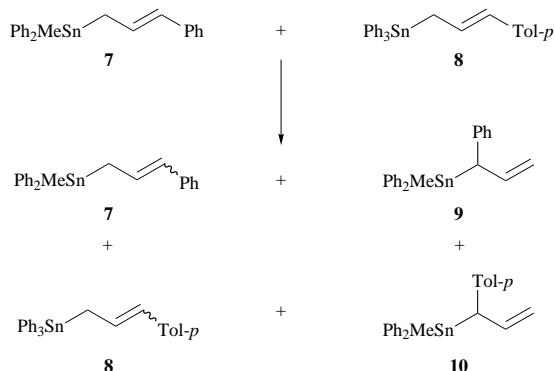
the tin have no influence on the photorearrangement. In addition, [3-(pyren-1-yl)prop-2-enyl]triphenylstannane **3d** having an α -pyrenyl group in the allylic moiety also gave a regioisomeric mixture of products **3d** and **4d** in the ratio 1:7 even under irradiation with light of longer wavelength than 400 nm (run 19 in Table 2). These results revealed clearly that the present photochemical 1,3-rearrangement of cinnamyl(trialkyl)stannanes should involve direct photoexcitation of the cinnamyl π system. This was further supported by an inspection of electronic absorption spectra of these allylic stannanes. (*E*)-Cinnamyl(triphenyl)stannane **3a** and (*E*)-cinnamyl(tributyl)stannane **3c** absorb light at nearly the same wavelength [λ_{\max} (log ϵ) for **3a**: 276 nm (4.38); for **3c**: 273 nm (4.36)], whereas compound **3d** absorbs light of longer wavelength [λ_{\max} = 366 nm (log ϵ = 4.54)] than do analogues **3a** and **3c**. Therefore, these absorption maxima are *not* due to a triphenyltin or tributyltin moiety but *are* due to allylic moieties in these allylstannanes.

Intramolecularity of the present photochemical 1,3-stannyl migration was examined by a crossover experiment (Scheme 5). When an equimolar mixture of cinnamyl(methyl)diphenylstannane **7** and [3-(*p*-tolyl)prop-2-enyl]triphenylstannane **8** in chloroform was photolysed for 1 h, intramolecular rearrangement products, 1-phenylprop-2-enyl(methyl)diphenylstannane **9** (38%) and [1-(*p*-tolyl)prop-2-enyl]triphenylstannane **10** (46%)

Table 3 Photoisomerization of crotyl- and prenyl-tins **11**

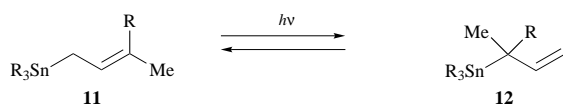
Run	Allyltin	Irradn (λ /nm)	Solvent (additive)	Irradn time (t/h)	Ratio of 11 : 12 ^a	Total yield (%) ^b
1	11a	280	CHCl ₃	0.5	100:0	70
2	11b	280	CHCl ₃	0.5	92:8	53
3	11b	280	CHCl ₃	1	92:8	30
4	11b	254	CHCl ₃	1	88:12	49
5	11e	280	C ₆ H ₆ (CH ₂ Br ₂) ^c	0.5	84:16	72
6	11e	280	C ₆ H ₆ (CH ₂ Br ₂) ^c	1	78:22	44
7	11e	280	C ₆ H ₆ (CH ₂ Br ₂) ^c	1.5	77:23	32
8	11c	280	C ₆ H ₆ (TEMPO) ^d	3	100:0	65
9	11d	280	C ₆ H ₆ (TEMPO) ^d	3	94:6	54
10	11e	280	C ₆ H ₆ (TEMPO) ^d	3	72:28	48

^a Ratios were determined by ¹H NMR spectra. ^b Yields were determined by ¹H NMR spectra using *p*-cyanobenzaldehyde as internal standard. ^c Dibromomethane (3 equiv.) was added. ^d TEMPO (0.2 equiv.) was added.

**Scheme 5** Conditions: *hν* (>320 nm), 1 h, CHCl₃, N₂

were obtained together with the recovery of reactants **7** (2.4%) and **8** (4%). No crossover products were detected in the reaction mixture. Thus, the photochemical 1,3-stannyl migration of cinnamylstannanes involves photoexcitation of the cinnamyl π system and proceeds intramolecularly *via* an orbital symmetry allowed concerted [1,3]-sigmatropic mechanism⁵ accompanying a side reaction of (cinnamyl)C–Sn bond fission. In contrast to the reported thermal rearrangement,² the present photo-rearrangement proceeds towards the opposite direction, giving sterically more crowded allylstannanes as the major product at the photostationary state.

Photoisomerization of but-2-enylstannane (crotylstannane) and 3-methylbut-2-enylstannane (prenylstannane) was also examined (Scheme 6), and the results are summarized in Table



a; R = Buⁿ, R = H; **b**; R = Ph, R = H; **c**; R = Buⁿ, R = Me;
d; R₃ = Buⁿ₂Ph, R = Me; **e**; R = Ph, R = Me

Scheme 6

3. Crotyl(tributyl)stannane **11a** and prenyl(tributyl)stannane **11c** were inert under irradiation with the light through a Pyrex filter (>280 nm), whereas the corresponding (triphenyl)stannanes, **11b** and **11e**, did undergo 1,3-stannyl rearrangement under the same conditions to give a mixture of compounds **11b** and **12b** or **11e** and **12e**, respectively, in which the starting linear tin compound (**11b** or **11e**) was the major regioisomer.

In addition, the photoisomerization of prenyl(dibutyl)phenylstannane **11d** was also observed although photoequilibrium again lay close to the starting prenylstannanes (run 9). Thus, in contrast to cinnamylstannanes, photoisomerization of crotyl- and prenyl-stannanes depended on the substituent at the tin atom, *i.e.* the 1,3-stannyl migration could be observed when the stannanes had phenyl group(s) at the tin centre. These results suggest that the photochemical 1,3-stannyl migration in crotyl-

and prenyl-stannanes involves not direct photoexcitation of the allylic π system but should involve an aromatic π - π^* excitation of phenyl substituents at the tin atom as reported in photochemical 1,3-silyl migration of allylic silanes with aromatic substituents at the silicon centre.⁴ Further work should be required to solve the origin of the different mechanism between cinnamylstannanes and crotyl- or prenyl-stannanes.

Experimental

Mps were determined on a Yanaco melting point apparatus and are uncorrected. The ¹H NMR spectra were recorded on a JEOL JNM GX270 FT spectrometer with tetramethylsilane (TMS) as internal standard: coupling constants (*J*) are given in Hz. The IR spectra were recorded on a Hitachi 260-50 instrument. The UV spectra were measured on a JASCO UVICEC-510 or on a Shimadzu UV3100 spectrometer. Preparative TLC (silica gel 60 PF₂₅₄) was used after being dried in an air oven at 120 °C for 2 h. Flash chromatography was performed on silica gel 60 (E. Merck). All solvents and organic halides were distilled and dried before use by standard procedures.

Materials

(*E*)-Cinnamyl(triphenyl)stannane **3a**,¹³ (*E*)-cinnamyl(trimethyl)stannane **3b**,¹⁴ (*E*)-cinnamyl(tributyl)stannane **3c**,¹⁵ allyl(tributyl)stannane **5**,¹⁵ but-2-enyl(tributyl)stannane **11a**,¹⁶ but-2-enyl(triphenyl)stannane **11b**¹⁶ and 3-methylbut-2-enyl(tributyl)stannane **11c**¹⁵ were prepared using previously reported methods.

(*E*)-[3-(Pyren-1-yl)prop-2-enyl]triphenylstannane **3d**. Butyllithium (14.8 ml of a 1.61 mol dm⁻³ solution in hexane, 24 mmol) was added dropwise to a solution of 1-bromopyrene (5.62 g, 20 mmol) in diethyl ether (80 ml)–benzene (20 ml) at room temperature under nitrogen. After stirring of the mixture for 30 min, 3-bromopropene (3.15 g, 26 mmol) was added to the solution and the mixture was stirred for 20 min before being quenched by the addition of saturated aq. NH₄Cl in an ice-bath. The mixture was extracted with diethyl ether (50 ml \times 3), and the organic layer was washed with brine, dried (Na₂SO₄), and concentrated under reduced pressure. Flash chromatography of the residue on silica gel, using hexane as eluent, gave 3-(pyren-1-yl)propene (3.2 g, 66%) as a pale yellow oil.

Butyllithium (6.2 ml, 10 mmol) was added dropwise to a solution of the foregoing 3-(pyren-1-yl)propene (2.42 g, 10 mmol) in THF (20 ml) at –70 °C under nitrogen, followed by a solution of triphenyltin chloride (3.85 g, 10 mmol) in THF (10 ml) at –30 °C. The mixture was allowed to warm to room temperature, was stirred for 1.5 h at that temperature, and was quenched by aq. KF (10%). The resulting precipitate was filtered off and the filtrate was extracted with diethyl ether. The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated under reduced pressure to afford a crude yellowish crystalline product. Recrystallization of the crude product from benzene–hexane and then from chloroform–diethyl

ether gave the *title compound 3d* (0.9 g, 28%) as yellow crystals, mp 143 °C (Found: C, 75.55; H, 4.43. C₃₇H₂₈Sn requires C, 75.16; H, 4.77%); δ_{H} 2.81 (2H, d, *J* 8.6), 6.69 (1H, dt, *J* 15.4 and 8.6) and 7.29–8.11 (25H, m, one olefinic and ArH); δ_{C} 18.5, 123.5, 123.7, 124.6, 124.9, 125.0, 125.8, 126.6, 126.9, 127.3, 127.5, 128.3, 128.7, 129.2, 129.9, 131.1, 131.6, 132.2, 133.1, 136.9, 137.2, 137.4 and 138.3; λ_{max} CHCl₃/nm 288 (log ϵ 3.70) and 366 (3.83).

(*E*)-Cinnamyl(methyl)diphenylstannane 7. This tin reagent was prepared by the coupling reaction of cinnamylmagnesium chloride with methylphenyltin iodide¹⁷ following a previously described method.¹³ The crude tin reagent thus obtained was purified by flash chromatography on silica gel with hexane as eluent: *oil* (Found: C, 65.08; H, 5.66. C₂₂H₂₂Sn requires C, 65.23; H, 5.47%); δ_{H} 0.52 (3H, s), 2.37 (2H, d, *J* 8.3, CH₂), 6.28 (1H, d, *J* 15.6), 6.43 (1H, dt, *J* 15.9 and 8.3) and 7.10–7.58 (15H, m); ν_{max} /cm⁻¹ 3060, 3020, 1635, 1600, 1435, 1085, 958, 750, 730 and 700.

(*E*)-[3-(*p*-Tolyl)prop-2-enyl]triphenylstannane 8. This *tin reagent* was prepared by the coupling reaction of 3-(*p*-tolyl)prop-2-enylmagnesium chloride with triphenyltin chloride following a previously described method.¹³ mp 86–87 °C (from methanol) (Found: C, 69.87; H, 5.51. C₂₈H₂₆Sn requires C, 69.89; H, 5.45%); δ_{H} 2.30 (3H, s), 2.60 (2H, d, *J* 8.1, CH₂), 6.30 (1H, d, *J* 15.6), 6.42 (1H, dt, *J* 15, and 8.1), 7.02–7.10 (4H, m) and 7.25–7.63 (15H, m).

3-Methylbut-2-enyl(dibutyl)phenylstannane 11d. This tin reagent was prepared by the coupling reaction of 3-methylbut-2-enylmagnesium chloride with dibutylphenyltin iodide¹⁷ following a previously described method.¹⁵ The crude tin reagent thus obtained was purified by column chromatography on alumina with hexane as eluent: *oil* (Found: C, 59.82; H, 8.86. C₁₉H₃₂Sn requires C, 60.19; H, 8.51%); δ_{H} 0.66 (6H, t, *J* 7.1), 1.04–1.09 (4H, m), 1.25–1.39 (4H, m), 1.48–1.60 (4H, m), 1.54 (3H, s), 1.67 (3H, s), 1.88 (2H, d, *J* 8.8), 5.34 (1H, t, *J* 8.8) and 7.30–7.47 (5H, m); ν_{max} /cm⁻¹ 3060, 2960, 2925, 2850, 1460, 1430, 1375, 1075, 725 and 700.

3-Methylbut-2-enyl(triphenyl)stannane 11e. This *tin reagent* was prepared by the reaction of triphenyltin-lithium with 3-methylbut-2-enyl bromide following a previously described method.¹⁵ mp 61–63 °C (from methanol) (Found: C, 65.69; H, 5.55. C₂₃H₂₄Sn requires C, 65.91; H, 5.77%); δ_{H} 1.43 (3H, s), 1.64 (3H, s), 2.35 (2H, d, *J* 8.8), 5.46 (1H, br t, *J* 8.8) and 7.34–7.62 (15H, m).

General procedure for irradiation

Irradiation was carried out with a 300-W high-pressure Hg arc lamp through a saturated aq. CuSO₄ filter about 1 cm in thickness (>320 nm), or through a Pyrex filter (>280 nm), or through a saturated solution of CuSO₄ and NaNO₂ in aq. NH₄OH ~1 cm in thickness (>400 nm).¹⁸ Irradiation with light of 254 nm was carried out with a 60-W low-pressure Hg arc lamp in a quartz vessel. An allyltin compound in benzene or in benzene containing 2,6-di-*tert*-butyl- α -(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*p*-tolylloxyl (galvinoxyl) or TEMPO was purged with nitrogen and irradiated for 1 h. After evaporation off of the solvent, the residue was analysed by means of ¹H NMR spectroscopy, from which the product ratio was determined by integration of signal intensities. The products were isolated by preparative TLC (PLC) developing with 9:1 hexane–dichloromethane.

Irradiation of an allyltin compound in chloroform or in benzene solution containing organic halides was carried out under similar conditions to those described above, but the work-up procedure was different from that above. After irradiation, the reaction mixture was washed with saturated aq. NaHCO₃, and the organic phase was dried (Na₂SO₄). After evaporation off of the solvent, the residue was analysed by means of ¹H NMR spectroscopy, from which the product ratio was determined by integration of signal intensities. In some cases, the yield of

products was also determined by integration of their signal intensities using *p*-cyanobenzaldehyde as internal standard. The product was isolated by PLC, developing with 9:1 hexane–dichloromethane. The results are given in Tables 2 and 3, and in Fig. 1.

Typical irradiation procedure for (*E*)-cinnamyl(triphenyl)stannane 3a in benzene under anaerobic or aerobic conditions

A nitrogen-purged solution of compound **3a** (46.7 mg, 0.1 mmol) in benzene (5 ml) was irradiated through saturated aq. CuSO₄ with a high-pressure Hg lamp for 1 h. The solvent was removed under reduced pressure and ¹H NMR measurement of the residue showed no formation of a 1,3-stannyl migration product. The residue was chromatographed on PLC, developing with 9:1 hexane–dichloromethane. The *R*_f 0.18 band contained 4 mg of hexaphenyldistannane: mp 230–232 °C (lit.,¹⁹ 229–232 °C). The *R*_f 0.57 band contained 36.4 mg (78%) of compound **3a** (*E/Z* = 94:6). The *R*_f 0.77 band contained 5 mg of (*E*)-1,4-diphenylhexa-1,5-diene^{3b} contaminated by 1,6-diphenylhexa-1,5-diene (ratio 92:8): δ_{H} 2.64 (2H, dd, *J* 7.3 and 7, 3-H₂), 3.43 (1H, dt, *J* 7.3, 4-H), 5.07 (2H, m, 6-H₂), 5.96–6.06 (1H, m, 5-H), 6.12 (1H, dt, *J* 7, 2-H), 6.39 (1H, d, *J* 15, 1-H) and 7.06–7.43 (10H, m, ArH); ν_{max} (CHCl₃)/cm⁻¹ 3080, 3000, 2920, 1638, 1600, 1495, 1452, 1075, 1030, 990, 970 and 920.

A benzene solution of compound **3a** was purged with oxygen for 15 min and irradiated under the above conditions. The reaction mixture was washed with saturated aq. NaHCO₃, and the organic layer was dried (Na₂SO₄). After evaporation of the mixture, the product was isolated by TLC, developing with hexane–dichloromethane (9:1) to give a regioisomeric mixture of compounds **3a** and **4a** (ratio **3a**:**4a** = 11:89) in 51% yield.

Spectroscopic and physical properties of rearranged allylic stannanes 4 and 12

Spectroscopic properties of 1-phenylprop-2-enyl(tributyl)stannane **4c**, but-3-en-2-yl(tributyl)stannane **12a**, and 2-methylbut-3-en-2-yl(tributyl)stannane **12c** agreed with the data reported in ref. 2.

1-Phenylprop-2-enyl(triphenyl)stannane 4a. Mp 104 °C (from methanol) (Found: C, 69.02; H, 5.19. C₂₇H₂₄Sn requires C, 69.42; H, 5.18%); δ_{H} 4.16 (1H, d, *J* 9.5, 1-H), 4.81–5.10 (2H, m, 3-H₂), 6.44 (1H, dt, *J* 17 and 10, 2-H), 7.02–7.20 (5H, m, ArH) and 7.25–7.50 (15H, m, ArH); δ_{C} 42.9, 111.6, 124.8, 127.2, 128.4, 128.6, 129.0, 137.4, 138.1, 138.8, 142.2.

1-Phenylprop-2-enyl(trimethyl)stannane 4b. Oil; δ_{H} 0.06 (9H, s, SnMe₃), 3.48 (1H, d, *J* 10.3, 1-H), 4.79–4.94 (2H, m, 3-H₂), 6.33 (1H, dt, *J* 16.8 and 10.1, 2-H) and 7.03–7.41 (5H, m, ArH).

[1-(Pyren-1-yl)prop-2-enyl]triphenylstannane 4d. This compound isomerized to compound **3d** with partial decomposition on TLC. It was isolated as follows: After irradiation of compound **3d** in benzene containing 3 equivalent of dibromomethane with light of wavelength >400 nm for 40 min, the solvent was removed under reduced pressure. Diethyl ether was added to the residue and the resulting ethereal solution was washed with aq. KF (10%), dried over Na₂SO₄ Evaporation of the solution gave an oil, which was triturated with chloroform–hexane and left overnight in a refrigerator (~–20 °C) to give compound **4d** as crystals: mp 116–118 °C (Found: C, 74.97; H, 4.52. C₃₇H₂₈Sn requires C, 75.16; H, 4.77%); δ_{H} 4.96–5.12 (2H, m, 3-H₂), 5.24 (1H, d, *J* 8.5, 1-H), 6.62–6.80 (1H, d, 2-H), 7.18–7.45 (15H, m, Ph₃Sn) and 7.85–8.25 (9H, m, ArH); δ_{C} 39.6, 112.3, 123.2, 124.5, 124.7, 125.1, 126.0, 126.3, 126.9, 127.4, 127.6, 128.1, 128.4, 128.7, 128.8, 129.0, 130.9, 131.6, 136.5, 136.8, 137.2, 137.5, 138.3 and 139.9; ν_{max} (CHCl₃)/cm⁻¹ 3060, 3050, 2920, 1620, 1600, 1585, 1480, 1430, 1075, 1020, 1000, 900 and 854.

But-3-en-2-yl(triphenyl)stannane 12b. Mp 74–75 °C; δ_{H} 1.52 (3H, d, *J* 7.3, CH₃), 2.88 (1H, dq, *J* 7.2 and 7.1, 2-H), 4.84 (1H, d, *J* 10, 4-H), 4.89 (1H, d, *J* 17.1, 4-H), 6.28 (1H, ddd, *J* 17.1, 10 and 7.1, 3-H) and 7.36–7.62 (15H, m, ArH); ν_{max} (KBr)/cm⁻¹

3050, 2950, 2900, 1620, 1480, 1430, 1140, 1070, 1020, 1000, 960, 850, 730 and 700.

2-Methylbut-3-en-2-yl(dibutyl)phenylstannane 12d. *Oil* (Found: C, 59.82; H, 8.86. C₁₉H₃₂Sn requires C, 60.19; H, 8.51%); δ_{H} 0.85–1.80 (24H, m, Me₂ + Bu₂), 4.62 (1H, dd, *J* 17.3 and 1.5, 4-H), 4.73 (1H, dd, *J* 10.5 and 1.5, 4-H), 6.07 (1H, dd, *J* 17.3 and 10.5, 3-H) and 7.28–7.57 (5H, m, ArH).

2-Methylbut-3-en-2-yl(triphenyl)stannane 12e. Mp 67–69 °C; δ_{H} 1.49 (6H, s, Me₂), 4.75–4.87 (2 H, m, 4-H₂), 6.26 (1H, dd, *J* 17.2 and 10.6, 3-H), 7.35–7.56 (15H, m, ArH); ν_{max} /cm⁻¹ 3045, 3015, 2930, 2850, 1620, 1475, 1424, 1115, 1072, 995, 890, 723 and 700.

Photochemical crossover reaction between cinnamyl(methyl-diphenyl)stannane 7 and [3-(*p*-tolyl)prop-2-enyl]triphenylstannane 8

An equimolar mixture of compounds 7 (20.3 mg, 0.05 mmol) and 8 (24 mg, 0.05 mmol) in a chloroform solution was photolysed with >320 nm light under nitrogen for 1 h. The reaction mixture was washed with saturated aq. NaHCO₃, and the organic phase was dried over Na₂SO₄. After evaporation of the mixture, careful chromatographic separation of the residue on TLC developing with hexane gave a mixture of compound 7 (*E:Z* = 33:67) and 1-phenylprop-2-enyl(methyl)diphenylstannane 9 (ratio 7:9 = 6:94) and a mixture of compounds 8 (*E:Z* = 29:71) and [1-(*p*-tolyl)prop-2-enyl]triphenylstannane 10 (ratio 8:10 = 8:92) in total yields of 40 and 50%, respectively. ¹H NMR data for compound 9: δ_{H} 0.43 (3H, s, SnMe), 3.91 (1H, d, *J* 9.8, 1-H), 4.82–5.05 (2H, m, 3-H₂), 6.38 (1H, dt, *J* 16.8 and 10, 2-H) and 7.03–7.53 (15H, m, ArH); for compound 10: δ_{H} 2.28 (3H, s, *p*-Me), 4.13 (1H, d, *J* 9.5, 1-H), 4.83–5.05 (2H, m, 3-H₂), 6.35–6.49 (1 H, m, 2-H) and 7.01–7.68 (19H, m, ArH).

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