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Note

Palladium complex-catalyzed germylation of allylic halides using (germyl)stannanes

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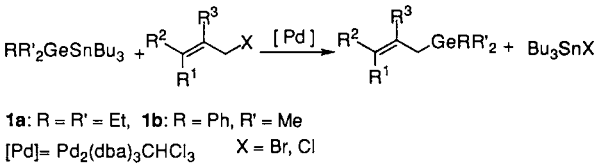
Abstract

(Triethylgermyl)tributylstannane reacts metal-selectively with allylic halides at room temperature (r.t.) in the presence of tris(dibenzylideneacetone)dipalladium, $Pd_2(dba)_3CHCl_3$, to provide an alternative route to allylgermanes. (Dimethylphenylgermyl)tributylstannane regio- and stereoselectively reacts more readily with allylic halides than (triethylgermyl)tributylstannane affording the corresponding allylgermanes in quantitative yields. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Germylstannanes; Palladium catalysis; Metathesis; Allylgermanes; Allyl halides

1. Introduction

Allylsilanes are of great importance in organic synthesis. Hence, a variety of methods for their synthesis [1] and use have been studied [2]. In contrast, the synthesis and use of allylgermanes have been very limited. However, interest in their use has recently increased [3]. Up to now, several routes for the synthesis of allylgermanes have been reported: (1) reactions of an allylmagnesium halide [4] or an allyllithium reagent [5] with halogenated germanes; (2) hydrogermylation of 1,3-dienes [6]; (3) double germylation of 1,3-dienes [7], and (4) germylation of allylic acetates (or allyl sulfides) using a bis(germyl)cuprate [8], in addition to our own previous work [9,10]. For the synthesis of allylgermanes, allylic halides or acetates are readily accessible substrates. Among these methods, the first synthetic reaction is not regiospecific e.g. during the synthesis of cinnamylgermane [8]. In the fourth one, only a single germyl group in a bis(germyl)cuprate is involved. Finally, our own methods employ allylic halides and digermanes [9a,b] or (germyl)silanes [9c] and the reactions proceeded metal-selectively resulting in the regio- and stereoselective formation of allylgermanes. However, they were accompanied by small amounts of by-products such as allylsilanes in the latter reaction. In the closely related study, we recently demonstrated that (triethylgermyl)tributylstannane **1a** reacted with allyl halides metal-selectively to provide an alternative route to the allylgermanes [10]. In this paper, we report the full results for the regio- and stereoselective synthesis of allylgermane using **1a** or (dimethylphenylgermyl)tributylstannane **1b** (Scheme 1).



Scheme 1.

2. Results and discussion

Stirring a benzene solution of a 1:1:0.005 mixture of **1a**, allyl bromide and $Pd_2(dba)_3CHCl_3$ (dba; dibenzyli-

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Table 1
The influence of the reaction conditions on the yield of allyltriethylgermane in reaction (**1**)

Run	GeSn [a] (mmol)	X in allyl-X (mmol)	[Pd] (mol %)	PPh_3 (mmol)	PhH (ml)	Conditions (°C, *h*)	Yield [b] (%)
1	1.01	Br(1.00)	A [c](0.5)	None	1	120, 5	80
2	1.01	Br(2.18)	A(3.0)	0.12	1	100, 10	37
3	1.01	Br(1.00)	A(0.5)	None	1	80, 5	71
4	1.00	Br(2.00)	B [d](1.0)	None	1	80, 10	12
5	1.02	Br(2.03)	A(0.5)	None	1	80, 10	84
6	1.00	Br(2.07)	A(0.5)	0.02	1	80, 10	14
7	1.03	Br(2.52)	A(1.5)	None	None	r.t., 17	83
8	1.00	Br(2.0)	A(1.5)	0.06	None	r.t., 360	69
9	1.00	Cl(2.00)	A(0.5)	None	None	r.t., 36	95
10	1.00	Cl(2.00)	A(1.5)	None	None	r.t., 7	92
11	1.00	Cl(2.00)	C [e](1.0)	None	None	r.t., 10	67

[a] $Et_3GeSnBu_3$ (**1a**).

[b] Product is allyltriethylgermane, GLC yields of which were based on the **1a** used.

[c] A, $Pd_2(dba)_3CHCl_3$.

[d] B, $PdCl_2(PPh_3)_2$.

[e] C, $Pd(dba)_2$.

deneacetone) at 120°C under nitrogen gave the allyltriethylgermane (80% yield, entry 1 in Table 1) along with bromotributylstannane.

Further inspection of the reaction conditions disclosed that the reaction could also proceed at 80°C to give the allylgermane (71% yield, entry 3). In these experiments, the formation of allyltributylstannane or bromotriethylgermane was not observed at all.

Quite interestingly, during the reaction using a 1:2:0.015 mixture of **1a**, allyl bromide and $Pd_2(dba)_3$-$CHCl_3$ without benzene solvent, germylation occurred even at r.t. (near 10–25°C) to give the allylgermane (83% yield, entry 7). The use of triphenylphosphine as a ligand on palladium made the reaction much slower. To obtain an acceptable yield, a longer reaction time was required (entry 8). The use of the allyl chloride instead of the bromide also gave a reasonable yield of the allyltriethylgermane (entries 9 and 10). Dichlorobis(triphenylphosphine)palladium also catalyzed the reaction of the allyl bromide with **1a**, but the catalytic activity of the complex was much lower than that of $Pd_2(dba)_3$ (entry 4). $Pd(dba)_2$ catalyzed the reaction similar to $Pd_2(dba)_3$ to form the allylgermane in good yield (entry 11).

Results for the $Pd_2(dba)_3$-catalyzed germylation of several allylic halides using **1a** at r.t. are summarized in Table 2.

The reaction of crotyl chloride gave crotyltriethylgermane in 88% yield together with 3-(triethylgermyl)-1-butene (6% yield) (entry 2). A similar isomer distribution was also observed during the reaction of crotyl bromide(entry 4). Interestingly, crotyltriethylgermane was also formed during the reaction with 3-chloro-1-butene (entry 3). From prenyl chloride, the expected dehalogenative germylation product was also formed in a good yield (entry 5). Cyclic allylic bromides such as 3-bromocyclohexene easily underwent the

Table 2
Palladium-catalyzed r.t. germylation of 2-alkenyl halides (R–X) using (germyl)stannane **1a** [a]

Run	R–X	Time (h)	Product	Yield (%) [b]
1	$CH_2{=}CHCH_2Cl$	7	$CH_2{=}CHCH_2GeEt_3$ [c]	92
2	$CH_3CH{=}CHCH_2Cl$ [d]	14	*trans*-$CH_3CH{=}CHCH_2$-$GeEt_3$ [e]	88
			$CH_2{=}CHCH(GeEt_3)CH_3$	6
3	$CH_2{=}CHCHClCH_3$	14	*trans*-$CH_3CH{=}CHCH_2$-$GeEt_3$ [e]	74
			$CH_2{=}CHCH(GeEt_3)CH_3$	6
4	$CH_3CH{=}CHCH_2Br$ [f]	14	*trans*-$CH_3CH{=}CHCH_2$-$GeEt_3$	85
			$CH_2{=}CHCH(GeEt_3)CH_3$	3
5	$(CH_3)_2C{=}CHCH_2Cl$	9	$(CH_3)_2C{=}CHCH_2GeEt_3$ [g]	63
6	$PhCH{=}CHCH_2Cl$	10	$PhCH{=}CHCH_2GeEt_3$ [h]	22
7	$PhCH{=}CHCH_2Br$	10	$PhCH{=}CHCH_2GeEt_3$ [h]	20
8	3-Br-cyclohexene	11	3-(Et_3Ge)-cyclohexene [i]	76

[a] All reactions were carried out at r.t. using a 1:2:0.015 mixture of **1a**, the halide and $Pd_2(dba)_3CHCl_3$ under argon or nitrogen.

[b] GLC yields based on the **1a** used.

[c] See Ref. [3g].

[d] A *cis* and *trans* mixture. Four percent of 3-chloro-1-butene was included.

[e] See Ref. [6a].

[f] A *cis* and *trans* mixture. Fourteen percent of 3-bromo-1-butene was included.

[g] See Ref. [11].

[h] See Ref. [12].

[i] See Ref. [13].

Table 3
Palladium-catalyzed r.t. germylation of 2-alkenyl chlorides (R–Cl) using **1b** [a]

Run	R–Cl	Time (h)	Product (isomer ratio) [b]	Yield (%) [c]
1	$CH_2=CHCH_2Cl$	2	$CH_2=CHCH_2GeMe_2Ph$ [d]	Quant.(95)
2	$CH_3CH=CHCH_2Cl$ [e]	4	*trans*-$CH_3CH=CHCH_2GeMe_2Ph$(88) [f] *cis*-$CH_3CH=CHCH_2GeMe_2Ph$(12)	Quant.(64) [g]
3	$CH_2=CHCHClCH_3$	3	*trans*-$CH_3CH=CHCH_2GeMe_2Ph$(79) [f] *cis*-$CH_3CH=CHCH_2GeMe_2Ph$(21)	Quant.(70) [g]
4	$(CH_3)_2C=CHCH_2Cl$	6	$(CH_3)_2C=CHCH_2GeMe_2Ph$ [h]	Quant.
5	$PhCH=CHCH_2Cl$	3	*trans*-$PhCH=CHCH_2GeMe_2Ph$(84) *cis*-$PhCH=CHCH_2GeMe_2Ph$ (4) $PhCH(GeMe_2Ph)CH=CH_2$(12)	Quant.(70) [g]

[a] All reactions were carried out at r.t. by using a 1:2–3:0.005 mixture of **1b**, the halide and $Pd_2(dba)_3CHCl_3$.

[b] Isomer ratio was determined by NMR using a sample collected by GLC.

[c] GLC yields based on the **1b** used. Isolated yields are shown in parentheses {Isolation was done by treating the resulting mixture with an aqueous solution of KF [19] followed by column chromatography (silica gel, hexane)}.

[d] See Ref. [14].

[e] A *cis* and *trans* mixture.

[f] See Ref. [9c].

[g] Total yields of product isomers.

[h] See Section 3.

germylation to afford the corresponding 3-(triethylgermyl)cyclohexene (entry 8). In contrast, *trans*-cinnamyltriethylgermane from *trans*-cinnamyl chloride or the bromide was formed only in ca. 20% yield (entries 6 and 7). Hoping to improve the yield, we examined the reaction of the cinnamyl chloride with **1b** in the presence of the palladium catalyst. As expected, the reaction proceeded rapidly at r.t. to produce a quantitative yield of the cinnamyldimethylphenylgermanes. Similar increased reactivity of a metal–metal bond caused by introduction of a phenyl group into bimetallic compounds is also seen in other reactions of a disilane [1i], a digermane [9b], or a (germyl)silane [9c].

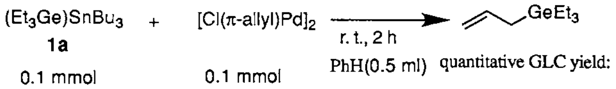
Other examples of germylation using **1b** are summarized in Table 3. Germylation of the allyl chloride, crotyl chloride, 3-chloro-1-butene and prenyl chloride with **1b** also proceeded more rapidly than that with **1a** to form the corresponding products in quantitative yields. Interestingly, during the germylation of 3-chloro-1-butene, the formation of crotyldimethylphenylgermanes dominated (entry 3).

We emphasize the exclusive formation of allylgermanes in the present reaction. This is in contrast with the previously reported reactions with (germyl)silanes which were always accompanied by small amounts of allylsilanes as by-products [10].

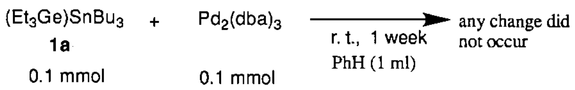
We next attempted the reactions of **1a** with the chloro(π-allyl)palladium dimer (Scheme 2) and with tris(dibenzylideneacetone)dipalladium (Scheme 3), aimed at understanding the reaction mechanism.

The former reaction gave the allyltriethylgermane in quantitative yield, whereas a benzene solution of $Pd_2(dba)_3$ and **1a** stirred for 1 week at r.t. remained unaltered.

The allylic halide has been reported to oxidatively add to the dibenzylideneacetone-palladium complex in organic media at r.t. giving the chloro(π-allyl)palladium complex [15]. Therefore, the oxidative addition of allyl chloride to the palladium complex seems to be a reasonable initial step in this catalysis. However, we cannot entirely exclude the possibility of the initial addition of a (germyl)stannane molecule to the palladium atom as the primary event. Hence, we propose the mechanism shown in Fig. 1. However, the reason for the predominant carbon–germanium bond formation or tin–chlorine bond formation is unclear at the moment. As shown in Table 3, **1b** reacted with cinnamyl chloride at r.t. to give the dechlorinative germylation products in quantitative GLC yield. The product isomer distribution, determined by NMR, was 84:4:12 for the *trans*: *cis*: α-substitution product (Scheme 4). This selectivity for the *trans*-isomer was slightly lower than that in the previously reported germylation using 1,2-diphenyltetramethyldigermane (isomer ratio: *trans*/*cis* = 97/3) (Scheme 5) [9b]. The difference in the isomer distributions between the reactions using **1b** and 1,2-diphenyltetramethyldigermane can not be precisely explained at



Scheme 2.



Scheme 3.

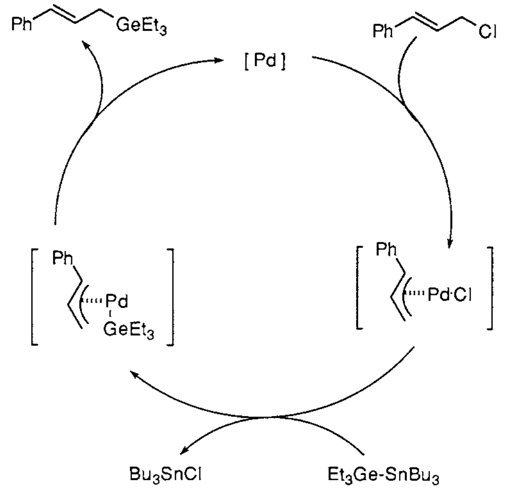
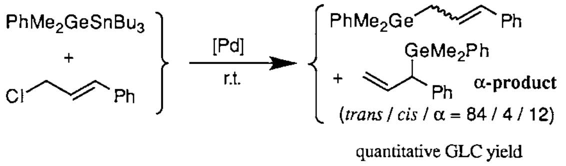
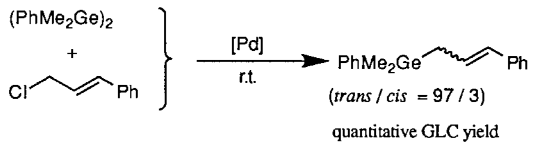


Fig. 1. The tentative mechanism for the germylation with a (germyl) stannane.



Scheme 4.



Scheme 5.

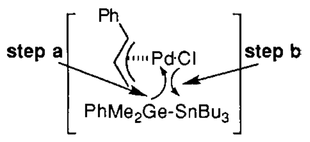


Fig. 2.

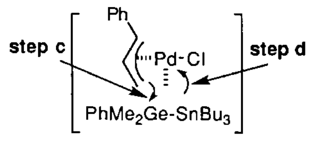


Fig. 3.

present, but may be closely related to the metathesis step in Fig. 1.

Two possible metathesis variants are illustrated in Figs. 2 and 3. In the form shown in Fig. 2, the tin–chlorine bond formation (step b) occurs faster than step a, and results in a germyl(π-cinnamyl)palladium complex similar to that resulting in the reaction of 1,2-diphenyltetramethyldigermane and chlorostannane. Both intermediates would be anticipated to yield similar isomer distributions, not, as is actually observed, different ones. In the second variant (Fig. 3), the carbon–germanium bond formation (step c) occurs faster than step d and results in the formation of cinnamylgermane and chloro(stannnyl)palladium.

The stannyl group in **1b** shown in Fig. 3 seems to exert an influence on the product distribution. Faster carbon-germanium bond formation than the tin–chlorine bond formation in Fig. 3 seems to be the most probable explanation for the difference in the product distributions arising from the reactions using **1b** and 1,2-diphenyltetramethyldigermane.

3. Experimental

3.1. Measurement and materials

GLC analyses were performed using an Ohkura model 103 instrument (tcd detector; 0.6 $\phi \times$ 100–200 cm stainless columns; Silicone KF-96 (10–20%) on Celite 545 SK (60–80 mesh). Mass spectra were obtained with a JEOL JMSAX-500 spectrometer with a DA7000 data system. ^{1}H-NMR spectra were recorded at 400 MHz on a Varian UNITY-400 spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Allylic halides were purchased as extra pure reagents from Tokyo Kasei Kogyo Co., Ltd., and distilled prior to use. (Triethylgermyl)tributylstannane and (dimethylphenylgermyl)tri-butylstannane were prepared according to the synthesis of (trimethylsilyl)tributylstannane [16]. Tris(dibenzylideneacetone)dipalladium [15], bis(dibenzylideneacetone)palladium [17], and dichlorobis(triphenylphosphine)palladium [18] were prepared according to the literature procedures. The chloro(π-allyl)palladium dimmer was purchased from Aldrich Chemicals Co., Inc.

3.2. A typical procedure for the synthesis of the allylgermanes

A mixture of $Pd_2(dba)_3$–$CHCl_3$ (0.0025 mmol), **1b** (0.3 mmol), *trans*-cinnamyl chloride (1 mmol) in a screw-cap sample tube was stirred at r.t. under argon. This reaction was complete within 3 h to form a mixture of 84:4:12, the ratio being determined by NMR, of *trans*-cinnamyldimethylphenylgermane, *cis*-cinnamyldi-methylphenylgermane and 3-(dimethylphenylgermyl)-3-phenylpropene in quantitative combined GLC yield. Ether (10 ml) was added to the resulting mixture which was then treated with an aqueous (10 ml) solution of KF(1 g) [19]. The precipitated fluorotributylstannane was then removed by filtration. The ether layer was separated, and dried using $MgSO_4$. The concentrate of the ether solution was purified by column chromatography (silica gel, hexane) to spectroscopically give the pure product isomers in a total yield of 70%. The ^{1}H-NMR and MS spectra of the products were in good agreement with those previously reported [9b].

Similarly, prenyldimethylphenylgermane was formed in a quantitative GLC yield: ^{1}H-NMR ($CDCl_3$) δ 7.47–7.43 (*m*, 2H), 7.46–7.2 (*m*, 3H), 5.21 (*tm*, 1H), 1.78 (*d*, 2H, $J = 8.8$ Hz), 1.67 (*s*, 3H), 1.51 (*s*, 3H) 0.36 (*s*, 6H) ppm. HRMS (EI): Calc for $C_{13}H_{20}Ge$ 250.0777. Found: 250.0815.

3.3. Reaction of **1a** with chloro(π-allyl)palladium dimmer

A benzene (0.5 ml) solution of **1a** (0.1 mmol) and the chloro(π-allyl)palladium dimmer (0.1 mmol) in a screw-cap sample tube was stirred at r.t. under argon. The reaction was monitored by GLC. After 2 h of stirring, **1a** was completely consumed. The allyltriethylgermane was formed in a quantitative GLC yield.

3.4. Reaction of **1a** with $Pd_2(dba)_3CHCl_3$

A benzene (1 ml) solution of **1a** (0.1 mmol) and tris(dibenzylideneacetone)dipalladium (0.1 mmol) in a screw-cap sample tube was stirred at r.t. under argon. The reaction was monitored by GLC. However, even after 1 week, no change in **1a** was observed.

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