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Note

An alternative route to allylgermanes by the palladium-catalyzed reaction of germylsilanes with allylic halides

Kazuyoshi Ono, Hisao Ishizuka, Taichi Nakano *

Department of Material Science and Technology, School of High-Technology for Human Welfare, Tokai University, 317 Nishino, Numazu, Shizuoka 410-0321, Japan

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Abstract

$\text{Pd}(\text{dba})_2$ (bis(dibenzylideneacetone)palladium complex) effectively catalyzes the reaction of (dimethylphenylgermyl)-trimethylsilane with 2-alkenyl halides to bring about metal-, regio- and stereoselective metathesis resulting in the formation of 2-alkenylphenylgermanes with good yields. On the other hand, the reaction of (chlorodimethylgermyl)trimethylsilane with 2-alkenyl halides is effected by a palladium–phosphine complex to give 2-alkenylchloro-germanes selectively. Germylation of 3,4-dichloro-1-butene with (dimethylphenylgermyl)trimethylsilane forms 1,4-bis(dimethylphenylgermyl)-2-butene with a high yield. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Allylsilanes [1] and allylstannanes [2] are valuable reagents in organic synthesis. In contrast, the synthetic use of allylgermanes [3] is very limited. The main reason is the apparent lack of appropriate synthetic methods for the preparation of stereo-defined allylgermanes. Several reactions are currently available; (a) allylation of chloro-germanes with allylmagnesium chloride [4] or allyl lithium [5]; (b) hydrogermylations of dienes [6] or allenes [7]; and (c) germylation of allyl acetates using germylcuprates(I) [8] or of allyl chlorides using digermanes [9]. Recently, we reported that (triethylgermyl)tributylstannane reacted with 2-alkenyl chlorides in the presence of $\text{Pd}_2(\text{dba})_3$ at room temperature undergoing a metal-controlled metathesis affording 2-alkenylgermanes with good yields [10]. In closely related work, we examined the reaction of (germyl)-silanes with 2-alkenyl halides aiming at a selective

formation of allylgermanes. Unfortunately, we found that the reaction of (triethylgermyl)trimethylsilane with allyl chloride in the presence of $\text{Pd}_2(\text{dba})_3$ gave allyltriethylgermane and allyltrimethylsilane with yields of 22 and 12%, respectively. To overcome this difficulty, we examined the reactions of (dimethylphenylgermyl)-trimethylsilane **1a** and (chlorodimethylgermyl)trimethylsilane **1b** with allylic halides in the presence of a transition metal catalyst and found that the selective formation of allylgermane occurred. In the metathesis of phenyl or chloro substituted homobimetallics such as disilanes or digermanes with allylic chlorides, selective formation of 2-alkenyl(phenyl)metallanes or 2-alkenyl(chloro)metallanes has been reported [9b, 11]. However, to date, it is not known whether the metathesis of heterobimetallics such as a (phenylgermyl)silane or a (chloro-germyl)silane with allylic halides occurs metal-, regio- and stereoselectively. We would like to report herein the first example demonstrating that the metal-, regio- and stereoselective metathesis does indeed take place in the presence of $\text{Pd}(\text{dba})_2$ or $\text{Pd}_2(\text{dba})_3\text{-4PPH}_3$ to provide an alternative synthesis of 2-alkenylgermanes.

* Corresponding author. Fax: +81-6-559681155.

2. Results and discussion

Stirring a 1:2:0.005 mixture of the (germyl)silane **1a**, allyl chloride and Pd₂(dba)₃ at room temperature (r.t.) led to metal selective metathesis to furnish allyldimethylphenylgermane (61%) and allyltrimethylsilane (3%). Chlorotrimethylsilane and chlorodimethylphenylgermane as by-products, respectively, of the allylgermane and the allylsilane were also formed in corresponding yields. Use of such solvents as benzene, toluene, cumene or THF brought about good germanium selectivity (entries 2–5 in Table 1). Dimethylformamide (DMF), a basic solvent, was found to be unsuitable for the present purpose (entry 6 in Table 1).

After screening the reaction conditions, use of 1 mol% of Pd(dba)₂ led to completion of metathesis within 4 h affording allyldimethylphenylgermane at a 70% yield with the formation of a 3% yield of allyltrimethylsilane (Scheme 1, entry 7 in Table 1). Palladium–phosphine complexes such as Pd(OAc)₂–2PPh₃ or PdCl₂(PPh₃)₂ also catalyzed the reaction, but the yields of the corresponding allylgermane were only 36

and 48%, respectively (entries 9 and 10 in the Table 1).

Dichlorotris(triphenylphosphine)ruthenium(II) effected metathesis at r.t. to afford allyldimethylphenylgermane in 54% yield with a 10% yield of allyltrimethylsilane. However, when the RuCl₂(PPh₃)₃ catalysis was carried out at 150°C, the yield of the allylgermane was improved from 54 to 70% and the ratio of the allylgermane to the allylsilane was improved from 84/16 to 96/4, respectively (entry 12 in the Table 1). The reason for this somewhat unexpected result is, however, at present unclear. Other tested catalysts such as Pd(dba)₂–LiCl, RhCl(PPh₃)₃, NiCl₂(PPh₃)₂ and NiBr₂(PPh₃)₂ were inferior to Pd(dba)₂, Pd₂(dba)₃ and RuCl₂(PPh₃)₃.

In the germylation using the (germyl)silane **1b**, triphenylphosphine as a ligand was necessary (Scheme 2). The metathesis in the presence of Pd₂(dba)₃ alone gave allylchlorodimethylgermane and allyltrimethylsilane only with yields of 13 and 2%, respectively (entry 2 in the Table 2). RuCl₂(PPh₃)₃ appeared to be less effective (entry 4 in the Table 2).

Table 1
Comparison of conditions in the reaction of (dimethylphenylgermyl)trimethylsilane **1a** with allyl chloride^a

Entry	Catalyst (mol%) ^b	Ligand (mol%) ^d	Solvent (ml)	Conditions (°C, h)	Yield (%) ^c		Metal selectivity
					[A] ^e [B] ^f	[A]/[B]	
1	Pd ₂ (dba) ₃ (0.5)	None	None	r.t., 5	61	3	95/5
2	Pd ₂ (dba) ₃ (0.5)	None	PhH (1)	40, 10	62	16	79/21
3	Pd ₂ (dba) ₃ (0.5)	None	PhMe (1)	40, 10	59	5	92/8
4	Pd ₂ (dba) ₃ (0.5)	None	Cumene (1)	40, 10	60	8	88/12
5	Pd ₂ (dba) ₃ (0.5)	None	THF (1)	40, 10	54	4	93/7
6	Pd ₂ (dba) ₃ (0.5)	None	DMF (1)	40, 10	20	34	37/63
7	Pd(dba) ₂ (1.0)	None	None	r.t., 4	70	3	96/4
8	Pd(dba) ₂ –LiCl (2.0)	None	DMF(1)	r.t., 200	12	13	48/52
9	Pd(OAc) ₂ (1.0)	PPh ₃ (2.0)	None	r.t., 850	36	16	69/31
10	PdCl ₂ (PPh ₃) ₂ (1.0)	None	None	r.t., 350	48	9	84/16
11	RuCl ₂ (PPh ₃) ₃ (1.0)	None	None	r.t., 2	54	10	84/16
12	RuCl ₂ (PPh ₃) ₃ (0.1)	None	None	150, 10	70	3	96/4
13	RhCl(PPh ₃) ₃	None	None	150, 25	0	22	0/100
14	NiCl ₂ (PPh ₃) ₂	None	None	150, 25	5	20	20/80
15	NiBr ₂ (PPh ₃) ₂	None	None	150, 25	19	10	66/34

^a (Germyl)silane **1a**/allyl chloride, 1 mmol/2–3 mmol. The (germyl)silane **1a** was almost completely consumed.

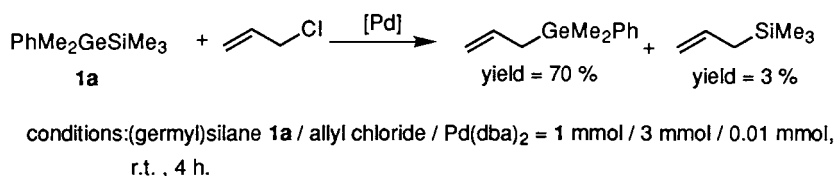
^b (mmols of the catalyst/mmols of (germyl)silane **1a**) × 100.

^c Yields were determined by GLC and based on the (germyl)silane **1a** charged. Thermal conductivity corrections were not made.

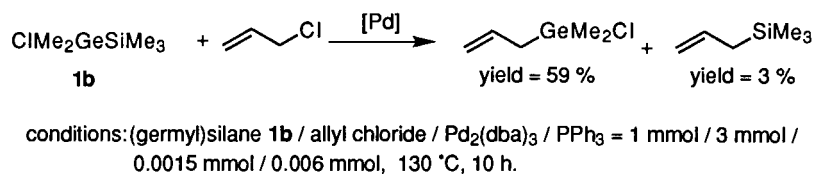
^d (mmols of PPh₃/mmols of (germyl)silane **1a**) × 100.

^e [A], allyldimethylphenylgermane.

^f [B], allyltrimethylsilane.



Scheme 1.



Scheme 2.

Table 2

Comparison of conditions in the reaction of (chlorodimethylgermyl)trimethylsilane **1b** with allyl chloride ^a

Entry	Catalyst (mol%) ^b	Ligand (mol%) ^d	Conditions (°C, h)	Yield (%) ^c		Metal selectivity
				[A] ^e [B] ^f	[A]/[B]	
1	Pd ₂ (dba) ₃ (0.15)	PPh ₃ (0.6)	130, 10	59	3	95/5
2	Pd ₂ (dba) ₃ (0.15)	None	150, 10	13	2	87/13
3	Pd ₂ (dba) ₃ (0.15)	PPh ₃ (0.6)	100, 10	3	3	50/50
4	RuCl ₂ (PPh ₃) ₃ (0.1)	None	150, 10	28	3	90/10

^a (Germyl)silane **1b**/allyl chloride:1 mmol/3 mmol.^b (mmols of the catalyst/mmol of (germyl)silane **1b**) × 100.^c Yields were determined by GLC and based on the (germyl)silane **1b** charged. Thermal conductivity corrections were not made.^d (mmols of PPh₃/mmols of (germyl)silane **1b**) × 100.^e [A], allylchlorodimethylgermane.^f [B], allyltrimethylsilane.

Table 3

Palladium-catalyzed reaction of (germyl)silanes (RMe₂GeSiMe₃) **1a** or **1b** with several allylic halides ^a

Entry	R in RGeSi	Halide	Catalyst (mol%) ^b	Conditions (°C, h)	Yield/% ^c		Metal selectivity
					[A] ^d [B] ^e	[A]/[B]	
1	Ph	CH ₂ =CHCH ₂ Cl	C (0.5) ^f	r.t., 5	61	3	95/5
2	Ph	CH ₂ =CHCH ₂ Cl	D (1.0) ^g	r.t., 4	70	3	96/4
3	Ph	CH ₂ =CHCH ₂ Br	C (0.5)	r.t., 8	53	5	91/9
4	Ph	CH ₂ =CMeCH ₂ Cl	D (1.0)	r.t., 5	94	6	94/6
5	Ph	CH ₃ CH=CHCH ₂ Cl ^h	D (1.0)	r.t., 3	97	Trace	³ 99.5/ ² 0.5
6	Ph	CH ₃ CHClCH=CH ₂	D (1.0)	r.t., 6	99	Trace	³ 99.5/ ² 0.5
7	Ph	Me ₂ C=CHCH ₂ Cl	D (1.0)	r.t., 3	86	Trace	³ 99.5/ ² 0.5
8	Ph	<i>trans</i> - PhCH=CHCH ₂ Cl	D (1.0)	r.t., 7	86 ⁱ	– ^j	–
9	Cl	CH ₂ =CHCH ₂ Cl	E (0.15) ^k	130, 10	59	3	95/5
10	Cl	Me ₂ C=CHCH ₂ Cl	E (0.15)	130, 10	46	9	84/16
11	Cl	<i>trans</i> - PhCH=CHCH ₂ Cl	E (0.15)	130, 10	57 ^l	4	93/7

^a (silyl)germane **1a** or **1b**/halide/1 mmol/2–3 mmol. Structural determination in these products was made by NMR and MS spectra.^b (mmols of the catalyst/mmol of (germyl)silane **1a** or **1b**) × 100.^c Yields were determined by GLC based on the (germyl)silane **1a** or **1b** used.^d [A], 2-alkenyldimethylphenylgermane.^e [B], 2-alkenyltrimethylsilane.^f C, Pd₂(dba)₃.^g D, Pd(dba)₂.^h A *trans*- and *cis*-isomeric mixture.ⁱ *trans*-Cinnamylchlorodimethylgermane/its *cis*-isomer/3-phenyl-3-(chlorodimethylgermyl)propene: 79/12/9.^j Cinnamyltrimethylsilane was not detected by GLC analysis, but chlorodimethylphenylgermane was formed in 12% yield.^k E, Pd₂(dba)₃-4PPh₃.^l *trans*-Chlorocinnamyltrimethylsilane.

Table 3 summarizes results for the germylation of several 2-alkenyl halides with the (germyl)silane **1a** catalyzed by Pd(dba)₂ and with the (germyl)silane **1b**

affected by Pd₂(dba)₃-4PPh₃ combination catalyst. As can be seen from Table 3, the (germyl)silane **1a** easily reacted with allyl bromide, 3-chloro-2-methylpropene

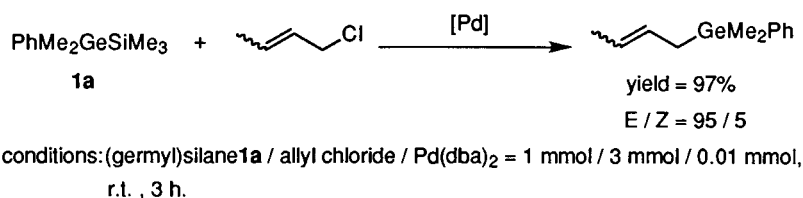
and 4-chloro-2-methyl-2-butene to afford corresponding allylgermanes in 53–99% yields. The most striking features in the reactions are their high regio- and stereoselectivities. In fact, the Pd(dba)₂-catalyzed germylation of 1-chloro-2-butenes using the (germyl)silane **1a** gave *trans*-1-(dimethylphenylgermyl)-2-butene and its *cis* isomer in 92 and 5% yields (Scheme 3). Similar germylation of 3-chloro-1-butene using the (germyl)silane **1a** gave the same product in the same isomer ratio with a combined yield of 99% (Scheme 4). In both reactions, no 3-(dimethylphenylgermyl)-1-butene formed.

These stereoselectivities were much higher than those in the previously reported germylation of 1-chloro-2-butene and 3-chloro-1-butene using 1,2-diphenyltetramethyldigermene [9b]. However, an exceptional case is the germylation of *trans*-cinnamyl chloride using the (germyl)silane **1a** (entry 8 in the Table 3). The reaction formed a 79:12:9 mixture of *trans*-cinnamyl-dimethylphenylgermane, its *cis* isomer and 3-phenyl-3-(chlorodimethylgermyl)propene with a combined yield of 86%, the regio- and stereoselectivities of which were somewhat lower than those in the germylation using 1,2-diphenyltetramethyldigermene [9b]. In this reaction, cinnamyltrimethylsilane was not detected in GLC analysis, but the chlorodimethylphenylgermane as a by-product of the cinnamylsilane formed with a 12% yield. The (germyl)silane **1b** reacted with prenyl chloride to

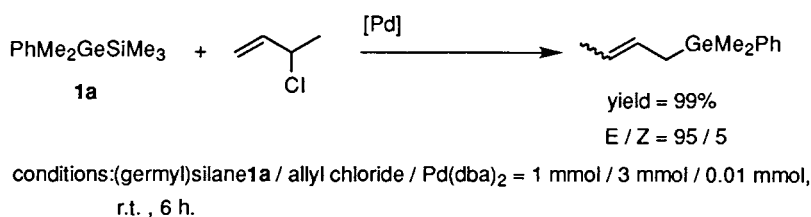
give prenyldimethylphenylgermane and prenyltrimethylsilane in 46 and 9% yields, respectively. Quite interestingly, in the germylation of *trans*-cinnamyl chloride using the (germyl)silane **1b**, the *trans* isomer of cinnamylchlorodimethylgermane was the dominant product (57%). The yield of cinnamyltrimethylsilane was 4%. In contrast, the germylation using (germyl)stannane gave the cinnamylgermane in only 20% yield [10]. Finally, we examined the selective germylation of 3,4-dichloro-1-butene using (germyl)silane **1a** in the presence of Pd(dba)₂ (Scheme 5).

As expected, 1,4-bis(dimethylphenylgermyl)-2-butenes were produced as a 93:7 mixture of *trans*- and *cis* isomers with a combined yield of 82%. The formation of 1,4-bis(dimethylphenylgermyl)-2-butene is reasonably explained via Scheme 6. However, the tentative intermediate **2a** was not detected at all during the course of the reaction, suggesting that the rate of the second reaction is much faster than that of the first.

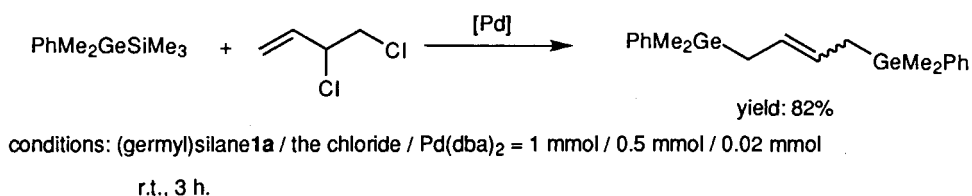
In conclusion, the Pd(dba)₂-catalyzed reaction of (dimethylphenylgermyl)trimethylsilane with 2-alkenyl halides opens up an alternative and selective synthesis of 2-alkenylgermanes. Similarly, the reaction of (chlorodimethylgermyl)trimethylsilane with allylic chlorides in the presence of palladium–phosphine complex catalyst also gave 2-alkenylchlorodimethylgermanes selectively in good yields. The formation of allylgermanes



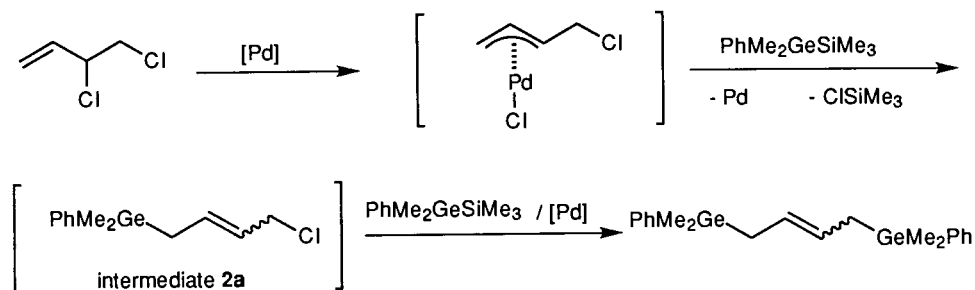
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

using the (germyl)silanes **1a** and **1b** took place with high regio- and stereoselectivity. $\text{RuCl}_2(\text{PPh}_3)_3$ also effected the metal selective metathesis of the (germyl)silane **1a** with allyl chloride giving allyldimethylphenylgermane in good yield. In further studies we shall investigate the germylation of other 2-alkenyl chlorides and attempt to provide a mechanism for the selective carbon–germanium bond formation observed using germylsilanes.

3. Experimental

A mixture of the (germyl)silane **1a** (1 mmol), crotyl chloride (2 mmol) and bis(dibenzylideneacetone)palladium (0.005 mmol) was stirred at r.t. for 3 h. Gas chromatography of the resulting mixture (Ohkura model 103; 0.4×100 cm columns; 10–20% Silicone KF-96 on 60–80 Celite 545 AW; tc detector) revealed that the (germyl)silane **1a** was completely consumed and crotyldimethylphenylgermane was formed in 97% yield with trace amounts of crotyltrimethylsilane. $^1\text{H-NMR}(\text{CDCl}_3)$: δ 0.37 (s, 6H), 1.63 (m, 3H), 1.78 (m, 2 H), 5.23 (m, 1 H), 5.44 (m, 1 H), 7.26–7.36 (m, 3 H), 7.44–7.47 (m, 2 H). LRMS (EI): 236 (M^+), 221 ($[\text{M}^+ - \text{Me}]$), 181 ($[\text{M}^+ - \text{crotyl}]$, base peak). HRMS (EI): Found; 236.0602, Anal. Calc. for $\text{C}_{12}\text{H}_{18}\text{Ge}$; 236.0620.

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