Palladium-Catalyzed Dehalogenative Germylation of Allylic Halides with Triethylgermyltributylstannane at Room Temperature

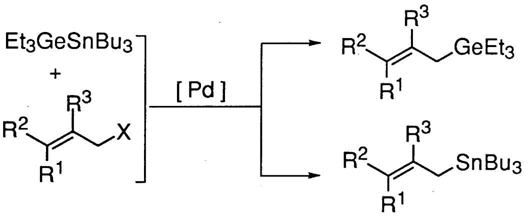
Taichi Nakano,* Kazuyoshi Ono, and Toshihiko Migita
Department of Material Science and Technology, School of High-Technology for Human Welfare, Tokai University, Numazu, Shizuoka 410-03

(Received April 26, 1996)

Triethylgermyltributylstannane was found to react with allylic halides at room temperature in the presence of a catalytic amount of $Pd_2(dba)_3CHCl_3$ to bring about regioselective dehalogenative germylation giving 2-alkenyltriethylgermanes in good yields. Using triphenylphosphine as a ligand of the palladium caused to slow the rate of the present reaction.

Disilanes such as hexamethyldisilane or chloromethyldisilanes are well known to react with organic halides such as allylic halides,[1] benzylic halides,[2] vinylic halides,[3] or aromatic halides[4] in the presence of tetrakis(triphenylphosphine)palladium(0) giving dehalogenative silylation products in good yields. However, only a few reports have been published for the group VIII metal-catalyzed germylation of organic halides with digermanes to date. Thus, hexamethyldigermane[5] was reported to react with benzoyl chloride in the presence of palladium catalyst to form benzoyltrimethylgermane. 1,2-Dichlorotetramethyldigermane[6] was reported to react with bromobenzene, benzyl bromide, benzyl chloride, and vinylic halides in the presence of $Pd(PPh_3)_4$ yielding the corresponding organomonogermanes in good yields. However, palladium-catalyzed reaction of hexaethyldigermane with *p*-bromotoluene was reported to give *p,p*'-di(tolyl) as a major product (60%) along with low yield of *p*-tolyltriethylgermane (35%).[2a]

Recently, we first reported that the reaction of hexaethyldigermane with allylic halides occurred at 170 °C in the presence of tris(dibenzylideneacetone)dipalladium(0) to cause the regioselective dehalogenative germylation of the halides giving 2-alkenylgermanes in good yields.[7] Convenient and regioselective synthesis of 2-alkenylgermanes under milder conditions is of much importance because of potential utilities of allylic germanes in organic synthesis.[8]



(1)

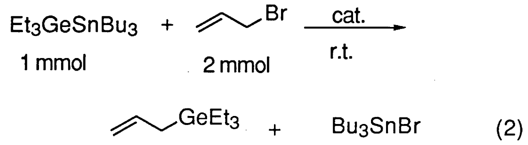
We investigated the novel reaction of allylic halides with triethylgermyltributylstannane[9] catalyzed by palladium complex (Eq. 1), aiming at regioselective synthesis of allylic germanes.

At the beginning, we examined such reaction conditions as concentration of the palladium catalyst, molar ratio of substrates, and temperature in the reaction of triethylgermyltributylstannane with allyl bromide. Stirring a benzene (1 ml) solution of 1: 2 mixture of the germylstannane and allyl bromide at 80 °C in 10 h did not cause any reaction. But, in the presence of 0.5 mol% of tris(dibenzylideneacetone)dipalladium(0) based on the germylstannane charged, the expected reaction occurred to form allyltriethylgermane in 84% yield.[10] In this reaction the formation of allyltributylstannane or bromotriethylgermane was not observed at all. Further inspection disclosed that the reaction proceeded even at room temperature to give the allylgermane in 83% yield (Eq. 2). However, in the presence of triphenylphosphine, prolonged stirring was required to obtain an acceptable yield (Eq. 2). The results were summarized in Table 1.

Table 1.
Comparison of the reaction conditions in the reaction (2)

GeSn[a] (mmol)	Allyl-Br (mmol)	[Pd][b] mol%	PPh_3 (mmol)	PhH (ml)	conditions °C, h	yield[c] %
1.01	1.00	0.5	none	1	120, 5	80
1.01	2.18	3.0	0.06	1	100, 10	37
1.01	1.00	0.5	none	1	80, 5	71
1.02	2.03	0.5	none	1	80, 10	84
1.00	2.07	0.5	0.02	1	80, 10	14
1.03	2.52	1.5	none	none	r.t., 17	83

[a] $Et_3GeSnBu_3$. [b] $Pd_2(dba)_3CHCl_3$. [c] Allyltriethylgermane.



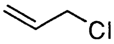
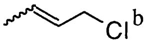
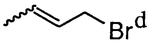
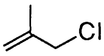
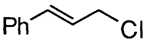
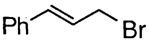
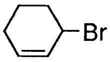
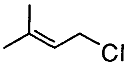
(2)

cat.: $Pd_2(dba)_3$ 17 h, product yield; 83%
cat.: $Pd_2(dba)_3$, 4 PPh_3 360 h, product yield; 69%

Other allylic halides were allowed to react with the germylstannane under similar conditions. Results obtained were shown in Table 2. The reaction of crotyl chloride gave crotyltriethylgermane in 88% yield together with 1-methy-2-propenyltriethylgermane (6% yield). Similar results were observed in the reaction of crotyl bromide. From methallyl chloride, prenyl chloride, and 3-bromocyclohexene were formed regioselectively the expected dehalogenative germylation products in good yields. In contrast, *trans*-cinnamyltriethylgermane was obtained only in near 20% yields from the corresponding *trans*-cinnamyl chloride and the bromide under similar conditions.

The low yield of the cinnamyltriethylgermane[11] seems to be due to insufficient oxidative addition ability of a cinnamyl halide to tris(dibenzylideneacetone)dipalladium under the conditions used. In case of allyl chloride, it has been reported that chloro π-allylpalladium complex is formed at room temperature.[12]

Table 2.
Palladium-catalyzed room temperature germylation of 2-alkenyl halides (R-X)[a]

$Et_3GeSnBu_3$ (mmol)	R-X (mmol)		time h	yield %
1.15		(2.32)	7	92
1.03		(2.04)	10	88 6^c
1.00		(2.07)	14	85 3^c
1.03		(2.06)	10	97
1.04		(2.04)	10	22
1.03		(2.17)	10	20
1.02		(2.17)	11	76
1.03		(2.04)	9	63

[a] All reactions were carried out using 1.5 mol% of $Pd_2(dba)_3$ based on the germylstannane charged. Product isomer ratios were determined by ^1H NMR. [b] A *cis* and *trans* mixture. Four per cent of 3-chloro-1-butene was included. [c] 1-methyl-2-propenyltriethylgermane. [d] A *cis* and *trans* mixture. Fourteen per cent of 3-bromo-1-butene was included.

Triphenylphosphine seems to interfere with the oxidative addition of an allylic halide to the palladium complex. Further work on the mechanism is underway.

References and Notes

1 For example, H. Matsumoto, T. Yako, S. Nagashima, T. Motegi, and Y. Nagai, *J. Organomet. Chem.*, **147**, 97 (1978).

2 For examples, a) C. Azarian, S. S. Dua, C. Eaborn, and D. R. M. Walton, *J. Organomet. Chem.*, **117**, C55 (1976); b) H. Matsumoto, M. Kasahara, I. Matsubara, M. Takahashi, T. Nakano, and Y. Nagai, *Chem. Lett.*, **1982**, 399; c) H. Matsumoto, M. Kasahara, I. Matsubara, M. Takahashi, T. Arai, M. Hasegawa, T. Nakano, and Y. Nagai, *J. Organomet. Chem.*, **250**, 99 (1983).

3 H. Matsumoto, S. Nagashima, T. Kato, and Y. Nagai, *Angew. Chem.*, **90**, 288 (1978).

4 H. Matsumoto, S. Nagashima, K. Yoshihiro, and Y. Nagai, *J. Organomet. Chem.*, **85**, C1 (1975).

5 K. Yamamoto, A. Hayashi, S. Suzuki, and J. Tsuji, *Organometallics*, **6**, 979 (1987).

6 N. P. Reddy, T. Hayashi, and M. Tanaka, *Chem. Lett.*, **1991**, 677.

7 T. Nakano, H. Yamashita, T. Enokido, K. Ono, and T. Migita, *Main Group Chem.*, **1**, 179 (1996).

8 H. Sano, Y. Miyazaki, M. Okawara, and Y. Ueno, *Synthesis*, **1986**, 776; K. Nakanishi, K. Mizuno, and Y. Otsuji, *Bull. Chem. Soc. Jpn.*, **66**, 2371 (1993).

9 Triethylgermyltributylstannane: bp 123-130 °C/ 3 mmHg. IR(neat) 2900, 2925, 2860, 1463, 1550, and 1375 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.48(m, 6H), 1.30(m, 6H), 1.06 (m, 9H), and 0.90(m, 21H). HRMS (70 eV) m/z Found: 450.1520. Calcd for $C_{18}H_{42}GeSn$, M^+: 450.1529.

10 A typical procedure is as follows. A mixture of $Pd_2(dba)_3$-$CHCl_3$ (0.005 mmol), triethylgermyltributylstannane (1 mmol), allyl bromide (2 mmol) was stirred at room temperature under argon. The reaction was traced with gas chromatograph (Ohkura model 103 connected with thermal conductivity detector and 0.4 x 200 cm column packed with 20% Silicone DCQF-1 coated on the 60-80 mesh Celite 545 SK). After 17 h, allyltriethylgermane was formed in 83% yield, the structure of which was confirmed by IR, ^1H NMR, and MS analysis.

11 J. Yamaguchi, Y. Tamada, and T. Takeda, *Bull. Chem. Soc.Jpn*, **66**, 607 (1993).

12 T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organomet. Chem.*, **65**, 253 (1974).