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A First Palladium-Catalyzed Aryldegermylation of Styryltrimethylgermanes

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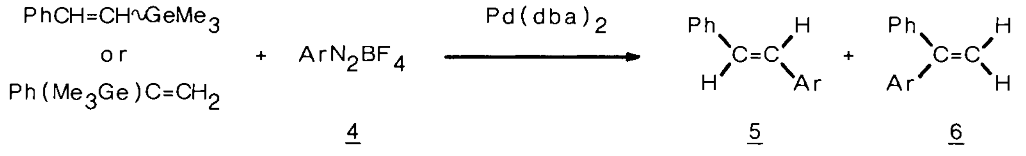
Both β-(E)- and β-(Z)-styryltrimethylgermanes easily reacted with arenediazonium tetrafluoroborates under palladium catalysis to give aryldegermylated products, (E)-PhCH=CHAr and Ph(Ar)C=CH_2. On the other hand, the aryldegermylation of α-styrylgermane gave (E)-stilbene derivatives with high stereo- and regioselectivities.

Vinylsilanes[1)] and vinylstannanes[2)] have been extensively utilized as important intermediates in organic synthesis. Few electrophilic[3)] and transition metal-mediated transformations of alkenylgermanes have been yet reported while a wide variety of preparations[4)] were well documented. Herein, we wish to report a very facile aryldegermylation of styryltrimethylgermanes[5)][(E)-PhCH=CH-$GeMe_3$(1), (Z)-PhCH=$CHGeMe_3$(2), and Ph(Me_3Ge)C=CH_2(3)] by arylpalladium tetrafluoroborates($[Ar\text{-}Pd]^+BF_4^-$: 4') generated from arenediazonium tetrafluoroborates (ArN_2BF_4: 4) with bis(dibenzylidenacetone)palladium(0)[$Pd(dba)_2$](Eq. 1). The results are summarized in Table 1.

The arylation of styrylgermanes easily gave aryldegermylated products, (E)-stilbene(5) and 1,1-diphenylethylene(6) derivatives, in good yields, in a manner similar to aryldesilylation of styrylsilanes by $[Ar\text{-}Pd]^+BF_4^-$.[6)] An addition of $Pd(dba)_2$(5.0 mol%) to a solution of styrylgermanes(0.50 mmol) and ArN_2BF_4(0.25 mmol) in CH_3CN(5 ml) at 25 °C afforded rapid gas evolution and clear reddish yellow solution. In all cases, gas evolution ceased within 30 min, but the



(1)

Ar=4-MeC_6H_4(4a), Ph(4b), 4-BrC_6H_4(4c), and 4-$NO_2C_6H_4$(4d)

Table 1. Palladium-Catalyzed Arylation of Styryltrimethylgermanes with ArN_2BF_4 [a)]

Germanes [α:β-(E):β-(Z)]	Ar of 4	Rates[b)]	Yields[c)] %	Products[c)] 5		6
1(0:94:6)	4-MeC_6H_4(4a)	1.3	82	52(5a)	:	48(6a)
	Ph(4b)[d)]	1.0	83	66(5b)	:	34(6b)
	4-BrC_6H_4(4c)	0.53	87	64(5c)	:	36(6c)
	4-$NO_2C_6H_4$(4d)	0.31	81	85(5d)	:	15(6d)
2(0:18:82)	4a	1.2	85	64(5a)	:	36(6a)
	4b	1.0	88	73(5b)	:	27(6b)
	4c	0.75	96	74(5c)	:	26(6c)
	4d	0.42	95	88(5d)	:	12(6d)
3(100:0:0)	4a	1.1	85	100(5a)	:	0
	4b[e)]	1.0	92[f)]	100(5b)	:	0
	4c	0.44	85	100(5c)	:	0
	4d	0.22	88	100(5d)	:	0

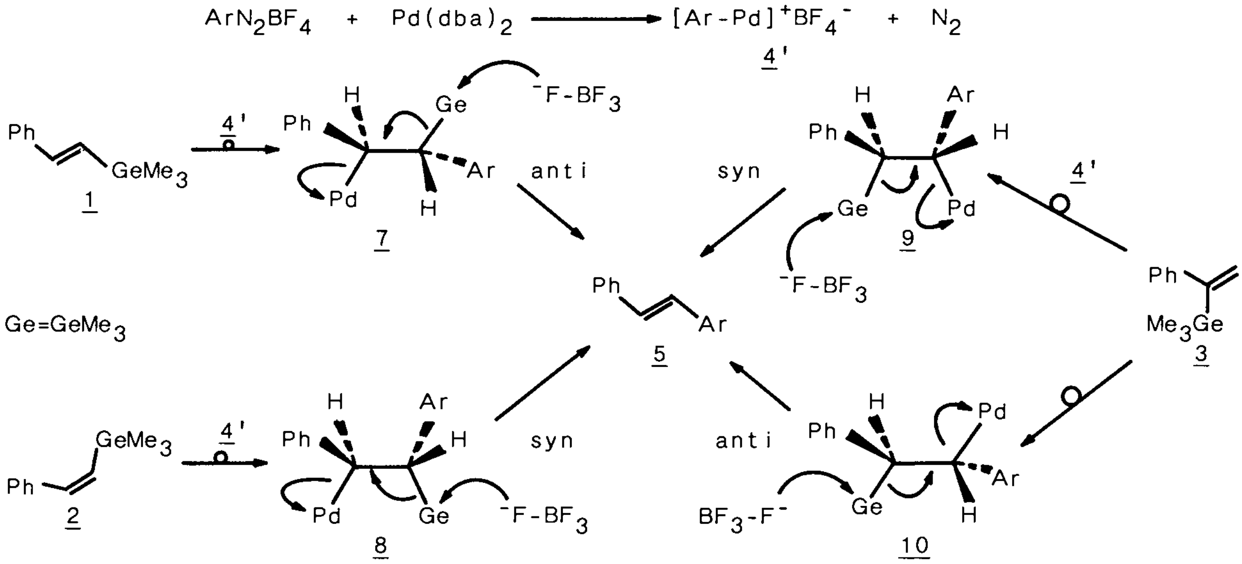
a) Unless otherwise noted the reactions were carried out 0.25 mmol scale to ArN_2BF_4, germanes/ArN_2BF_4/$Pd(dba)_2$=0.50/0.25/0.0125. b) Values are relative rates: $(Rate)_{Ar}/(Rate)_{Ph}$. Steady state rates at early stage, $(Rate)_{Ar}$, estimated by N_2 gas evolution(%) a min at 25±1 °C were corrected to case of 5.0 mol% of Pd catalysis. c) GC yields were based on ArN_2BF_4. d) 0.20 mmol scale. e) 0.50 mmol scale. f) Isolated yields.

mixture was stirred for about 2 h to the complete reaction. A GC analysis of the reaction mixture and the ^1H-NMR spectra of the isolated products showed the formation of arylated styrene derivatives. In all these aryldegermylation, (Z)-stilbene, (Z)-5, could not be detected by GC and NMR analyses. Starting germanes and products did not isomerize during the reaction.

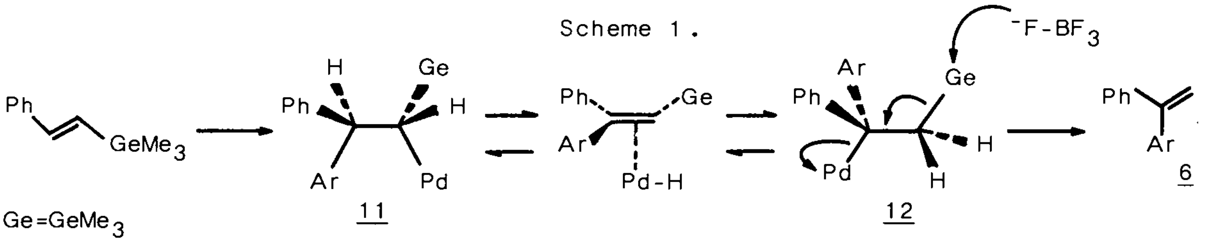
The arylation of (E)-PhCH=CH$GeMe_3$(1) with 4a gave 5a and 6a(5a/6a=52/48, 82 %). The reaction of (Z)-PhCH=CH$GeMe_3$(2) with 4a also produced 5a and 6a(5a/6a=64/36, 85%). The aryldegermylation of Ph(Me_3Ge)C=CH_2 with 4a only gave 5a(85 %). In all arylations, electron-withdrawing substituents on aromatic ring of ArN_2BF_4 reduced the rates of aryldegermylation considerably. The aryldegermylation of α-styrylgermane proceeded with high stereo- and regioselectivities in contrast to that of β-(E)- and (Z)-styrylgermanes.

Recently, we reported aryldesilylation of styrylsilanes[6)] and aryldestannylation of styrylstannanes[7)] by $[Ar\text{-}Pd]^+BF_4^-$. The elimination route of silyl group at the aryldesilylation may be very different from that of stannyl group at the aryldestannylation.[8)]

The present aryldegermylation can be explained by the aryldesilylation mechanism described for the reactions (E)- and (Z)-PhCH=CH$SiMe_3$, and Ph(Me_3Si)C=



Scheme 1.



Scheme 2.

CH_2[6)](Schemes 1 and 2).

The orientation of the addition of $[Ar\text{-}Pd]^+BF_4^-$(4') to 1 determined the ratios of 5 and 6. The orientation was affected by the steric factors of the substituents on C-C double bond[10)] and σ-π conjugation of C-Ge bond. The aryldegermylation of β-(E)-styryltrimethylgermane proceeded via anti-1,2-elimination of Pd(0) and Me_3Ge groups from the adduct, threo-$PhCH(Pd^+)CH(Ar)GeMe_3$(7).[6a,b)] The formation of $Ph(Ar)C{=}CH_2$(6) is easily explained by the anti-elimination of Pd(0) and germyl groups from the conformer(12) generated through the intramolecular addition-elimination of H-Pd species from the adduct(11). The aryldegermylation of β-(Z)-germane did through syn-elimination route from most stable conformer, erythro-adduct(8).[6a,b)]

On the other hand, the reaction of 4' with α-germane only gave the adduct, $Ph(Me_3Ge)(Pd^+)CCH_2Ar$, because of the steric effect of Ph and Me_3Ge groups on 3. The elimination of Pd(0) moiety and Me_3Ge group from the intermediates(9 and /or 10) generated, via the addition-elimination of H-Pd species, from the first adduct can be accounted for by syn- and/or anti-route.[6c)]

This arylation provides the first example of transition metal-catalyzed carbon-carbon bond formation using alkenylgermanes.[11)]

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5) Preparations of styryltrimethylgermanes(1-3): (E)-PhCH=CHGeMe$_3$(1) and Ph(Me$_3$Ge)C=CH$_2$(3) were obtained by Grignard reaction of corresponding styrylmagnesium bromide with Me$_3$GeBr in THF. (Z)-PhCH=CHGeMe$_3$(2) was prepared from the Ti-catalyzed Grignard exchange reaction of trimethylgermylphenylacetylene[F. Sato, H. Ishikawa, M. Sato, Tetrahedron Lett., 22, 85(1981)]. (E)-Ph^{a}CH^b=CH^{c}GeMe$_3^d$(1): ^{1}H-NMR(solvent: CCl$_4$, internal standard: CH$_2$Cl$_2$)δH^{a}7.15-7.50(m, 5H), H^{b}6.74(d, 1H, J$_{bc}$=18.2 Hz), H^{c}6.69(d, 1H, J$_{cb}$=18.2 Hz), H^{d}0.29(s, 9H). (Z)-Ph^{a}CH^b=CH^{c}GeMe$_3^d$(2): δH^{a}7.29(s, 5H), H^{b}7.38(d, 1H, J$_{bc}$=13.8 Hz), H^{c}6.00 (d, 1H, J$_{cb}$=13.8 Hz), H^{d}0.28(s, 9H). Ph^a(Me$_3^d$Ge)C=CH$_2^{bc}$(3): δH^{a}7.21(s, 5H), H^{b}5.87(d, 1H, J$_{bc}$=2.50 Hz), H^{c}5.52(d, 1H, J$_{cb}$=2.50 Hz), H^{d}0.43(s, 9H).

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7) K. Kikukawa, H. Umekawa, and T. Matsuda, J. Organomet. Chem., 311, C44 (1986); The phenyldestannylation of PhCH=CHSnBu$_3$(E/Z=83/17) and Ph(Bu$_3$Sn)C=CH$_2$ readily gave (E)-5/(Z)-5=86/14 and (E)-5/(Z)-5=18/82, respectively.

8) Alkenylstannanes usually react with arylpalladium species via transmetallation mechanism9a) except for the arylation of α-styrylstannanes by [Ar-Pd]$^+$-BF$_4^-$.7) On the other hand, palladium-catalyzed arylations of alkenylsilanes generally proceed through addition-elimination mechanism6,9b) except for the cross-coupling reaction of alkenylsilanes or alkenylfluorosilanes with aryl or alkenyl iodide in the presence of TASF.9c)

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