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A First Palladium-Catalyzed Aryldegermylation of Styryltrimethylgermanes

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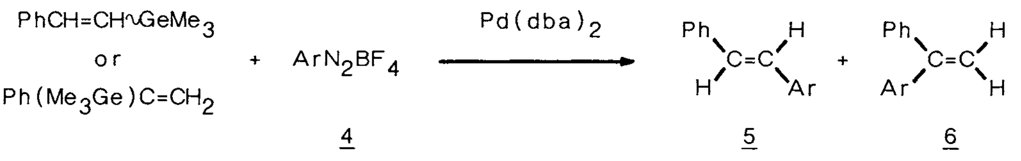
Both β-(E)- and β-(Z)-styryltrimethylgermanes easily reacted with arenediazonium tetrafluoroborates under palladium catalysis to give aryldegermylated products, (E)-PhCH=CHAr and Ph(Ar)C=CH_2. On the other hand, the aryldegermylation of α-styrylgermane gave (E)-stilbene derivatives with high stereo- 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-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-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$_2$BF$_4$a)

Germanes [α:β-(E):β-(Z)]	Ar of 4	Rates b)	Yields c) %	Products c) 5		6
1(0:94:6)	4-MeC$_6$H$_4$(4a)	1.3	82	52(5a)	:	48(6a)
	Ph(4b)d)	1.0	83	66(5b)	:	34(6b)
	4-BrC$_6$H$_4$(4c)	0.53	87	64(5c)	:	36(6c)
	4-NO$_2$C$_6$H$_4$(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
	4be)	1.0	92f)	100(5b)	:	0
	4c	0.44	85	100(5c)	:	0
	4d	0.22	88	100(5d)	:	0

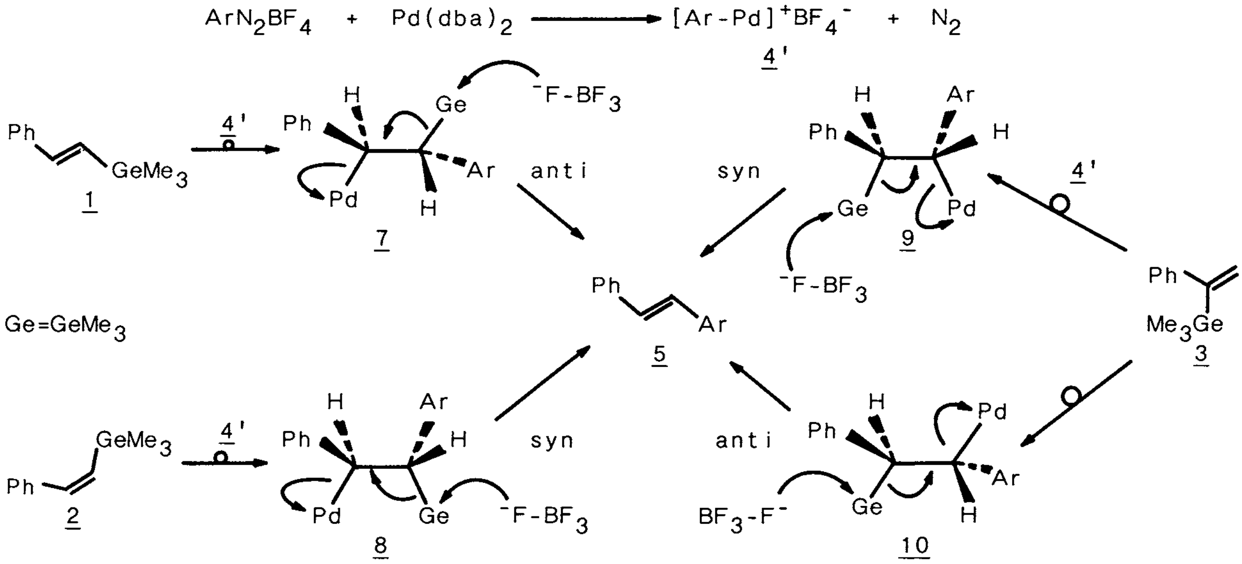
a) Unless otherwise noted the reactions were carried out 0.25 mmol scale to ArN$_2$BF$_4$, germanes/ArN$_2$BF$_4$/Pd(dba)$_2$=0.50/0.25/0.0125. b) Values are relative rates: (Rate)$_{Ar}$/(Rate)$_{Ph}$. Steady state rates at early stage, (Rate)$_{Ar}$, estimated by N$_2$ gas evolution(%) a min at 25±1 °C were corrected to case of 5.0 mol% of Pd catalysis. c) GC yields were based on ArN$_2$BF$_4$. 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 ^{1}H-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.

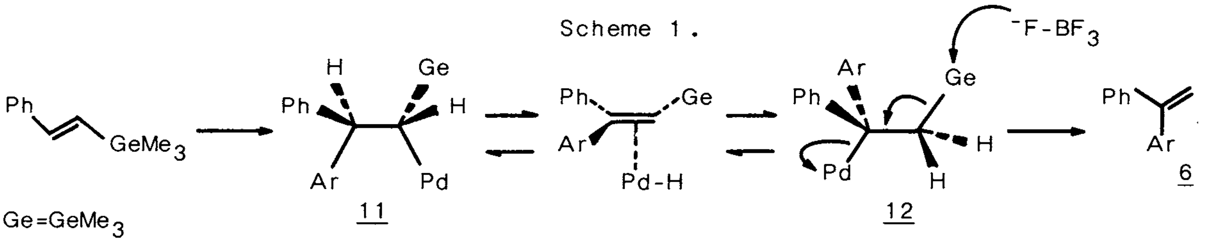
The arylation of (E)-PhCH=CHGeMe$_3$(1) with 4a gave 5a and 6a(5a/6a=52/48, 82 %). The reaction of (Z)-PhCH=CHGeMe$_3$(2) with 4a also produced 5a and 6a(5a/6a=64/36, 85%). The aryldegermylation of Ph(Me$_3$Ge)C=CH$_2$ with 4a only gave 5a(85 %). In all arylations, electron-withdrawing substituents on aromatic ring of ArN$_2$BF$_4$ 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 styrylsilanes6) and aryldestannylation of styrylstannanes7) by [Ar-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=CHSiMe$_3$, and Ph(Me$_3$Si)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 $Ph(Me_3Ge)C{=}CH_2$(3) were obtained by Grignard reaction of corresponding styrylmagnesium bromide with Me_3GeBr 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)-$Ph^aCH^b{=}CH^cGeMe_3^d$(1): ^{1}H-NMR(solvent: CCl_4, internal standard: CH_2Cl_2)δH^a7.15-7.50(m, 5H), H^b6.74(d, 1H, J_{bc}=18.2 Hz), H^c6.69(d, 1H, J_{cb}=18.2 Hz), H^d0.29(s, 9H). (Z)-$Ph^aCH^b{=}CH^cGeMe_3^d$(2): δH^a7.29(s, 5H), H^b7.38(d, 1H, J_{bc}=13.8 Hz), H^c6.00 (d, 1H, J_{cb}=13.8 Hz), H^d0.28(s, 9H). $Ph^a(Me_3^dGe)C{=}CH_2^{bc}$(3): δH^a7.21(s, 5H), H^b5.87(d, 1H, J_{bc}=2.50 Hz), H^c5.52(d, 1H, J_{cb}=2.50 Hz), H^d0.43(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 $Ph(Bu_3Sn)C{=}CH_2$ 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 mechanism[9a] except for the arylation of α-styrylstannanes by $[Ar\text{-}Pd]^+\text{-}BF_4^-$.[7] On the other hand, palladium-catalyzed arylations of alkenylsilanes generally proceed through addition-elimination mechanism[6,9b] 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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