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STEREOCHEMISTRY OF REACTION OF (E)- AND (Z)-β-TRIMETHYLSILYLSTYRENE WITH ARYLPALLADIUM TETRAFLUOROBORATES GENERATED FROM ARENEDIAZONIUM TETRAFLUOROBORATES AND PALLADIUM(0)

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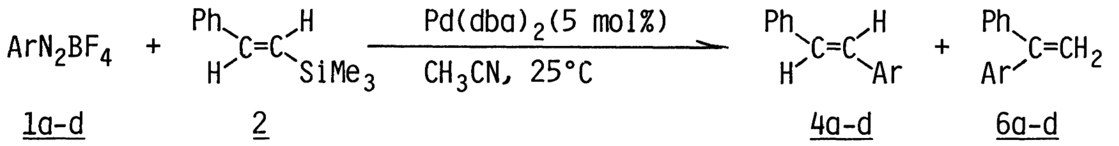
(E)- and (Z)-$PhCH=CHSiMe_3$ react easily with $[ArPd]^+BF_4^-$ to give (E)-PhCH=CHAr and $Ph(Ar)C=CH_2$ at 25 °C. Stereochemistry of the desilylation is disclosed by using (E)- and (Z)-$PhCH=CDSiMe_3$, that is, *syn*-addition of Ar-Pd species followed by *anti*-elimination of Pd and Me_3Si moiety for (E)-isomer and *syn*-elimination for (Z)-isomer are proposed.

Regio- and stereospecific substitution of organosilicons, especially vinylsilanes, by wide range of electrophiles have been extensively utilized in organic synthesis.[1)] However, only a few transition metal mediated reactions of organosilicons have been reported.[1)] Herein we report a very facile reaction of (E)-and (Z)-β-trimethylsilylstyrene(2 and 3) with Ar-Pd species, which is renerated from arenediazonium tetrafluoroborates(1) and bis(dibenzylideneacetone)Palladium(0) ($Pd(dba)_2$),[2)] to produce arylated styrenes. The stereochemical feature of the reaction is discolosed by using (E)- and (Z)-β-*d*-β-trimethylstyrene, $PhCH=CDSiMe_3$.

Addition of 5 mol% of $Pd(dba)_2$ to a solution of 1(0.5 mmol) and 2(1 mmol) in acetonitrile(5 ml) at 25 °C caused rapid gas evolution and gave clear yellow solution. The NMR spectra of the isolated products showed the formation of (E)-PhCH=CHAr(4) and $Ph(Ar)C=CH_2$(6) in excellent yields irrespective of the substituents on 1, although electron-withdrawing substituents reduced the rates considerably (Eq. 1 and Table 1). No resonance assignable to (Z)-PhCH=CHAr(5) was observed in the NMR spectra, though a trace of 5a was detected by GC in the reaction with 1a. The gas evolution corresponded to the total yields of 4 and 6, and completed in 12 min (1a), 12 min(1b), 19 min(1c), and 27 min(1d). In the absence of the palladium catalyst, any appreciable change could not be observed besides very slow decomposition of 2 to styrene.



(1)

(a, Ar=Ph, b, Ar=4-Me-C_6H_4, c, Ar=4-Br-C_6H_4, d, Ar=4-NO_2-C_6H_4)

In the reaction with (Z)-isomer, 3, higher catalyst concentration(10 mol%) was required to obtain reasonable rates and yields. It is notable that the reaction

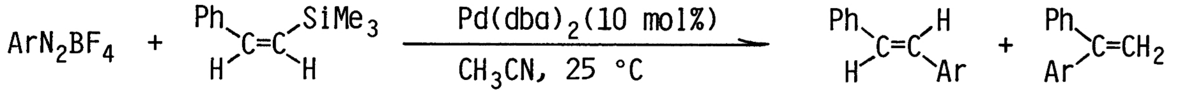
Table 1. Palladium(0)-Catalyzed Arylation of $PhCH=CHSiMe_3$ by ArN_2BF_4(Eqs. 1 and 2)[a]

ArN_2BF_4	$PhCH=CHSiMe_3$	$Pd(dba)_2$ mol%	Rates[b] $\times 10^7$ mol/s	Products (% composition)		Yields[c] %
1a	2	5	11	4a(67)	6a(33)	98
1b	2	5	13	4b(58)	6b(42)	97
1c	2	5	7.8	4c(65)	6c(35)	100
1d	2	5	3.8	4d(86)	6d(14)	99
1a	3	10	6.4	4a(80)	6a(20)	97
1b	3	10	4.3	4b(70)	6b(30)	68
1c	3	10	5.0	4c(76)	6c(24)	100
1d	3	10	6.8	4d(76)	6d(24)	84

a) The reactions were started by the addition of $Pd(dba)_2$ to a solution of ArN_2BF_4(0.5 mmol) and (E)- or (Z)-$PhCH=CHSiMe_3$(1 mmol) in CH_3CN(5 ml) at 25 °C.

b) Steady state rates estimated by gas evolution at early stage.

c) GC yields based on ArN_2BF_4.

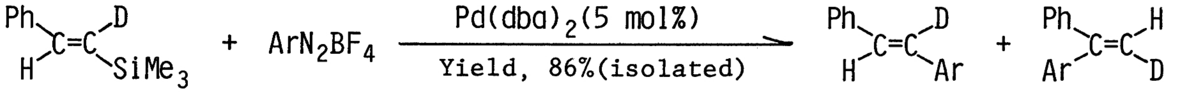


(2)

1a-d 3 4a-d 6a-d

with 3 also gave only trace or no 5(Eq. 2 and Table 1). No isomerization of 2 and 3 was observed during the reactions. Isomerization of 5 to 4 is one of possible reasons for the loss of stereospecificity of the present reactions. However, the reaction of 1b with 3 or 2 in the presence of both 4a and 5a showed that no isomerization occurred in either isomer under the present reaction conditions.

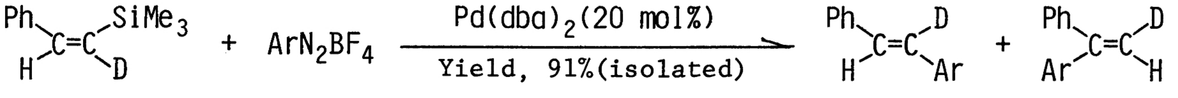
The reaction of (E)- and (Z)-$PhCH=CDSiMe_3$(7 and 8)[3] with 1d showed interesting stereochemical feature of the present reaction(Eqs. 3 and 4). Both 7 and 8 gave (E)-β-*d*-β-4-nitrophenylstyrene(9) as the major product. Whereas the minor product, (Z)- or (E)-β-*d*-α-4-nitrophenylstyrne(10 or 11), was obtained stereospecificically from 7 and 8,[4] respectively. Deuterium was completely retained in the products.



(3)

7 1d($Ar=4\text{-}NO_2\text{-}C_6H_4$) 9 10

(D content, 86%) (9 : 10 = 89 : 11)



(4)

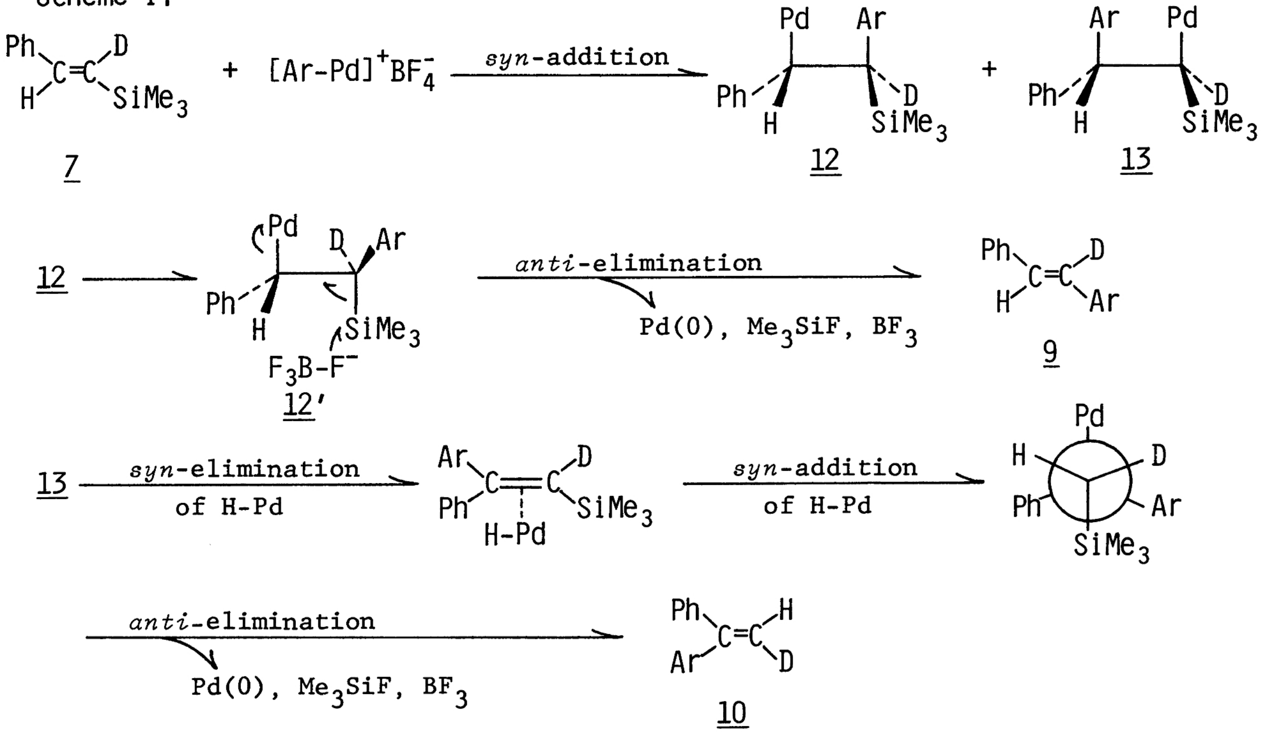
8 1d 9 11

(D content, 97%) (9 : 11 = 83 : 17)

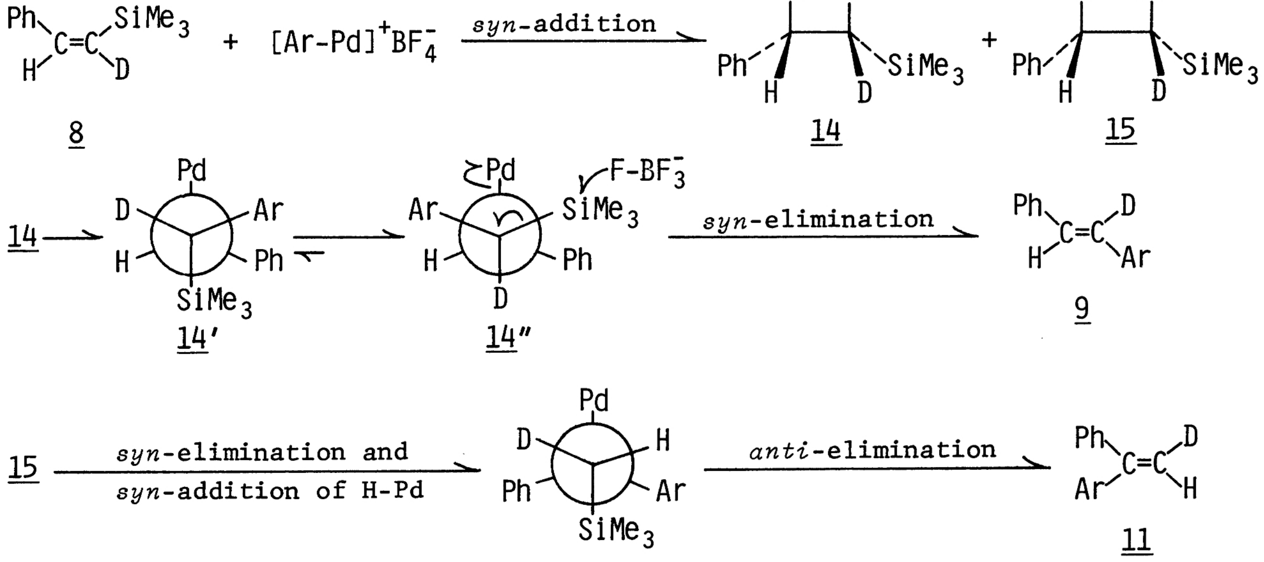
Reactions of or (E)-PhCH=CHSiF$_5^{2-}$ with palladium(II) salts have been described to form vinylpalladium intermediates through addition-elimination[5)] or transmetallation[6)] process, respectively, with retention of the geometry, but the corresponding (Z)-isomers have not been examined. In the present reaction system, the transmetallation process seems to be incompatible with the loss of regioselectivity(the formation of 6, 10,or 11) and of stereospecificity.

Since Ar-Pd species add to olefins easily at ambient temperature,[7)] the addition of Ar-Pd species to alkenylsilanes can be reasonably expected as an initial step in the present reaction as shown in Schemes 1 and 2.

Scheme 1.



Scheme 2.



The elimination of Pd and Me_3Si moiety from the adduct 12 or 14 is a plausible pathway to give where an assistance of fluoride ion seems to be an important step of the Si-C bond cleavage. The important role of fluoride ion in the present desilylation can be revealed by the formation of (Z)-$PhCH{=}C(SiMe_3)Ph$ as a main product in the reaction of 2 with Ph-Pd(OAc) in the absence of fluoride ion.$^{8)}$ The adduct 12 may undergo *anti*-elimination of Pd and Me_3Si group from the most stable conformer 12′ to give 9 as in the common elimination of β-heteroatomsubstituted silanes.$^{1)}$ Whereas the formation of 9 from 8 necessitates *syn*-elimination from the adduct 14. In this case *anti*-elimination requires more sterically congested conformer 14′than that leading *syn*-elimination, conformer 14″.$^{9)}$ The stereospecific formation of 10 or 11 can be reasonably interpreted by supposing an initial isomerization of 13(or 15) *via syn*-elimination and *syn*-addition of H-Pd and following *anti*-elimination of Pd and Me_3Si.

References

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2) K. Kikukawa, K. Kono, F. Wada, and T. Matsuda, *J. Org. Chem.*, 48, 1333 (1983).

3) (E)- and (Z)-$PhCH{=}CDSiMe_3$(7 and 8) were prepared by the following reaction sequences and the D contents were determined by NMR.

   i) $PhC{\equiv}CD \xrightarrow{\text{1)}HSiMe_2Cl/H_2PtCl_6\quad\text{2)}MeMgBr}$ (E)-$PhCH{=}CDSiMe_3$(D content, 86%)

   ii) $PhC{\equiv}CSiMe_3 \xrightarrow{\text{1)}HAl(i\text{-}Bu)_2\quad\text{2)}D_2O/D_2SO_4}$(Z)-$PhCH{=}CDSiMe_3$(D content, 97%)

4) The structure of 9, 10, and 11 was determined by comparison of their NMR with those of 4d and 6d, and of NMR of their epoxides derived by peroxybenzoic acid oxidation with those of epoxides of 4d and 6d. (H. Güsten and M. Salzwedel, *Tetrahedron*, 23, 173 (1967); G. Ceccarelli, G. Berti, G. Lippi, and B. Macchia, *Org. Magn. Reson.*, 2, 379 (1970)). Oxydation of 9 by $NaIO_4$-OsO_4 gave PhCHO and ArCDO. The NMR of 10 and 11 showed that 10 obtained in eq. 3 was contaminated with about 30% of 11 and 11 in eq. 4 was contaminated with 10% of 10. Since spontaneous isomerization of 10 and 11 was observed during storage in $CDCl_3$, the contamination might be attributed to the isomerization of initially formed products.

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8) K. Kikukawa, F. Wada, and T. Matsuda, Unpublished data. Ph-Pd(OAc) was generated by reaction of $Pd(OAc)_2$ and PPh_3 (K. Kikukawa and T. Matsuda, *J. Organometal. Chem.*, 235, 243 (1982)).

9) The mode of elimination of Me_3Si-X(X=Br, Cl) from *t*-BuCH(X)CH(X)$SiMe_3$ has been reported to be affected by the stability of the conformer. (R. B. Miller and G. McGarvey, *J. Org. Chem.*, 43, 4424 (1978)).

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