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Palladium-Catalyzed Regio- and Stereoselective Aryldesilylation of α -Silylstyrenes with Arenediazonium Salts

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 α -Trialkylsilylstyrenes[Ph(R₃Si)C=CH₂: R=Me(<u>1</u>), Et(<u>2</u>), and Ph (3)] easily reacted with arenediazonium tetrafluoroborates[ArN₂⁺BF₄⁻ (4)] to give (E)-PhCH=CHAr under palladium(0) catalysis. The bulky substituents on silicon gave better stereoselectivity.

Regio- and stereospecific desilylation of β -substituted vinylsilanes with a wide variety of $electrophiles^{1}$ and $organopalladium compounds^{2}$ have been well known. Palladium-catalyzed aryldesilylation of (E)-and (Z)-PhCH=CHSiMe3 with arenediazonium salts(ArN₂X), however, proceeds with loss of regio- and stereo-

 $Pd(dba)_{2}$ (E)-or (Z)-PhCH=CHSiMe₃ + ArN₂⁺X⁻ (E)-PhCH=CHAr + Ph(Ar)C=CH₂ (1)

specificity(Eq. 1).³⁾ In contrast to β -substituted vinylsilanes, few α -substituted vinylsilanes have been examined in the desilylation reaction. Now, we wish to report regio- and stereoselective arylation of α -trialkylsilylstyrenes $(1-3)^{4}$ with $ArN_2BF_4(4)$ in the presence of bis(dibenzylidenacetone)palladium(0) [Pd(dba)₂].

An addition of 10 mol% of Pd(dba)₂ to a solution 1-3 and 4(molar ratio=2/1) in acetonitrile(5 ml) at 25 °C afforded rapid gas evolution and clear reddish



R=Me(1), Et(2), and Ph(3) $Ar=Ph(\underline{a}), 4-MePh(\underline{b}), 4-BrPh(\underline{c}), and 4-NO_2Ph(\underline{d})$

Ph C=CH R ₃ Si R	2 ArN2 ⁺ BF4 ⁻ Ar	Pd(dba) ₂ mol%	Rates ^b) %min ⁻¹	Yields ^{C)} %	$\frac{Products}{Ph} \\ H \\ C=C \\ Ar \\ \frac{5}{2}$	ra	$\frac{Ph}{C=C}$
Me(<u>1</u>)	Ph(<u>4a</u>) ^{e)}	10	58	100	96(<u>5a</u>)	:	4(<u>6a</u>)
	$4-MePh(\underline{4b})^{f}$	1.1	2.5	45	>99(<u>5b</u>)	:	t ⁱ⁾
	$4-MePh(\underline{4b})^{f}$	5.0	14	82	>99(<u>5b</u>)	:	t ⁱ⁾
	$4-MePh(\underline{4b})^{f}$	10	62	97	>99(<u>5b</u>)	:	t ⁱ⁾
	4-BrPh(<u>4c</u>)e)	10	35	98	98(<u>5c</u>)	:	2(<u>6c</u>)
	$4-NO_2Ph(\underline{4d})^{f}$	10	27	96	96(<u>5d</u>)	:	4(<u>6d</u>)
Et(<u>2</u>)	Ph(<u>4a</u>) ^{e)}	10	12	61	100(<u>5a</u>)	:	0
	Ph(<u>4a</u>) ^{g)}	29	29	78	100(<u>5a</u>)	:	0
	$4-MePh(\underline{4b})g)$	10	13	60	100(<u>5b</u>)	:	0
	4-BrPh(<u>4c</u>) ^{e)}	10	8.5	55	100(<u>5c</u>)	:	0
	$4-NO_2Ph(\underline{4d})^e$	10	6.9	67	100(<u>5d</u>)	:	0
Ph(<u>3</u>)	Ph(<u>4a</u>) ^{h)}	10	4.1	43	100(<u>5a</u>)	:	0

Table 1. Arylation of α -Silylstyrenes(<u>1-3</u>) by ArN₂BF₄(<u>4</u>) under Pd(dba)₂^a)

a) $Ph(R_3Si)C=CH_2/ArN_2BF_4=2/1$. b) Steady state rates at early stage estimated by the gas evolution at 25±1 °C. c) GC yields based on <u>4</u> used. d) Determined by GC analysis. e) 0.5 mmol scale. f) 1.0 mmol scale. g) 0.25 mmol scale. h) 0.18 mmol scale. i) Trace amount.

yellow solution. A GC analysis of the reaction mixture and the NMR spectra of the isolated products showed the formation of stilbene derivatives(Eq. 2 and Table 1).

In contrast to the reactions of β -silylstyrenes(Eq. 1),³) ipso-substituted products, 1,1-diphenylethylene derivatives(<u>7</u>), could not be detected in all the reactions examined here, but (E)-stilbene derivatives(<u>5</u>) were selectively produced. A control reaction of <u>1</u> with <u>4b</u> in the presence of <u>5a</u> and <u>6a</u> clearly showed that no isomerization occurred in either product isomers, <u>5a</u> and <u>6a</u>, under these particular reaction conditions.⁵) Irrespective of the substituents on <u>4</u>, the reaction of <u>1</u> were completed within 10 min, and gave the products in excellent yields. The bulky substituents on silicon considerably reduced the rates and yields, but increased stereoselectivity.

Present regio- and stereoselective aryldesilylation may be explained by the same mechanism³) described for the reaction of (E)- and (Z)-PhCH=CHSiMe₃(Scheme 1). The reactions of zero-valent palladium with $\underline{4}$ easily generate the arylpal-ladium species([Ar-Pd]⁺BF₄⁻: $\underline{4}$ ').⁶) The Ar-Pd species easily add to olefins at



Scheme 1.

ambient temparature.⁷⁾ The steric and electronic effects of Ph and R₃Si groups on <u>1-3</u> may determine the orientation of the syn-addition of Ar-Pd species to α silylstyrenes and more preferentially give the adduct <u>8</u> than <u>9</u>. In the adduct <u>8</u>, palladium should be transposed with the neighbouring carbon to undergo desilylation. Two isomeric adducts <u>10</u> and <u>11</u> can be obtained from the corresponding conformers <u>8'</u> and <u>8</u>", respectively, via intramolecular syn-elimination and re-addition of an H-Pd species. The stereochemistry of the elimination of Pd(0) and Me₃Si moieties depends on the stability of the conformers.³⁾ The bulky substituents(R=Et and Ph) on silicon destabilize not only the conformer <u>8</u>", but also the conformer <u>10</u>'. The syn-elimination from the stable conformer <u>10</u> produces <u>5</u>, and may explain the present stereoselectivity. Although anti-elimination is the most common process for organosilanes with a leaving group at the β -position, ^{1b, c)} syn-elimination is also frequently observed.^{3,8})

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References

- a) T. H. Chan and I. Fleming, Synthesis, <u>1979</u>, 761; b) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London(1981), p. 44; c) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin (1983), p. 79.
- 2) W. P. Weber, R. A. Flex, A. K. Willard, and K. E. Koenig, Tetrahedron Lett., <u>1971</u>, 4701; J. Yoshida, K. Tamao, H. Yamamoto, R. Kakui, T. Uchida, and M. Kumada, Organometallics, <u>1</u>, 542(1982); A. Hallberg and C. Westerlund, Chem. Lett., <u>1982</u>, 1993; A. Hallberg and K. Karabelas, Tetrahedron Lett., <u>1985</u>, 3131; J. Org. Chem., <u>51</u>, 5286(1986).
- 3) K. Kikukawa, K. Ikenaga, F. Wada, and T. Matsuda, Chem. Lett., <u>1983</u>, 1337;
 K. Ikenaga, K. Kikukawa, and T. Matsuda, J. Chem. Soc., Perkin Trans. 1, <u>1986</u>, 1959.
- 4) Ph(Me₃Si)C=CH₂(<u>1</u>) was obtained, in 61% yield, by Grignard reaction of Ph(BrMg)C=CH₂ with Me₃SiCl in THF. Ph(Et₃Si)C=CH₂(<u>2</u>) and Ph(Ph₃Si)C=CH₂(<u>3</u>) were prepared from the Ni-catalyzed Grignard cross-coupling reaction[cf. K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, and M. Kumada, Bull. Chem. Soc. Jpn., <u>49</u>, 1958(1976)].

$$R_{3}SiCH=CH_{2} \xrightarrow{Br_{2} Et_{2}NH} R_{3}Si(Br)C=CH_{2} \xrightarrow{PhMgBr} Ph(R_{3}Si)C=CH_{2}$$

NiCl₂(dppp)

These yields in the last step were $75\%(\underline{2})$ and $95\%(\underline{3})$. $Ph^{a}(Me_{3}{}^{b}Si)C=CH_{2}{}^{cd}$ (<u>1</u>): ¹H NMR(solvent: CCl₄, internal standard: CH₂Cl₂) δ H^a7.21(s 5H), H^b0.22 (s 9H), H^c5.62(d 1H J_{cd}=3.00 Hz), H^d5.83(d 1H J_{dc}=3.00 Hz). Ph^a(Et₃^bSi)C=CH₂^{cd}(\underline{2}): H^a7.17(s 5H), H^b0.35-1.21(m 15H), H^c5.58(d 1H J_{cd}=3.44 Hz), H^d 5.87(d 1H J_{dc}=3.44 Hz). Ph^a(Ph₃^bSi)C=CH₂^{cd}(\underline{3}): H^a7.20(s 5H), H^b7.26-7.65(m 15H), H^c5.72(d 1H J_{cd}=2.76 Hz), H^d6.30(d 1H J_{dc}=2.76 Hz); m.p. 132-133 °C.

- 5) The conditions of reaction of $Ph(Me_3Si)C=CH_2(\underline{1})$ with $4-MePhN_2BF_4(\underline{4b})$ in the presence of (E)- and (Z)-PhCH=CHPh(<u>5a</u> and <u>6a</u>): <u>1</u>=2.0 mmol, <u>4</u>b=1.0 mmol, <u>5a=</u> 0.47 mmol, <u>6a</u>=0.27 mmol, Pd(dba)_2=0.1 mmol, and CH_3CN=5 ml at 25 °C.
- R. Yamashita, K. Kikukawa, F. Wada, and T. Matsuda, J. Organomet. Chem., <u>201</u>, 463(1980).
- 7) K. Kikukawa, K. Nagira, F. Wada, and T. Matsuda, Tetrahedron, 37, 31(1981).
- 8) The tighter coordination of OAc⁻ to palladium than BF_4^- may promote the synelimination of H-Pd-OAc from RCH(AcOPd)CH(SiMe₃)Ar[K. Ikenaga, K. Kikukawa, and T. Matsuda, J. Org. Chem., <u>52</u>, 1276(1987)]; The mode of syn-elimination of Me₃SiX(X=Br and Cl) from ^tBuCH(X)CH(X)SiMe₃ depends upon the stability of the conformer[R. B. Miller and G. McGarvey, J. Org. Chem., <u>43</u>, 4424(1978)]; In the basic conditions of Peterson reaction, syn-elimination of hetero atom and silyl group is observed[Ref. 1c, p. 62; P. F. Hudrlik and D. Peterson, Tetrahedron Lett., <u>1975</u>, 1133; J. Am. Chem. Soc., <u>97</u>, 1464(1975)].

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