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

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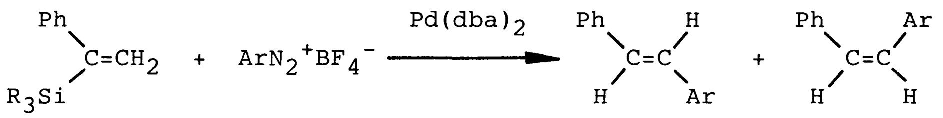
α-Trialkylsilylstyrenes[$Ph(R_3Si)C=CH_2$: R=Me(1), Et(2), and Ph (3)] easily reacted with arenediazonium tetrafluoroborates[$ArN_2^+BF_4^-$ (4)] to give (E)-PhCH=CHAr under palladium(0) catalysis. The bulky substituents on silicon gave better stereoselectivity.

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)-$PhCH=CHSiMe_3$ with arenediazonium salts(ArN_2X), however, proceeds with loss of regio- and stereo-

$$\text{(E)- or (Z)-}PhCH=CHSiMe_3 + ArN_2^+X^- \xrightarrow{Pd(dba)_2} \text{(E)-}PhCH=CHAr + Ph(Ar)C=CH_2 \qquad (1)$$

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



(2)

1-3 4a-d 5a-d 6a-d

R=Me(1), Et(2), and Ph(3)

Ar=Ph(a), 4-MePh(b), 4-BrPh(c), and 4-NO_2Ph(d)

Table 1. Arylation of α-Silylstyrenes(1-3) by ArN_2BF_4(4) under $Pd(dba)_2$[a)]

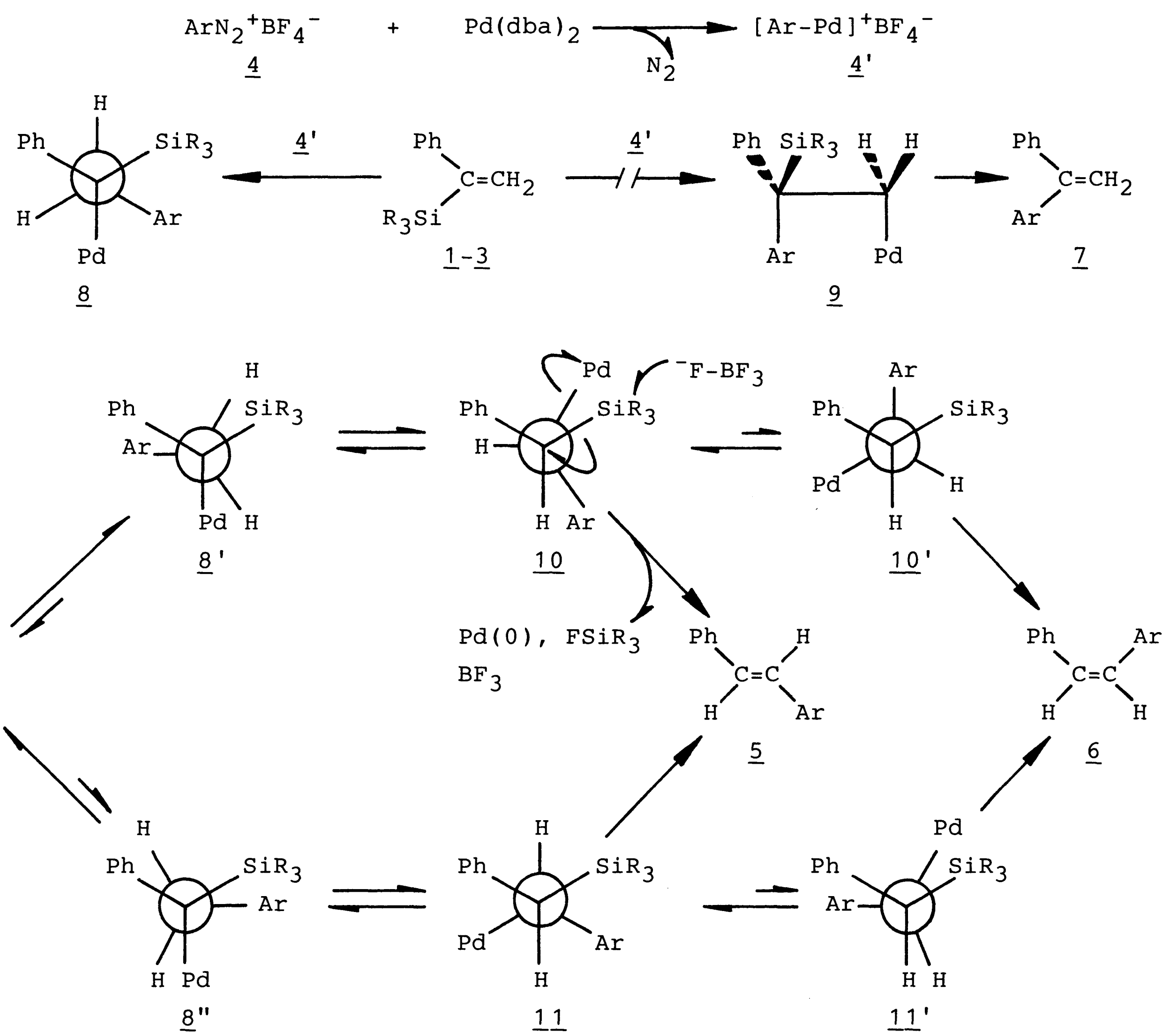
$Ph(R_3Si)C=CH_2$ R	$ArN_2{}^+BF_4{}^-$ Ar	$Pd(dba)_2$ mol%	Rates[b)] $\%min^{-1}$	Yields[c)] %	Products ratio/%[d)] (E)-PhCH=CHAr 5		(Z)-PhCH=CHAr 6
Me(1)	Ph(4a)[e)]	10	58	100	96(5a)	:	4(6a)
	4-MePh(4b)[f)]	1.1	2.5	45	>99(5b)	:	t[i)]
	4-MePh(4b)[f)]	5.0	14	82	>99(5b)	:	t[i)]
	4-MePh(4b)[f)]	10	62	97	>99(5b)	:	t[i)]
	4-BrPh(4c)[e)]	10	35	98	98(5c)	:	2(6c)
	$4-NO_2Ph$(4d)[f)]	10	27	96	96(5d)	:	4(6d)
Et(2)	Ph(4a)[e)]	10	12	61	100(5a)	:	0
	Ph(4a)[g)]	29	29	78	100(5a)	:	0
	4-MePh(4b)[g)]	10	13	60	100(5b)	:	0
	4-BrPh(4c)[e)]	10	8.5	55	100(5c)	:	0
	$4-NO_2Ph$(4d)[e)]	10	6.9	67	100(5d)	:	0
Ph(3)	Ph(4a)[h)]	10	4.1	43	100(5a)	:	0

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 4 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(7), could not be detected in all the reactions examined here, but (E)-stilbene derivatives(5) were selectively produced. A control reaction of 1 with 4b in the presence of 5a and 6a clearly showed that no isomerization occurred in either product isomers, 5a and 6a, under these particular reaction conditions.[5)] Irrespective of the substituents on 4, the reaction of 1 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 mechanism[3)] described for the reaction of (E)- and (Z)-$PhCH=CHSiMe_3$(Scheme 1). The reactions of zero-valent palladium with 4 easily generate the arylpalladium species($[Ar-Pd]^+BF_4{}^-$: 4').[6)] The Ar-Pd species easily add to olefins at



Scheme 1.

ambient temparature.[7)] The steric and electronic effects of Ph and R_3Si groups on 1-3 may determine the orientation of the syn-addition of Ar-Pd species to α-silylstyrenes and more preferentially give the adduct 8 than 9. In the adduct 8, palladium should be transposed with the neighbouring carbon to undergo desilylation. Two isomeric adducts 10 and 11 can be obtained from the corresponding conformers 8' and 8", respectively, via intramolecular syn-elimination and re-addition of an H-Pd species. The stereochemistry of the elimination of Pd(0) and Me_3Si moieties depends on the stability of the conformers.[3)] The bulky substituents(R=Et and Ph) on silicon destabilize not only the conformer 8", but also the conformer 10'. The syn-elimination from the stable conformer 10 produces 5, 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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4) $Ph(Me_3Si)C{=}CH_2$(1) was obtained, in 61% yield, by Grignard reaction of $Ph(BrMg)C{=}CH_2$ with Me_3SiCl in THF. $Ph(Et_3Si)C{=}CH_2$(2) and $Ph(Ph_3Si)C{=}CH_2$(3) 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., 49, 1958(1976)].

$$R_3SiCH{=}CH_2 \xrightarrow{Br_2 \quad Et_2NH} R_3Si(Br)C{=}CH_2 \xrightarrow[NiCl_2(dppp)]{PhMgBr} Ph(R_3Si)C{=}CH_2$$

These yields in the last step were 75%(2) and 95%(3). $Ph^a(Me_3{}^bSi)C{=}CH_2{}^{cd}$ (1): ^1H NMR(solvent: CCl_4, internal standard: CH_2Cl_2)δH^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). $Ph^a(Et_3{}^bSi)C{=}CH_2{}^{cd}$(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). $Ph^a(Ph_3{}^bSi)C{=}CH_2{}^{cd}$(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 $Ph(Me_3Si)C{=}CH_2$(1) with $4\text{-}MePhN_2BF_4$(4b) in the presence of (E)- and (Z)-PhCH=CHPh(5a and 6a): 1=2.0 mmol, 4b=1.0 mmol, 5a=0.47 mmol, 6a=0.27 mmol, $Pd(dba)_2$=0.1 mmol, and CH_3CN=5 ml at 25 °C.

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8) The tighter coordination of OAc^- to palladium than $BF_4{}^-$ may promote the syn-elimination of H-Pd-OAc from $RCH(AcOPd)CH(SiMe_3)Ar$[K. Ikenaga, K. Kikukawa, and T. Matsuda, J. Org. Chem., 52, 1276(1987)]; The mode of syn-elimination of Me_3SiX(X=Br and Cl) from $^tBuCH(X)CH(X)SiMe_3$ depends upon the stability of the conformer[R. B. Miller and G. McGarvey, J. Org. Chem., 43, 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., 1975, 1133; J. Am. Chem. Soc., 97, 1464(1975)].

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