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REACTION OF DIAZONIUM SALTS WITH TRANSITION METALS

IX *. REACTION OF VINYLTRIMETHYLSILANE WITH ARENEDIAZONIUM TETRAFLUOROBORATES UNDER PALLADIUM(0) CATALYSIS

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Summary

Arenediazonium tetrafluoroborates (ArN_2BF_4 where Ar = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-IC_6H_4 and 4-$NO_2C_6H_4$) reacted easily with CH_2=$CHSiMe_3$ at 25 °C to give ArCH=CH_2, (*E*)-ArCH=$CHSiMe_3$ and Ar(Me_3Si)C=CH_2 in excellent yields under palladium(0) catalysis. (*E*)-ArCH=$CHSiMe_3$ compounds were obtained predominantly and isolated in good yields by using an excess of CH_2=$CHSiMe_3$ over ArN_2BF_4. Protodesilylation of the reaction mixture afforded styrene derivatives.

Introduction

Palladium-catalyzed reactions of arenediazonium salts (ArN_2X; **1**) involve arylpalladium species (ArPdX) as a key intermediate [1–5]. The increased reactivity of **1** to zero-valent palladium as compared to that of aryl iodides (or bromides) provides an excellent method for the chemoselective preparation of ArPdX bearing iodine or bromine substituents on the aromatic ring. Simple transformation of **1** to alkyl- and acylarenes has been accomplished through transmetallation of in situ formed ArPdX [5] and aroylpalladium species [4] with organotin compounds, respectively.

Regiospecific substitution and stereospecific substitution of organosilicons, especially vinylsilanes, by various electrophiles have been extensively utilized in organic syntheses [6]. However, not so many transition metal mediated C–C coupling reactions via organosilicons have been reported because of the low reactivity of the Si–C bond for transmetallation with transition metals. It has been reported that the reaction of (*E*)-PhCH=$CHSiMe_3$ or (*E*)-PhCH=$CHSiF_5^{2-}$ with palladium(II) salts results in the formation of the (*E*)-PhCH=CHPd-intermediate through an addition-

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* For Part VIII, see ref. 5.

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elimination (eq. 1) [7] or a transmetallation (eq. 2) [8] mechanism, respectively.

$$(E)\text{-PhCH=CHSiMe}_3 + \text{PdCl}_2 \rightarrow [\text{PhCH(Cl)CH(PdCl)SiMe}_3] \xrightarrow[-\text{Me}_3\text{SiCl}]{} [(E)\text{-PhCH=CHPdCl}] \qquad (1)$$

$$(E)\text{-PhCH=CHSiF}_5^{2-} + \text{Pd(OAc)}_2 \rightarrow [(E)\text{-PhCH=CHPd(OAc)}] \qquad (2)$$

Herein we report a very facile reaction of vinyltrimethylsilane (**2**) with **1** catalyzed by palladium(0).

Results and discussion

Rapid gas evolution occurred on the addition of 2 mol% of bis(dibenzylideneacetone)palladium(0) (**3**) to a solution of **1** (0.5 mmol) and **2** (1.5 mmol) in acetonitrile (5 ml) at 25 °C, and was completed within 10–60 min depending on the substituents on **1**. Interestingly, (E)-ArCH=CHSiMe$_3$ (**5a–5e**) and Ar(Me$_3$Si)C=CH$_2$ (**6a–6e**) were obtained together with ArCH=CH$_2$ (**4a–4e**) (eq. 3 and Table 1). Figure 1 shows the time course of the reaction with **1a**.

$$\underset{(\mathbf{1a\text{–}1e})}{\text{ArN}_2\text{BF}_4} + \underset{(\mathbf{2})}{\text{CH}_2\text{=CHSiMe}_3} \xrightarrow{\text{Pd(dba)}_2\,(\mathbf{3})/\text{CH}_3\text{CN, }25\,^\circ\text{C}} \underset{(\mathbf{4a\text{–}4e})}{\text{ArCH=CH}_2} + \underset{(\mathbf{5a\text{–}5e})}{(E)\text{-ArCH=CHSiMe}_3} + \underset{(\mathbf{6a\text{–}6e})}{\text{Ar(Me}_3\text{Si)C=CH}_2} \qquad (3)$$

(**a**, Ar = Ph; **b**, Ar = 4-MeC$_6$H$_4$; **c**, Ar = 4-BrC$_6$H$_4$;
d, Ar = 4-IC$_6$H$_4$; **e**, Ar = 4-NO$_2$C$_6$H$_4$)

TABLE 1

PALLADIUM-CATALYZED REACTION OF ArN$_2$BF$_4$ (1) AND VINYLTRIMETHYLSILANE (2) (eq. 3) [a]

Entry	ArN$_2$BF$_4$	Molar ratio 2/1	Products [b]			Yields [c] (%)	Isolated yields (%) [d]	
			4	5	6		4 [e]	5
1	**1a**	1	82	14	4	80	–	–
2	**1a**	2	68	28	4	100	–	–
3	**1a**	3	54	41	5	98	–	–
4	**1a**	5	40	55	5	96	–	–
5	**1a**	10	24	71	5	100	–	–
6	**1b**	3	91	6	3	100	(–) [f]	–
7	**1b**	10	65	32	3	100	–	29
8	**1c**	3	37	58	5	100	67	–
9	**1c**	10	7	88	5	(97) [g]	–	67
10	**1d**	3	60	35	5	100	42	–
11	**1d**	10	41	54	5	100	–	35
12	**1e**	3	23	70	7	79	–	–
13	**1e**	10	11	84	5	100	–	83

[a] Unless noted otherwise, the reactions were carried out by the addition of **3** (0.01 mmol) to a solution of **1** (0.5 mmol) and **2** (0.5–5.0 mmol) in CH$_3$CN (5 ml) at 25 °C. [b] The mol% compositions of the products were determined by direct GC analysis of the reaction mixtures. [c] GC yields based on **1**. [d] For isolation, 5 mmol of **1**, 15 or 50 mmol of **2**, and 0.1 mmol of **3** were used in 50 ml of CH$_3$CN at room temperature. [e] After desilylation by concentrated HCl. [f] 4-Methylstyrene formed in this system polymerized spontaneously. [g] Isolated yields of crude mixture.

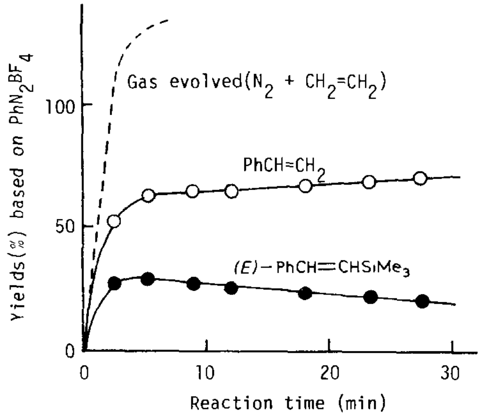


Fig. 1. Time course of the reaction of PhN_2BF_4 with CH_2=$CHSiMe_3$. PhN_2BF_4 = 0.5 mmol, CH_2=$CHSiMe_3$ = 1.5 mmol, $Pd(dba)_2$ = 0.027 mmol, CH_3CN = 5 ml, 25.0 °C. -○-: PhCH=CH_2; -●-: (*E*)-PhCH=$CHSiMe_3$; ------: gases evolved (N_2 + CH_2=CH_2).

Desilylation of **5** to **4** was found to be very slow under the present reaction conditions, and most of **4** is considered to form without the intervention of **5**. The addition of concentrated HCl to the reaction mixture protodesilylated **5a**–**5d** smoothly to give **4a**–**4d**, whereas **5e** and **6a**–**6e** remained unchanged under ordinary desilylation conditions. After the desilylation, **4a**–**4d** could be easily isolated by distillation and/or column chromatography (silica gel/hexane). Since **1** with various kinds of substituents is readily available, the present reaction affords a convenient method of preparing styrene derivatives, i.e. **2** seems to be an advantageous ethylene equivalent for vinylation of **1** [9].

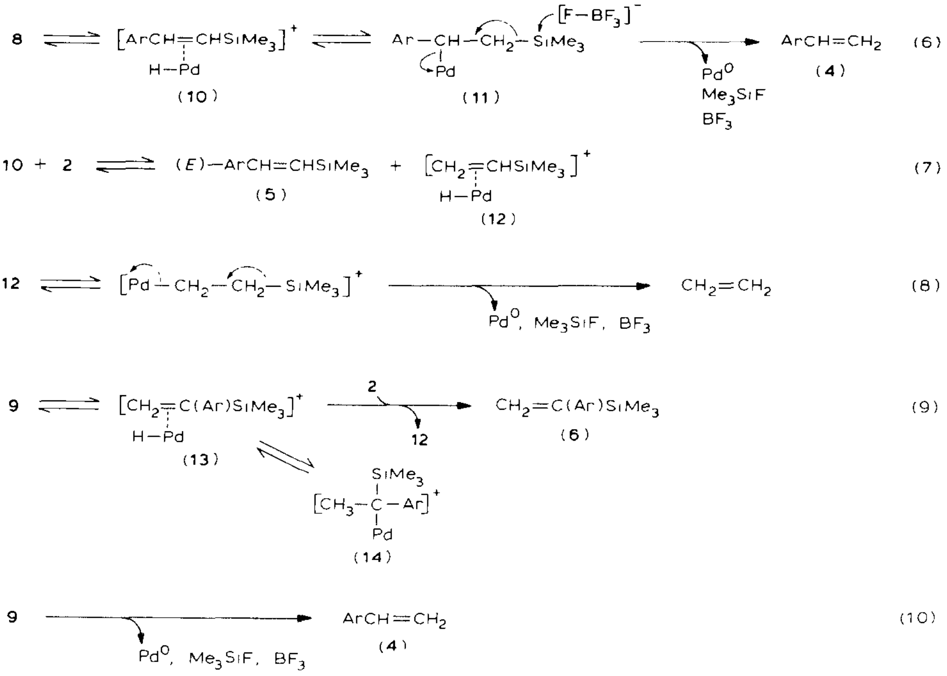
When **2** was used in a large excess (**2**/**1** = 10), compounds **5a**–**5e** were obtained predominantly and the gas evolution increased considerably with an increase in ethylene content. Thus, the formation of ethylene may be related to that of **5a**–**5e**. Vacuum distillation and/or column chromatography (silica gel/hexane) gave **5b**–**5e** in moderate to good yields. Despite the requirement of a large excess of **2**, the present reaction provides a convenient method of the preparation of **5** with the substituents being reactive for organometals or metal hydrides.

Recently, Hallberg and Westerlund reported a palladium-catalyzed reaction of **2** with aryl iodides in the presence of triethylamine to give **4** together with **5** and **6** [10]. The reaction required a relatively high temperature and a long reaction time (75–125 °C, 0.5–48 h). The mild conditions of the present reaction system enable successful preparation of **4** or **5** bearing halogen (bromine and iodine) substituents.

Some palladium-mediated reactions of organosilicons previously reported have been described to proceed via a transmetallation process [8,11]. However, the formation of **5** and **6** in the present reaction system requires an alternative path. The addition of Ar–Pd species followed by the elimination of H–Pd and/or Me_3Si and Pd^0 might be a plausible pathway, as described in the following equations where the assistance of the fluoride ion is an important factor in cleaving the Si–C bond (eq. 6, 8 and 10) [12].

$$\underset{(\mathbf{1})}{ArN_2BF_4} + Pd^0 \xrightarrow[N_2]{} \underset{(\mathbf{7})}{[Ar\text{-}Pd\text{-}]^+BF_4^-} \qquad (4)$$

$$7 + \underset{(\mathbf{2})}{CH_2{=}CHSiMe_3} \rightarrow \underset{(\mathbf{8})}{[Ar{-}CH_2CH(Pd)SiMe_3]^+} + \underset{(\mathbf{9})}{[Pd{-}CH_2CH(Ar)SiMe_3]^+} \qquad (5)$$



The formation of Me_3SiF was observed by GC analysis. Such desilylation may produce **4** from **9** directly (eq. 10) or from **8** after the isomerization to **11** via elimination and re-addition of H–Pd (eq. 6). The preferential formation of **5** when an increased amount of **2** is used and/or in the presence of an electron-withdrawing group on **1** can be easily recognized by postulating the existence of an equilibrium between **10** and **12** (eq. 7). In contrast to the formation of **5**, that of **6** was insensitive to the molar ratio of **2** to **1**. The regiochemistry is determined by the addition step of the Ar–Pd species (eq. 5). The preferential formation of **8** is clearly expected from the steric and electronic effects of the trimethylsilyl group. As mentioned before, compounds **6a**–**6e** were very difficult to protodesilylate under the conditions which easily protodesilylated **5a**–**5d** (eq. 11 and 12).

$$\underset{(\mathbf{6})}{CH_2{=}C(Ar)SiMe_3} + H^+ \nrightarrow \left[\overset{+}{C}H_2{-}CH(Ar)SiMe_3\right] \rightarrow \underset{(\mathbf{4})}{ArCH{=}CH_2} \qquad (11)$$

$$\underset{(\mathbf{5})}{(E)\text{-}ArCH{=}CHSiMe_3} + H^+ \rightarrow \left[Ar\overset{+}{C}H{-}CH_2SiMe_3\right] \rightarrow \underset{(\mathbf{4})}{ArCH{=}CH_2} \qquad (12)$$

This result suggests that the direct desilylation of **9** through eq. 10 may be very slow. Furthermore, the equilibrium between **9** and **13** (or **14**) (eq. 9) may lie to the right. Thus, **9** might decompose exclusively through **13** (eq. 9) instead of the direct desilylation (eq. 10). Consequently, the formation of **6** may not depend on the amount of **2**, but may reflect the regioselectivity of the addition step to form **8** and **9** (eq. 5).

The formation of **5** and **6** inevitably produces the H–Pd^{II} species, which is trapped by **2** to form **12**. The resulting complex, **12**, regenerates zero-valent palladium, an active catalyst, with the formation of ethylene (eq. 8). Thus, **2** works as a base as in the Heck olefin arylation [13]. Although the evolved ethylene was only qualitatively analyzed, the gas evolution of more than 100% in Fig. 1 might reflect the formation of ethylene. The reaction of **1** with **5a** exclusively produced desilylated products, PhCH=CHAr [12]. Since **2** is a better ligand with Pd^{II} than **5**, the present reaction produces undesilylated products, **5** and **6**.

Vinyltrimethoxysilane (**15**) also reacted smoothly with **1**, but only low yields of **4** were obtained as identifiable products (eq. 13). The low yields might be attributed,

$$\underset{(\mathbf{1})}{\mathrm{ArN_2BF_4}}+\underset{(\mathbf{15})}{\mathrm{CH_2{=}CHSi(OMe)_3}}\xrightarrow[(\mathbf{15}/\mathbf{1}=1.5)]{\mathbf{3}\,(2\ \mathrm{mol\%})/\mathrm{CH_3CN,\ r.t}}\begin{array}{l}\mathrm{ArCH{=}CH_2}\\ \mathbf{4a},\ 43\%\ (\mathrm{GC})\\ \left.\begin{array}{l}\mathbf{4b},\ 17\%\\ \mathbf{4c},\ 27\%\\ \mathbf{4e},\ 20\%\end{array}\right\}(\mathrm{isolated})\end{array}\qquad(13)$$

in part, to polymerization of arylated products containing a trimethoxysilyl group to polysiloxanes in the presence of BF_3. The addition of concentrated HCl or CsF did not affect the yields.

Experimental

Materials. Acetonitrile was distilled from phosphorus pentoxide (twice) and calcium hydride under nitrogen. Arenediazonium tetrafluoroborates were prepared by the usual method [14] and stored under nitrogen at −20 °C. Bis(dibenzylideneacetone)palladium(0) was prepared by the method of ref. 15. Vinyltrimethylsilane and vinyltrimethoxysilane were used as received.

General procedure. The reactions were started by the addition of **3** (2 mol%) to a solution of **1** (0.5 mmol), **2** (0.5–5.0 mmol) and CH_3CN (5 ml) in a thermostated cell (25 °C) equipped with a side arm and a serum cap. Gas evolution was measured by a gas buret connected to the side arm. After completion of the gas evolution, a chloroform solution of an appropriate internal standard was added to the reaction mixture. The products and their yields were analyzed by GC (Silicone SE-30 with FID).

The time course of the reaction was determined with **1a** (0.5 mmol), **2** (1.5 mmol), **3** (0.027 mmol) and diamyl ether (internal standard) in CH_3CN (5 ml) at 25 °C. Samples were withdrawn at appropriate time intervals by a micro-syringe and directly analyzed on GC with FID.

For isolation of the products, 5 mmol of **1** and 50 ml of CH_3CN were used at room temperature. After completion of the reaction, 100 ml of hexane or diethyl ether was added. The mixture was washed with aqueous sodium carbonate and brine, and then dried over anhydrous magnesium sulfate. The solvents were removed on a rotary evaporator, and the residue was chromatographed on silica gel (hexane) or was distilled (Kugelrohr). In the reaction of **1** with **15**, 10 mmol of **1**, 15 mmol of **15**, 0.2 mmol of **3** and 50 ml of CH_3CN were used at room temperature.

TABLE 2

NMR SPECTRAL DATA OF $ArCH{=}CH_2$ (**4**), (*E*)-$ArCH{=}CHSiMe_3$ (**5**) AND $Ar(Me_3Si)C{=}CH_2$ [a]

	Ar H^b C=C H^a H^c						Ar H^b C=C H^a SiMe$_3$			Ar H^a C=C Me$_3$Si H^b		
Ar	H^a	H^b	H^c	J_{ab}	J_{ac}	J_{bc}	H^a	H^b	J_{ab}	H^a	H^b	J_{ab}
4-MeC_6H_4	6.54	5.51	5.02	17.6	10.4	1.1	6.78	6.22	19.6	5.70	5.49	3.1
4-BrC_6H_4	6.52	5.70	5.16	17.5	10.8	0.9	6.65	6.25	18.0	5.66	5.48	2.9
4-IC_6H_4	6.41	5.57	5.03	18.0	10.4	1.2	6.73	6.30	19.6	5.65	5.45	3.0
4-$NO_2C_6H_4$	6.68	5.79	5.38	16.9	10.4	0.8	6.83	6.40	19.0	5.71	5.57	2.8

[a] Measured in CCl_4, ppm from TMS, and coupling constants in Hz.

Identification of products

The structures of **4a**–**4c** and **5a** were determined by comparison of their NMR and IR spectra and their retention times on GC with those of authentic samples. NMR and IR spectra were used to confirm the formation of **4a**–**4e** and **5a**–**5e**. Elemental analysis was also used for the new compounds **4d** and **5c**–**5e**. Since the amount of **6a**–**6e** was too small to isolate these compounds in a pure form, the structures of **6a**–**6e** were assumed by NMR of the mixture of the crude products, by the resonance of the vinylidene proton ($CH_2{=}$). More than a trace amount of any other products could not be observed in GC and NMR. Table 2 shows the NMR spectral data of **4b**–**4e**, **5b**–**5e** and **6b**–**6e**.

4-Iodostyrene (**4d**) (nc), m.p. 40–41°C. Found: C, 41.76; H, 3.07. (C_8H_7I) calcd.: C, 41.79; H, 3.08%. (*E*)-4-Bromostyryltrimethylsilane (**5c**) (nc), m.p. 42–43°C; IR (cm^{-1}) ν(C=C) 1605, δ(CH of *trans*-CH=CH) 996. Found: C, 51.77; H, 5.92. ($C_{11}H_{15}BrSi$) calcd.: C, 51.63; H, 5.92%.

(*E*)-4-Iodostyryltrimethylsilane (**5d**) (nc), m.p. 24–25°C; IR (cm^{-1}) ν(C=C) 1605, δ(CH of *trans*-CH=CH) 990. Found: C, 44.13; H, 5.23. ($C_{11}H_{15}ISi$) calcd.: C, 43.72; H, 5.00%. (*E*)-4-Nitrostyryltrimethylsilane (**5e**) (nc), m.p. 61–62°C; IR (cm^{-1}) ν(C=C) 1590, δ(CH of *trans*-CH=CH) 995. Found: C, 60.14; H, 6.85; N, 6.33. ($C_{11}H_{15}NO_2Si$) calcd.: C, 59.68; H, 6.79; N, 6.43%.

References

1 K. Kikukawa, K. Nagira, F. Wada and T. Matsuda, Tetrahedron, 37(1981) 31
2 K. Nagira, K. Kikukawa, F. Wada and T Matsuda, J. Org. Chem., 45(1980) 2365
3 K. Kikukawa, K. Kono, K. Nagira, F. Wada and T. Matsuda, J. Org. Chem., 46(1981) 4413.
4 K. Kikukawa, K. Kono, F. Wada and T Matsuda, Chem. Lett., (1982) 35.
5 K. Kikukawa, K. Kono, F. Wada and T. Matsuda, J. Org. Chem, 48(1983) 1333
6 T.H. Chan and I. Fleming, Synthesis, (1979) 761; E.W. Colvin, Silicon in Organic Synthesis, Butterworths, London, 1981, p. 44; W.P. Weber, Silicon Reagents for Organic Synthesis, Springer-Verlag, Berlin, 1983, p. 79.
7 W.P. Weber, R.A. Felix, A.K Willard and K.W. Koenig, Tetrahedron Lett, (1971) 4701
8 J. Yoshida, K. Tamao, H. Yamamoto, R Kakui, T Uchida and K. Kumada, Organometallics, 1(1982) 542.
9 K. Kikukawa, N. Terao, K. Nagira, F. Wada and T. Matsuda, Bull. Chem. Soc. Jpn., 52(1979) 2609
10 A. Hallberg and C. Westerlund, Chem Lett., (1982) 1993.
11 I.S. Akhrem, N.M. Chistovalova, E.I. Mysov and M.E. Vol'pin, J. Organomet Chem., 72(1974) 163
12 K. Kikukawa, K. Ikenaga, F. Wada and T. Matsuda, Chem. Lett., (1983) 1337
13 R.F. Heck, Acc. Chem. Res., 12(1979) 146.
14 A. Roe, Org. React., 5(1949) 193.
15 T. Ukai, H. Kawazura, Y. Ishii, J J Bonnet and J.A Ibers, J. Organomet Chem, 65(1974) 253.