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Substituent Effect of 3,3,3-Trifluoropropyl Group on Organic Silanols. Palladium-Mediated Mizoroki–Heck Type and Cross-Coupling Reactions

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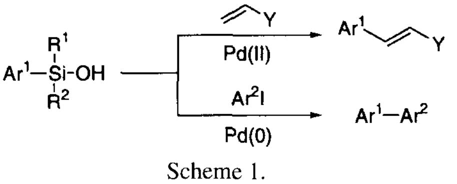
The Mizoroki–Heck type reaction of methyl(phenyl)-(3,3,3-trifluoropropyl)silanol (**1a**) with ethyl acrylate in the presence of $Pd(OAc)_2$ (10 mol%) and $Cu(OAc)_2$/LiOAc gave ethyl cinnamate in 70% yield. The palladium-catalyzed cross-coupling of **1a** with 4-iodomethoxybenzene in the presence of Ag_2O also afforded 4-methoxybiphenyl in 51% yield.

We have reported that several silanols have exhibited unique reactivities, which seem to be based on the effect of a hydroxy group on silicon.[1,2] The hydroxy group induces the enhanced reactivity on the transformation of a neighboring functional group.[3] The carbon–silicon bond is activated by the hydroxy group to result in undergoing palladium-catalyzed carbon–carbon bond-forming reactions. Indeed, the reaction with olefinic compounds in the presence of stoichiometric palladium(II) or the combined use of a catalytic palladium and a copper(II) salt proceeded to give Mizoroki–Heck type products.[4] In addition, the palladium-catalyzed cross-coupling reaction also proceeded in the presence of silver(I) salt as a cocatalyst (Scheme 1).[5]

On the other hand, we recently reported the synthesis and optical resolution of chiral silanols, in which novel silanols with a 3,3,3-trifluoropropyl group as a substituent were afforded.[6] Since various organic groups with fluorine substituent(s) have shown a remarkable electronic and/or steric effect,[7] the reactions of such chiral silanols with an aryl- or alkenyl substituent, thereby, have become a center of our major concern. We herein report that these silanols with a 3,3,3-trifluoropropyl group appear to be more reactive than the corresponding silanol with two methyl groups **3**, which was previously reported for palladium-catalyzed reactions.



Scheme 1.

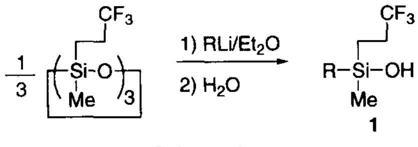
The synthesis of silanols with a 3,3,3-trifluoropropyl group was carried out by the reaction of 1,3,5-tris(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane (D_3^F) with aryl- or alkenyllithium in 53—84% yield (Scheme 2). We compared the palladium-catalyzed reactions of **1a** with the corresponding **3a**.

As previously reported,[4] the reaction of dimethyl(phenyl)-silanol (**3a**) with ethyl acrylate at 100 °C for 3 h furnishes ethyl cinnamate (**2a**) in 55% yield. On the other hand, the reaction of **1a** under similar conditions resulted in giving 70% of the product. To this end, the reactivity of the silanol bearing a 3,3,3-trifluoropropyl group appeared, despite being sterically more congested, comparable to **3**. Other olefins also effected a similar Mizoroki-Heck type reaction in moderate-to-good yields, as shown in Table 1.

Palladium-catalyzed cross-coupling reactions of (trifluoropropyl)silanols with several aryl iodides were also performed in the presence of silver(I) oxide as an activator in a similar manner to that of **3**.[5] The reaction of silanol **1b** with iodobenzene in the presence of 5 mol% of $[Pd(PPh_3)_4]$ and silver(I) oxide (100 mol%) in THF at 60 °C for 7 h proceeded to give **4a** in 74% yield. The cross-coupling reaction using the silanol with the dimethylsilyl substituent, **3b**, under similar conditions afforded a coupled product in only 46% yield. Consequently, the cross-coupling reaction with a silanol **1** bearing a 3,3,3-trifluoropropyl group as a substituent was found to proceed faster than that of **3**.

The results concerning reaction of silanols **1** with aryl iodides are given in Table 2. Aryl- and alkenylsilanols afforded the corresponding coupling products in good-to-excellent yields within a reaction period of 7 h; it is noteworthy to compare this with the fact that the reactions of **3** required a longer reaction period (36 h) to produce a good yield. In particular, the cross-coupling of an alkenylsilanol **1d** with 4-iodomethoxybenzene is remarkably rapid to give **4f** in 79% yield within a reaction period of 2 h (89% yield for 7 h).

In summary, aryl- and alkenyl(3,3,3-trifluoropropyl)-(methyl)silanols reacted with organic halides and olefinic



Scheme 2.

Table 1. Mizoroki–Heck Type Reaction of Silanol

Silanol	Y	Product (%)
$PhSiMe_2OH$ (**3a**)	CO_2Et	**2a** (55)
PhSiR′MeOH (**1a**)[a]		(70)
	COMe	**2b** (79)
	CN	**2c** (43)[b]
	Ph	**2d** (59)

a) R′ = $CF_3CH_2CH_2$. b) $E/Z = 5/2$.

Table 2. Cross-Couling of Silanol with Ar^2I[a)]

Silanol		Ar^2	Product (%)
$PhSiMe_2OH$	(**3a**)	4-$MeOC_6H_4$	**4a** (30)[b)]
PhSiMeROH	(**1a**)[c)]		(51)
4-$MeOC_6H_4$-$SiMe_2OH$	(**3b**)	Ph	(46)
4-$MeOC_6H_4$-SiMeROH	(**1b**)[c)]		(74)
		4-$MeCOC_6H_4$	**4b** (92)
		4-MeC_6H_4	**4c** (68)
4-$MeOC_6H_4$-SiMeROH	(**1c**)[c)]	Ph	**4d** (42)
		4-$MeCOC_6H_4$	**4e** (89)
(*E*)-PhCH=CH-SiMeROH	(**1d**)[c)]	4-$MeOC_6H_4$	**4f** (79)[d)]
			(89)
		Ph	**4g** (91)

a) Reaction time: 7 h, otherwise noted. b) Reaction time: 36 h.
c) R = $CF_3CH_2CH_2$. d) Reaction time: 2 h.

compounds in the presence of a palladium complex. The reactivity of silanols with a 3,3,3-trifluoropropyl group in the Mizoroki–Heck type reaction was comparable to that of **3**, and the cross-coupling reaction with several aryl iodides took place more rapidly than that of **3**.

Experimental

The synthesis of silanols with 3,3,3-trifluoropropyl group was carried out in a similar manner as reported.[1,6] The spectroscopic data and physical properties of new silanols are shown below.

4-Methoxyphenyl(methyl)(3,3,3-trifluoropropyl)silanol (1b): 69% yield; bp 170 °C/1.0 Torr (bath temp) (1 Torr = 133.322 Pa); ^{1}H NMR ($CDCl_3$) δ = 0.42 (s, 3 H), 1.04 (m, 2 H), 1.96 (s, 1 H), 2.09 (m, 2 H), 3.83 (s, 3 H), 6.95 (d, J = 8.4 Hz, 2 H), 7.49 (d, J = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ = −2.2, 8.5, 28.0 (q, J = 30 Hz), 54.9, 113.8, 127.4, 127.7 (q, J = 275 Hz), 134.8, 161.1; IR (neat) 3340 (br), 3023, 2959, 2907, 2841, 1597, 1368, 1119, 1032, 897, 770 cm^{-1}. Found: C, 50.32; H, 5.92%. Calcd for $C_{11}H_{15}F_3O_2Si$: C, 49.98; H, 5.72%.

Methyl(4-methylphenyl)(3,3,3-trifluoropropyl)silanol (1c): 76% yield; bp 140 °C/0.5 Torr (bath temp) (1 Torr = 133.322 Pa); ^{1}H NMR ($CDCl_3$) δ = 0.43 (s, 3 H), 1.05 (m, 2 H), 1.96 (s, 1 H), 2.09 (m, 2 H), 2.37 (s, 3 H), 7.23 (d, J = 7.5 Hz, 2 H), 7.46 (d, J = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ = −2.2, 8.4, 21.4, 28.0 (q, J = 30 Hz), 127.7 (q, J = 275 Hz), 128.9, 132.7, 133.2, 140.2; IR (neat) 3300 (br), 3071, 3017, 2963, 1605, 1447, 1266, 1210, 1067, 897, 720 cm^{-1}. Found: C, 53.06; H, 5.91%. Calcd for $C_{11}H_{15}F_3OSi$: C, 53.21; H, 6.09%.

General Procedure for Mizoroki–Heck Type Reaction of Silanols with Olefins. To a solution of palladium(II) acetate (4.5 mg, 0.02 mmol, 10 mol%), copper(II) acetate (0.11 g, 0.6 mmol), and lithium acetate (26.4 mg, 0.4 mmol) in DMF (1 mL) placed in a screw-capped sealed glass tube were successively added an olefin (0.2 mmol) and a silanol (0.2 mmol) at room temperature. The mixture was heated with stirring at 100 °C for 3 h and then, after cooling, passed through a Celite pad, which was washed with 10 mL of diethyl ether. The filtrate was washed with 1 M HCl aq (10 mL, 1 M = 1 mol dm^{-3}), saturated $NaHCO_3$ aq (10 mL), and brine (10 mL). The ethereal solution was dried over $MgSO_4$ and concentrated under reduced pressure to leave a crude oil, which was purified by flush column chromatography on silica gel to give **2a**—**d** in 43—79% yield. The products were identical to authentic samples.

General Procedure for the Cross-Coupling of Silanols with Aryl Iodides. To a mixture of $[Pd(PPh_3)_4]$ (11.6 mg, 0.01 mmol, 5 mol%) and Ag_2O (46.3 mg, 0.2 mmol) in THF (2 mL) placed in a Schlenck tube was successively added a silanol (0.24 mmol) and an aryl iodide (0.2 mmol). The resulting mixture was then heated at 60 °C and stirring was continued for 7 h. The mixture was passed through a Celite pad and washed with diethyl ether. The filtrate was washed with 1 M HCl aq (10 mL), saturated $NaHCO_3$ aq (10 mL), and brine (10 mL). The ethereal solution was dried over $MgSO_4$ and concentrated under reduced pressure to leave a crude product, which was purified by column chromatography on silica gel to give **4** in up to 92% yield. The products were identical to authentic samples.

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