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PALLADIUM-MEDIATED SILYLATION OF ORGANIC HALIDES WITH DISILANE/F$^-$ REAGENT

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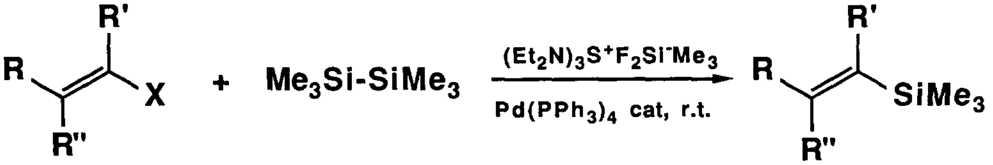
Under catalytic influence of tetrakis(triphenylphosphine)palladium, tris(diethylamino)sulfonium trimethyldifluorosilicate promoted the reaction of vinyl halides with hexamethyldisilane to give corresponding vinyl silanes in good yields chemoselectively and stereospecifically.

The coupling reaction of disilanes with various organic halides under the catalytic influence of transition metal complexes has afforded a useful method for the preparation of such versatile organosilicon compounds as arylsilanes,[1] allylsilanes,[2] benzylsilanes,[3] and acylsilanes.[4] However, the low reactivity of disilanes requires usually drastic conditions (high temperature and long reaction time)[1a] and therefore limited its synthetic application. To achieve successful silylation of vinyl halides, polychlorinated disilanes must be employed,[5] as the electronegative substitutent facilitates the transition metal catalyzed Si-Si bond cleavage.[2a] In spite of these modifications, handling of the resulting chlorovinylsilanes is rather troublesome due to the moisture-sensitive character of the products.

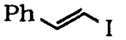
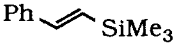
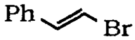
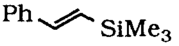
In contrast, fluoride ion induces the cleavage of Si-Si bond of hexamethyldisilane under extremely mild conditions to produce metal-free silyl anion species.[6] Taking advantage of the hexaalkyldisilane and fluoride ion reagent system, we have found that trimethylsilylation of vinyl halides does take place at room temperature by using tetrakis(triphenylphosphine)palladium as a catalyst, hexamethyldisilane and tris(diethylamino)sulfonium difluoro(trimethyl)silicate (TASF).



A typical procedure follows: A tetrahydrofuran (THF) solution of TASF (1.0 M solution, 0.35 ml, 0.35 mmol) was added to hexamethyldisilane (58 mg, 0.40 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) dissolved in HMPA (0.3 ml) at 0 oC under argon atmosphere, and the resultant solution was stirred at room temperature for 10 min. (*E*)-1-Iodooctene (72 mg, 0.30 mmol) was injected with the aid of a syringe, and the reaction mixture was stirred for 5 h at room temperature. After completion of the reaction, bulk of the solvent was removed by passing the reaction mixture through a silica gel column (pentane eluent). Evaporation of the pentane under atmospheric pressure gave (*E*)-1-trimethylsilyl-1-octene (38 mg, 68% yield). The silylation was applied to various vinyl haldies, and the results are summarized in Table 1.

A small excess of the fluoride ion to substrates is essential for the effective reaction; Use of lesser amount of the reagent resulted in lowering the yields of vinylsilanes, even if the reaction was carried out at an elevated temperature. Of various fluorides, TASF was the best. Tetrabutylammonium fluoride (TBAF) was proved to be slightly inferior due possibly to the contaminative moisture. Metal fluorides like KF and CsF were essentially ineffective owing to insolubility of these fluorides in the reaction media.

Table 1 Trimethylsilylation of Vinyl Halides

Run	Halide	Time (h)[a]	Product (% yield)[b]
1		2	 (82)
2		10	 (32)
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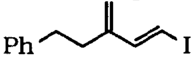
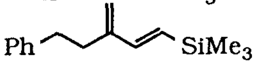
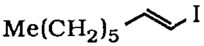
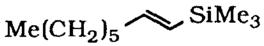
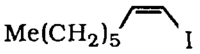
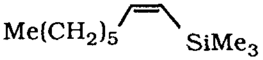
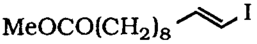
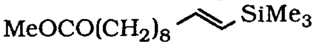
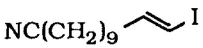
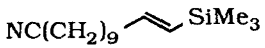
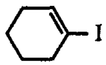
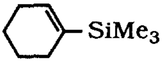
4		3	 (64)
5		5	 (74)
6		12	 (62)
7		3	 (92)
8		4	 (53)
9		10	 (82)

a: Satisfactory spectral data were obtained for all compounds.
b: Isolated yields.

We extensively examined the catalytic activity of various palladium complexes for the successful reaction in the presence of TASF and found that the best results were obtained on using $Pd(PPh_3)_4$ as the catalyst, with which moderate to high yields of vinylsilanes were obtained as the almost sole product. Several other catalysts including Pd(II) complexes showed the activity for the homocoupling reaction of the vinyl halides in addition to the desired silylation.

For the smooth reaction, co-existence of an aprotic polar solvent like HMPA is particularly essential. Less polar solvent THF or acetonitrile retarded the reaction considerably.

Salient features of the herein disclosed reaction are summarized as follows:

(1) The reaction proceeds stereospecifically with retention of the C=C bond geometry in the vinyl iodides, and thus stereochemically pure (*E*)- and (Z)-vinylsilanes could be obtained in good yields from the corresponding (*E*)- and (Z)-vinyliodides respectively (see runs 1, 3, 5, and 6).

(2) The reactions could be carried out without protection of a wide variety of functional groups *e.g.* ester and nitrile. In this respect the TASF-promoted silylation sharply contrasts with the precedent ones, which involve silylation of organolithium or -magnesium compounds and hence affect such functional sites.

(3) Unlike many other transition metal catalyzed silylation with disilanes, the reaction conditions are so mild that it is possible to introduce trimethylsilyl moiety to thermally labile substrates. For example, (*E*)-1-iodo-3-(2-phenylethyl)-1,3-butadiene was transformed to (*E*)-1-(trimethylsilyl)-1,3-butadiene efficiently (run 4).

Table 2 Trimethylsilylation of Aryl Iodides

Run	Halide	Time (h)	Catalyst (mol%)	Product (% yield)[a]
1	$4\text{-Me-}C_6H_4\text{-I}$	15	$Pd(PPh_3)_4$ (5)	$4\text{-Me-}C_6H_4\text{-SiMe}_3$ (20)
2	$4\text{-Me-}C_6H_4\text{-I}$	15	$Pd(PPh_3)_4$ (20)	$4\text{-Me-}C_6H_4\text{-SiMe}_3$ (100)
3	1-Naphthyl-I	5	$Pd(PPh_3)_4$ (20)	1-Naphthyl-$SiMe_3$ (100)
4	Ph-I	48	$Pd(PPh_3)_4$ (5)	Ph-$SiMe_3$ (32)[b]
5	Ph-I	24	$PdCl_2(PPh_3)_2$ (5)	Ph-$SiMe_3$ (32)[b]
6	Ph-I	24	$PdCl_2(PEt_3)_2$ (5)	Ph-$SiMe_3$ (28)[b]
7	Ph-I	24	$(\eta^3\text{-}C_3H_5PdCl)_2$ (2.5)	Ph-$SiMe_3$ (38)[b]
8	Ph-I	24	$PdCl_2(MeCN)_2$ (5)	Ph-$SiMe_3$ (32)[b]

a: Isolated yield unless otherwise stated.
b: Yield determined by GLC.

Under the same conditions, aromatic halides were silylated, but this silylation turned out to be less effective (Table 2). The turnover of the catalyst was at best 5 to 6. By using 20 mol% of the catalyst, the conversion was raised to almost 100%. Although we screened several palladium catalysts, we could not improve the results strikingly.

Though the reaction mechanism remains yet to be studied, the silylation reaction reported herein may involve, firstly, oxidative addition of the organic halides to Pd(0) species, secondly, transmetallation of the resulting alkenyl- or arylpalladium(II) species with silyl anion and/or pentacoordinated silicate generated by the reaction of fluoride ion and hexamethyldisilane to afford alkenyl- or aryl(trimethylsilyl)palladium species, and finally reductive elimination to give rise to the vinylsilanes or arylsilanes as well as the active Pd(0) species.

Further synthetic applications are in progress in our Laboratories.

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