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A WIDE RANGE OF ORGANOSILICON COMPOUNDS COUPLES WITH ENOL AND ARYL TRIFLATES IN THE PRESENCE OF Pd CATALYST AND FLUORIDE ION

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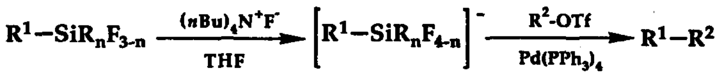
Under the influence of tetrakis(triphenylphosphine)palladium and tetrabutylammonium fluoride, the title reaction took place with alkenyl, alkynyl, aryl, and alkylsilanes to give the corresponding coupled products in good yields with high chemoselectivity and stereospecificity.

Organometallic compounds undergo cross-coupling reaction usually with organic halides with the aid of a transition-metal catalyst.[1] Recently, enol triflates[2] and phosphates[3] have been grown to be alternative or mostly more versatile substrates, since these esters are regioselectively prepared by means of the well-established enolate chemistry.[4] In view of a wide structural variety and the ready availability of organosilicon compounds, the application of organosilicon reagents[5] to the transition-metal catalyzed reaction with the enol esters should have the advantages over the conventional methods. We report that in the presence of fluoride ion various types of organosilicon compounds undergo the palladium-catalyzed cross-coupling with enol and aryl triflates under mild conditions with high stereospecificity and chemoselectivity.[6]

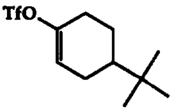
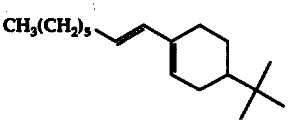
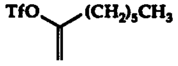
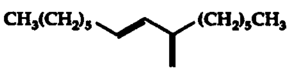
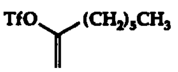
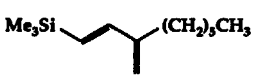
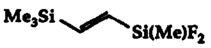
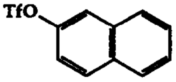
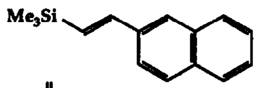
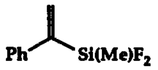
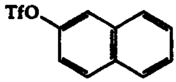
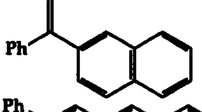
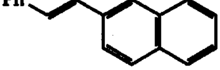
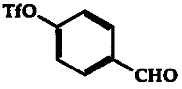
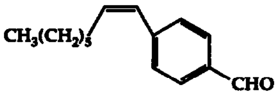
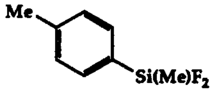
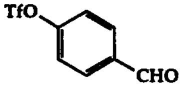
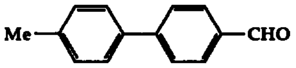
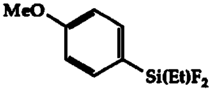
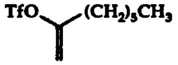
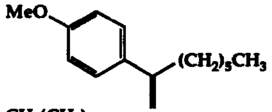
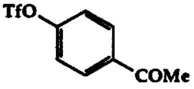
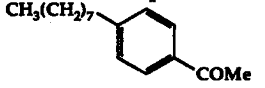
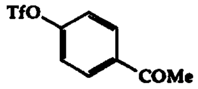
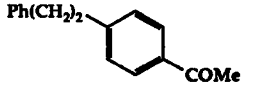
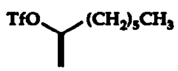
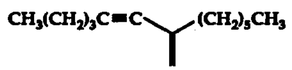


$$R^1{-}SiR_nF_{3\text{-}n} \xrightarrow[\text{THF}]{(n\text{Bu})_4N^+F^-} \left[R^1{-}SiR_nF_{4\text{-}n}\right]^- \xrightarrow[\text{Pd(PPh}_3)_4]{R^2\text{-OTf}} R^1{-}R^2$$

$n = 0, 1, 2$
R^1: alkenyl, alkynyl, aryl, alkyl
R^2: alkenyl, aryl
R : Me, Et

Table 1 summarizes the results and demonstrates that almost all types of organosilicon compounds can take part in the coupling reaction. Entries 1 and 2 show (*E*)-1-octenyltrifluorosilane and (*E*)-1-octenylmethydifluorosilane, available by the fluorination of the corresponding chlorosilanes,[7] reacted with 4-*tert*-butylcyclohexenyl triflate in the presence of 1 equiv of tetrabutylammonium fluoride (TBAF) (1.1 M in THF solution) and 5 mol% of tetrakis-

Table 1. TBAF/Pd(PPh_3)$_4$ Mediated Cross-Coupling of Organosilanes with Triflates[a]

run	organosilane	triflate	reaction time (h)	product(s)	% yield[b]
1	 n = 0		0.5		87
2	n = 1		0.5		99
3	n = 2		0.5		71
4	n = 3		24		0
5	n = 1		4		82
6			5		90
7			5		74
8			5	 	51 26
9			5		73
10			4		92
11			5		62
12	$CH_3(CH_2)_7SiF_3$		2.5		65
13	$Ph(CH_2)_2SiF_3$		2.5		71
14[c]	$CH_3(CH_2)_3C{\equiv}CSiMe_3$		1.5		81

[a]: Unless otherwise stated, all the reactions were carried out at 50 °C by using the organosilane (1.2 equiv) and the triflate (1.0 equiv) in the presence of TBAF (1.2 equiv) and Pd(PPh_3)$_4$ (3 - 5 mol%) in THF.

[b]: Isolated yields are given.

[c]: Reaction was carried out at room temperature.

(triphenylphosphine)palladium in THF solvent at 50 °C to afford 1-((*E*)-1-octenyl)-4-*tert*-butylcyclohex-1-ene in excellent yields. The corresponding fluorodimethylsilyl substituted olefin was less reactive, and the trimethylsilyl derivative did not show any reactivity (entries 3 and 4).[8] TBAF as the F^- reagent is essential for the success of the reaction; tris(diethylamino)sulfonium difluorotrimethylsilicate or potassium fluoride gave no coupled products. In contrast to the coupling reaction of triflates with organostannanes which require lithium chloride for a smooth transmetalation,[2b] the TBAF promoted reaction of the organosilanes proceeded well in the absence of lithium chloride. Presumably, the fluoride ion replaced the triflate ion to generate a reactive alkenylpalladium fluoride species which was capable of the transmetalation with the pentavalent alkenylsilicates.[5b] High degree of chemoselectivity observed in the silicon-based coupling reaction also deserve a comment. As seen in entires 9, 10, 12, and 13, the ketone and aldehyde carbonyls involved in the triflate substrates remained intact under the reaction conditions. The stereospecificity of the reaction was confirmed by the reaction of (*E*)- and (*Z*)-1-octenyldifluoromethylsilane (cf. entries 2 and 9). The coupling reaction usually takes place at the *ipso*-position: the C-Si bond is definitely converted into the C-C bond. However, the reaction of 1-methyldifluorosilylstyrene with 2-naphthyl triflate afforded, in addition to a normal coupled product, a fair amount of 2-(2-naphthyl)styrene (entry 8).[9] Only the aryl groups of arylalkyldifluorosilanes[5f] participated in the coupling reaction with an aryl triflate (entry 10) or an enol triflate (entry 11) in preference to the alkyl groups to give an alkenylarene or an asymmetric biaryl respectively as the sole product. This observation sharply contrasts to the fact that aryltin reagents do not show any reactivity towards enol triflates.[2b] Under the typical reaction conditions, even the alkyl groups of alkyltrifluorosilanes[7] cleanly coupled with aryl triflates to afford the desired arylalkanes in good yields (entries 12 and 13). This is particularly striking in view of the fact that the alkylpalladium intermediates having β-hydrogens are thermally rather labile.

Following procedure for the preparation of (*E*)-1-trimethylsilyl-3-methylene-1-nonene is representative (Table 1, entry 6). To a THF (10 mL) solution of 1-octen-2-yl triflate (0.78 g, 3.0 mmol) and tetrakis(triphenylphosphine)palladium (0.10 g, 0.090 mmol, 3 mol%) were added successively (*E*)-2-trimethylsilyl-1-methyldifluorosilylethene (0.63 g, 3.5 mmol) and a THF solution of TBAF (1.1 M, 3.2 mL, 3.5 mmol) under an argon atmosphere, and the mixture was heated at 60 °C for 5 h. Concentration under reduced pressure and purification by column chromatography (silica gel) using hexane gave the pure product as a colorless oil (0.57 g, 90% yield).

In conclusion, we have presented a general cross-coupling method which employs stable organosilanes and triflates. The new method is characterized by its high stereospecificity and chemoselectivity comparable to or better in some cases than other organometallic reagents. Studies on its applications as well as the mechanistic details are currently undertaken and will be described in the near future.

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