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PENTACOORDINATE ORGANOSILICON COMPOUNDS IN ORGANIC SYNTHESIS: CROSS-COUPLING OF ALKENYLSILICONATES WITH ORGANIC HALIDES AND TRIFLATES CATALYZED BY PALLADIUM COMPLEX[1]

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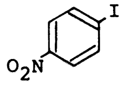
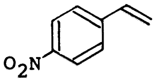
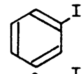
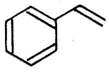
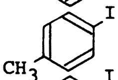
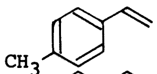
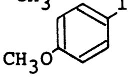
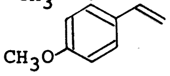
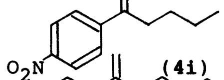
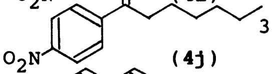
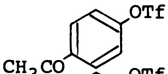
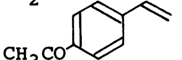
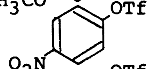
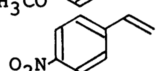
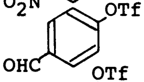
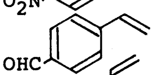
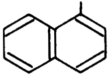
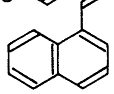
Pentacoordinate triethylammonium bis(catecholato)alkenylsiliconates, readily prepared from alkenyltrialkoxysilane, catechol, and triethylamine, react with aryl iodides, vinylic iodides and aryl triflates catalyzed by a palladium complex to give the corresponding cross-coupled products in a stereospecific mode.

KEYWORDS ——— pentacoordinate organosilicon compound; cross-coupling; palladium catalyst; organic halide; C(sp^2) halide; aryl triflate; stereoselective reaction; triethylammonium bis(catecholato)alkenylsiliconate

The selective carbon-carbon bond formation continues to be of current importance in organic synthesis. One of the previous methods for such purpose was based on the transition metal-catalyzed cross-coupling reactions of organometallics with organic halides.[2] We have recently demonstrated that pentacoordinate allylsiliconates, relative to tetracoordinate allylsilanes, reveal remarkably enhanced reactivity towards carbonyl compounds, and are convenient and useful reagents for the selective allylation without catalysts.[3] In the course of our studies on the use of highly coordinate organosilicon compounds in organic synthesis and from standpoints of biological and pharmacological activity,[4] we have found new stereo- and chemoselective cross-coupling reactions of purified pentacoordinate alkenylsiliconates with organic halides and triflates mediated by a palladium catalyst (eq. 1).[5] The cross-coupling can be also attained by the "one pot" operation without isolation of **1**. The results are listed in Table I.

At the outset of the work, the reaction of vinylsiliconate (**1a**) with 4-iodonitrobenzene (**2a**) was examined in detail under various conditions. A palladium complex like Pd(PPh$_3$)$_4$, PdCl$_2$(PhCN)$_2$, and [PdCl(C$_3$H$_5$)]$_2$, works as a catalyst to give the corresponding cross-coupling product, 4-nitrostyrene (**4a**) in 76-84% yields, but nickel complexes are not effective for the conversion. The addition of triethyl phosphite gave better results among various phosphines and phosphites such as PPh$_3$, P(OPh)$_3$, 1,2-bis(diphenylphosphino)ethane (dppe), and

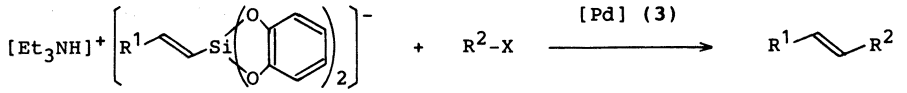
Table I. Pd-Catalyzed Cross-Coupling of **1** with Organic Halides and Triflates (**2**)[a]

Entry	1	2	Catalyst (3)	Time(h)	Products (4)[b]	%Yield
1	**1a**	 (**2a**)	$PdCl_2(PhCN)_2$	60	 (**4a**)	84
2	**1a**	**2a**	$[PdCl(C_3H_5)]_2$	60	**4a**	76
3	**1a**	 (**2b**)	$[PdCl(C_3H_5)]_2$	60	 (**4b**)	30[c]
4	**1a**	 (**2c**)	$[PdCl(PhCN)]_2$	60	 (**4c**)	38
5	**1a**	 (**2d**)	$PdCl_2(PhCN)_2$	60	 (**4d**)	35
6	**1a**	**2d**	$PdCl_2(PhCN)_2$	110	**4d**	47
7	**1a**	 (**2e**)	$PdCl_2(PhCN)_2$	60	 (**4e**)	29
8	**1a**	 (**2f**)	$[PdCl(C_3H_5)]_2$	40	 (**4f**)	21[c]
9	**1b**	**2b**	$[PdCl(C_3H_5)]_2$	48	 (**4g**)	48
					$Ph_2C=CH_2$ (**4h**)	25
10	**1c**	**2a**	$PdCl_2(PhCN)_2$	40	 (**4i**)	54
11	**1d**	**2a**	$PdCl_2(PhCN)_2$	110	 (**4j**)	33
12	**1a**	 (**2g**)	$Pd(PPh_3)_4$[d]	60	 (**4k**)	52
13	**1a**	 (**2h**)	$Pd(PPh_3)_4$[d]	12	 (**4a**)	57
14	**1a**	 (**2i**)	$Pd(PPh_3)_4$[d]	60	 (**4l**)	41
15	**1a**	 (**2j**)	$Pd(PPh_3)_4$[d]	60	 (**4m**)	32

[a] Unless noted, all reactions were carried out in the presence of 5 mol% of the catalyst and 10 mol% of $P(OEt)_3$ in dioxane at reflux. [b] All samples gave satisfactory ^1H NMR and IR spectra. [c] Determined by GLC. [d] LiCl (3 eq.) was added.

reaction mixture and the resulting mixture was stirred for 30 min and extracted with ether (20 x 3 ml). The combined organic layer was washed with 10% NaOH (20 ml), water (20 x 3 ml), and a brine (20 ml). After drying over anhydrous Na_2SO_4, the solvent was removed in vacuo. The residue was purified by the preparative TLC.

Further studies directed to useful carbon-carbon bond forming reactions utilizing the above promoter are currently in progress.



(1)

1a, R^1 = H
b, = Ph
c, = $CH_3(CH_2)_3$
d, = $CH_3(CH_2)_5$

2

4

1,3-bis(diphenylphosphino)propane (dppp) examined. Satisfactory results were obtained by using $[PdCl(C_3H_5)]_2$ and $PdCl_2(PhCN)_2$ in dioxane at reflux, though THF and DMF were not adequate as solvents.

Substituted iodobenzenes (**2a**, **2c**, and **2d**) and iodobenzene (**2b**) reacted with vinylsiliconate (**1a**) to afford the corresponding substituted styrene derivatives (**4a–d**). With bromobenzene the coupling reaction was quite slow, resulting in low yields of the coupled products. Treatment of **1a** with 1-iodooctene (**2e**) and β-bromostyrene (**2f**) gave the cross-coupled products in a stereospecific manner. However reactions of 1-alkenylsiliconates (**1b–d**) with iodobenzenes proceeded with loss of site-specificity, 1,1-disubstituted alkenes being obtained along with the normal cross-coupled products in some cases. Thus the reaction of **1c** with **2a** afforded 1,1-diphenylethylene (**4g**) and 1,2-diphenylethylene (**4h**) in 48% and 25% yields, respectively. From 1-hexenylsiliconate (**1c**) and 1-octenylsiliconate (**1d**), 1-butyl-1-(4-nitrophenyl)ethylene (**4i**) and 1-hexyl-1-(4-nitrophenyl)ethylene (**4j**) were produced in 54% and 33% yields. When alkenylsiliconate (**1b**) and phenylsiliconate (**5**) reacted without **2** under similar conditions, homo-coupling products were obtained in 58% and 75% yields, respectively.

It should be noted that organic trifluoromethanesulfonates (triflates) (**2g–j**) also react with **1** to give results similar to organic halides (**2a–f**). In this case $Pd(PPh_3)_4$ was a rather effective catalyst for the conversion. It was found that lithium chloride was also an important co-promoter for this reaction.10)

The present cross-coupling reaction can be achieved by "one pot" operation from organotrialkoxysilane. Thus after treatment of vinyltrimethoxysilane with two equivalents of catechol and triethylamine under neat conditions at room temperature, 4-iodonitrobenzene (**2a**), a catalytic amount of $[PdCl(C_3H_5)]_2$, and dioxane as a solvent were added, and the reaction mixture was stirred at reflux to afford p-nitrostyrene (**4a**).

Formation of cross-couples products may be explained by a mechanism similar to that proposed for the palladium and nickel-catalyzed reactions of organometallics with organic halides.11,12) However a detailed mechanism of the formation of 1,1-disubstituted alkenes remains obscure, though similar coupling reactions involving the rearrangement of an alkenyl group have been observed in the palladium-catalyzed cross-coupling of alkenylmercurials13) and -boranes.14)

A general procedure is as follows. A mixture of an alkenylsiliconate (**1**) (0.5 mmol), an organic halide (**2**) (0.5 mmol), a palladium complex (**3**) (0.025 mmol), and triethylphosphite (0.05 mmol) in dioxane (2 ml) was stirred at reflux temperature. After cooling, ether and saturated aq. $NaHCO_3$ were added to the

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