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Cobalt-catalyzed mono-coupling of R_3SiCH_2MgCl with 1,2-dihalogenoethylene: a general route to γ-substituted (*E*)-allylsilanes

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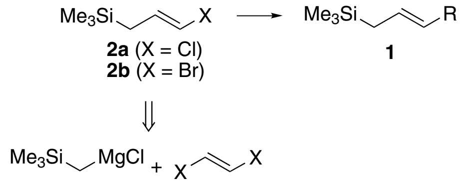
Abstract—The reaction of trimethylsilylmethylmagnesium chloride ($TMSCH_2MgCl$) with 1,2-dihalogenoethylene in the presence of 1 mol% of Co(II) or Co(III) acetylacetonate in THF or THF–NMP proceeded exclusively in a mono-coupling pathway to provide 3-trimethylsilyl-1-halogeno-1-propene with >99% of *E* geometry in high yield, which was converted to a variety of γ-substituted allylsilanes by Ni- or Pd-catalyzed coupling with organometallic compounds.

Allylsilanes are versatile compounds in organic synthesis useful as an allylating reagent or a starting material.[1] Therefore, numerous methods have been developed for their preparation, and several substituted allylsilanes as well as simple unsubstituted ones have become obtainable from commercial sources. γ-Substituted allylsilane **1** is an important member in the chemistry field that has been widely used in inter- and intramolecular reactions in the presence of a Lewis acid or F^- with a variety of electrophiles such as carbonyl, imino and iminium compounds and α,β-unsaturated carbonyl compounds, where high regio- and/or stereoselectivity has often been attained. Therefore, development of a general method for their preparation is desired.[2] Herein we describe an efficient preparation of (*E*)-3-silyl-1-halogeno-1-propene (**2**)[3] by a selective Co-catalyzed mono-coupling of 1,2-dihalogenoethylene with $TMSCH_2MgCl$ (TMS = trimethylsilyl), which allows a general access to (*E*)-γ-substituted allylsilanes **1** by the metal-catalyzed cross-coupling with a variety of organometallic reagents (Scheme 1).

First, we investigated a transition metal-catalyzed coupling reaction of (*E*)-1,2-dichloroethylene (>99% *E*), which is commercially available at low price, with $TMSCH_2MgCl$ to find conditions for selective production of mono-coupling product **2a**. Thus, (*E*)-1,2-dichloroethylene (4.0 mmol) was treated with $TMSCH_2MgCl$[4] (2.0 mmol) in the presence of 1 mol% of Ni, Pd, Co or Fe catalyst precursor. As can be seen from Table 1 summarizing the results, nickel-catalyzed reactions[5] afforded a mixture of (*E*)-3-trimethylsilyl-1-chloro-1-propene (**2a**) and 1,4-bis(trimethylsilyl)-2-butene (**3**) (entries 1–4).[6] It was noteworthy that the reaction with Ni–PPh_3 complexes gave **2a** predominantly (entries 1 and 2) but Ni-complexes with a bidentate phosphine ligand such as $Cl_2Ni(dppp)$ and $Cl_2Ni(dppb)$ catalyzed production of **3** mainly (entries 3 and 4). As shown in entries 6–8, to our delight, the reaction catalyzed by $Co(acac)_2$ or $Co(acac)_3$ proceeded smoothly with nearly complete selectivity of mono-coupling to provide **2a** in excellent yield, the isomeric purity of which was found to be >99% *E* by GC and 500 MHz ^1H NMR analyses.[7] In these reactions, use of NMP (*N*-methylpyrrolidin-2-one) as an additive affected the reaction rate but not the yield and selectivity (entries 6 and 7). Cahiez and Avedissian originally reported the reaction of 1,2-dichloroethylene with alkyl-Grignard reagents providing



Scheme 1.

Keywords: Allylsilane; Co-catalyst; Cross-coupling.

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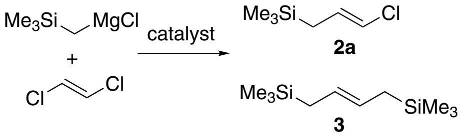
Table 1[a]



Entry	Catalyst (1 mol %)	Conditions	Yield, %[b]	
			2a	**3**
1[c]	$Br_2Ni(PPh_3)_2 + 2PPh_3$	0 °C, 30 min, benzene–ether	78	15
2	$Cl_2Ni(PPh_3)_2 + 2PPh_3$	0 °C to rt, 2.5 h, ether	33	20
3	$Cl_2Ni(dppp)_2$	0 °C to rt, 2.5 h, ether	10	87
4	$Cl_2Ni(dppb)_2$	0 °C to rt, 2.5 h, ether	5	32
5	$Cl_2Pd(PPh_3)_2$	0 °C to rt, 12 h, THF–ether	Trace	Trace
6	$Co(acac)_3$	0 °C, 5 h, THF	86	0
7	$Co(acac)_3$	0 °C, 15 min, THF–NMP (4:1)	88	0
8	$Co(acac)_2$[d]	0 °C, 15 min, THF–NMP (4:1)	81	0
9	$Fe(acac)_2$	0 °C to rt, 1.5 h, THF–NMP (4:1)	Trace	Trace

dppp: 1,3-bis(diphenylphosphino)propane.
dppb: 1,4-bis(diphenylphosphino)butane.
acac: acetylacetonato.

[a] Reactions were performed using 2.0 mmol of Grignard reagent, 4.0 mmol of 1,2-dichloroethylene and 1 mol % of catalyst.

[b] GC yield.

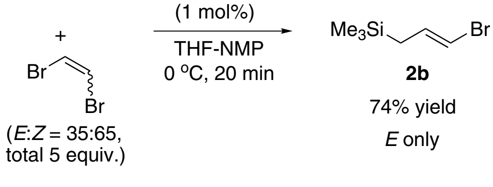
[c] See Ref. 1. 1,2-Dichloroethylene (5 equiv) was used.

[d] Tetrahydrate was used.

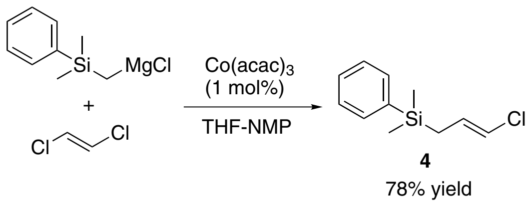
mono-coupling products exclusively where addition of NMP as a co-solvent was suggested for attaining good yield.[8] The yield of the reaction carried out here was somewhat better than those of the reaction with the usual alkyl-Grignard reagents reported by Cahiez. It can be assumed that the absence of β-hydride in $TMSCH_2MgCl$ might avoid other reaction(s) than the desired coupling. With these results, we carried out 20 mmol scale synthesis and **2a** could be isolated in pure form by distillation in 90% yield. Pd- and Fe-compounds did not catalyze this reaction (entries 5 and 9).

Next we tried a Co-catalyzed coupling of $TMSCH_2MgCl$ with (*Z*)-1,2-dichloroethylene and, unfortunately, found that the reaction did not proceed at all. However, the results prompted us to carry out the reaction with a mixture of (*E*)- and (*Z*)-1,2-dibromoethylene, which is commercially available at low price. Thus, a mixture of *E*- and *Z*-isomers of 1,2-dibromoethylene ($E/Z = 35{:}65$, total 5 equiv) was treated with $TMSCH_2MgCl$ in the presence of 1 mol % of $Co(acac)_2$ in THF–NMP (Scheme 2). As expected, only (*E*)-3-trimethylsilyl-1-bromopropene (**2b**) was produced in good yield of 74%.

Similarly, γ-halogenoallylsilanes having a silyl moiety other than trimethylsilyl could be prepared without loss of yield and selectivity (Scheme 3).[7]



Scheme 2.



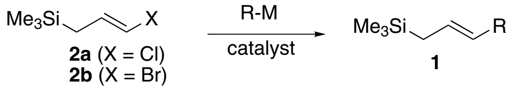
Scheme 3.

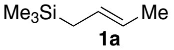
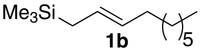
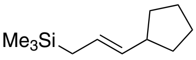
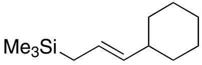
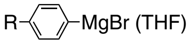
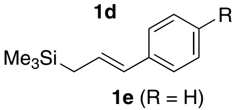
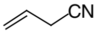
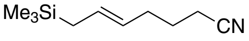
With γ-halo-(*E*)-allylsilanes **2a** and **2b** in hand, we carried out their conversion to **1** by transition metal-catalyzed coupling reactions. As can be seen from Table 2 summarizing the several representative results, **1** with methyl as well as normal and secondary alkyl and aryl groups could be readily prepared by the Ni-catalyzed coupling with the corresponding Grignard reagent (Kumada–Tamao reaction).[5] It is noteworthy that the Suzuki–Miyaura coupling[9] of bromide **2b** with boranes was effective for synthesis of **1** having a functional group as shown in entry 7.

In addition the use of **2** as a substrate for metal-catalyzed coupling reactions, as illustrated in Scheme 4, **2a** and **2b** are useful as an equivalent of 3-silyl-1-propynyl and 3-silyl-1-propenyl anions. Thus, treatment of **2a** with LDA (2 equiv) and the following addition of aldehyde afforded the corresponding adduct, whereas (*E*)-allylic alcohol was obtained by treatment of **2b** with *t*-BuLi and then aldehyde.[10]

In conclusion, we have developed a selective mono-coupling reaction of R_3SiCH_2MgCl with 1,2-dihalogenoethylene, which opens up a general method for preparation of γ-substituted (*E*)-allylic silanes. Further study for the preparation and synthetic utilization of functionalized allylsilanes is underway in our laboratories.

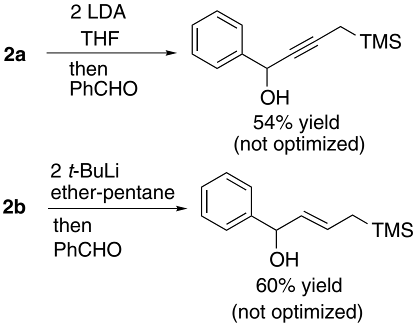
Table 2



Entry	2	R–M (solvent) catalyst (mol%)	Product	Yield, %[a]
1	**2a**	MeMgI (ether) $Cl_2Ni(dppp)$ (2)	 **1a**	95[b]
2	**2a**	n-$C_6H_{13}MgBr$ (THF) $Cl_2Ni(dppp)$ (2)	 **1b**	83
3	**2a**	c-C_5H_9MgCl (ether) $Cl_2Ni(dppp)$ (2)	 **1c**	59
4	**2a**	c-$C_6H_{11}MgCl$ (ether) $Cl_2Ni(dppp)$ (2)	 **1d**	93
5	**2a**		 **1e** (R = H) **1f** (R = Me)	91
6		$Cl_2Ni(dppp)$ (2)		95
7	**2b**	 9-BBN (4) $Cl_2Pd(dppf)$ K_3PO_4	 **1g**	58

[a] Isolated yield unless otherwise indicated. Reaction was not optimized.

[b] GC yield.



Scheme 4.

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3. An *E*- and *Z*-mixture of **2a** or **2b** has been prepared from the corresponding 1,3-dihalopropene by the reaction with Cl_3SiH and the following methylation with MeMgBr. For preparation and synthetic utilization of **2**, see: (a) for **2a**, Ochiai, M.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1980**, 1118; (b) Ochiai, M.; Fujita, E. *Tetrahedron Lett.* **1980**, *21*, 4369; For **2b**: (c) Nishiyama, H.; Narimatsu, S.; Itoh, K. *Tetrahedron Lett.* **1981**, *22*, 5289; (d) Angell, R.; Parsons, P. J.; Naylor, A.; Tyrrell, E. *Synlett* **1992**, 599; (e) Parsons, P. J.; Angell, R.; Naylor, A.; Tyrell, E. *J. Chem. Soc., Chem. Commun.* **1993**, 366.
4. Prepared from $TMSCH_2Cl$ and magnesium turnings in ether or THF and titrated by using acid and base. Yields shown in Table 1 and Scheme 2 were based on the amount of the Grignard reagent used.
5. Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.
6. One of the authors (S.O.) reported the preparation of **2a** by the reaction shown in entry 1 in Table 1, in which **2a** was obtained by distillation as a benzene solution: Okamoto, S.; Tani, K.; Sato, F.; Sharpless, K. B.; Zargarian, D. *Tetrahedron Lett.* **1993**, *34*, 2509.
7. H NMR ($CDCl_3$, 500 MHz): **2a**: δ 5.87 (dt, $J = 13$, 8.5 Hz, 1H), 5.51 (d, $J = 13$ Hz, 1H), 1.48 (d, $J = 8.5$ Hz, 2H), 0.03 (s, 9H); **2b**: δ 6.16 (dt, $J = 13$, 8.5 Hz, 1H), 5.82 (dt, $J = 13$, 1.0 Hz, 1H), 1.52 (dd, $J = 1.0$, 8.5 Hz, 2H), 0.06 (s, 9H); **4**: δ 7.39–7.57 (m, 5H), 5.90 (ddt, $J = 1.0$, 13, 8.5 Hz, 1H), 5.77 (dd, $J = 1.0$, 13 Hz, 1H), 1.75 (d, $J = 8.5$ Hz, 2H), 0.35 (s, 6H).
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9. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
10. $CrCl_2$-mediated reaction of **2b** with aldehydes providing δ-trimethylsilyl allylic alcohols has been reported: see Refs. 3d,e.