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Selective Cross Coupling via Oxovanadium(V)-Induced Oxidative Desilylation of Benzylic Silanes

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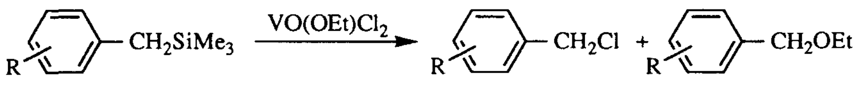
Abstract: Benzylic silanes bearing an electron-donating group at the *ortho*- or *para*-position underwent the oxovanadium(V)-induced one-electron oxidative desilylation due to low ionization potential, which was applied to the intermolecular regioselective coupling with allylic silanes or silyl enol ether.

Desilylation of organosilicon compounds based on one-electron oxidation is useful to generate radicals or cationic species through further one-electron oxidation, providing a versatile route to electrophilic synthetic equivalents. Desilylation by chemical,[1] electrochemical,[2] or photochemical oxidation[3,4] has been developed from this point of view. Oxovanadium compounds are revealed to be Lewis acids with one-electron oxidation capability, which has been applied to oxidative desilylation of silyl enol ethers[5] and allylic silanes.[6] A combination of $VO(OR)Cl_2$ and Me_3SiOTf, which is a more reactive oxidant,[7] is required for desilylation of benzyltrimethylsilane (**1f**) in dichloromethane maybe due to redox potential. We herein describe that benzylic silanes bearing an electron-donating group undergo the oxidative carbon-silicon bond cleavage selectively with oxovanadium(V) compounds to permit a novel intermolecular carbon-carbon bond formation.

Treatment of the benzylic silane **1** with $VO(OEt)Cl_2$ (3 equiv.) in acetonitrile under nitrogen resulted in chlorination to the benzylic chloride **2** (eq. 1). The ethyl ether **3** was also obtained as a minor product. The selective formation of **3a** was performed in ethanol as a solvent. The other solvents listed in Table 1 gave poor results for the oxidative desilylation of **1** to **2** and **3**.



(1)

1 **2** **3**

The susceptibility of benzylic silanes to oxidation in acetonitrile depended on the substituent and its position. A facile oxidative transformation was observed with benzylsilanes bearing an electron-donating group. The yield of the oxidation product was lowered in the order of the *para*-, *ortho*-, and *meta*-substituted ones. Tolylsilanes underwent the selective chlorination. The unsubstituted benzylic silane **1f** and chloro-substituted one **1g** were less oxidizable. On the contrary, **1h** bearing the cyano group was not oxidized under the conditions employed here.

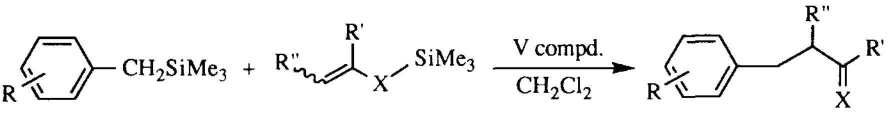
This reactivity tendency is accounted for by their ionization potentials based on AM1 or PM3 molecular orbital calculation: the more reactive benzylic silane possesses the lower ionization potential.[8] A good relation was obtained between yields and calculated ionization potentials. Such a correlation was not observed with σ or $\sigma^{\bullet}$, but with σ^{+}. These results are likely to be in consistent with the proposal that benzylic carbon-hydrogen bond homolysis correlates with the ionic substituent parameter σ^{+}.[9]

Table 1. Substituent Effect for Oxidative Desilylation of Benzylic Silanes[a]

1	Solvent	NMR Yield, % **2+3** (**2** : **3**)	Recovery of **1**	Ionization Potential, eV[b] PM3	AM1
a (R = *p*-MeO)	MeCN	99 (2 : 1)	trace	8.51	8.59
a	EtOH[c]	76 (7 : 93)	5		
a	Et_2O[d]	29 (>99 : 1)	70		
a	PhMe[d]	trace	21		
a	Hexane[d]	5 (>99 : 1)	63		
a	CH_2Cl_2[d]	complex mixture			
b (R = *o*-MeO)	MeCN	92 (14 : 1)	trace	8.60	8.68
c (R = *m*-MeO)	MeCN	70 (>99 : 1)	22	8.74	8.79
d (R = *p*-Me)	MeCN	71 (>99 : 1)	19	8.71	8.82
e (R = *m*-Me)	MeCN	42 (>99 : 1)	54	8.84	8.97
f (R = H)	MeCN	28 (>99 : 1)	64	8.89	9.24
g (R = *p*-Cl)	MeCN	25 (>99 : 1)	74	8.79	9.03
h (R = *p*-CN)	MeCN	<1 (>99 : 1)	>99	9.25	9.39

[a] Reaction: -30 °C, 2 h; r t, 4 h unless otherwise stated. [b] Calculated by MOPAC (ver. 6. 1).
[c] Reaction: -75 °C, 2 h; r t, 6 h. [d] Reaction: -75 °C, 2 h; r t, 4 h.

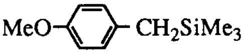
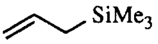
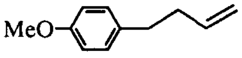
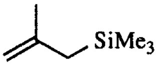
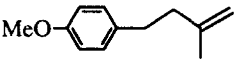
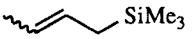
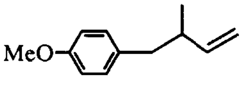
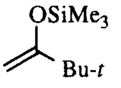
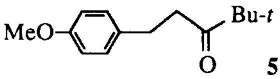
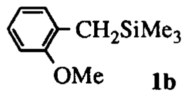
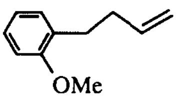
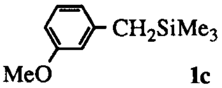
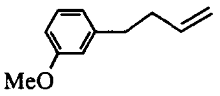
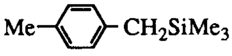
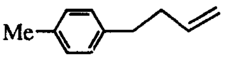
A carbon-carbon bond formation via oxidative desilylation of benzylic silanes has not been developed so far. A selective intermolecular coupling (eq. 2) is achieved by the $VO(OEt)Cl_2$-induced reaction of **1a** with allyltrimethylsilane (**4a**), which is not susceptible to oxidation with $VO(OEt)Cl_2$ under the conditions employed here. A different solvent effect was observed. The allylated product **5a** was produced in a good yield in dichloromethane, but a poor result was obtained in acetonitrile (-30 °C, 2 h; room temperature, 4 h: **2a**, 52%; **3a**, 26%; **5a**, 14% by ^1H NMR). Methallyltrimethylsilane (**4b**) and crotyltrimethylsilane (**4c**) were successfully used instead of **4a** (Table 2). It should be noted that the regioselective carbon-carbon bond formation was achieved with **4c**. The silyl enol ether **4d** also served as an acceptor. The oxidative coupling did not proceed well with the less oxidizable benzylic silanes. Use of the oxidant consisting of $VO(OEt)Cl_2$-Me_3SiOTf resulted in the more facile coupling.



(2)

1 **4** X = CH_2, O (3 equiv.) **5**

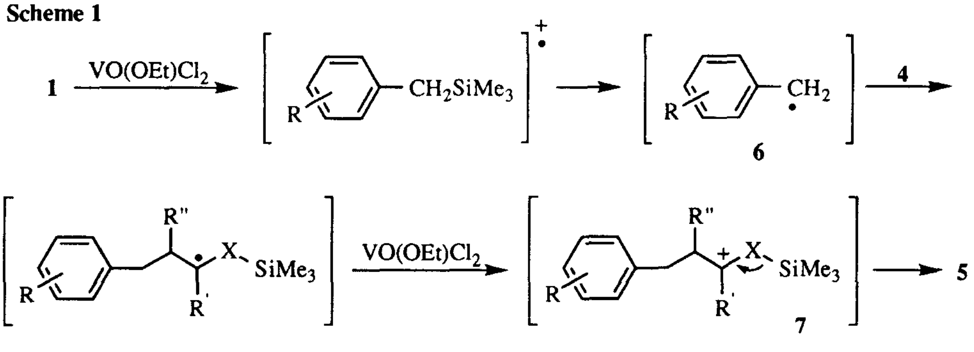
Table 2. Oxidative Coupling of Benzylic Silanes

1	4	V compd.[a]	5	Yield, %
 **1a**	 **4a**	$VO(OEt)Cl_2$ (3 equiv.)	 **5a**	67
1a	 **4b**	$VO(OEt)Cl_2$ (3 equiv.)	 **5b**	89
1a	 **4c**	$VO(OEt)Cl_2$ (3 equiv.)	 **5c**	76
1a	 **4d**	$VO(OEt)Cl_2$ (3 equiv.)	 **5d**	45
 **1b**	**4a**	$VO(OEt)Cl_2$ (3 equiv.) $VO(OEt)Cl_2$-Me_3SiOTf[b] (3 : 1 equiv.)	 **5e**	21 46
 **1c**	**4a**	$VO(OEt)Cl_2$-Me_3SiOTf[b] (3 : 1 equiv.)	 **5f**	19
 **1d**	**4a**	$VO(OEt)Cl_2$-Me_3SiOTf[b] (3 : 1 equiv.)	 **5g**	36

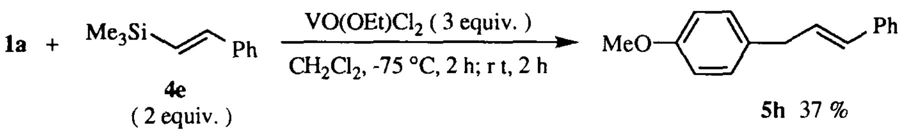
[a] Reaction: -75 °C, 2 h; r t, 4 h unless otherwise stated. [b] Reaction: 0 °C, 2 h; r t, 6 h.

A reaction course for the oxidative desilylation of benzylic silanes is probably explained as follows (Scheme 1). The benzylic silane **1** undergoes one-electron oxidation with the oxovanadium(V) species to generate the cation radical followed by desilylation to the benzylic radical **6**. This step correlates the redox potential of benzylic silanes. Thus generated radical **6** adds to the allylic silane or silyl enol ether **4**. The subsequent one-electron oxidation and desilylation leads to the coupling adduct **5**. Another pass involves the further oxidation of the radical **6** prior to the intermolecular bond formation. The observed regioselectivity is considered to be attributed to the stabilization of the adduct cation **7** ($X=CH_2$) by the β-silyl group. Oxidation with $VO(OR)Cl_2$ permits the intermolecular cross coupling with allylic silanes and silyl enol ether based on the chemoselective desilylation of benzylic silanes.

Scheme 1



Oxidative coupling of **1a** with β-trimethylsilylstyrene (**4e**) led to the regioselective formation of **5h** (eq. 3). On the contrary, the coupling reaction with α-trimethylsilylstyrene was not attained.



(3)

Organosilicon compounds are considered to be synthetic equivalents of electrophiles via one-electron oxidative desilylation. The above-mentioned results provide probably the first example for the desilylative intermolecular carbon-carbon bond formation of benzylic silanes induced by transition metals.

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