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Oxovanadium-Induced Oxidative Desilylation of Allylic and Benzylic Silanes

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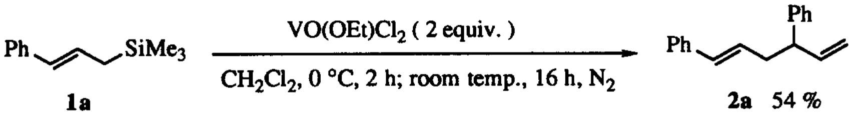
Abstract: Cinnamyltrimethylsilane underwent desilylation via one-electron oxidation with $VO(OEt)Cl_2$, which was applied to the cross-coupling with the less oxidizable allylic silanes to give the corresponding 1,5-hexadienes. Chlorination or aromatization based on desilylation was observed on treatment of benzyltrimethylsilane or 3-ethoxycarbonyl-2-methyl-5-trimethylsilyl-5-phenyl-4,5-dihydrofuran with $VO(OEt)Cl_2$-Me_3SiOTf, respectively.

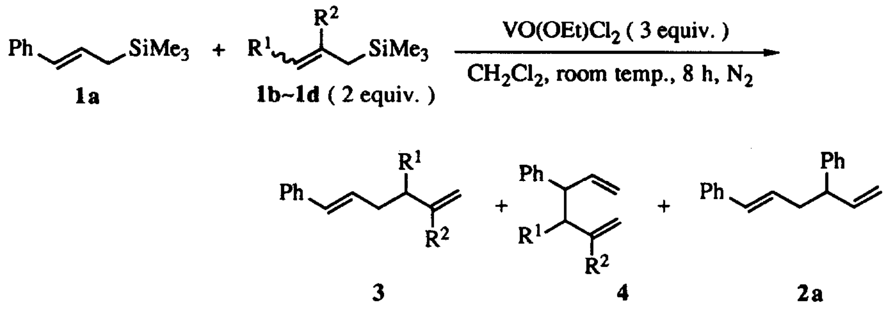
Desilylative transformation of organosilicon compounds constitutes an important tool in organic syntheses as exemplified in the fluoride-mediated desilylation to generate carbanion intermediates.[1] Chemical,[2] electrochemical,[3] or photochemical oxidation[4] has been reported to induce oxidative desilylation. Oxidation with transition metal complexes in a high oxidation state is expected to promote such a reaction. Pentavalent oxovanadium compounds have been revealed to serve as a Lewis acid with one-electron oxidation capability.[5] The versatile cross-coupling of silyl enol ethers to 1,4-diketones is achieved by the chemoselective one-electron oxidation with $VO(OR)Cl_2$.[6] We herein describe a novel oxidative carbon-silicon bond cleavage of allylic and benzylic silanes with oxovanadium(V) compounds.

Treatment of cinnamyltrimethylsilane (**1a**) with $VO(OEt)Cl_2$ in dichloromethane led to the oxidative coupling to form the 1,5-hexadiene **2a** regioselectively (eq.1). Allyltrimethylsilane (**1b**) and methallyltrimethylsilane (**1c**) did not undergo desilylation under the similar conditions, suggesting that the oxidation reaction depends on the redox potential of allylic silanes as observed in oxidative desilylation of silyl enol ethers.[6]



(1)

The reactivity difference is successfully extended to the selective cross-coupling of allylic silanes. Oxidation of **1a** with $VO(OEt)Cl_2$ in the presence of the less oxidizable allylic silanes **1b**-**d** gave the corresponding dienes **3** and **4** with a small amount of **2a** (eq. 2, Table 1).[7] The carbon-carbon bond is formed at both α and γ positions of **1a**, but only at γ position of **1c**-**d**.



(2)

Table.1 Oxidative Cross-Coupling of Allylic Silanes

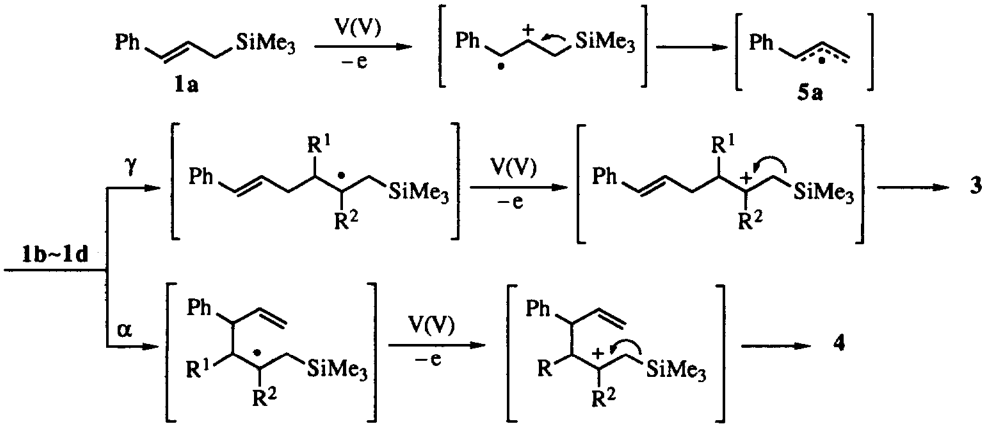
Allylic Silane **1**	Glc Yields, %	
	3 + **4** (**3** : **4**)[a]	**2a**[b]
1b ($R^1 = R^2 = H$)	40 (2.5 : 1)	12
1c ($R^1 = H$, $R^2 = Me$)	51 (1.5 : 1)	6
1d ($R^1 = Me$, $R^2 = H$)	56 (2.0 : 1)	7

a) Ratio was determined by glc.

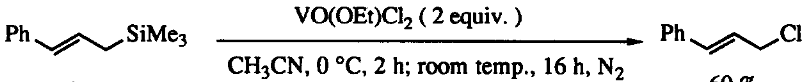
b) Based on the allylic radical intermediate.

The reaction course for the coupling reaction of allylic silanes is probably explained as follows (Scheme 1). The allylic silane **1a** undergoes one-electron oxidation with the oxovanadium(V) species to generate the cation radical followed by desilylation to the allylic radical **5a**. The generation of the allylic radical was supported by the formation of cinnamyl bromide in the reaction of **1a** with VO(OEt)Cl2 and bromotrichloromethane. The intermolecular carbon-carbon bond formation of the radical **5a** or the further oxidized allylic cation with the second allylic silane gives the coupling adduct via desilylation. Regioselectivity of the addition reaction is considered to be attributed to the stabilization of the adduct cation by the β-trimethylsilyl group.

Scheme 1



The choice of a solvent drastically changed the reaction product. Oxidation of **1a** in acetonitrile instead of dichloromethane resulted in chlorination without formation of **2a** (eq. 3). Coordination of acetonitrile to oxovanadium species seems to prevent the intermolecular carbon-carbon bond formation.



1a 60 % (3)

Benzyltrimethylsilane is also expected to undergo the oxovanadium(V)-induced oxidative desilylation, but turned out to be less oxidizable with VO(OEt)Cl2. The oxovanadium species generated from VO(OEt)Cl2 and Me3SiOTf, the more efficient one-electron oxidant in the dehydrogenative aromatization,[8] was found to be effective to give benzyl chloride via desilylation (eq. 4). The increase in the amounts of VO(OEt)Cl2 and Me3SiOTf raised the yield as shown in Table 2. Lithium chloride did not work as a chlorine source, being in contrast to the VO(OEt)Cl2-induced oxidative ring-opening reaction of cyclobutanone.[5b]

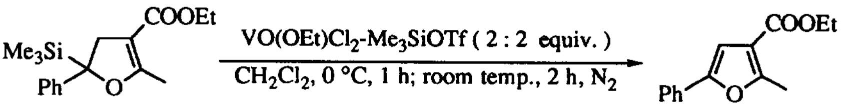
$$PhCH_2SiMe_3 \xrightarrow[CH_2Cl_2,\ \text{room temp., 24 h, } N_2]{VO(OEt)Cl_2\text{-}Me_3SiOTf} PhCH_2Cl \quad (4)$$

Table 2. Oxidative Desilylation of Benzyltrimethylsilane

$VO(OEt)Cl_2$-Me_3SiOTf equiv.	Additive	Glc Yield, % $PhCH_2Cl$
4 : 4	—	32
2 : 2	—	20
1 : 1	—	14
1 : 1	LiCl (10 equiv.)	12

The similar one-electron oxidation seems to be operative as mentioned above. A cation radical intermediate is involved to give benzyl radical through the cleavage of the carbon-silicon bond. Chlorination to benzyl chloride takes place at this stage or towards the cation via further one-electron oxidation with the oxovanadium(V) species.

These findings prompted us to apply this system to the oxidative aromatization[5a] of the trimethylsilyl-substituted dihydrofuran **6** (eq. 5). VO(OEt)Cl2 is not so effective for this transformation, which requires the severe reaction conditions (2 equiv. of VO(OEt)Cl2 in refluxing ethanol under oxygen for 2 h; 24% yield). The oxidation reaction with VO(OEt)Cl2-Me3SiOTf smoothly proceeded even at a lower temperature under nitrogen giving the furan **7** quantitatively in 70% conversion.



6 **7** (5)

An important point is that substitution with trimethylsilyl group is considered to raise HOMO of the dihydrofuran.[9] The HOMO is likely to be susceptible to the facile interaction with the oxovanadium(V) compound for desilylation via one-electron oxidation. Further one-electron oxidation and deprotonation explains the aromatization. The benzyl radical and cation obtained by desilylation also appears to be stabilized by the vinyl ether moiety.

One-electron oxidation with oxovanadium(V) compounds is useful for the chemoselective cleavage of a carbon-silicon bond. Further investigations including mechanistic aspect are now in progress.

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7. A representative procedure for the oxidative cross-coupling of allylic silanes is as follows. To a solution of $VO(OEt)Cl_2$ (3.0 mmol) in dichloromethane (4 mL) was added **1b** (2.0 mmol) at room temperature, followed by dropwise addition of **1a** (1.0 mmol) over 1 h. The mixture was stirred for 8 h at room temperature. Ether (15 mL) and 5% aqueous $Na_2S_2O_3$ (0.5 mL) were added to the reaction mixture, which was extracted with ether (2 x 20 mL) followed by addition of conc. HCl (0.5 mL) and extraction with ether (3 x 20 mL). The combined ethereal solution was washed with saturated $NaHCO_3$ and brine, dried, and concentrated. The residue was analyzed by glc (PEG 20 M, 2.1 m and OV-17, 2.1 m, 200 °C).
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