Highly selective coupling of organoboron compounds *via* oxovanadium(v)-induced oxidation

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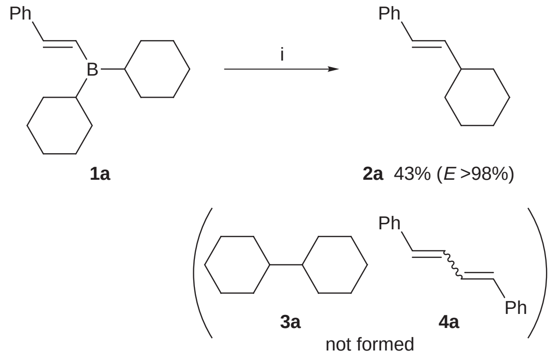
Reaction of organoboranes or organoborane ate complexes (obtained by treatment with Bu^{n}Li or CsF) with oxovanadium(v) compounds results in the intramolecular oxidative coupling of organic groups on the boranes or borates.

One-electron oxidation of organometallics with metallic oxidants is expected to offer synthetically useful transformations *via* intermediates with a higher oxidation state involving organometallic radical cation species.[1] An oxovanadium(v) compound, VO(OR)X_2, has been revealed to be an efficient one-electron oxidant,[1*a*,2] as exemplified by oxidative desilylation of organosilicon compounds.[3] The reaction path is explained by the intermediacy of radical cations and radicals *via* desilylation, which provides a versatile route to electrophilic synthetic equivalents. Carbon–carbon bond forming reactions *via* oxidation of organoboranes using metallic oxidants have not been investigated except for a few transformations of functional groups.[4] We herein report a novel ligand coupling of organoboron compounds induced by an oxovanadium(v) compound.

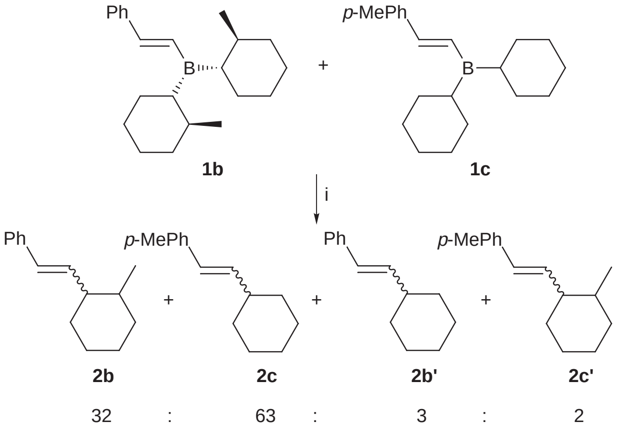
When organoborane compound **1a**, derived from phenylacetylene and dicyclohexylborane,[5] was treated with 3 equiv.[6] of VO(OEt)Cl_2 at room temperature in CH_2Cl_2, [(*E*)-2-phenylethenyl]cyclohexane **2a** was selectively produced without the formation of bi(cyclohexyl) **3a** and 1,4-diphenylbutadiene **4a**, as shown in Scheme 1. It should be noted that the coupling reaction occurs selectively.

To gain insight into the reaction pathway, the following crossover reaction was examined (Scheme 2). When an equimolar mixture of bis(2-methylcyclohexyl)[(*E*)-2-phenylethenyl]borane **1b** and dicyclohexyl[(*E*)-2-(4-methylphenyl)ethenyl]borane **1c** was treated with VO(OEt)Cl_2, 1-methyl-2-(2-phenylethenyl)cyclohexane **2b** and [2-(4-methylphenyl)ethenyl]cyclohexane **2c** were produced, with only trace amounts of crossover products **2b′** and **2c′**. Although trace amounts of crossover products were obtained, the result may imply that the coupling reaction proceeds intramolecularly.

The corresponding ate complexes of the organoboranes are expected to undergo more facile oxidation. A higher yield was attained in the reaction of the borate **5a** generated from **1a** and Bu^{n}Li (Scheme 3).[7] No butylated product was detected in the reaction mixture, indicating that the organic groups are effectively differentiated in the coupling reaction. The stereoisomer was, however, obtained in a small amount. Use of VO(OPr^i)$_2$Cl, which has a lower oxidation capability, decreased the yield. CH_2Cl_2 was found to be superior to Et_2O as a solvent.



Scheme 1 *Reagents and conditions*: i, VO(OEt)Cl_2 (3 equiv.), CH_2Cl_2, room temp., 2 h

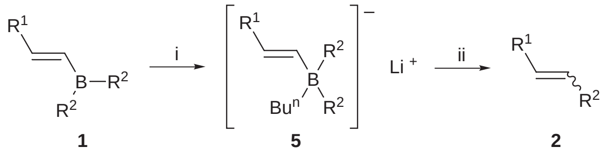


Scheme 2 *Reagents and conditions*: i, VO(OEt)Cl_2 (3 equiv.), CH_2Cl_2, −78 °C, 4 h

Representative results for the borate **5** are summarized in Table 1. A distinct substituent effect was observed with R^1. Starting from the 2-(4-methylphenyl)ethenyl- and 2-(ethoxycarbonyl)ethenyl-substituted boranes **1c** and **1e**, highly stereoselective coupling reactions were performed, but the organoborate derived from **1f** did not couple under the reaction conditions. These findings suggest that the coupling reaction is controlled by the electronic nature of the substituents in **5**. The reaction of the ate complex **5d** with VO(OEt)Cl_2 afforded 1-phenylhex-1-ene **2g** as the main product, in sharp contrast to the abovementioned observation. The cyclopentyl group was found to scarcely participate in the coupling reaction under the conditions described, but oxidation with VO(OPr^i)$_2$Cl led to the incorporation of the cyclopentyl group together with **2g**.

Use of CsF or TBAF to form organoborate **6a**[7] improved the stereoselectivity, giving the *E* isomer exclusively (Scheme 4).

Although the reaction path is ambiguous, the intramolecular ligand coupling is achieved *via* oxidation with the oxovanadium(v) compound. The oxidation of alkenylborates with iodine is known to give the corresponding coupling products as a single stereoisomer, in which an ionic mechanism is proposed generally.[5*a*,8] On the other hand, the present oxovanadium-



Scheme 3 *Reagents and conditions*: i, Bu^{n}Li (1 equiv.), −78 °C, 1 h; ii, VO(OEt)Cl_2 (3 equiv.)

Table 1 Oxidative cross-coupling reaction of borate **5**[a]

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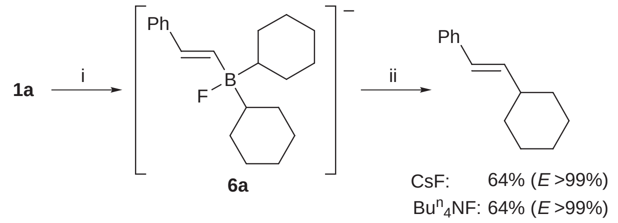
	R^1	R^2	Oxovanadium	Solvent	Product	Yield (%)[b]	*E*:*Z*[c]
1a	Ph	cyclohexyl	$VO(OEt)Cl_2$	CH_2Cl_2	**2a**	82 (70)	92:8
1a	Ph	cyclohexyl	$VO(OPr^i)_2Cl$	CH_2Cl_2	**2a**	69	92:8
1a	Ph	cyclohexyl	$VO(OEt)Cl_2$	Et_2O	**2a**	52	69:31
1b	Ph	2-methylcyclohexyl	$VO(OEt)Cl_2$	CH_2Cl_2	**2b**	47 (30)[d]	92:8
1c	$4\text{-}MeC_6H_4$	cyclohexyl	$VO(OEt)Cl_2$	CH_2Cl_2	**2c**	65 (55)	96:4
1d	$4\text{-}MeC_6H_4$	cyclopentyl	$VO(OEt)Cl_2$	CH_2Cl_2	**2d**	trace[e]	—
1d	$4\text{-}MeC_6H_4$	cyclopentyl	$VO(OPr^i)_2Cl$	CH_2Cl_2	**2d**	(21)[f]	93:7
1e	EtO_2C	cyclohexyl	$VO(OEt)Cl_2$	CH_2Cl_2	**2e**	95 (60)	97:3
1f	*n*-hexyl	cyclohexyl	$VO(OEt)Cl_2$	CH_2Cl_2	**2f**	not detected	

[a] All reactions were performed at room temperature for 2 h unless otherwise stated. [b] Determined by ^1H NMR spectroscopy based on the alkyne. Isolated yield is shown in a parentheses. [c] The olefinic geometry. [d] Reaction temperature is −78 °C, *syn*:*anti* = 50:50. PhCH=CHBu **2g** was isolated in 10% yield (*E*:*Z* = 93:7). [e] **2g** was isolated in 40% yield (*E*:*Z* = 85:15). [f] **2g** was isolated in 20% yield (*E*:*Z* = 95:5).



Scheme 4 *Reagents and conditions:* i, CsF or TBAF (1 equiv.), CH_2Cl_2, room temp., 1 h; ii, $VO(OEt)Cl_2$ (3 equiv.), CH_2Cl_2, room temp., 2 h

induced reaction of **5** provides the coupling products with *E* configuration preferentially. Taking this stereochemical observation into account in the oxidation of **5**, a radical-like species is assumed to be involved as an intermediate in the intramolecular coupling step, since a radical species is generated by aerobic oxidation of triethylborane[9] and electrochemical oxidation of borates.[10] Further investigations are now in progress.

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Notes and References

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