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A Novel Oxovanadium(V)-Induced Oxidation of Organoaluminum Compounds. Highly Selective Coupling of Organic Substituents on Aluminum

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The redox processes of organometallics are important in synthetic transformations, especially in transition-metal-induced reactions.[1] Transmetalation and electronic interaction are able to participate in the control of such a process.[2] From this point of view, main-group organometallics such as silicon, aluminum, and boron have limited usage due to their restricted redox processes. A versatile one-electron oxidation method for organosilicon compounds has been developed by using oxovanadium(V) compounds in a previous paper,[3,4] permitting oxidative desilylation via radical cations and radicals. Oxidative transformations of organoaluminum compounds usually lead to alcohols,[5] but to the best of our knowledge, the investigation on selective carbon−carbon bond formation of organic substituents on aluminum has not been undertaken with the aid of metallic oxidants. This is partly due to the difficulty in the selection of metallic oxidants. Herein we report a highly selective coupling of organoaluminum compounds induced by oxovanadium(V) compounds.

The addition of 1-alkynyllithium (1.1 equiv) to the 1-octenylaluminum[6] at −78 °C, followed by treatment with $VO(OEt)Cl_2$, led to a novel cross-coupling of organic substituents on aluminum, giving the corresponding *trans*-enyne **2** with excellent stereoselectivity (Scheme 1). Interestingly, the homo-coupled diene and isobutylated products were not obtained at all, although the diyne probably from excess alkynyllithium was formed as a byproduct.[7] Representative results of the cross-coupling reaction are shown in Table 1. The addition of the ate complex to the solution of $VO(OEt)Cl_2$ raised the yield of **2** (Table 1, entries 1 and 2). Similar conditions can be employed with some other 1-alkynyllithiums, affording the conjugate *trans*-enynes **2** in good yields via highly selective carbon−carbon bond formation (Table 1, entries 3−5). Stoichiometric or excess amounts of $VO(OEt)Cl_2$ are required for this transformation, and the absence of $VO(OEt)Cl_2$ only resulted in the recovery of 1-octene and the starting alkyne.

Scheme 1

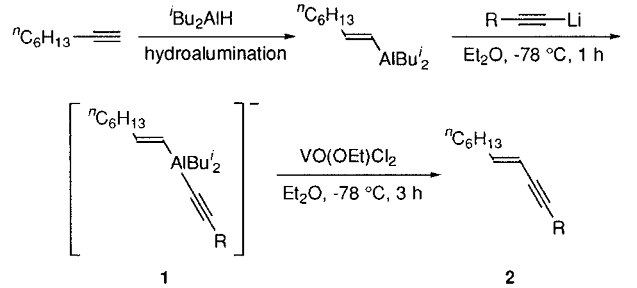
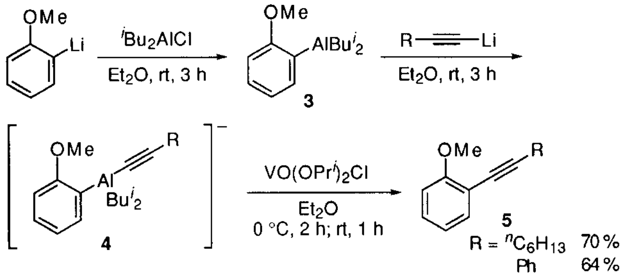


Table 1. The Cross-Coupling Reaction of the Ate Complex **1**[a]

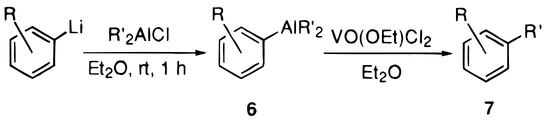
entry	**1**, R	**2**, yield, %[b]
1	Ph	80 (76)
2	Ph	56[c]
3	n-C_6H_{13}	84 (70)
4	Me_3Si	77 (68)
5	$PhCH_2OCH_2$	72 (65)

[a] $VO(OEt)Cl_2$, 3 equiv. The reaction conditions are shown in Scheme 1. The ate complex **1** was added to the solution of $VO(OEt)Cl_2$ unless otherwise stated. [b] Determined by ^1H NMR based on 1-octyne. Isolated yields are shown in parentheses. [c] $VO(OEt)Cl_2$ was added to the solution of the ate complex **1**.

Scheme 2



Scheme 3



When the aryl-substituted aluminum **3**[8] was used instead of the 1-alkenylaluminum, the intramolecular coupling of the ate complex **4** took place selectively between aryl and 1-alkynyl groups (Scheme 2). Use of $VO(OPr^i)_2Cl$ with the lower oxidation capability[9] gave rise to the coupling product **5** and only trace amount of isobutylated product despite the higher reaction temperature (0 °C). Again, the alkynyl group is introduced to

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(1) Efficiency of redox-active ligands in the transition-metal-catalyzed oxidation reactions has been investigated: (a) Hirao, T.; Higuchi, M.; Hatano, B.; Ikeda, I. *Tetrahedron Lett.* **1995**, *36*, 5925. (b) Higuchi, M.; Yamaguchi, S.; Hirao, T. *Synlett* **1996**, 1213. (c) Hirao, T.; Murakami, T.; Ohno, M.; Ohshiro, Y. *Chem. Lett.* **1989**, 785; **1991**, 299.

(2) For recent reviews for radical generation from organic compounds by metallic reagents, see: (a) Iqbal. J.; Bhatia. B.; Nayyar. N. K. *Chem. Rev.* **1994**, *94*, 519. (b) Dalko. P. I. *Tetrahedron* **1995**, *51*, 7579. (c) Arai, N.; Narasaka, K. *Yuki Gousei Kagaku Kyoukaishi* **1996**, *54*, 964. (d) Hirao, T. *Chem. Rev.* **1997**, *97*, 2707. For oxidation of d^0 organometallics, see: (e) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (f) Burk, M. J.; Tumas, W.; Ward, M. D.; Wheeler, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 6133.

(3) (a) Fujii, T.; Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1992**, *33*, 5823. (b) Fujii, T.; Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1993**, *34*, 5601. (c) Hirao, T.; Fujii, T.; Ohshiro, Y. *Tetrahedron Lett.* **1994**, *35*, 8005. (d) Hirao, T.; Fujii, T.; Ohshiro, Y. *Tetrahedron* **1994**, *50*, 10207.

(4) For oxidative transformations of organosilicon compounds by using other metallic oxidants, see: (a) Ito, Y.; Konoike, T.; Saegusa, T. *J. Am. Chem. Soc.* **1975**, *97*, 649. (b) Kobayashi, Y.; Taguchi, T.; Morikawa, T.; Tokuno, E.; Sekiguchi, S. *Chem. Pharm. Bull.* **1980**, *28*, 262. (c) Baciocchi, E.; Casu, A.; Ruzziconi, R. *Synlett* **1990**, 679. For a review, see: ref 2c, d.

(5) (a) Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1994; Vol. 11, pp 277−311. (b) Zietz, J. R., Jr.; Robinson, G. C.; Lindsay, K. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, S. G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, pp 365−464.

(6) Zweifel, G.; Miller, J. A. *Org. React.* **1984**, *32*, 375.

(7) The enyne **2** and the diyne were easily separable by recycling GPC equipped with JAI-GEL-1H and -2H columns (Japan Analytical Industry Co. Ltd.) using chloroform as an eluent.

(8) Arylaluminum **3** was prepared by treatment of the aryllithium, which was derived by treatment of the bromobenzene derivative with butyllithium (0.63 mL, 1.6 M in hexane) in ether at room temperature, with diisobutylaluminum chloride in ether at room temperature. Diisobutylaluminum chloride was prepared by treatment of triisobutylaluminum with isobutylaluminum dichloride at 80 °C.

(9) The following reactivity order has been reported; $VO(OR)Cl_2-AgOTf$ or $Me_3SiOTf > VO(OR)Cl_2 > VO(OR)_3 > VO(acac)_2$. Hirao, T.; Mori, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2399; *J. Org. Chem.* **1990**, *55*, 358; *Chem. Lett.* **1991**, 783.

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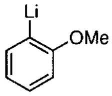
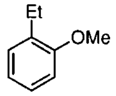
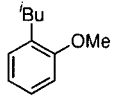
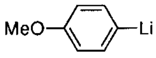
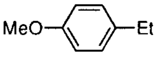
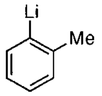
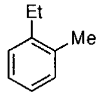
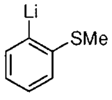
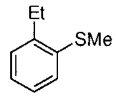
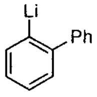
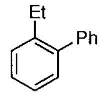
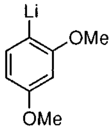
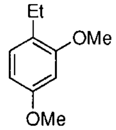
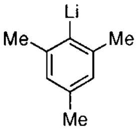
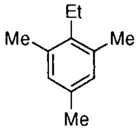
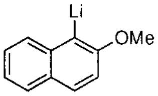
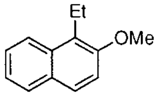
Table 2. The Cross-Coupling Reaction of the Arylaluminum **6**[a]

entry	aryllithium	reaction temp.	7, isolated yield, %[b]	
1		rt		80
2		rt		55[c, d]
3		rt		24[e, f]
4		rt		44[c, e, g]
5		rt		70[h]
6		rt		65
7		rfx		64
8		rfx		90
9		rt		58
10		rfx		53
11		rt		91

[a] $VO(OEt)Cl_2$, 3 equiv. The arylaluminum **6** was added to the ether solution of $VO(OEt)Cl_2$. Reaction time, 2 h. [b] The biaryl product was obtained in <5% yield unless otherwise stated. [c] $VO(O\text{-}i\text{-}Pr)_2Cl$ was used instead of $VO(OEt)Cl_2$. [d] The biaryl product, 13%. [e] $i\text{-}Bu_2AlCl$ was used instead of Et_2AlCl. [f] The biaryl product, 54%. [g] The biaryl product, 22%. [h] The biaryl product, 26%.

the sp^2-carbon (*o*-anisyl group) of aluminum ligand rather than the sp^3-carbon (isobutyl group). On the other hand, the selectivity of reaction with $VO(OEt)Cl_2$ was lower and the alkylation product and biaryl were formed as byproducts.

Although tri(organo)aluminum compounds are considered to be less reactive than the corresponding ate complexes, the reaction of aryldiethylaluminums **6** (obtained from aryllithiums and diethylaluminum chloride) with $VO(OEt)Cl_2$ in ether at the room or refluxing temperature surprisingly led to a novel ethylation reaction (Scheme 3). The absence of $VO(OEt)Cl_2$ again resulted in the recovery of the arene. As exemplified in Table 2, the procedure can be applied to a wide variety of arylaluminums bearing an electron-donating group, indicating that intramolecular coupling of the organic groups of organoaluminums is performed selectively. The methylthio group was found to be intact under the conditions, but the similar coupling was not observed in the case of the 2-cyanophenyl derivative. The electronic nature of the substituents in **6** appears to be an important factor to control the reaction.[10] The carbon−carbon bond formation occurred even with the disubstituted phenyllithium (Table 2, entries 9−10). The naphthyllithium was also converted to the ethylated product (Table 2, entry 11).

It should be noted that the coupling reaction depends on the substituent of oxovanadium(V) compounds. Use of $VO(OPr^i)_2Cl$ decreased the yield of the ethylation product (Table 2, entry 2). Staring from diisobuthylaluminum derivative, the yield of the expected coupling product drastically decreased with the major formation of the biaryl (Table 2, entry 3). This result is probably due to the steric effect, but an improved conversion to the desired coupling product was attained by using $VO(OPr^i)_2Cl$ instead of $VO(OEt)Cl_2$ (Table 2, entry 4). Both redox and steric control interactions are considered to operate in these transformations.

Although the intramolecular coupling mechanism is ambiguous, coordination of oxo atom of oxovanadium(V) to organoaluminums has been reported.[11] Such an intermetallic interaction and/or transmetalation may induce the oxidation of organoaluminum compounds.[11,12] In conclusion, these novel transformations for the formal reductive elimination on aluminum are for the first time achieved by oxidation of the organoaluminum ate complexes and arylaluminums with the oxovanadium(V) compound.[13] This method is expected to be promising with regard to its synthetic potential.

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Supporting Information Available: Experimental procedures and spectral data (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(10) The calculated ionization potentials of **6** based on MOPAC are correlated to their reactivities.

(11) Feher, F. J.; Blanski, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 5886.

(12) The electrochemical oxidation of diethyl(2-methoxyphenyl)aluminum afforded a small amount of the corresponding biaryl.

(13) For an electrophile-induced 1,2-migration reaction, see: Takagi, K.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 1440.