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Oxovanadium(V)-induced oxidative transformations of main-group organometallics

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Contents

Abstract

Oxovanadium(V) compounds induce one-electron oxidative desilylation of organosilicon compounds such as silyl enol ethers, allylic silanes, and benzylic silanes, permitting chemoselective coupling with the less oxidizable organosilicon compounds. The oxovanadium(V)-induced oxidation of benzylsilane and benzyltin compounds is carried out under an oxygen atmosphere to afford the aromatic aldehydes (ketones) and/or carboxylic acids. The catalytic reaction proceeds with benzyltins. Oxidative ligand coupling of dialkylarylaluminums is achieved by treatment with oxovanadium(V) compounds, leading to the formation of the alkylarenes. The ate complex derived from 1-alkenyllithium and arylaluminum or 1-alkenylaluminum undergoes the more facile oxidation to give the corresponding ligand coupling product selectively. The similar oxidation of organoborons or ate complexes also results in the oxidative coupling of organic groups on boron. This method is applied to the oxidative ligand coupling of organozinc compounds and ate complexes. In particular, the organozincates prepared from iodoarenes and Me_3ZnLi or bromoarenes and Me_4ZnLi_2 are oxidized with higher selectivity. Vicinal alkylation with diorganozincs or ate complexes at both the α and β positions of 2-cycloalkenones is performed by treatment with oxovanadium(V) compounds.

Keywords: Electron transfer; Transmetallation; Oxidation; Main-group organometallic; Redox interaction; Ligand coupling

1. Introduction

Redox interaction between a metal and a metal or a ligand (or an organic group) through inner- or outer-sphere electron transfer is envisaged to change the oxidation state of these components. Precise regulation of the redox process based on the electronic interaction between HOMO and LUMO orbitals is required for this purpose, which allows one to develop novel and selective methods for oxidative or reductive transformations of the ligands or organic groups under redox potential control. In this context, one-electron redox reactions with transition metal complexes can generate radicals via anionic or cationic radical species. Another reaction

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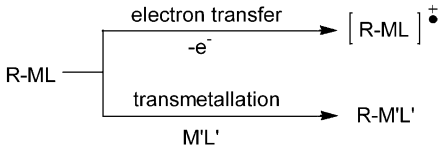
path lies in the interaction between different metallic compounds to induce transmetallation, resulting in change in the reactivities of the original organometallic compounds.

Vanadium compounds in a high oxidation state are able to induce oxidative transformations. Pentavalent vanadium compounds, which exist in one of five possible configurations (e.g. $VOCl_3$, tetrahedral; VF_5, octahedral), are generally considered to be one-electron oxidants which utilize the V(V)–V(IV) couple. The redox potential of this couple increases with acidity, so the reactions are usually carried out in acidic aqueous media. One-electron oxidation is also possible with the V(IV)–V(III) couple (E_0, 0.38 V), but the V(V)–V(III) couple (E_0, 0.68 V) is less useful for organic oxidation.

A variety of oxidative transformations with vanadium oxidants have been developed [1], as exemplified by the oxidative coupling of phenols. The scope of synthetic reactions can be broadened even further by exploiting the versatility of vanadium compounds as an oxidant [2]. $VO(OR)X_2$ can act as a Lewis acid towards carbonyl compounds, which permits their oxidative transformations. Scheme 1 summarizes this synthetic utility [3,4].

As described above, oxidation of main-group organometallic compounds with a metallic oxidant is expected to induce oxidative transformations via redox interaction between them or transmetallation (Scheme 2). This review focuses on such a reaction induced by oxovanadium(V) compounds, which provides a variety of novel synthetic methods.

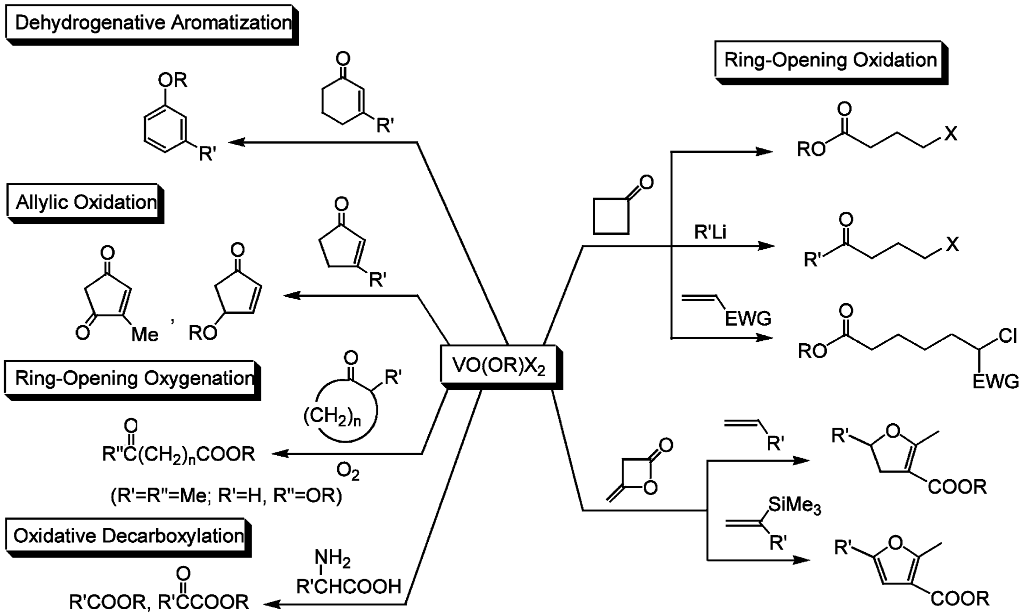


Scheme 2.

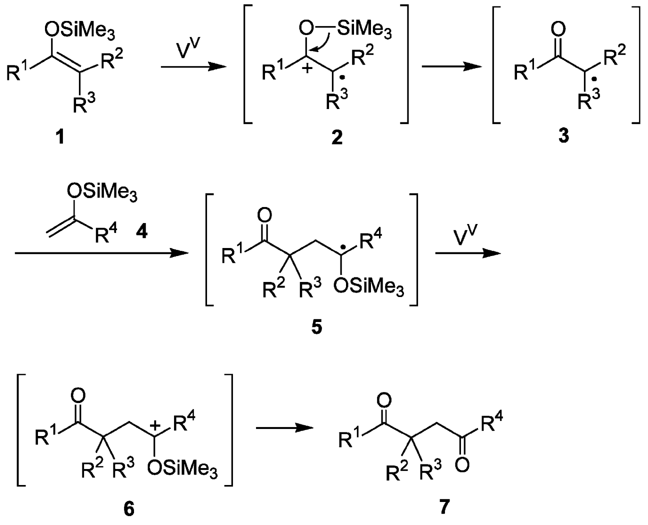
2. Oxidative transformation of organosilicon compounds

Silyl enol ethers are susceptible to one-electron oxidation [5]. $VO(OR)Cl_2$ [6] is capable of inducing chemoselective homo- or cross-coupling of silyl enol ethers (**1**) to give the corresponding 1,4-diketones (**7**) via regioselective carbon–carbon bond formation (Scheme 3) [7,8]. One-electron oxidation of the silyl enol ether (**1**) with an oxovanadium(V) species affords the radical cation **2**. This radical cation is then desilylated to the radical **3**. The radical **3** adds intermolecularly to another silyl enol ether (**4**) to form the adduct **5**, which is further oxidized by the oxovanadium(V) species to form the cation **6**. Finally, this cation undergoes desilylation to yield the 1,4-diketone (**7**). The silyl ketene acetals (**8**) undergo the more facile oxidation for the cross-coupling with the silyl enol ethers (**4**) to give the γ-keto esters (**9**) (Eq. (1)). The one-electron oxidation process depends on the redox potentials of the substrates and oxovanadium(V) compounds. The more readily oxidizable silyl enol ethers work as radical precursors and the less oxidizable ones are recognized as radicophiles.

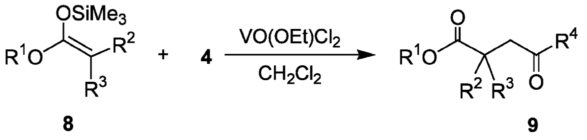
Carbon–silicon bond cleavage has definite synthetic potential. The chemoselective cross-coupling reaction of



Scheme 1.

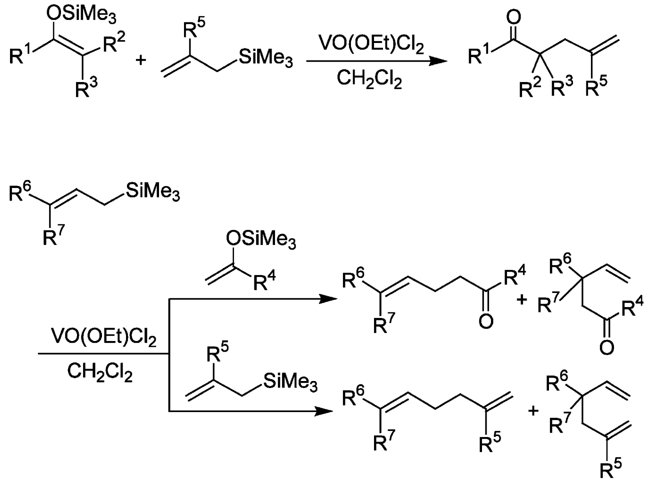


Scheme 3.



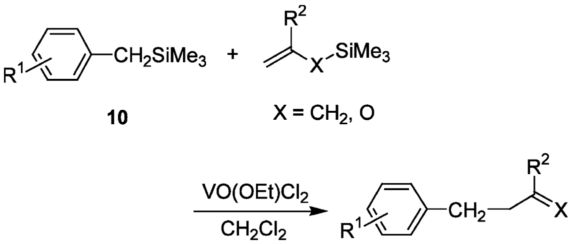
(1)

silyl enol ethers and allylic silanes is induced by $VO(OR)Cl_2$ (Scheme 4) [9]. As described above, their redox potentials, which can be predicted from MOPAC calculated ionization potentials, determine whether they act as radical precursors or acceptors. Oxovanadium(V) reagents differentiate the oxidation process effectively. The reactivity order is as follows; $VO(OR)Cl_2$–AgOTf or $Me_3SiOTf > VO(OR)Cl_2 > VO(OR)_2Cl > VO(OR)_3$ [3]. $VO(OR)Cl_2$ is a versatile oxidant which is able to promote the chemoselective coupling via oxidative desilylation of organosilicon compounds under controlled conditions.



Scheme 4.

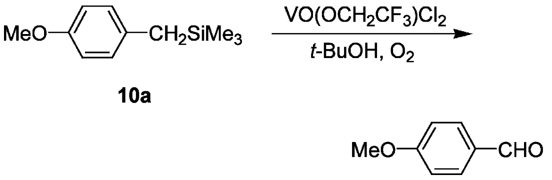
The similar chemoselective oxidative desilylation is also achieved with benzylic silanes. The electron-donating group on the arene ring lowers the ionization potential of the benzylsilane (**10**), thus activating it for desilylation. The desilylation reaction is applied to intermolecular regioselective coupling of the substituted benzylic silane with an allylic silane or silyl enol ether (Eq. (2)) [10].



(2)

Oxidation of organosilicon compounds provides a useful route to synthetic equivalents for cationic intermediates for the selective carbon–carbon bond formation.

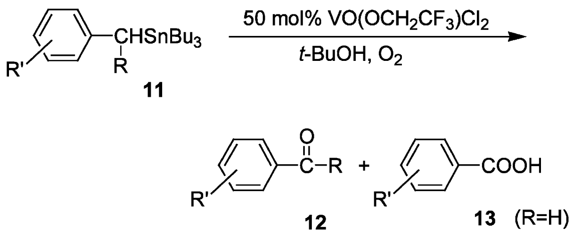
The reaction of 4-methoxybenzyltrimethylsilane (**10a**) with $VO(OR)Cl_2$ is carried out in *t*-BuOH under an oxygen atmosphere affords the aldehyde [11]. $VO(OCH_2CF_3)Cl_2$ [8] exhibits a higher reactivity than $VO(OEt)Cl_2$ (Eq. (3)). The oxidation path is explained below, as compared with the oxidative transformation of benzyltins.



(3)

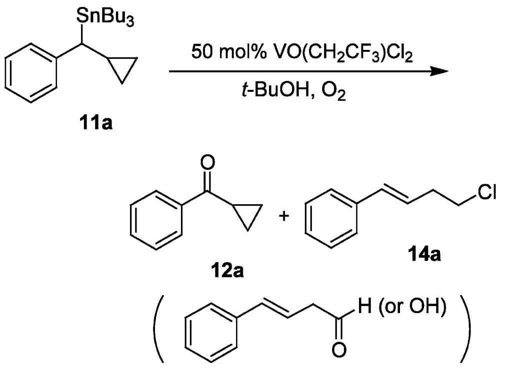
3. Oxidative transformation of organotin compounds

Allylic tins and benzylic tins are known to undergo a more facile oxidation than the corresponding silicon compounds [12], and are converted to the alcohols or their derivatives by a metallic oxidant such as Mn(IV), Ce(IV), Tl(III), or Fe(III) [13]. The oxidation of the benzyltributyltins (**11**) with $VO(OCH_2CF_3)Cl_2$ in *t*-BuOH under an oxygen atmosphere leads to the aldehydes (**12**) (ketones) and the corresponding carboxylic acids (**13**) (Eq. (4)) [11,14]. The susceptibility to oxidation depends on the substituent on the arene ring of **11**. $VO(OPr^i)_2Cl$ and $VO(OCH_2CF_3)Cl_2$ are superior to a weaker oxidant such as $VO(acac)_2$, $VO(OPr^i)_3$, or $VO(OEt)_3$. Furthermore, a catalytic reaction proceeds with $VO(OCH_2CF_3)Cl_2$.



(4)

1-Cyclopropyl-1-phenylmethyltributyltin (**11a**) is oxidized to the cyclopropyl ketone (**12a**) as a major product (Eq. (5)). As for ring-opened compounds, neither the aldehyde nor the carboxylic acid is detected, although only a small amount of the chloride **14a** is obtained.



(5)

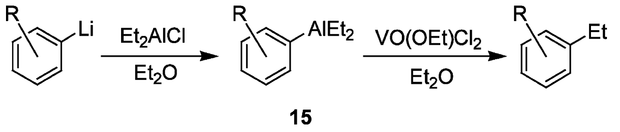
Plausible reaction paths are illustrated in Scheme 5. In the case of benzylsilanes, an electron transfer mechanism is considered to operate as mentioned above. Although benzyltin compounds undergo the more facile oxidation than benzylsilanes, an electron transfer process may not be favorable judging from the reactivities of the cyclopropylmethyltin (**11a**). This result suggests that either the electron transfer process or homolytic scission of carbon–vanadium bond of a benzylvanadium species is a minor pathway, and the ketone **12a** may be derived by transmetallation through a non-radical process. A low-valent vanadium species generated in situ is oxidized under an oxygen atmosphere to regenerate a vanadium species in its high oxidation state for catalytic reactions [15].

4. Oxidative transformation of organoaluminum compounds

The redox processes of organometallics are important in synthetic transformations, especially in transition metal-induced reactions. The transition metal-catalyzed cross-coupling reactions of main-group organometallic compounds with organic halides provide versatile synthetic tools in organic synthesis. As mentioned in the introduction, the transmetallation and/or electronic interaction are able to widen the reactivities of main-group organometallic compounds. One-electron oxidation of d^0-transition metal complexes such as titanocenes, zirconocenes, and/or platinum complexes with metallic oxidants permits synthetically useful transformations via organometallic radical cation species as key intermediates [16]. In these reactions, selective coupling is achieved between two ligands on the transition metal, providing a useful method for carbon–carbon bond formation.

Main-group organometallics have limited usage due to their restricted redox processes. Oxidative transformations of organoaluminum compounds usually provide alcohols, [17] but to the best of our knowledge, selective carbon–carbon bond formation of organic substituents on aluminum has not been investigated.

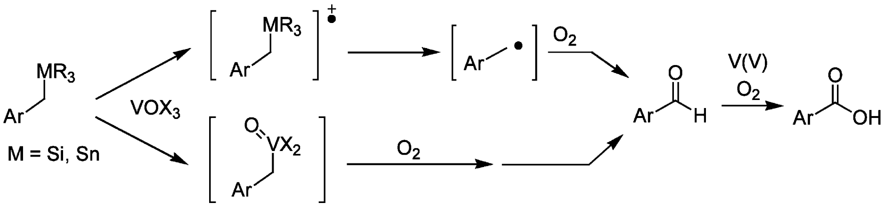
The oxidation of the aryldiethylaluminums (**15**), obtained from aryllithiums and diethylaluminum chloride, with $VO(OEt)Cl_2$ results in novel ethylation (Scheme 6) [18]. This method can be applied to a wide variety of arylaluminums bearing an electron-donating group, which permits the selective ligand coupling of the organic groups of organoaluminums.



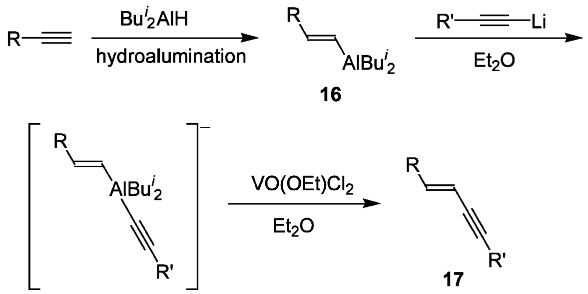
Scheme 6.

The addition of 1-alkynyllithium to the 1-alkenylaluminum (**16**), followed by treatment with $VO(OEt)Cl_2$, leads to the coupling of organic substituents on aluminum, giving the corresponding *trans*-enyne (**17**) via chemoselective and stereoselective bond formation between sp carbon and sp^2 carbon (Scheme 7). The homo-coupled diene is not obtained, although the diyne is probably derived by oxidative homo-coupling of excess alkynyllithium is formed as a byproduct [19].

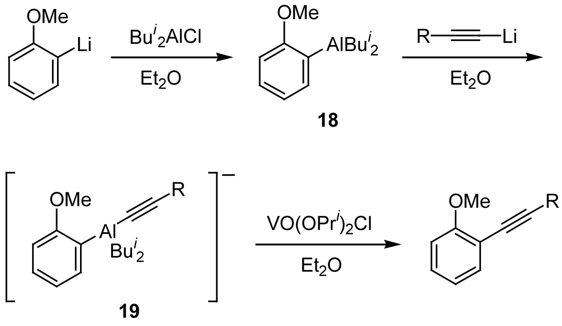
When the aryl-substituted aluminum **18** is used instead of the 1-alkenylaluminum, the ligand coupling of the ate complex **19** is induced by $VO(OPr^i)_2Cl$ with



Scheme 5.



Scheme 7.



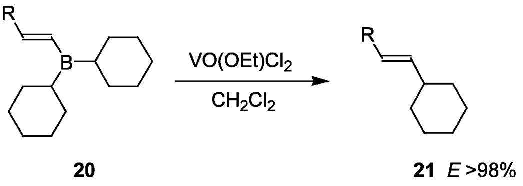
Scheme 8.

the lower oxidation capability to give the aryl-1-alkynyl coupling product selectively (Scheme 8).

Although the coupling mechanism is ambiguous, coordination of an oxo atom of oxovanadium(V) species to organoaluminums has been reported [20]. Such an interaction might promote electron transfer or transmetallation for the oxidative coupling. The transformations for formal reductive elimination on aluminum are considered to be achieved for the first time.

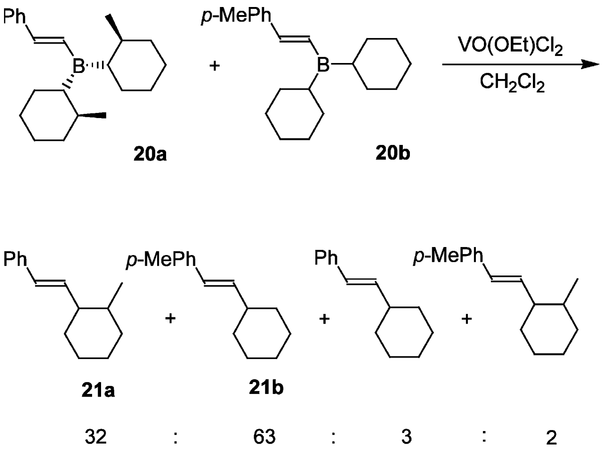
5. Oxidative transformation of organoboron compounds

The organoboron compound **20**, derived from dicyclohexylborane and phenylacetylene or acetylenecarboxylic ester, is oxidized with $VO(OEt)Cl_2$ to give the (*E*)-ethenylcyclohexane (**21**) selectively without the formation of di cyclohexyl and 1,4-butadiene derivative, as shown in Eq. (6) [21].



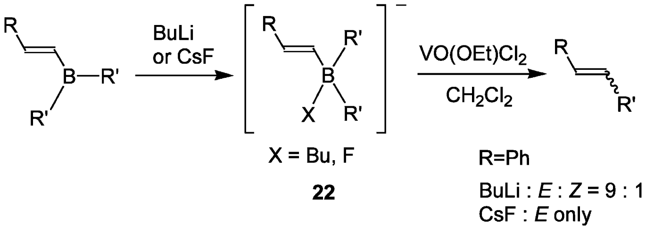
(6)

When an equimolar mixture of bis(2-methylcyclohexyl)[(*E*)-2-(4-methylphenylethenyl)]borane (**20a**) and dicyclohexyl[(*E*)-2-(4-methlyphenyl)ethenyl]borane (**20b**) is treated with $VO(OEt)Cl_2$, 1-methyl-2-(2-phenylethenyl)cyclohexane (**21a**) and [2-(4-methylphenyl)ethenyl]cyclohexane (**21b**) are predominantly produced, with only trace amounts of the crossover products (Eq. (7)). The result suggests that the coupling reaction proceeds mostly in an intramolecular fashion.



(7)

The ate complexes **22** of the organoborons undergo the more facile oxidation with $VO(OEt)Cl_2$, as observed in the oxidation of the aluminum ate complexes. The organic groups are effectively differentiated in the coupling reaction. Although the *Z* isomer is obtained in a small amount, use of CsF or TBAF [22] to form the organoborate improves the stereoselectivity, giving the *E* isomer exclusively (Scheme 9).

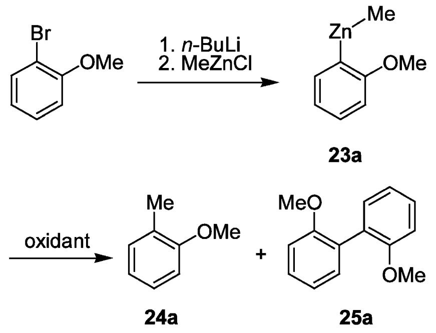


Scheme 9.

Taking these observation into account, an electronic interaction with oxovanadium(V) species is assumed to operate in the coupling step. Alkenyltrialkylborates are known to undergo the coupling reaction induced by I_2 or BrCN, giving the corresponding alkylated alkenes [23]. Biaryl formation also occurs by electrochemical, photochemical, and chemical oxidation, for example with Ir(IV), of tetraarylborates [24]. The oxovanadium(V)-induced ligand coupling provides another versatile method for the carbon–carbon bond formation on boron.

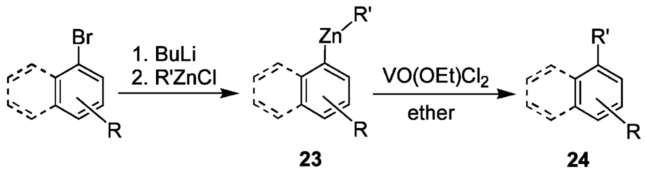
6. Oxidative transformation of organozinc compounds

Organozinc compounds can tolerate a broad range of functionalities. Cross-coupling reactions between orga-



oxidant	equiv	**24a** + **25a** yield, %	(**25a** : **25a**)
Cp_2FePF_6	3	33	(0 / 100)
$AgBF_4$	6	55	(31 / 69)
$VO(OEt)Cl_2$	3	82	(68 / 32)

Scheme 10.



Scheme 11.

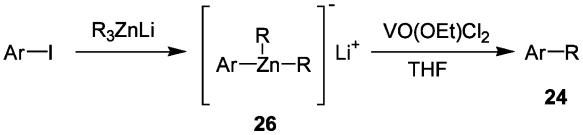
nozinc reagents and electrophiles such as organic halides are catalyzed by transition metal complexes [25]. However, examples of the selective cross-coupling of two ligands of organozinc compounds are limited to few cases, which include 1,2-migration of zincate carbenoids and intramolecular coupling reaction of organozinc compounds by organocopper reagents [26]. Thus, the development of such a selective ligand coupling of zinc reagents is a challenging subject in organozinc chemistry, which is accomplished by the oxidation of organozinc compounds.

The organozinc compound **23a**, which is prepared in situ by transmetallation of the methylzinc chloride with the aryllithium, is oxidized with Cp_2FePF_6, to give the homo-coupling compound **25a**, selectively (Scheme 10). Among the oxidants employed, $AgBF_4$ serves as a useful oxidizing agent to give the desired cross-coupling compound **24a**, probably via an one-electron oxidation process. Using $VO(OEt)Cl_2$ instead of $AgBF_4$, the cross-coupling reaction proceeds in preference to the homo-coupling one [27]. Higher selectivity for the cross-coupling is observed with $VO(OEt)Cl_2$ than $VO(O\text{-}Pr^i)Cl_2$ or $VO(OPr^i)_2Cl$.

The coupling reaction of organozinc compounds **23** bearing an *o*-methoxy, *o*-phenyl, or *o*-methylthio group on the arene ring proceeds smoothly, but the *o*-cyano-substituted alkylarylzinc exhibits a lower reactivity. Organoaluminum compounds having an electron-withdrawing substituent do not undergo oxidative coupling under the similar conditions. Alkyl and 1-alkynyl groups can couple with the aryl group successfully (Scheme 11).

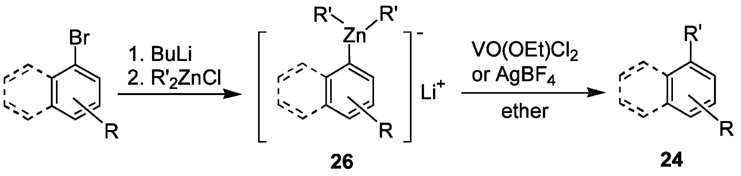
Triorganozincates (**26**) are oxidized with $VO(OEt)Cl_2$ very smoothly to give the corresponding cross-coupling compounds **24** in high yields (Scheme 12) [27]. Selective carbon–carbon bond formation between alkyl groups and *o*-methoxy-substituted aryl groups also occurs with $AgBF_4$.

As described above, aryl–aryl homo-coupling compounds are occasionally formed as byproducts. On the other hand, homo-coupling reactions of aryllithium compounds proceed by the action of oxovanadium(V) compounds [19]. When the organozinc compounds are prepared from organolithiums, the homo-coupling may be derived by the oxidation of organolithium compounds remaining in situ. Reaction of ate complexes, R_3ZnLi [28], provides a direct method for the preparation of arylzincates from aryl iodides through iodine–zinc exchange without the use of the aryllithium derivatives as starting reagents. Oxidation of the so-obtained zinc ate complexes **26** results in the exclusive formation of the cross-coupling products **24** as shown in Scheme 13 [27].

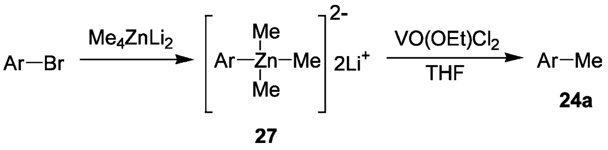


Scheme 13.

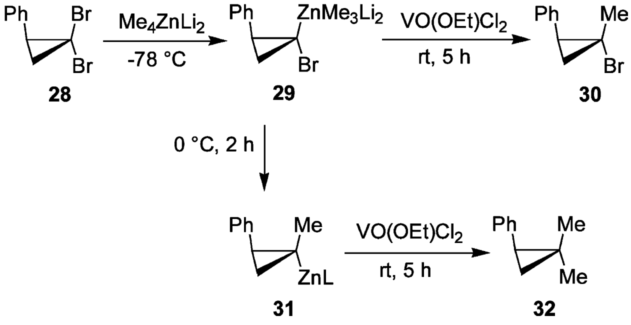
The organozincates (**27**), prepared from various bromoarenes and Me_4ZnLi_2 [29], are also oxidized by $VO(OEt)Cl_2$ to give the expected methylarene (**24a**) (Scheme 14) [30]. Thus, the coupling between sp^2-carbon (aryl group) and sp^3-carbon (methyl group) of aryltrimethylzincates is achieved chemoselectively. Although the mechanism remains obscure, the reaction is presumed to proceed by either a process of transmetallation or one-electron oxidation between the organozincate complex and oxovanadium(V) species.



Scheme 12.



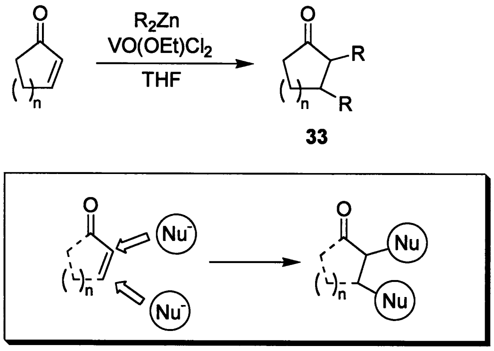
Scheme 14.



Scheme 15.

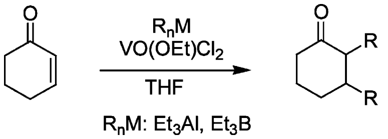
The oxovanadium(V)-induced oxidative transformation is applied to the selective carbon–carbon bond formation between sp^3-carbons [30]. A bromine–zinc exchange reaction of **28** selectively occurs at the position *cis* to the phenyl group by treatment with Me_4ZnLi_2 at −78 °C [31]. Oxidation of the so-obtained zincate **29** with $VO(OEt)Cl_2$ leads to the stereoselective formation of 1-bromo-1-methyl-2-phenylcyclopropane (**30**). On the other hand, when the reaction mixture is warmed up to 0 °C, followed by treatment of $VO(OEt)Cl_2$, dimethylation takes place to give the dimethylcyclopropane (**32**) via the organozinc (**31**) (Scheme 15).

Dialkylzinc reagent (R_2Zn) is recognized as a mild nucleophile in the presence of an additional promoter such as a Lewis acid [32]. Characteristics of oxovanadium(V) compounds as a Lewis acid and one-electron oxidant permit vicinal dialkylation at both the α and β positions of α,β-unsaturated carbonyl compounds with dialkylzinc reagents (Scheme 16) [33]. For example, reaction of 2-cyclohexenone with dimethylzinc in the presence of $VO(OEt)Cl_2$ affords 2,3-dimethylcyclohexanone. Use of the stronger Lewis acid, $VO(OEt)Cl_2 > VO(OPr^i)Cl_2 > VO(OPr^i)_2Cl$, gives a better result.

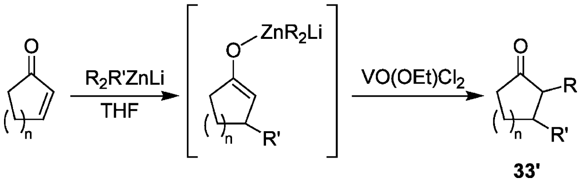


Scheme 16.

This method can be applied to vicinal alkylation with triethylaluminum or triethylborane compounds as shown in Eq. (8) [33]. In contrast, the similar oxidation reaction is not observed with organocuprate reagents.

 (8)

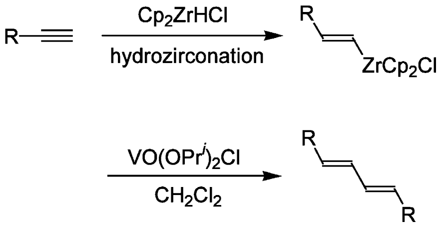
Contrary to dialkylzincs, lithium trialkylzincates (R_3ZnLi) have enough nucleophilicity for conjugate addition without the aid of a Lewis acid. Treatment with $R_2R'ZnLi$, followed by oxidation with $VO(OEt)Cl_2$, leads to the efficient vicinal dialkylation to give the cycloalkanones **33′** (Scheme 17). A better yield is obtained with the organozinc compound prepared from a $ZnCl_2$–TMEDA complex and BuLi. It is noteworthy that two different alkyl groups can be introduced regioselectively. For example, use of $BuMe_2ZnLi$ results in the selective formation of 3-butyl-2-methylcycloalkanone.



Scheme 17.

7. Oxidative transformation of organozirconium compounds

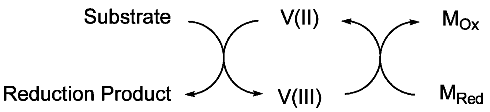
The oxidation reaction of (*E*)-1-alkenylchlorozirconocenes with an $VO(OPr^i)_2Cl$ leads to the homocoupling, giving the (*E,E*)-diene stereoselectively (Scheme 18) [34]. (*E*)-1-Alkenyl-1-alkynylzirconocenes undergo the oxovanadium(V)-induced cross-coupling of organic substituents on zirconium, to form the (*E*)-enynes stereoselectively.



Scheme 18.

8. Conclusion

Oxovanadium(V) compounds are potential oxidants to induce the oxidation of a variety of main-group organometallic compounds based on their characteristics. Oxidation capability and redox potential are effectively controlled by the substituent of oxovanadium(V) compounds. Transmetallation and/or electron transfer mechanism are considered to operate in the oxidative transformations mentioned in this review. Although the precise reaction route, especially for the oxidative ligand coupling, requires more investigation, the intermetallic interaction between vanadium species and main-group organometallics might permit one to induce a selective oxidation reaction. On the other hand, low-valent vanadium compounds are employed in the reductive transformations. Catalytic reactions for one-electron reduction have been achieved in our laboratory by using a multi-component catalytic system (Scheme 19) [35,36]. Both synthetic methods are expected to be promising from the viewpoint of synthetic chemistry and inorganic or organometallic chemistry.



Scheme 19.

Acknowledgements

The work in this review was mostly carried out by the members in our laboratory, whose names are cited in the references.

References

[1] Review: T. Hirao, Chem. Rev. 97 (1997) 2707.

[2] Recent papers, for example: (a) M. Kirihara, M. Ichinose, S. Takizawa, T. Momose, Chem. Commun. (1998) 1691;
(b) D.-G. Piao, K. Inoue, H. Shibasaki, Y. Taniguchi, T. Kitamura, Y. Fujiwara, J. Organometal. Chem. (1999) 574;
(c) D.R. Hwang, C.Y. Chu, S.K. Wang, B.J. Uang, Synlett (1999) 77;
(d) D.R. Hwang, C.P. Chen, B.J. Uang, Chem. Commun. (1999) 1207;
(e) C.T. Chen, S.W. Hon, S.S. Weng, Synlett (1999) 816;
(f) J. Hartung, P. Schmidt, Synlett (2000) 367;
(g) U. Bora, G. Bose, M.K. Chaudhuri, S.S. Dhar, R. Gopinath, A.T. Khan, B.K. Patel, Org. Lett. 2 (2000) 247;
(h) R. Gopinath, B.K. Patel, Org. Lett. 2 (2000) 577;
(i) C.Y. Chu, D.R. Hwang, S.K. Wang, B.J. Uang, Chem. Commun. (2001) 980.

[3] (a) T. Hirao, M. Mori, Y. Ohshiro, Bull. Chem. Soc. Jpn. 62 (1989) 2399;
(b) T. Hirao, M. Mori, Y. Ohshiro, J. Org. Chem. 55 (1990) 358;
(c) T. Hirao, M. Mori, Y. Ohshiro, Chem. Lett. (1991) 783.

[4] (a) T. Hirao, Y. Ohshiro, Tetrahedron Lett. 31 (1990) 3917;
(b) T. Hirao, S. Mikami, M. Mori, Y. Ohshiro, Tetrahedron Lett. 32 (1991) 1741;
(c) T. Hirao, T. Fujii, Y. Ohshiro, J. Organomet. Chem. 407 (1991) C1;
(d) T. Hirao, T. Fujii, S.-I. Miyata, Y. Ohshiro, J. Org. Chem. 56 (1991) 2264;
(e) T. Hirao, T. Fujii, T. Tanaka, Y. Ohshiro, J. Chem. Soc. Perkin Trans. 1 (1994) 3;
(f) T. Hirao, T. Fujii, T. Tanaka, Y. Ohshiro, Synlett (1994) 845;
(g) T. Hirao, M. Sakaguchi, T. Ishikawa, I. Ikeda, Synth. Commun. 25 (1995) 2579.

[5] (a) Y. Ito, T. Konoike, T. Saegusa, J. Am. Chem. Soc. 97 (1975) 649;
(b) Y. Kobayashi, T. Taguchi, T. Morikawa, E. Tokuno, S. Sekiguchi, Chem. Pharm. Bull. 28 (1980) 262;
(c) E. Baciocchi, A. Casu, R. Ruzziconi, Synlett (1990) 679.

[6] H. Funk, W. Weiss, M. Zeising, Z. Anorg. Allg. Chem. 36 (1958) 296.

[7] T. Fujii, T. Hirao, Y. Ohshiro, Tetrahedron Lett. 33 (1992) 5823.

[8] K. Ryter, T. Livinghouse, J. Am. Chem. Soc. 120 (1998) 2658.

[9] (a) T. Fujii, T. Hirao, Y. Ohshiro, Tetrahedron Lett. 34 (1993) 5601;
(b) T. Hirao, T. Fujii, Y. Ohshiro, Tetrahedron 50 (1994) 10207.

[10] T. Hirao, T. Fujii, Y. Ohshiro, Tetrahedron Lett. 35 (1994) 8005.

[11] T. Hirao, C. Morimoto, T. Takada, H. Sakurai, Tetrahedron Lett. 42 (2001) 1961.

[12] (a) M. Pereyre, J.-P. Quintard, A. Rahm, Tin in Organic Synthesis, Butterworths, London, 1987;
(b) P.G. Harrison, Chemistry of Tin, Blackie & Son, New York, 1989.

[13] (a) E. Baciocchi, T. Del Giacco, C. Rol, G.V. Sebastiani, Tetrahedron Lett. 30 (1989) 3573;
(b) W.C. Still, J. Am. Chem. Soc. 99 (1977) 4186;
(c) M. Ochiai, E. Fujita, M. Arimoto, H. Yamaguchi, Chem. Pharm. Bull. 32 (1984) 887;
(d) M. Ochiai, E. Fujita, M. Arimoto, H. Yamaguchi, Chem. Pharm. Bull. 32 (1984) 5027;
(e) E.J. Corey, J.C. Walker, J. Am. Chem. Soc. 109 (1987) 8108.

[14] T. Hirao, C. Morimoto, T. Takada, H. Sakurai, Tetrahedron 57 (2001) 5073.

[15] K. Yamamoto, E. Tsuchida, H. Nishide, M. Jikei, K. Oyaizu, Macromolecules 26 (1993) 3432.

[16] (a) R.F. Jordan, R.E. JaPointe, C.S. Bajgure, S.F. Echols, R. Willet, J. Am. Chem Soc. 109 (1987) 4111;
(b) S.L. Borkowsky, N.C. Baenziger, R.F. Jordan, Organometallic 12 (1993) 486;
(c) M.J. Burk, W. Tumas, M.D. Ward, D.R. Wheeler, J. Am. Chem. Soc. 112 (1990) 6133;
(d) M. Sato, E. Mogi, S. Kumakura, Organometallics 14 (1995) 3157;
(e) Y. Hayashi, M. Osawa, Y. Wakatsuki, J. Organomet. Chem. 542 (1997) 241.

[17] (a) J.J. Eisch, in: E.W. Abel, F.G.A. Stone, S.G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 11, Pergamon Press, Oxford, 1994, p. 277;
(b) J.R. Zietz, Jr, G.C. Robinson, K.L. Lindsay, in: S.G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon Press, Oxford, 1982, p. 354.

[18] T. Ishikawa, A. Ogawa, T. Hirao, J. Am. Chem. Soc. 120 (1998) 5124.

[19] T. Ishikawa, A. Ogawa, T. Hirao, Organometallics 17 (1998) 5713.

[20] F.J. Feher, R.L. Blanski, J. Am. Chem. Soc. 114 (1992) 5886.

[21] T. Ishikawa, S. Nonaka, A. Ogawa, T. Hirao, Chem. Commun. (1998) 1209.

[22] (a) E. Negishi, M.J. Idacavage, K.-W. Chin, T. Yoshida, A. Abramovitch, M. E. Goettel, A. Silveira, H.D. Bretherick, J. Chem. Soc. Perkin Trans. 2 (1978) 1225;
(b) L. Garnier, B. Plunian, J. Morter, M. Vaultier, Tetrahedron Lett. 37 (1996) 6699;
(c) M.T. Reetz, C.M. Niemeryer, K. Harms, Angew. Chem. Int. Ed. Engl. 30 (1991) 1472.

[23] A. Pelter, K. Smith, H.C. Brown, Borane Reagents, Academic Press, London, 1988.

[24] (a) D.H. Geske, J. Phys. Chem. 63 (1959) 1062;
(b) D.H. Geske, J. Phys. Chem. 66 (1962) 1743;
(c) A. Pelter, R. Pardasani, P. Pardasani, Tetrahedron 56 (2000) 7339;
(d) P. Abley, J. Halpern, J. Chem. Soc., Chem. Commun. (1971) 1238.

[25] (a) K. Oshima, Transition metal catalyzed reactions of organozinc compounds, in: L.S. Liebeskind (Ed.), Advance in Organometallic Chemistry, vol. 2, JAI Press, London, 1991, p. 101;
(b) E. Erdik, Tetrahedron 48 (1992) 9577.

[26] (a) M. Iyoda, S.M.H. Kabir, A. Vorasingha, Y. Kuwatani, M. Yosihda, Tetrahedron Lett. 39 (1998) 5393;
(b) T. Harada, K. Iwazaki, D. Hara, K. Hattori, A. Oku, J. Org. Chem. 62 (1997) 8966;
(c) T. Harada, T. Katsuhira, K. Takeshi, O. Atusshi, I. Katsuhiro, M. Keiji, A. Oku, J. Am. Chem. Soc. 118 (1996) 11377.

[27] T. Hirao, T. Takada, A. Ogawa, J. Org. Chem. 65 (2000) 1511.

[28] Y. Kondo, N. Takazawa, C. Yamazaki, T. Sakamoto, J. Org. Chem. 59 (1994) 4717.

[29] M. Uchiyama, M. Kameda, O. Mishima, N. Yokoyama, M. Koike, Y. Kondo, T. Sakamoto, J. Am. Chem. Soc. 120 (1998) 4934.

[30] T. Takada, H. Sakurai, T. Hirao, J. Org. Chem. 66 (2001) 300.

[31] T. Harada, T. Katsuhira, K. Hattori, A. Oku, J. Org. Chem. 58 (1993) 2958.

[32] (a) P. Knochel, J.J.A. Perea, P. Jones, Tetrahedron 54 (1998) 8275;
(b) P. Knochel, R.D. Singer, Chem. Rev. 93 (1993) 2117 (and references therein).

[33] T. Hirao, T. Takada, H. Sakurai, Org. Lett. 2 (2000) 3659.

[34] T. Ishikawa, A. Ogawa, T. Hirao, J. Organomet. Chem. 575 (1999) 76.

[35] (a) T. Hirao, K. Hirano, T. Hasegawa, I. Ikeda, Y. Ohshiro, J. Org. Chem. 58 (1993) 6529;
(b) T. Hirao, T. Hasegawa, Y. Muguruma, I. Ikeda, J. Org. Chem. 61 (1996) 366;
(c) T. Hirao, M. Asahara, Y. Muguruma, A. Ogawa, J. Org. Chem. 63 (1998) 2812;
(d) T. Hirao, B. Hatano, M. Asahara, Y. Muguruma, A. Ogawa, Tetrahedron Lett. 39 (1998) 5247;
(e) B. Hatano, A. Ogawa, T. Hirao, J. Org. Chem. 63 (1998) 9421;
(f) T. Hirao, B. Hatano, Y. Imamoto, A. Ogawa, J. Org. Chem. 64 (1999) 7665;
(g) T. Hirao, H. Takeuchi, A. Ogawa, H. Sakurai, Synlett (2000) 1658;
(h) L. Zhou, T. Hirao, Tetrahedron Lett. 41 (2000) 8517;
(i) L. Zhou, T. Hirao, Tetrahedron 57 (2001) 6927.

[36] Review: T. Hirao, Synlett (1999) 175.