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Oxidation of benzylsilanes and benzyltins by oxovanadium(V) compound and molecular oxygen

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Dedicated to Professor Barry M. Trost on the occasion of his 60th birthday

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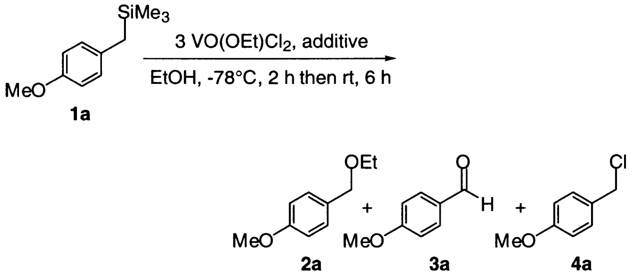
Abstract—Benzylsilane and benzyltin compounds were oxidized by oxovanadium(V) compound under an oxygen atmosphere to afford the corresponding aromatic aldehydes (ketones) and/or carboxylic acids. In the reaction of benzyltins, oxovanadium(V) compound can be reduced to 0.5 molar amounts. The reaction of benzylsilanes is considered to proceed via electron-transfer process. On the other hand, benzyltins may undergo transmetallation to generate benzylvanadium species, which are directly transferred to the carbonyl compounds via non-radical process. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Many organometallic compounds are readily oxidized to generate reactive species. Controlling the reaction pathway to the reactive intermediates by the choice of oxidant, reaction conditions, etc. is a key to construct a new type of reaction.[1] Based on this concept, we have focused on the development of novel reactions by oxovanadium(V)-induced oxidation[2] of main-group organometallics, as exemplified by selective ligand coupling reactions of organoaluminum,[3] boron,[4] zirconium[5] and zinc compounds,[6] and carbon–carbon bond forming reactions of silyl enolates, allylsilanes and benzylsilanes.[7,8]

Transformation of group 14 organometallic compounds, such as organosilicon and organotin compounds, into other functional groups has provided a variety of synthetic tools. For example, oxidative conversion of organosilicon compounds to the corresponding alcohols by hydrogen peroxide,[9] and oxidation of benzylic and allylic silanes via one-electron transfer process induced by photolysis[10] or $(NH_4)_2Ce(NO_2)_6$[11] are widely applied in organic synthesis. Allyltins and benzyltins are known to undergo more facile oxidation than the corresponding silicon compounds,[12] and their conversion to the alcohols or their derivatives is performed by metallic oxidants such as Mn(IV),[13] Ce(IV)[11] or Tl(III),[14] organic oxidants such as MCPBA,[15] or photo-induced electron transfer conditions.[10] Recent reports from our laboratory also demonstrated that oxovanadium(V) compound works as an excellent oxidant towards allylsilanes and benzylsilanes.[8]

In the course of our study, the development of the oxovanadium-induced oxidation of benzylsilanes to oxygen-containing compounds was attempted. When 4-methoxybenzyltrimethylsilane (**1a**) was treated with 3 molar amounts of $VO(OEt)Cl_2$ in EtOH under an argon atmosphere, 4-methoxybenzyl ethyl ether (**2a**) was obtained in 80% yield, accompanied by 4-methoxybenzaldehyde (**3a**) and 4-methoxybenzyl chloride (**4a**) in 7 and 9% yields, respectively. Addition of stoichiometric H_2O did not change the yield of **2a**–**4a**, whereas the yield of **3a** was drastically increased to 40% when the reaction was performed under an oxygen atmosphere (eq. 1).



additive	atmosphere	2a	3a	4a
none	Ar	80%	7%	9%
H_2O	Ar	77%	8%	12%
none	O_2	51%	40%	5%

(1)

Only two examples have been concerned with the direct transformation of benzylic silanes/tins to the corresponding

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Keywords: oxidation; oxovanadium; benzylsilane; benzyltin; molecular oxygen.

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Table 1. Oxidation of benzylic silanes **1** by oxovanadium(V) compound under an oxygen atmosphere

Entry	**1**	Solvent	Oxovanadium (molar amount)	Conditions (temp., time)	Yields (%)			
					2(R)	**3**	**4**	Recovery of **1**
1	**1a**	CH_3CN	$VO(OEt)Cl_2$ (3)	rt, 2 h	16(Et)	12	15	–
2	**1a**	Et_2O	$VO(OEt)Cl_2$ (3)	rt, 24 h	–	trace	–	–
3	**1a**	CH_2Cl_2	$VO(OEt)Cl_2$ (3)	rt, 48 h		Complex mixture		
4	**1a**	DMF	$VO(OEt)Cl_2$ (3)	rt, 48 h	–	10	–	88
5	**1a**	DMF	$VO(OEt)Cl_2$ (3)	50°C, 30 h	14(Et)	53	12	–
6	**1a**	EtOH	$VO(OEt)Cl_2$ (3)	rt, 6 h	51(Et)	40	5	–
7	**1a**	*t*-PrOH	$VO(OEt)Cl_2$ (3)	rt, 24 h	17(*t*-Pr)	32	trace	–
8	**1a**	*t*-PrOH	$VO(OEt)Cl_2$ (3)	0°C, 24 h	8(*t*-Pr)	44	4	–
9	**1a**	*t*-BuOH	$VO(OEt)Cl_2$ (3)	rt, 24 h	trace(*t*-Bu)	19	trace	41
10	**1a**	*t*-BuOH	$VO(OEt)Cl_2$ (3)	rt, 48 h	9(*t*-Bu)	45	2	–
11	**1a**	*t*-BuOH	$VO(OEt)Cl_2$ (1)	rt, 48 h	trace(*t*-Bu)	54	trace	trace
12	**1a**	*t*-BuOH	$VO(OEt)Cl_2$ (0.5)	rt, 48 h	–	14	–	59
13	**1a**	*t*-BuOH	$VO(OCH_2CF_3)Cl_2$ (3)	50°C, 20 h	4(*t*-Bu)	88	–	–
14	**1a**	*t*-BuOH	$VO(OCH_2CF_3)Cl_2$ (1)	50°C, 72 h	–	22	–	65
15[a]	**1a**	*t*-BuOH	$VO(OCH_2CF_3)Cl_2$ (3)	50°C, 48 h	trace(*t*-Bu)	18	4	72
16	**1b**	*t*-BuOH	$VO(OCH_2CF_3)Cl_2$ (3)	70°C, 72 h	3(*t*-Bu)	2	6	40
17	**1c**	*t*-BuOH	$VO(OCH_2CF_3)Cl_2$ (3)	70°C, 72 h	–	trace	–	15
18	**1d**	*t*-BuOH	$VO(OCH_2CF_3)Cl_2$ (3)	70°C, 72 h	–	20	–	53

[a] Under an argon atmosphere.

aromatic carbonyl compounds using a metallic oxidant.[16,17] Treatment of 1-tributylstannyl-1-phenyl-2-propene with $FeBr_3$ under an oxygen atmosphere affords phenyl vinyl ketone in 70% yield,[18] but no simple benzylic tins were attempted in this study. Iron–porphyrin complex catalyzed oxidation reactions of benzylic silanes/tins with PhIO were shown to give benzaldehydes in 5–20% yields together with several products, which are possibly derived from benzyl radical intermediates.[19] The results shown in eq. 1 prompted us to develop a new method for the oxidative transformation of benzylic silanes/tins to the corresponding carbonyl compounds and/or carboxyl compounds with oxovanadium(V)–O_2.[20]

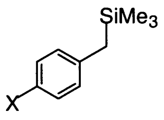
2. Results and discussion

First, 4-methoxybenzyltrimethylsilane (**1a**) was chosen as a substrate and reaction conditions were optimized under an oxygen atmosphere as listed in Table 1. In the presence of 3 molar amounts of $VO(OEt)Cl_2$, solvent effect was monitored (entries 1–10). In CH_3CN, Et_2O, or CH_2Cl_2 solution, oxidation did not occur clearly and the yield of 4-methoxybenzaldehyde (**3a**) was very low (entries 1–3). In DMF, oxidation proceeded very slowly to give **3a** in 10% yield with 88% recovery of **1a** after 48 h at room temperature (entry 4). When the reaction was carried out at 50°C for 30 h, the yield of **3a** was increased to 53% together with the benzyl ether **2a** and benzyl chloride **4a** in 14 and 12% yields, respectively (entry 5). In alcohol solution, the yield of **3a** was generally better, but the two processes, aldehyde formation and ether formation, were competitive especially in EtOH as shown in entry 6. In order to reduce the ether formation, less nucleophilic alcohols were chosen. In *i*-PrOH, ether formation could not be suppressed, but the selectivity was increased when the reaction was performed at 0°C rather than at room temperature (entries 7 and 8). In *t*-BuOH solution, 41% of benzylsilane **1a** still remained after 24 h at room temperature, whereas **1a** was completely consumed after 48 h, giving **3a** in 45% yield (entries 9 and 10). Next, conditions of vanadium oxidants were examined. Interestingly, the reaction became clear to give **3a** in 54% yield when the amount of $VO(OEt)Cl_2$ was reduced to equimolar. However, with further reduction of the oxidant to 0.5 molar amounts, the reaction did not proceed smoothly (entries 11 and 12). Recently, $VO(OCH_2CF_3)Cl_2$ was reported to exhibit an excellent reactivity for promoting one-electron oxidative cyclization and unsymmetrical coupling of silyl enol ethers.[21] $VO(OCH_2CF_3)Cl_2$ was also found to be effective for the oxidation of **1a**. When **1a** was treated with 3 molar amounts of $VO(OCH_2CF_3)Cl_2$ in *t*-BuOH under an oxygen atmosphere, desired aldehyde **3a** was obtained in 88% yield (entry 13). The yield of **3a** was decreased to 22% with equimolar amount of $VO(OCH_2CF_3)Cl_2$ and 65% of **1a** was recovered (entry 14). Finally, effect of molecular oxygen was reexamined (entry 15). The reaction was performed under the conditions listed in entry 13 and an argon atmosphere in place of an oxygen atmosphere to give **1a** and **3a** in 72 and 18% yields, respectively.

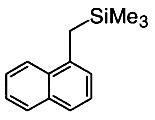
Table 2. Comparison of the reactivity between the benzylsilane and benzyltin

Entry	**1** or **7**	MR_3	X	Conditions	Yields (%)					
					2	**3**	**4**	**5**	**6**	**3**+**6**
1	**1a**	$SiMe_3$	OMe	O_2, 50°C, 20 h	4	88	–	–	–	88
2	**7a**	$SnBu_3$	OMe	O_2, rt, 2 h	–	48	38	14	–	48
3	**7a**	$SnBu_3$	OMe	Ar, rt, 2 h	–	24	15	43	–	24
4	**7b**	$SnBu_3$	Me	O_2, 50°C, 3 h	–	60	–	trace	19	79
5	**7b**	$SnBu_3$	Me	Ar, 50°C, 3 h	–	12	25	15	–	12

However, the above $VO(OCH_2CF_3)Cl_2$-induced procedure was not able to be applied to other benzylsilanes. As shown in entries 16–18, 4-methylbenzyl derivative **1b** and benzyltrimethylsilane (**1c**) were scarcely reactive, while α-naphthyl derivative **1d** partially underwent the oxidation.

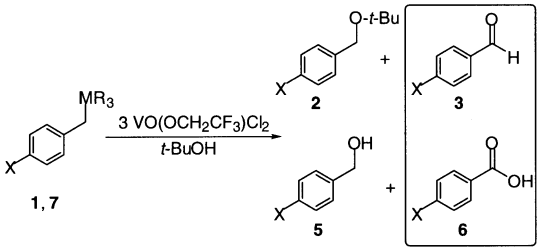


1b (X = Me)
1c (X = H)



1d

Since benzyltins are expected to undergo more facile oxidation than benzylsilanes, 4-methoxybenzyltributyltin (**7a**) was treated with 3 molar amounts of $VO(OCH_2CF_3)Cl_2$ in *t*-BuOH for the comparison with the benzylsilane **1a** (eq. 2, Table 2). When the reaction was performed under an oxygen atmosphere, **7a** completely disappeared after 2 h and the expected aldehyde **3a** was obtained in 48% yield (entry 2). 4-Methylbenzyltributyltin (**7b**) also underwent the smooth oxidation (50°C, 3 h), giving the aldehyde **3b** and the corresponding carboxylic acid **6b** in 60 and 19% yields, respectively (entry 4). On the other hand, when **7a** and **7b** were oxidized under an argon atmosphere, a mixture of the aldehyde, chloride, and alcohol products was obtained (entries 3 and 5).

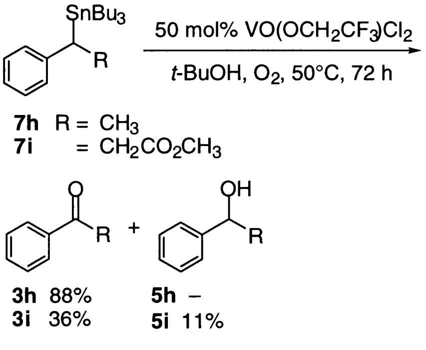


(2)

As indicated above, this oxovanadium(V)–O_2 induced oxidation is expected to be applied to a variety of benzyltin compounds. The reaction conditions were optimized using **7b** as a benzyltin compound as shown in Table 3. When a weak oxidant such as $VO(acac)_2$, $VO(OPr^i)_3$, or $VO(OEt)_3$ was used, the reaction did not proceed smoothly with a low yield of **3b** (entries 1–3), indicating that at least one chloride ligand is required on the oxovanadium(V) compound. When $VO(OPr^i)_2Cl$ was employed, the total yield of **3b** and **6b** was up to 83% although the formation of **5b** could not be suppressed (entry 4). Use of $VO(OCH_2CF_3)Cl_2$ resulted in the selective formation of **3b** and **6b** (79% total yield, entry 5). It should be noted that oxovanadium(V) compound could be reduced to 0.5 molar amounts. Catalytic activity of $VO(OPr^i)_2Cl$ was not enough to accomplish the reaction, and 29% of **7b** was recovered even after 72 h. On the other hand, $VO(OCH_2CF_3)Cl_2$ showed the superior catalytic activity, giving **6b** quantitatively (entries 6 and 7). 50 mol% of the oxovanadium(V) compound could induce a direct conversion of the benzyltin to the corresponding aromatic aldehyde and/or acid under an oxygen atmosphere, in which at least four equivalents of oxidant should be required.

Table 4 shows the examples for the reaction of various benzyltins under the oxovanadium-catalyzed oxidation conditions. Since 4-methoxybenzyltin **7a** was too susceptible for oxidative conditions, the use of milder oxidant, $VO(OPr^i)_2Cl$, was more suitable to afford the aldehyde **3a** and carboxylic acid **6a** in 63 and 15% yields, respectively (entries 1 and 2). As shown in entries 3–8, the better yield was obtained with the more electron-rich benzyltins although the reactivity of non-substituted benzyltin was somewhat low (entry 5). In particular, 4-methyl- and 2-methylbenzyltins underwent facile oxidation to give the acids **6** quantitatively (entries 3 and 4).

This transformation can be applied to secondary benzyltin compounds, giving the corresponding ketones (eqs. 3 and 4). 1-Phenylethyltributyltin (**7h**) was oxidized to acetophenone in 88% yield as a sole isolable product. The compound **7i**,[22] which possesses the ester function, also underwent the oxidation, giving the β-ketoester **3i** in 36% yield accompanied by the formation of the alcohol **5i** in 11% yield. When 1-cyclopropyl-1-phenylmethyltributyltin (**7j**)[23] was treated under the standard conditions, cyclopropylketone **3j** was mainly produced in 60% yield. As for ring-opened compounds, neither the aldehyde nor carboxylic acid was detected, but only chloride **4j** was isolated in 14% yield.

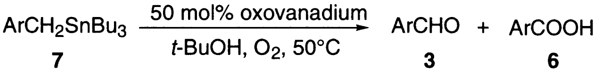


(3)

Table 3. Oxidation of **7b** by oxovanadium(V) compound under an oxygen atmosphere (all reactions were performed in *t*-BuOH at 50°C)

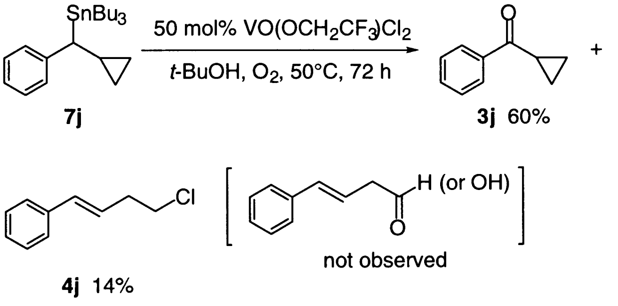
Entry	Oxovanadium (molar amount)	Time (h)	Yields (%)			
			3b	**6b**	**5b**	Recovery of **7b**
1	$VO(acac)_2$ (3)	3	5	–	4	75
2	$VO(OEt)_3$ (3)	3	20	–	37	20
3	$VO(OPr^i)_3$ (3)	3	36	–	45	–
4	$VO(OPr^i)_2Cl$ (3)	3	64	19	12	–
5	$VO(OCH_2CF_3)Cl_2$ (3)	3	60	19	trace	–
6	$VO(OPr^i)_2Cl$ (0.5)	72	40	–	3	29
7	$VO(OCH_2CF_3)Cl_2$ (0.5)	36	–	100	–	–

Table 4. Oxovanadium(V)-catalyzed oxidation of benzyltins



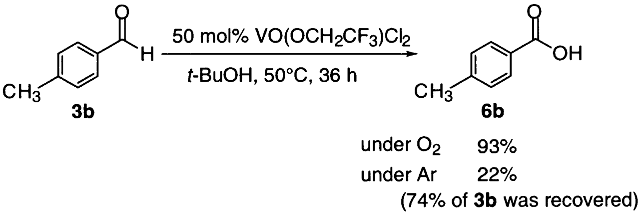
Entry	Ar (**7**)	Oxovanadium	Time (h)	Total yield (%) **3**+**6** (**3**/**6**)	Recovery of **7** (%)
1	4-MeO-C_6H_4 (**7a**)	$VO(OCH_2CF_3)Cl_2$	24	59 (55/4)[a,b]	–
2	4-MeO-C_6H_4 (**7a**)	$VO(OPr^i)_2Cl$	72	78 (63/15)[c]	–
3	4-Me-C_6H_4 (**7b**)	$VO(OCH_2CF_3)Cl_2$	36	100 (0/100)	–
4	2-Me-C_6H_4 (**7d**)	$VO(OCH_2CF_3)Cl_2$	72	100 (0/100)	–
5	C_6H_5 (**7c**)	$VO(OCH_2CF_3)Cl_2$	72	62 (41/21)	23
6	4-Cl-C_6H_4 (**7e**)	$VO(OCH_2CF_3)Cl_2$	72	95 (64/31)	4
7	4-NC-C_6H_4 (**7f**)	$VO(OCH_2CF_3)Cl_2$	72	25 (25/0)	18
8	1-Naphthyl (**7g**)	$VO(OCH_2CF_3)Cl_2$	24	86 (58/28)[d]	–

[a] The reaction was carried out at room temperature.
[b] Benzyl alcohol **5** was also obtained in 9% yield.
[c] Benzyl alcohol **5** was also obtained in 9% yield.
[d] Benzyl chloride **4** and benzyl alcohol **5** were obtained in 4 and 5% yields, respectively.



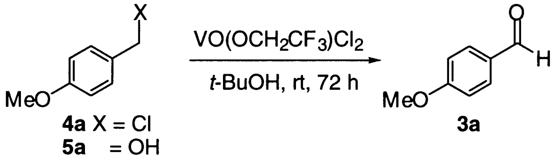
(4)

For understanding the reaction mechanism, a possible reaction intermediate should be assigned. In many cases, both aromatic aldehydes **3** and carboxylic acids **6** are the final oxidation products and benzylic ethers **2**, chlorides **4**, and alcohols **5** are usually detected as a minor product. As noted above, on treatment with 0.5 molar amounts of $VO(OCH_2CF_3)Cl_2$, **7b** was quantitatively converted to **6b**, and **3b** was not detected during the reaction. 4-Tolualdehyde (**3b**) was treated under the same conditions to produce **6b** in 93% yield (eq. 5), indicating that the aldehyde might be an initial product and its further oxidation proceeds to form the carboxylic acid. Under an argon atmosphere, on the other hand, oxidation of aldehyde to carboxylic acid did not proceed efficiently.



(5)

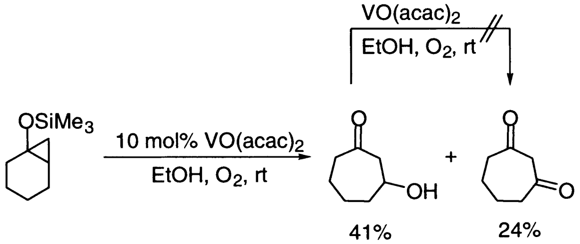
Then, possibility of the benzylic alcohol and chloride as reaction intermediates was studied by submitting them to the oxidation conditions (eq. 6 and Table 5). In every case, the reaction was very complicated to give the aldehyde **3a** only in 10–14% yield, respectively. These results indicate that benzylic alcohols/chlorides are not involved as a key intermediate. Kirihara also reported the similar phenomena.[24] Trimethylsilyl ethers of tertiary cyclopropanols were treated with $VO(acac)_2$–O_2 to afford β-hydroxyketones and β-diketones, while no β-diketone formation was observed when the β-hydroxyketone was oxidized under the same conditions (eq. 7).



(6)

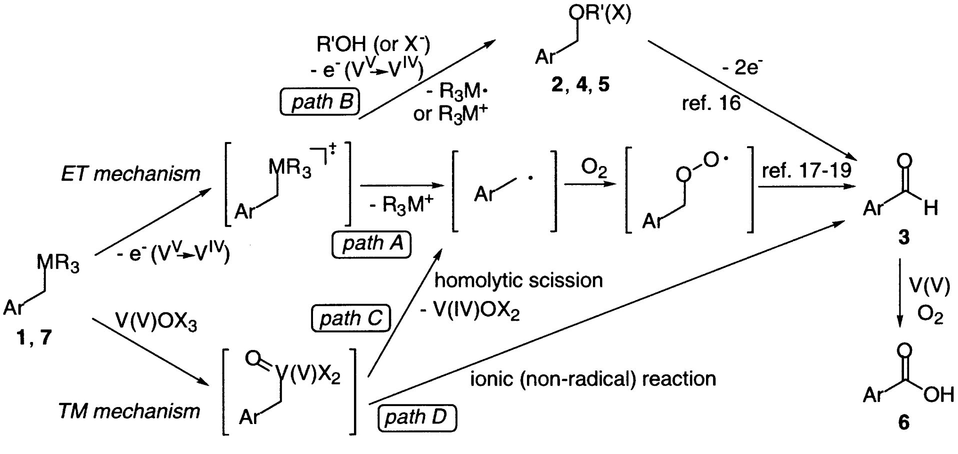
Table 5. Oxidation of the benzylic chloride **4a** and the alcohol **5a**

Entry	**4a** or **5a**	Atmosphere	Yield (%)	Recovery of **4a** or **5a** (%)
1	**4a**	O_2	14	19
2	**4a**	Ar	10	11
3	**5a**	O_2	14	7
4	**5a**	Ar	14	11



(7)

Two mechanisms, electron-transfer (ET) mechanism and transmetallation (TM) mechanism, are considered for this oxovanadium(V)–O_2 induced transformation reaction (Scheme 1). Initial step of ET mechanism involves one-electron transfer from benzylsilane/tin to oxovanadium(V) to generate a radical cation and vanadium(IV) species.[16,17] One of two possible routes from the thus-generated radical cation species is that nucleophilic attack by the solvent occurs on Si/Sn to give a benzyl radical equivalent via cleavage of Si–X/Sn–X bond (*path A*). Carbon-centered radicals are known to react with molecular oxygen to generate peroxyradicals, which are finally converted to aldehydes and carboxylic acids.[17–19,25] Another pathway is



Scheme 1. Electron-transfer (ET) and transmetallation (TM) mechanisms.

explained by nucleophilic attack at the benzylic position to produce $ArCH_2X$ **2**, **4** and/or **5** via removal of the Me_3Si/Bu_3Sn group. The benzylic products **2**, **4**, and/or **5** are assumed to be oxidatively converted to the aldehyde (*path B*).[16]

On the other hand, it is known that alkyl group transfer occurs from alkylsilane/tin compound to transition metal complex (TM mechanism). Therefore, the similar benzyl transfer might take place to form the benzylvanadium(V) species together with R_3SiX/R_3SnX. If the carbon–vanadium bond is cleaved homolytically to generate the benzyl radical and vanadium(IV), the reaction with molecular oxygen is likely to afford the aldehyde similarly as mentioned in ET mechanism (*path C*). Direct conversion from the benzylvanadium intermediate to the aldehyde is also conceivable (*path D*).

During the reaction, molecular oxygen reacts with carbon-centered radical to generate the peroxyradical, which is converted to the carbonyl compound. Molecular oxygen also oxidizes a low valent vanadium species to regenerate the vanadium species in its high oxidation state.[26]

Drastic substituent effect on the phenyl group of benzylsilanes suggests that the oxidation of benzylsilanes proceeds by ET mechanism. The relationships between the redox potentials ($E_{1/2}$) of benzylsilanes and the yields of **3** are as follows: **1a**, 0.85 V (88% yield); **1b**, 1.12 V (2%); **1c**, 1.22 V (trace); **1d**, 0.96 V (20%).[27] Reactivities of benzylsilanes appear to be dependent on their redox potentials. After one-electron oxidation, nucleophilic substitution at the benzyl position under an argon atmosphere (*path B*) leads to the benzyl ether **2** as a major product (eq. 1). Further oxidation to the carbonyl compound may not occur with ease under the conditions as shown in Table 5. Under an oxygen atmosphere, on the other hand, the benzyl radical is efficiently trapped by molecular oxygen to afford the carbonyl compound through *path A*.

Although benzyltin compounds undergo more facile oxidation rather than benzylsilanes ($E_{1/2}$: **1c**, 1.22 V; **7c**, 0.85 V),[27] electron-transfer process may not be favorable judging from the reactivities of cyclopropylmethyltin **7j**. As shown in eq. 4, cyclopropylketone **3j** was isolated in 60% yield and only chloride **4j** was observed as a minor product derived from the homoallylic radical species, which should be immediately generated from the cyclopropylmethyl radical. This result suggests that either ET process or homolytic scission of carbon–vanadium bond of a benzylvanadium species (*path C*) should be a minor pathway, and the ketone **3j** is derived by TM mechanism with *non-radical process* (*path D*).[28]

3. Conclusion

In conclusion, benzylsilane and benzyltin compounds were oxidized by oxovanadium(V) compound under an oxygen atmosphere to afford the corresponding aromatic aldehydes (ketones) and/or carboxylic acids directly. In the reaction of benzyltins, oxovanadium(V) compounds can be reduced to 0.5 molar amounts. Interestingly, benzylic alcohols or chlorides may not be involved as a key intermediate, indicating a direct pathway to the formation of carbonyl compounds. On the other hand, carboxylic acids are produced from the corresponding aldehydes by further oxidation under the oxovanadium–O_2 conditions.

Two possible mechanisms are considerable for the oxovanadium(V)–O_2-induced oxidation, electron-transfer (ET) mechanism and transmetallation (TM) mechanism, and the reaction pathway might be dependent on the substrate.

1. Reactivities of benzylsilanes are strongly controlled by their oxidation potentials, suggesting that the reaction of benzylsilanes may proceed via ET mechanism.
2. Benzyltins are oxidized mainly via non-radical process, judging from the reaction of cyclopropylmethyltin **7j**. TM mechanism is considered to operate in the oxidation.

As described above, the present reaction depends on the starting main-group metal compounds, substituents, and oxidation conditions, which even differentiate the oxidation pathway. These findings are considered to permit a versatile catalytic system for oxidative transformation of organometallic compounds.

4. Experimental

4.1. General

^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on a Varian Mercury 300 spectrometer. $CDCl_3$ was used as a solvent and residual chloroform (δ=7.24 ppm; ^{13}C, 77.0 ppm) or Me_4Si was used as an internal standard. Infrared spectra were recorded on Perkin–Elmer Model 1600 Series FT-IR. Mass spectra were measured on a JEOL JMS-DX-303 spectrometer using either electron impact (EI) or chemical ionization (CI) modes. Elemental analyses were carried out at the Analytical Center, Faculty of Engineering, Osaka University. Column chromatography was conducted on silica gel (Wakogel C-200). GPC was performed with Japan Analytical Industry LC-908 using chloroform as a solvent. *t*-BuOH was distilled from sodium *t*-butoxide and dried over 4 Å Molecular Sieves. Hexane was freshly distilled from CaH_2. THF was purchased from Kanto Chemical Co., Inc. as dehydrated stabilizer free grade, and was collected with argon stream introduced directly into the apparatus.

Benzylsilanes **1a–d** and benzyltins **7a–g** were prepared using a modified procedure for the reaction of the corresponding benzyl chlorides, Mg, and Me_3SiCl/Bu_3SnCl.[29] **7h**,[30] **7i**,[22] and **7j**[23] were synthesized according to the literature methods.

4-Methoxybenzyltrimethylsilane (1a) [17988-20-4]: ^{1}H NMR $\delta=-0.01$ (s, 9H), 2.01 (s, 2H), 3.78 (s, 3H), 6.79 (d, 2H, J=8.8 Hz), 6.92 (d, 2H, J=8.8 Hz). **4-Methylbenzyltrimethylsilane (1b)** [7450-04-6]: ^{1}H NMR δ=0.01 (s, 9H), 2.05 (s, 2H), 2.31 (s, 3H), 6.91 (d, 2H, J=8.3 Hz), 7.04 (d, 2H, J=8.3 Hz). **Benzyltrimethylsilane (1c)** [770-09-2]: ^{1}H NMR $\delta=-0.03$ (s, 9H), 2.06 (s, 2H), 6.97–7.23 (m, 5H). **1-Trimethylsilylmethylnaphthalene (1d)** [18410-58-7]: ^{1}H NMR δ=0.03 (s, 9H), 2.61 (s, 2H), 7.19 (d, 1H, J=6.9 Hz), 7.39 (dd, 1H, J=8.2, 6.9 Hz), 7.40–7.60 (m, 2H), 7.64 (d, 1H, J=8.2 Hz), 7.80–8.00 (m, 2H). **4-Tributyl-(4-methoxybenzyl)tin (7a)** [74260-40-5]: ^{1}H NMR δ=0.74–0.82 (m, 15H), 1.20–1.27 (m, 6H), 1.37–1.43 (m, 6H), 2.22 (s, 2H), 3.74 (s, 3H), 6.72 (d, 2H, J=8.1 Hz), 6.88 (d, 2H, J=8.1 Hz). **Tributyl-(4-methylbenzyl)tin (7b)** [74260-32-5]: ^{1}H NMR δ=0.76–0.89 (m, 15H), 1.22–1.29 (m, 6H), 1.39–1.41 (m, 6H), 2.24 (s, 2H), 2.25 (s, 3H), 6.85 (d, 2H, J=7.9 Hz), 6.95 (d, 2H, J=7.9 Hz). **Benzyltributyltin (7c)** [28493-54-1]: ^{1}H NMR δ=0.75–0.93 (m, 15H), 1.17–1.30 (m, 6H), 1.34–1.45 (m, 6H), 2.28 (s, 2H), 6.95–6.97 (m, 3H), 7.12–7.16 (m, 2H). **Tributyl-(2-methylbenzyl)tin (7d)** [174473-23-5]: ^{1}H NMR δ=0.74–0.86 (m, 15H), 1.19–1.26 (m, 6H), 1.36–1.53 (m, 6H), 2.17 (s, 3H), 2.26 (s, 2H), 6.85–7.05 (m, 4H); ^{13}C NMR δ=9.82, 13.77, 16.20, 20.31, 27.42, 29.07, 123.01, 125.76, 127.27, 129.67, 133.15, 141.95; IR (neat) 3009, 2956, 2924, 1601, 1487, 1460, 756, 743 cm^{-1}. Anal. Calcd for $C_{20}H_{36}Sn$: C, 60.78; H, 9.18. Found: C, 60.78; H, 8.99. **Tributyl-(4-chlorobenzyl)tin (7e)** [74260-39-2]: ^{1}H NMR δ=0.77–0.89 (m, 15H), 1.22–1.29 (m, 6H), 1.37–1.43 (m, 6H), 2.26 (s, 2H), 6.90 (d, 2H, J=8.4 Hz), 7.12 (d, 2H, J=8.4 Hz). **Tributyl-(4-cyanobenzyl)tin (7f)**: ^{1}H NMR δ=0.77–0.86 (m, 15H), 1.21–1.26 (m, 6H), 1.36–1.42 (m, 6H), 2.34 (s, 2H), 7.01 (d, 2H, J=8.1 Hz), 7.42 (d, 2H, J=8.1 Hz); ^{13}C NMR δ=9.68, 13.75, 19.93, 27.33, 28.98, 105.82, 119.64, 127.11, 131.92, 150.71; IR (neat) 3030, 2956, 2926, 2851, 2224, 1601, 1500, 1464, 1077, 837 cm^{-1}. Anal. Calcd for $C_{20}H_{33}NSn$: C, 59.14; H, 8.19; N, 3.45. Found: C, 59.07; H, 7.96; N, 3.45. **1-Tributylstannylmethylnaphthalene (7g)** [113688-53-2]: ^{1}H NMR δ=0.75–0.93 (m, 15H), 1.17–1.30 (m, 6H), 1.32–1.45 (m, 6H), 2.73 (s, 2H), 7.14 (d, 1H, J=6.6 Hz), 7.28 (dd, 1H, J=8.2 Hz, 6.6 Hz), 7.4–7.5 (m, 2H), 7.50 (d, 1H, J=8.2 Hz), 7.77–7.80 (m, 1H), 7.86–7.89 (m, 1H), ^{13}C NMR δ=10.08, 13.72, 15.94, 27.37, 29.03, 123.56, 123.58, 123.91, 124.82, 125.18, 125.58, 128.58, 130.83, 133.76, 140.19; IR (neat) 3058, 1577, 1508, 1394, 793, 774 cm^{-1}. Anal. Calcd for $C_{23}H_{36}Sn$: C, 64.06; H, 8.41. Found: C, 64.19; H, 8.13.

$VOCl_3$, $VO(acac)_2$, and $VO(OEt)_3$ are commercially available. $VO(OPr^i)_3$ was supplied from Nichia Chemical Industries Ltd.

4.2. Preparation of other oxovanadium(V) compounds[31]

To a well-dried 200 mL round-bottomed flask equipped with a condenser, magnetic stirring bar, and septum, hexane (120 mL) was added followed by trichlorooxovanadium(V) (1.73 g, 9.4 mL, 0.01 mol) under a stream of argon. The mixture was stirred at room temperature while the dry corresponding alcohol (1.1 or 2.2 molar amounts) was added dropwise via syringe with a constant flow of argon to remove HCl evolved from the reaction. Upon completion of the addition, the mixture was stirred for 1 h at room temperature. For dichloro(2,2,2-trifluoroethoxy)oxovanadium(V), the mixture was required to be heated to reflux for 30 min. The reflux condenser was then quickly replaced with a distillation head and the solvent was removed at atmospheric pressure. The product was distilled at reduced pressure to give the corresponding oxovanadium (V) compound as a yellow/orange liquid, which was stored under an inert atmosphere.

Dichloro(ethoxy)oxovanadium(V) [1801-77-0]: (78%, bp 55–60°C/5 mmHg). **Dichloro(isopropoxy)oxovanadium(V)** [1636-01-7]: (75%, bp 59–62°C/3 mmHg). **Chloro(diisopropoxy)oxovanadium(V)** [1636-00-6]: (83%, bp 55–58°C/1 mmHg). **Dichloro(2,2,2-trifluoroethoxy)oxovanadium(V)**: (82%, bp 80°C/115 mmHg).[21]

4.3. Oxidation of 4-methoxybenzyltrimethylsilane (1a) by $VO(OCH_2CF_3)Cl_2$ under an oxygen atmosphere

To a 20 mL two-necked round-bottomed flask equipped with a reflux condenser, magnetic stirring bar, septum, and a balloon charged with O_2 were added *t*-BuOH (2 mL), $VO(OCH_2CF_3)Cl_2$ (355.3 mg, 1.5 mmol), and then 4-methoxybenzylsilane **1a** (97.2 mg, 0.5 mmol), and the mixture was stirred at 50°C for 20 h. The reaction was quenched with 1 M HCl solution, and the mixture was extracted with Et_2O. The combined organic layer was washed with brine and was dried over $MgSO_4$. The organic solvent was evaporated and the resulting crude product was purified by silica gel column chromatography to give 4-methoxybenzaldehyde (**3a**, 88%) and 1-*t*-butoxymethyl-4-methoxybenzene (**2a**, 4%).[32]

4.4. General procedure for oxidation of benzyltins with 50 mol% of $VO(OCH_2CF_3)Cl_2$

To a 20 mL two-necked round-bottomed flask equipped with a reflux condenser, magnetic stirring bar, septum, and a balloon charged with O_2 were added *t*-BuOH (4 mL), $VO(OCH_2CF_3)Cl_2$ (118.4 mg, 0.5 mmol), and then benzyltin **7** (1 mmol), and the mixture was stirred under the conditions listed in Table 4. The reaction was quenched with 1 M HCl solution, and the mixture was extracted with Et_2O. The combined organic layer was washed with aqueous KF (if necessary) and brine, and was dried over $MgSO_4$. The organic solvent was evaporated and the resulting crude product was purified by silica gel column chromatography to give **3** and/or **6**.

All of the products are known compounds, and their spectral data are in good agreement with those of authentic samples. **4-Methoxybenzaldehyde (3a)**: [123-11-5]. **4-Methylbenzaldehyde (3b)**: [104-87-0]. **Benzaldehyde (3c)**: [100-52-7], **2-Methylbenzaldehyde (3d)**: [529-20-4]. **4-Chlorobenzaldehyde (3e)**: [104-88-1]. **4-Cyanobenzaldehyde (3f)**: [105-07-7]. **1-Naphthaldehyde (3g)**: [66-77-3]. **Acetophenone (3h)**: [98-86-2]. **Methyl 3-oxo-3-phenylpropionate (3i)**: [614-27-7]. **Cyclopropylphenyl ketone (3j)**. [3481-02-5]; **4-Methoxybenzoic acid (6a)**: [100-09-4]. **4-Methylbenzoic acid (6b)**: [99-94-5]. **Benzoic acid (6c)**: [65-85-0]. **2-Methylbenzoic acid (6d)**: [118-90-1]. **4-Chlorobenzoic acid (6e)**: [74-11-3]. **4-Cyanobenzoic acid (6f)**: [619-65-8]. **1-Naphthoic acid (6g)**: [86-55-5].

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