Pergamon

Tetrahedron Letters 42 (2001) 1961–1963

TETRAHEDRON
LETTERS

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

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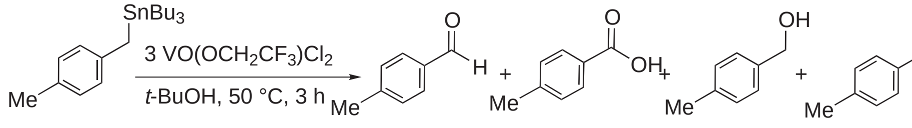
Received 9 January 2001; accepted 17 January 2001

Abstract—Benzyltin compounds were oxidized by oxovanadium(V) compound under an oxygen atmosphere to afford the corresponding aromatic aldehydes (ketone) and/or carboxylic acids. © 2001 Elsevier Science Ltd. All rights reserved.

Organotin compounds undergo facile oxidation to generate other functional groups via carbon–tin bond scission.[1] Among these reactions, transformation to the oxygen-containing group is one of the most important reactions from a synthetic viewpoint. In particular, allylic and benzylic tin compounds are readily converted to the corresponding alcohols or their derivatives by metallic oxidants such as Mn(IV),[2] Ce(IV),[3] or Tl(III),[4] organic oxidants such as MCPBA,[5] or photoinduced oxidation.[6] In the course of our study on oxovanadium(V)-induced oxidation of Group 14 metal compounds,[7,8] we found that benzylic tin compounds can be oxidized directly to the corresponding aromatic aldehydes (ketone) and/or carboxylic acids by oxovanadium(V) compound under an oxygen atmosphere.[9]

When 4-methylbenzyltributyltin (**1a**) was treated with 3 molar amounts of $VO(OCH_2CF_3)Cl_2$[10] in *t*-BuOH under an argon atmosphere, tolualdehyde **2a**, benzyl alcohol **4a**, and benzyl chloride **5a** were obtained in 38, 5 and 35% yields, respectively. The yield of aldehyde **2a** was increased to 60% together with carboxylic acid **3a** (19% yield) when the reaction was performed under an oxygen atmosphere (Eq. (1)).



(1)

	1a	2a	3a	4a	5a
Ar atmosphere		38%	0%	5%	35%
O_2 atmosphere		60%	19%	trace	trace

Table 1. Oxidation of **1a** by oxovanadium(V) compound under an oxygen atmosphere[a]

Entry	Oxovanadium (mol%)		Time (h)	Yields (%)			Recovery of **1a** (%)
				2a	**3a**	**4a**	
1	$VO(acac)_2$	(300)	3	5	–	4	75
2	$VO(OEt)_3$	(300)	3	20	–	37	20
3	$VO(OPr^i)_3$	(300)	3	36	–	45	–
4	$VO(OPr^i)_2Cl$	(300)	3	64	19	12	–
5	$VO(OCH_2CF_3)Cl_2$	(300)	3	60	19	Trace	–
6	$VO(OPr^i)_2Cl$	(50)	72	40	–	3	29
7	$VO(OCH_2CF_3)Cl_2$	(50)	36	–	100	–	–

[a] All reactions were performed at 50°C.

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PII: S0040-4039(01)00083-1

Table 2. Oxovanadium(V)-catalyzed oxidation of benzyltins

$$\underset{\mathbf{1}}{\mathrm{ArCH_2SnBu_3}} \xrightarrow[t\text{-BuOH, 50°C}]{\text{50 mol\% oxovanadium reagent, } O_2 \text{ atmosphere}} \underset{\mathbf{2}}{\mathrm{ArCHO}} + \underset{\mathbf{3}}{\mathrm{ArCOOH}}$$

Entry	Ar	Oxovanadium	Time (h)	Total yield (%) **2**+**3** (**2**/**3**)	Recovery of **1** (%)
1	4-MeO-C_6H_4	$VO(OCH_2CF_3)Cl_2$	24	59 (55/4)[a,b]	–
2	4-MeO-C_6H_4	$VO(OPr^i)_2Cl$	72	78 (63/15)[b]	–
3	4-Me-C_6H_4	$VO(OCH_2CF_3)Cl_2$	36	100 (0/100)	–
4	2-Me-C_6H_4	$VO(OCH_2CF_3)Cl_2$	72	100 (0/100)	–
5	C_6H_5	$VO(OCH_2CF_3)Cl_2$	72	62 (41/21)	23
6	4-Cl-C_6H_4	$VO(OCH_2CF_3)Cl_2$	72	95 (64/31)	4
7	4-NC-C_6H_4	$VO(OCH_2CF_3)Cl_2$	72	25 (25/0)	18
8	1-Naphthyl	$VO(OCH_2CF_3)Cl_2$	24	86 (58/38)[c]	–

[a] The reaction was carried out at room temperature.

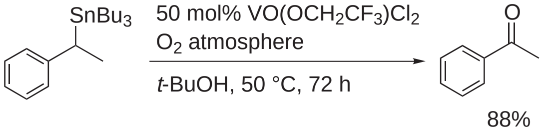
[b] Benzyl alcohol **4** was also obtained in 9% yield.

[c] Benzyl alcohol **4** and benzyl chloride **5** were obtained in 5 and 4% yields, respectively.

The reaction conditions were optimized and the representative results are shown in Table 1. 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 the low yield of **2a** (entries 1–3), indicating that at least one chloride ligand was required on oxovanadium(V) compound. When $VO(OPr^i)_2Cl$ was employed, the total yield of **2a** and **3a** was up to 83%, although the formation of **4a** could not be suppressed (entry 4). Use of $VO(OCH_2CF_3)Cl_2$ resulted in the selective formation of **2a** and **3a** (79% total yield, entry 5). It should be noted that the amount of oxovanadium(V) compound could be reduced to 0.5 molar amount. Catalytic activity of $VO(OPr^i)_2Cl$ was not enough to accomplish the reaction, and **1a** was recovered in 29% yield even after 72 h. On the other hand, $VO(OCH_2CF_3)Cl_2$ showed the superior catalytic activity, giving only **3a** quantitatively (entries 6 and 7). Oxovanadium(V) compound (50 mol%) can induce a direct conversion of the benzyltin to the corresponding aromatic aldehyde and/or acid under oxygen atmosphere, in which at least 4 equivalents of oxidant should be required.

Table 2 shows the examples for the reaction of various benzyltins under the oxovanadium-catalyzed oxidation conditions.[11] Since 4-methoxybenzyltin was too susceptible to oxidative conditions, the use of a milder oxidant, $VO(OPr^i)_2Cl$, was more suitable to afford the aldehyde **2** and carboxylic acid **3** 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-methyl-benzyltins underwent facile oxidation to give the acids **3** quantitatively (entries 3 and 4).

This transformation can be applied to secondary benzyltin compounds, giving the corresponding ketones selectively. As shown in Eq. (2), 1-phenylethyltributyltin was converted to acetophenone in 88% yield as a sole isolable product.



(2)

The precise reaction mechanism is unsolved, but the following results suggest a direct conversion to carbonyl/carboxyl compound. It is noteworthy that benzylic alcohol **4** is *not* involved as a key intermediate.[12] When 4-methoxybenzyl alcohol was treated under similar oxidation conditions as employed above, the reaction became very complicated, giving a complex mixture including the alcohol and the aldehyde in 11 and 14% yields, respectively. On the other hand, benzaldehydes **2** were quantitatively converted to the acids **3** under similar conditions. Therefore, the present oxovanadium-O_2 oxidation system appears to induce a transformation of benzyltins, not to the alcohols but to the aldehydes or their vanadium complexes directly, and the thus-formed species may be converted to the acids, especially effectively in the catalytic reaction.

As described above, a useful synthetic method for direct catalytic oxidation of benzyltins to the corresponding aldehydes/acids was achieved by the oxovanadium(V)-induced oxidation. These findings are considered to permit a versatile catalytic system for oxidative transformation of organometallic compounds.

Acknowledgements

The use of the facilities of the Analytical Center, Faculty of Engineering, Osaka University, is acknowledged. This work was partly supported by a Grant-in-Aid for Scientific Research (No. 11450341) from the Ministry of Education, Science, and Culture, Japan.

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9. Other examples for direct conversion of benzyltins to the carbonyl compounds; Corey, E. J.; Walker, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 8108; Bachiocchi, E.; Ioele, M. *J. Org. Chem.* **1995**, *60*, 5504.
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11. **General procedure**: To a 20 mL two-necked round-bottomed flask equipped with magnetic stirrer, septum, reflux condenser, and a balloon charged with O_2 was added *t*-BuOH (4 mL), $VO(OCH_2CF_3)Cl_2$ (0.5 mmol) and then benzyltin **1** (1 mmol), and the mixture was stirred under the conditions listed in the Table 2. The reaction was quenched with a 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 **2** and/or **3**.
12. Kirihara et al. also reported a similar phenomena in the oxidative ring-opening reaction of cyclopropanols: Kirihara, M.; Ichinose, M.; Takizawa, S.; Momose, T. *Chem. Commun.* **1998**, 1691.