Pergamon

Tetrahedron Letters 43 (2002) 1269–1271

TETRAHEDRON
LETTERS

A novel catalytic activity of bismuth(III) salts in palladium(II)-catalyzed atom economical Michael-type hydroarylation of nitroalkenes with aryltin compounds

Toshiyuki Ohe and Sakae Uemura*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

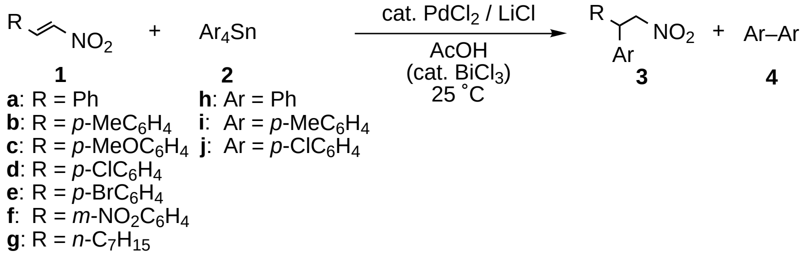
Received 12 November 2001; revised 13 December 2001; accepted 14 December 2001

Abstract—A novel catalytic effect of bismuth(III) salts such as $BiCl_3$, Bi_2O_3, and $Bi(NO_3)_3·5H_2O$ has been disclosed in new palladium(II)-catalyzed Michael-type hydroarylation of nitroalkenes with aryltin compounds. The reaction is atom economical in the tin compounds and slightly fewer than four aryl groups of tetraaryltins can be transferred to the products. © 2002 Elsevier Science Ltd. All rights reserved.

Recently, we have reported palladium(II)-catalyzed atom economical Michael-type hydroarylation of α,β-unsaturated ketones and aldehydes with aryltin compounds[1] as one of our series of studies on organic transformations using organoheteroatom compounds such as organoborons,[2] organoantimonys,[3] and organobismuths.[4] We now communicate our preliminary results of application of this reaction to nitroalkenes to give the corresponding hydroarylation products[5] where various bismuth(III) salts work as good catalysts for improving their yield. The catalysis of bismuth(III) salts on a variety of organic transformations including carbon-carbon bond forming reactions is of current interest.[6]

At first, β-nitrostyrene (**1a**, 2 mmol) was treated with tetraphenyltin (**2h**, 0.5 mmol) in the presence of $PdCl_2$ (0.02 mmol) and LiCl (4 mmol)[7] in AcOH (20 mL) at 25°C for 20 h. As a result, the Michael-type hydroarylation product, 2-nitro-1,1-diphenylethane (**3ah**), and biphenyl (**4h**) were obtained in 14% (0.28 mmol) and 23% (0.23 mmol) isolated yields, respectively (Eq. (1)). The use of five times $PdCl_2$ (0.10 mmol) resulted in the increase of both **3ah** (52% yield, 1.04 mmol) and **4h** (39% yield, 0.39 mmol) (Table 1, Entry 1). Here, the yield of **3ah** was much improved than that of **4h** and just above two phenyl moieties of **2h** were transferred to the product **3ah**.

Since we have already shown that antimony(III) chloride worked quite effectively in Pd(II)-catalyzed Michael-type hydroarylation of α,β-unsaturated ketones and aldehydes with organoborons,[2b,2c] we looked for various Lewis acidic metal salts to accomplish a highly atom economical transformation producing **3ah**. Eventually, it was disclosed that a variety of bismuth(III) salts such as $BiCl_3$, Bi_2O_3, and $Bi(NO_3)_3·5H_2O$ worked as quite effective catalysts for this



(1)

---

* Corresponding author.

PII: S0040-4039(01)02387-5

Table 1. Pd(II)-catalyzed hydroarylation of nitroalkenes (**1**) using aryltin compounds (**2**) in the presence and absence of Bi(III) salt[a]

Entry	**1**	**2**	Bi(III) salt	(mmol)	Isolated yield (%)[b]	
	R	Ar			**3**	**4**
1	Ph	Ph	$BiCl_3$	0.1	83 (52[c])	16 (39[c])
2	Ph	Ph	Bi_2O_3	0.05	85	15
3	Ph	Ph	$Bi(NO_3)_3 \cdot 5H_2O$	0.1	81	9
4	p-MeC_6H_4	Ph	$BiCl_3$	0.1	82 (59)	10 (31)
5	p-$MeOC_6H_4$	Ph	$BiCl_3$	0.1	81 (50)	15 (33)
6	p-ClC_6H_4	Ph	$BiCl_3$	0.1	88 (50)	6 (43)
7	p-BrC_6H_4	Ph	$BiCl_3$	0.1	85 (53)	13 (35)
8	m-$NO_2C_6H_4$	Ph	$BiCl_3$	0.1	77 (37)	16 (36)
9	n-C_7H_{15}	Ph	$BiCl_3$	0.1	78 (68)	3 (16)
10	Ph	p-MeC_6H_4	$BiCl_3$	0.1	76 (67[c])	17 (19[c])
11	p-ClC_6H_4	p-MeC_6H_4			(63)	(24)
12	Ph	p-ClC_6H_4	$BiCl_3$	0.1	13 (13[c])	62 (71[c])
13	Ph	Ph_3SnCl[d]	$BiCl_3$	0.1	27 (39[c])	37 (44[c])
14	Ph	Ph_2SnCl_2[e]	$BiCl_3$	0.1	70 (70[c])	13 (19[c])

[a] Reaction conditions: **1** (1 mmol), **2** (0.25 mmol), $PdCl_2$ (0.05 mmol) and LiCl (2 mmol) in AcOH (10 mL) at 25°C for 20 h.

[b] The yields obtained in the absence of Bi(III) salt are shown in parentheses. Based on **2**; 1 mmol as Ar group: 1 mmol of **3** and 0.5 mmol of **4** correspond to 100% yield, respectively.

[c] Double scale reaction.

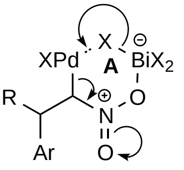
[d] 0.33 mmol.

[e] 0.5 mmol.

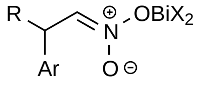
transformation[8,9] as in the cases of the so far known $BiCl_3$ catalysis in Mukaiyama-aldol and some Michael-type reactions.[10] Thus, the addition of $BiCl_3$ (0.1 molar amount of **1a**) improved the yield of **3ah** from 52% to 83% by the sacrifice of the yield of **4h** from 39% to 16% as shown in Entry 1. Similar trends were also observed in the reactions using various nitrostyrenes having a substituent at the aromatic ring and 1-nitro-1-nonene (Table 1). The most atom economical reaction we found so far is that between 1-(p-chlorophenyl)-2-nitroethene (**1d**) and tetraphenyltin (**2h**) in the presence of $BiCl_3$, where 88% of hydroarylation product **3dh** was isolated, showing that 3.52 phenyl moieties of Ph_4Sn were transferred to the product **3dh**. Some other phenyl moieties were employed to produce biphenyl (6% yield, 0.24 phenyl moieties) (Entry 6). At present, this catalytic reaction could not be applied to α-alkyl-substituted nitroalkenes such as 2-nitro-1-phenyl-1-propene and 1-nitro-1-cyclohexene.

Among other aryltin compounds examined, tetrakis(p-methylphenyl)tin (**2i**) and diphenyltin dichloride gave reasonable yield of the corresponding hydroarylation product, **3ai**, **3di**, and **3ah**, respectively (Entries 10, 11, and 14), but in the cases of tetrakis(p-chlorophenyl)tin (**2j**) (Entry 12), triphenyltin chloride (Entry 13), and tributylphenyltin the yield of **3** was lower even in the presence of $BiCl_3$. Other bismuth(III) salts such as Bi_2O_3, $Bi(NO_3)_3 \cdot 5H_2O$ were also revealed to be as effective as $BiCl_3$ (Entries 2 and 3).

The reaction seems to proceed via transmetallation of Sn(IV) moiety of aryltins by Pd(II) to give an ArPd(II)X (X = Cl or OAc) species which adds to nitroalkenes activated by coordination of Bi(III) salt to the oxygen of nitro group to afford such an alkylpalladium species as **A**. From the species **A**, a palladium species is eliminated in the state of divalent Pd to give a bismuth enolate **B**, protonolysis of which gives the hydroarylation product. Further study to widen the applicability of this hydroarylation including enantioselective reaction[11] and to clarify the reaction mechanism is now in progress.



A



B

References

1. Ohe, T.; Wakita, T.; Motofusa, S.-i.; Cho, C. S.; Ohe, K.; Uemura, S. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2149–2155.
2. (a) Cho, C. S.; Itotani, K.; Uemura, S. *J. Organomet. Chem.* **1993**, *443*, 253–259; (b) Cho, C. S.; Motofusa, S.-i.; Uemura, S. *Tetrahedron Lett.* **1994**, *35*, 1739–1742; (c) Cho, C. S.; Motofusa, S.-i.; Ohe, K.; Uemura, S.; Shim, S. C. *J. Org. Chem.* **1995**, *60*, 883–888; (d) Cho, C. S.; Uemura, S. *J. Organomet. Chem.* **1994**, *465*, 85–92; (e) Cho, C. S.; Ohe, T.; Uemura, S. *J. Organomet. Chem.* **1995**, *496*, 221–226.
3. (a) Cho, C. S.; Tanabe, K.; Uemura, S. *Tetrahedron Lett.* **1994**, *35*, 1275–1278; (b) Cho, C. S.; Motofusa, S.-i.; Ohe, K.; Uemura, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2341–2348; (c) Cho, C. S.; Tanabe, K.; Itoh, O.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 274–275; (d) Matoba, K.; Motofusa, S.-i.; Cho, C. S.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **1999**, *574*, 3–10.

4. (a) Cho, C. S.; Ohe, T.; Itoh, O.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1992**, 453–454; (b) Cho, C. S.; Yoshimori, Y.; Uemura, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 950–957.
5. Examples of transition metal-catalyzed or -mediated Michael-type conjugate addition to nitroalkenes using organoheteroatom compounds: (a) Organoboronic acids-Rh(I) (catalyzed), Hayashi, T.; Senda, T.; Ogasawara, M. *J. Am. Chem. Soc.* **2000**, *122*, 10716–10717; (b) dialkylzinc-Cu(II) (catalyzed), Alexakis, A.; Benhaim, C. *Org. Lett.* **2000**, *2*, 2579–2581; (c) Ongeri, S.; Piarulli, U.; Jackson, R. F. W.; Gennari, C. *Eur. J. Org. Chem.* **2001**, 803–807; (d) aryl iodide-Pd (mediated), Denmark, S. E.; Schnute, M. E. *J. Org. Chem.* **1995**, *60*, 1013–1019. Compared to these examples, where an excess amount of either organoborons or dialkylzinc and also a stoichiometric amount of Pd salt were employed, our present method is atom economical in organoheteroatom compounds by use of a catalytic amount of Pd salt.
6. *Organobismuth Chemistry*; Suzuki, H.; Matano, Y., Eds. Elsevier: London, 2001; Chapter 5.
7. The role of LiCl is to solubilize $PdCl_2$ and also to coordinate to organotins making transmetallation with Pd salt facile as reported in Ref. 1.
8. In the case of Pd(II)-catalyzed hydroarylation of α,β-unsaturated ketones and aldehydes using organoborons, $BiCl_3$ showed only a low catalytic activity as reported in Refs. 2b,c.
9. The metal salts such as $BF_3 \cdot Et_2O$, $AlCl_3$, and $InCl_3$ did not show any positive catalytic effect, while $SbCl_3$ showed a slightly less catalytic activity than $BiCl_3$.
10. (a) Ohki, H.; Wada, M.; Akiba, K.-y. *Tetrahedron Lett.* **1988**, *29*, 4719–4722; (b) Wada, M. *Yuki Gosei Kagaku Kyokaishi (J. Synth. Org. Chem. Jpn.)* **1990**, *48*, 960–961.
11. In the paper of Ref. 5a, a quite highly enantioselective hydroarylation of nitroalkenes was reported. Under our present conditions, the reaction did not proceed at all with $PhB(OH)_2$ in place of organotin compounds.