A Novel Transmetallation of Triarylstibanes into Arylboronate: Boro-induced Ipso-deantimonation and Its Theoretical Calculation

Shuji Yasuike,[1,2] Kazuhide Nakata,[3] Weiwei Qin,[1]
Toshiyuki Kaji,[2] and Jyoji Kurita*[1]
[1]*Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-1181*
[2]*Organization for Frontier Research in Preventive Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-1181*
[3]*Science Research Center, Hosei University, 2-17-1 Fujimi, Chiyoda-ku, Tokyo 102-8160*

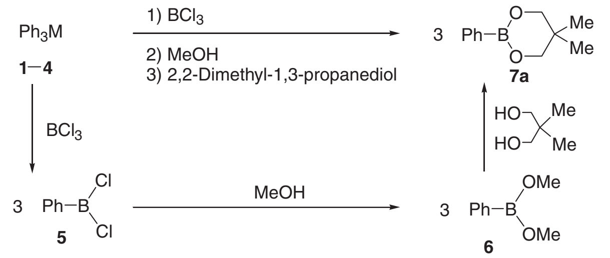
(Received August 1, 2006; CL-060876; E-mail: j-kurita@hokuriku-u.ac.jp)

Treatment of triarylstibanes with boron trichloride followed by derivatization with methanol and 1,3-propanediol afforded arylboronates in good yield with all three aryl groups on the antimony being utilized. Theoretical calculation of the reaction pathway revealed that the transformation proceeds through boro-induced ipso-deantimonation and the reactivity of Ph_3M ($M = P$, As, Sb, and Bi) should be governed by the stability of the corresponding cations Ar_2M^+.

The utility of arylboronic acids and their esters in organic synthesis has attracted much attention in recent years, particularly through developments in the Suzuki–Miyaura coupling reaction.[1,2] Several approaches for the synthesis of arylboron derivatives have been reported.[2–4] Among these, it is known that the propensity of arylsilanes[5] and -stannanes[6] to undergo ipso-substitution allows smooth transmetallation from silicon and tin to boron by treatment with boron halides (BX_3), leading to $ArBX_2$. However, the transmetallation of organo-pnictogen (group 15 element: P, As, Sb, and Bi) compounds into arylboron compounds has not been reported so far. Herein, we describe the first approach of the metal exchange reaction from group 15 element to boron. In the present studies, treatment of triarylstibanes (Ar_3Sb) with boron trichloride (BCl_3) followed by derivatization with methanol and 2,2-dimethyl-1,3-propanediol afforded boronates in good yield with all three aryl groups on the antimony being utilized.

We first examined the reaction of triphenylpnictogens **1**–**4** with BCl_3 (3.6 equiv.), followed by quenching with methanol and derivatization with 2,2-dimethyl-1,3-propanediol. The results including reaction conditions are summarized in Table 1. Triphenylstibane **3a** ($M = Sb$) was effectively converted to phenylboronate **7a**, though **1** ($M = P$) and **2** ($M = As$) showed no ability to transform (Entries 1–3). It should be noted that all three phenyl groups on the antimony participated in the reaction of **3a** with BCl_3. On the other hand, the reaction of **4** ($M = Bi$) with BCl_3 gave a side product $Ph_2B–O–BPh_2{\cdot}H_2O$, which might result from the reaction of Ph_2BCl with water during work-up of the reaction mixture. This result indicates that the Ph–Bi bond in **4** would be more reactive than the Ph–Sb bond in **3a**, and $PhBCl_2$ initially formed can react with the phenylbismuthane derivatives to form Ph_2BCl (Entries 4 and 5). Thus, only **3a** was converted to dichloroborane intermediate **5**, which was transformed to **7a** via **6** by successive treatment with methanol and 1,3-propanediol.[7] Also apparent was that treatment of Ph_2SbCl and $PhSbCl_2$ with BCl_3 (2.4 and 1.2 equiv., 0 °C/2 h) resulted in similar transmetallation to afford **7a** in 61 and 54% yields, respectively. These results revealed that the three phenyl groups on the antimony in **3a** reacted with BCl_3 one by one via Ph_2SbCl and $PhSbCl_2$.

Table 1. Reaction of Ph_3M ($M = P$, As, Sb, and Bi) with BCl_3[a]

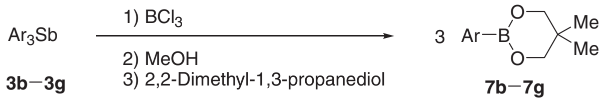


Entry	M	Conditions °C/h	Yield/%[c]	
			7a	Ph_3M:Recovery
1	P (**1**)	0/2	0	97
2	As (**2**)	0/2	0	98
3	Sb (**3a**)	0/2	88	0
4[b]	Bi (**4**)	0/2	35	0
5[b]	Bi (**4**)	−78/4	44	0

[a]All reactions were carried out using Ph_3M (1 mmol), BCl_3 (3.6 mmol), MeOH (3 mL), and 2,2-dimethyl-1,3-propanediol (10 mmol). [b]There was a by-product [$Ph_2B–O–BPh_2{\cdot}H_2O$ (Entry 4; 54%, Entry 5; 16%)]. [c]Isolated yield.

In order to evaluate the generality and applicability of this transmetallation, we attempted a reaction between BCl_3 and a variety of triarylstibanes, and the results are summarized in Table 2. Triarylstibanes **3b**–**3g** were treated under the standard conditions employed for entry 3 in Table 1. In all cases, the corresponding arylboronates **7b**–**7g** were formed in good yield

Table 2. Boro-induced ipso-deantimonation[a]



Entry	Substrate	Ar	Yield/%[b]
1	**3b**	4-Methoxyphenyl	57 (**7b**)
2	**3c**	4-Methylphenyl	85 (**7c**)
3	**3d**	4-Fluorophenyl	83 (**7d**)
4	**3e**	4-Chlorophenyl	92 (**7e**)
5	**3f**	2-Methylphenyl	68 (**7f**)
6	**3g**	1-Naphthyl	80 (**7g**)

[a]All reactions were carried out using Ar_3Sb (1 mmol), BCl_3 (3.6 mmol), MeOH (3 mL), and 2,2-dimethyl-1,3-propanediol (10 mmol). [b]Isolated yield.

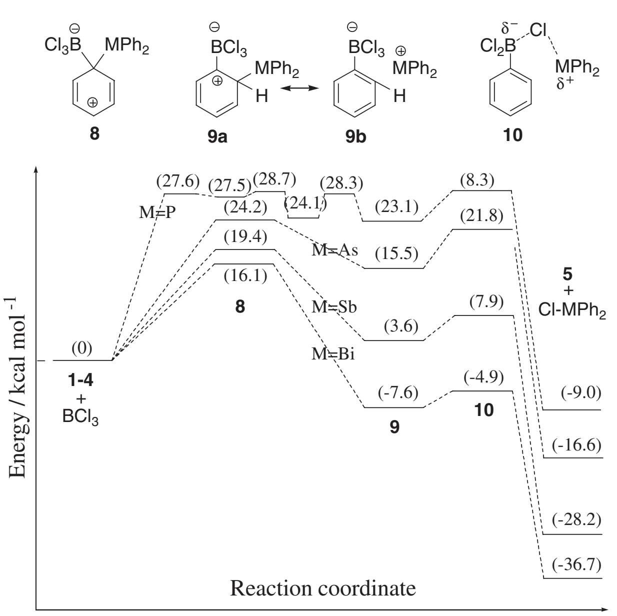


Figure 1. Calculated reaction coordinates for **1–4** to give **5**. Numbers in parentheses are relative energies against reactants.

with all three aryl groups on the antimony being used.[8] Also apparent was that the position of the substituent on the aryl group was retained during the reaction. These results imply that the reaction took place through boro-induced ipso-deantimonation, which will be the first example of the ipso-attack against organostibanes by boron halide.

We next examined a theoretical calculation (RHF/Lan L2DZ level) to reveal the difference in the reactivity toward the above transmetallation (Figure 1).[9] The reaction initially proceeds from an electrophilic attack of BCl_3 on the ipso-position of **1–4** to form transition state **8** whose structure is similar to those of Wheland complexes. The transformation of Ph_3M into **8** may be the rate-determining step for all substrates; activation energies are 16.1 kcal mol^{-1} for M = Bi, 19.4 kcal mol^{-1} for M = Sb, and 24.2 kcal mol^{-1} for M = As. Then, the Ph_2M moiety rearranges on the ortho-position to give intermediate **9** which can be described as a resonance hybrid between **9a** and **9b**. In the second step, one of the chloride ions moved rapidly toward M to give the product **5** and Ph_2MCl. Structures of the transition states **10** are similar to those of **9**. A similar pathway for **1** (M = P) was also found at the same theoretical level, though the Wheland complex **8** was obtained as an intermediate accompanied by two transition states in front and behind. The Ph_2P moiety in **9b** moved on other ortho-position in order to change the conformation of the phenyl rings, which make the chloride transfer feasible. Calculated activation energy of this reaction was 28.7 kcal mol^{-1}. All these proposed mechanisms are supported by the experimental results such as the ipso-attack and the order of reactivity. It has become apparent that the reactivity of this type of reaction is governed by the stability of the intermediate **9**, or, more essentially, by the stability of the cation Ar_2M^+. These results imply that information concerning the stability of the cations provides guidelines for the synthesis of various arylboronates.

In conclusion, we have disclosed a novel transmetallation of triarylstibanes into arylboronates based on boro-induced ipso-deantimonation and its divisional theoretical calculation of the reaction pathway was made. Synthetic application and work on the detailed reaction mechanism are in progress.

This work was supported by a Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Culture, Sports, Sciences and Technology of Japan (to J. K.); the "Academic Frontier" Project for Private Universities from the Ministry Education, Culture, Sports, Sciences and Technology of Japan (to S. Y. and T. K.); and the Specific Research Fund of Hokuriku University, which is gratefully acknowledged.

References and Notes

1 a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457. b) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633.

2 A. Suzuki, H. C. Brown, *Organic Syntheses via Boranes*, Aldrich Chemical Company, Inc., Milwaukee, Wisconsin, **2003**, Vol. 3.

3 a) D. S. Matteson, *The Chemistry of the Metal–Carbon Bond*, ed. by F. R. Hartley, S. Patai, Wiley, New York, **1987**, Vol. 4, p. 307. b) N. Miyaura, K. Maruoka, *Synthesis of Organometallic Compounds*, ed. by S. Kojima, Wiley, New York, **1997**, p. 345.

4 a) P.-E. Broutin, I. Čerňa, M. Campaniello, F. Leroux, F. Colobert, *Org. Lett.* **2004**, *6*, 4419. b) M. Murata, T. Oyama, S. Watanabe, Y. Masuda, *J. Org. Chem.* **2000**, *65*, 164, and reference cited therein.

5 For recent examples, see: a) Z. Zhao, V. Snieckus, *Org. Lett.* **2005**, *7*, 2523. b) E. Hupe, M. I. Calaza, P. Knochel, *Chem. Commun.* **2002**, 1390. c) M. Pottländer, N. Palmer, P. Knochel, *Synlett* **1996**, 573.

6 For recent examples, see: a) G. J. P. Britovsek, J. Ugolotti, A. J. P. White, *Organometallics* **2005**, *24*, 1685. b) M. Schulte, F. P. Gabbaï, *Can. J. Chem.* **2002**, *80*, 1308. c) B. Schilling, V. Kaiser, D. E. Kaufmann, *Chem. Ber.* **1997**, *130*, 923.

7 M. Lauer, H. Böhnke, R. Grotstollen, M. Salehnia, G. Wulff, *Chem. Ber.* **1985**, *118*, 246.

8 All reactions were carried out under argon using standard Schlenk techniques. Boron trichloride (1.0 M solution in dichloromethane, 3.6 mL, 3.6 mmol, 3.6 equiv.) was added to a stirred solution of triarylstibane **3a–3g** (1.0 mmol) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 2 h at the same temperature, and then allowed to warm at room temperature. The solvent was removed under reduced pressure and the residual oil was dissolved in methanol (3 mL). After stirring the mixture for 30 min at room temperature, 2,2-dimethyl-1,3-propanediol (1.06 g, 10 mmol) was added and stirring was continued for 1 h. The solvent was removed under reduced pressure and the crude product was purified by silica-gel column chromatography using hexane/CH_2Cl_2 as eluents. **7a**: 501 mg, mp 62–64.5 °C, **7b**: 376 mg, mp 54–56 °C, **7c**: 520 mg, mp 92–95 °C, **7d**: 517 mg, mp 65–67 °C, **7e**: 618 mg, mp 97–99 °C, **7f**: 416 mg, oil, **7g**: 576 mg, mp 68–70 °C.

9 All calculations were performed at the RHF/LanL2DZ level with Gaussian 03 program: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford CT, **2004**.

Published on the web (Advance View) November 11, 2006; doi:10.1246/cl.2006.1402