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Oxidation of *gem*-Borylsilylalkylcoppers to Acylsilanes with Air

Junichi Kondo,[†] Hiroshi Shinokubo,*[,‡] and Koichiro Oshima*[,†]

Department of Material Chemistry, Graduate School of Engineering,
Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan, and
Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku,
Kyoto 606-8502, Japan

oshima@orgrxn.mbox.media.kyoto-u.ac.jp; hshino@kuchem.kyoto-u.ac.jp

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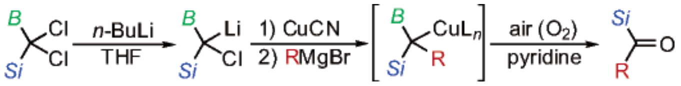
ABSTRACT



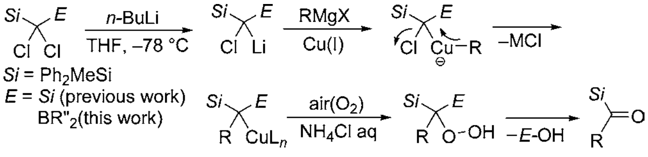
1-Boryl-1-silylalkylcoppers react with molecular oxygen in the presence of pyridine to afford acylsilanes efficiently. The one-pot process consists of two reactions: alkylation of 1-boryl-1-chloro-silylmethyllithium with Grignard reagents in the presence of copper(I) cyanide and aerobic oxidation of the alkylcopper species. This procedure enables us to access the divergent synthesis of acylsilanes.

Nowadays, organoboron compounds have fairly wide utilities and are indispensable not only for synthetic chemistry but also for modern science ranging from material science to life science.[1] Among a number of boron-based reagents, α-borylcarbanions, which are *gem*-dimetallic species, have been proven to be considerably useful synthetic intermediates to participate in Wittig-type olefination with carbonyl compounds to afford substituted alkenes.[1,2] In addition, this type of boron reagent is also known to react with dioxygen to give rise to carbonyl compounds.[3] These reagents are more effective with the assistance of their vacant orbital and small atom size in comparison to the silicon analogues. On the other hand, it was reported that the olefination reactions of carbonyl compounds with trimetallic species, α-boryl-α-silylcarbanions, provided borylalkenes via faster *β*-oxygen elimination of silicon than boron.[4]

Here, we wish to report the synthesis of acylsilanes[5] by aerobic oxidation of 1-boryl-1-silylalkylcoppers through selective elimination of the boryl group from intermediary peroxy species. In addition, we illustrate a facile preparative method for the synthesis of *gem*-borylsilylalkylcoppers via 1,2-migration on ate-type copper carbenoids.

We have previously reported that the reaction of 1,1-disilylalkylcoppers with air furnishes acylsilanes in both protic and aprotic conditions (Scheme 1).[6] The initial step is alkylative metalation of the lithium carbenoid with RMgX and a stoichiometric amount of CuCN to afford the 1,1-disilylalkylcopper, which is then converted to a peroxide

Scheme 1. Synthesis of Acylsilanes from Disilylalkylcoppers via Aerobic Oxidation



[†] Graduate School of Engineering, Kyoto University.

[‡] Graduate School of Science, Kyoto University.

(1) (a) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988. (b) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 11.

(2) (a) Matteson, D. S.; Moody, R. J.; Jesthi, P. K. *J. Am. Chem. Soc.* **1975**, *97*, 5608. (b) Mendoza, A.; Matteson, D. S. *J. Org. Chem.* **1979**, *44*, 1352. (c) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 1, p 689.

(3) Nakamura, M.; Hara, K.; Hatakeyama, T.; Nakamura, E. *Org. Lett.* **2001**, *3*, 3137.

(4) (a) Matteson, D. S.; Majumdar, D. *Organometallics* **1983**, *2*, 230. (b) Garad, M. V.; Pelter, A.; Singaram, B.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 637.

(5) For reviews on the synthesis and utility of acylsilanes, see: (a) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. (b) Page, P. C. B.; McKenzie, M. J.; Klair, S. S.; Rosenthal, S. Acylsilanes. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley-Interscience: New York, 1998; Vol. 2, Chapter 27, p 1599. (c) Page, P. C. B.; McKenzie, M. J. Product Subclass 25: Acylsilanes. In *Science of Synthesis*; Fleming, I., Ed.; Georg Thieme Verlag: Stuttgart; New York, 2002; Vol. 4, p 513.

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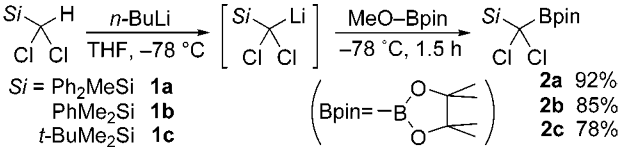
Scheme 2. Synthesis of Boryldichloromethylsilanes

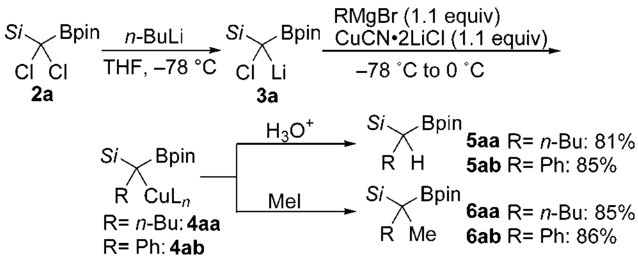


species upon the reaction with dioxygen. After this event, one of the silyl groups eliminates in the peroxide intermediate to yield silanol and acylsilane. We then contemplated replacement of one of the silyl groups with a boryl group with one question in our mind: which migrates, the silyl or boryl group?

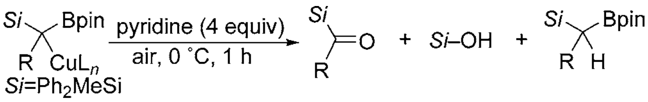
Treatment of dichloromethylsilane **1a**[7] with 1.0 equiv of *n*-BuLi in THF at −78 °C afforded silyldichloromethyllithium via deprotonation, which reacted with methoxy(pinacolato)borane to provide the desired boryldichloromethylsilane **2a** in excellent yield (Scheme 2). A series of boron-bearing dichloromethanes can be synthesized in a similar way as stable solids at room temperature under air.[8]

The addition of *n*-BuLi to a solution of boryldichloromethylsilane **2a** in THF at −78 °C provided borylchlorosilylmethyllithium **3a** as a yellow solution quantitatively through chlorine−lithium exchange. Fortunately, a byproduct via 1,2-migration of the butyl group on the boron center was not detected.[9] Organolithium **3a** was sequentially treated with 1.1 equiv of $CuCN\cdot 2LiCl$ and *n*-BuMgBr at −78 °C, and the mixture was warmed gradually to 0 °C. After quenching with dilute HCl aq under argon, we obtained the butylated product **5aa** in 81% yield. The use of PhMgBr also afforded the desired product **5ab** in 85% yield. An addition of methyl iodide instead of HCl aq to trap the intermediary copper species **4a** furnished the desired products **6aa** and **6ab**, respectively, in good yields (Scheme 3). In sharp contrast to 1,1-disilylalkylcoppers which cannot be utilized as nucleophiles in a carbon−carbon bond-forming process, replacement of silicon with boron gives the copper species sufficient reactivity.

Scheme 3. Preparation of 1-Boryl-1-silylalkylcoppers and Their Electrophilic Trapping



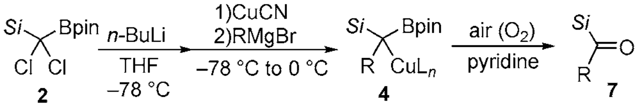
Scheme 4. Aerobic Oxidation of Alkylcoppers **4a** in Aprotic Conditions

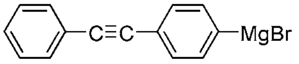
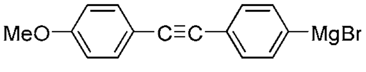


4aa R=*n*-Bu	**7aa** 55%	**8a** 32%	**5aa** 0%
4ab R=Ph	**7ab** 86%	**8a** 0%	**5ab** 0%

Next, we examined the aerobic oxidation of alkylcoppers **4aa** and **4ab**. The previous oxidation conditions with NH_4Cl aq afforded disappointing results due to hydrolysis of the copper species **4**. Aerobic oxidation of **4aa** in aprotic conditions with the presence of 4.0 equiv of pyridine proceeded smoothly to yield acylsilane **7aa** in moderate yield, along with the formation of silanol **8a**.[10] On the other hand, **4ab** was converted into benzoylsilane **7ab** in 86% yield without the formation of silanol (Scheme 4).

Table 1. Synthesis of Acylsilanes via Aerobic Oxidation of 1-Boryl-1-silylalkylcoppers[a]



entry	*Si*	RMgBr	**7** yield (%)
1	Ph_2MeSi	PhMgBr	**7ab** 86
2	Ph_2MeSi	mesitylMgBr	**7ac** 73
3	Ph_2MeSi	2-thienyllithium[b] + $MgBr_2$	**7ad** 72
4	Ph_2MeSi		**7ae** 65
5	Ph_2MeSi		**7af** 71
6	$PhMe_2Si$	*n*-Bu	**7ba** 81
7	$PhMe_2Si$	Ph	**7bb** 76
8	*t*-$BuMe_2Si$	*n*-Bu	**7ca** 76
9	*t*-$BuMe_2Si$	Ph	**7cb** 65

[a] Conditions: $CuCN\cdot 2LiCl$ (1.1 equiv), RMgBr (1.1 equiv), and pyridine (4.0 equiv) were employed. Si = Ph_2MeSi, $PhMe_2Si$, *t*-$BuMe_2Si$. [b] 2-Thienyllithium was prepared by an addition of *n*-BuLi (1.1 equiv) to thiophene (1.1 equiv) in THF.

Hence, we attempted the synthesis of aroylsilanes with various aryl Grignard reagents. Several features of the reaction are noteworthy. As shown in Table 1, mesityl Grignard reagent can be efficiently employed despite its low nucleophilicity due to the steric hindrance by ortho-disub-

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(6) Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2001**, *123*, 11109.

(7) Dichloromethylsilanes **1a**−**c** are easily prepared according to the reported procedure. (a) Bacquet, C.; Masure, D.; Normant, J. F. *Bull. Soc. Chim. Fr.* **1975**, 1797. (b) Shinokubo, H.; Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron* **1996**, *52*, 503.

(8) Hiyama et al. previously reported the synthesis of **2b** through *gem*-dimetalation of lithium carbenoids with silylboranes. See: Shimizu, M.; Kurahashi, T.; Kitagawa, H.; Shimono, K.; Hiyama, T. *J. Organomet. Chem.* **2003**, *686*, 286.

stitution (entry 2). The premixed reagent with 2-thienyllithium and magnesium bromide provided 2-thiophenecarbonylsilane **7ad** in good yield (entry 3), whereas 2-thienyllithium itself did not work at all, affording no trace of **7ad**. This reaction procedure can be applied to incorporation of silylcarbonyl groups into tolan derivatives as shown in entries 4 and 5. In contrast to our previous method where we observed a decrease in yields due to hydrolysis of benzylic copper species, the present protocol with pyridine does not provide hydrolysis product **5**. To our delight, similar copper reagents with other silyl groups such as $PhMe_2Si$ and t-$BuMe_2Si$ can be prepared from **2b** and **2c** in the same way, and their oxidative conversion to acylsilanes worked well without formation of silanols (entries 6−9). While our previous protocol needed silyl groups with at least one aryl group to enhance mobility, introduction of the boryl group enables the synthesis of acyltrialkylsilanes with a variety of silyl groups.

In conclusion, we have achieved the selective conversion of 1-boryl-1-silylalkylcoppers with molecular oxygen to the corresponding acylsilanes. In addition, we have developed a simple and efficient method to prepare various *gem*-borylsilylalkylcopper reagents via alkylation reaction of boryl silyl carbenoids with various Grignard reagents and copper cyanide. This one-pot process using air as the oxidant enables the divergent synthesis of acylsilanes.

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Supporting Information Available: Detailed experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) For reviews on the reactions of α-halo boronic esters, see: (a) Matteson, D. S. *Chem. Rev.* **1989**, *89*, 1535. (b) Matteson, D. S. *J. Organomet. Chem.* **1999**, *581*, 51.

(10) Silanol **8a** may result from competing migration of the silyl group. However, we could detect neither the presumed product, acylborane from β-elimination of silyl group, nor its hydrolyzed products.