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Communications

One-Pot Conversions of (Silylmethyl)cyclopropanes to Homoallylic Alcohols and 1,4-Diols Based on Haloborane-Induced Ring Opening

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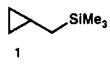
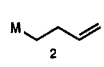
Summary: The reactions of (silylmethyl)cyclopropanes with haloboranes, such as BBr_3 and $BHBr_2$, result in desilylative ring opening to give homoallylboranes and boracyclopentanes, respectively. Coupled with subsequent oxidation procedure, these reactions provide ready access to homoallylic alcohols and 1,4-diols.

Introduction of a silyl group to the appropriate positions of organic molecules often functions as the key for the dramatic enhancement of their reactivity. Thus we have recently revealed that silylmethyl-substituted cyclopropanes **1** notably effect metal salt induced ring opening to give homoallylmetals **2**.[1] Both the β-effect of silicon[2] and the release of ring strain are essential for the ring opening to occur. We report herein the unique simple methods for the preparation of homoallylic alcohols **4** and 1,4-diols **6** from **1**, which were based on tribromoborane- or dibromoborane-induced facile ring opening of **1**.



1



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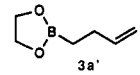
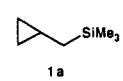
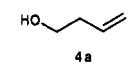
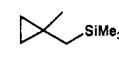
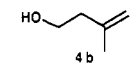
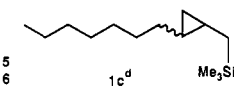
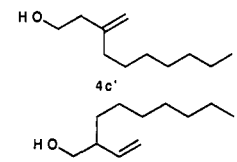
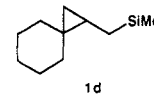
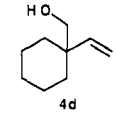
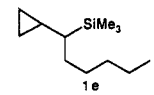
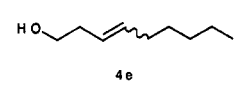


3a'

The reaction of **1a** with an equimolar amount of BBr_3[3] in CH_2Cl_2 at −78 to 25 °C for 0.5 h gave dibromohomoallylborane **3a**, which was isolated as the form of boronic ester **3a'** by further esterification with ethylene glycol bis(trimethylsilyl) ether.[4] Upon treatment of the crude homoallylborane **3a** with an alkaline solution of hydrogen peroxide at 50 °C for 0.5 h, homoallylic alcohol **4a** was

Table I. One-Pot Conversion of (Silylmethyl)cyclopropanes 1 to Homoallyl Alcohols 4 via Haloborative Ring Opening

entry	substrate	BBr_3 (equiv)[a]	product (yield,[b] %)
1		(1)	 (96)[c]
2	1a	(0.5)	4a (84)[c]
3		(1)	 (97)[c]
4	1b	(0.5)	4b (80)[c]
5		(1)	(70)(4c'/4c=86/14)[e]
6	1c[d]	(0.5)	 (71)(4c'/4c=87/13)[e]
			4c' 4c
7		(1)	 (72)
	1d		4d
8		(1)	 (93)[f]
	1e		4e

[a] Method: (a) BBr_3, CH_2Cl_2, −78 to 25 °C, 0.5 h; (b) 30% H_2O_2, 3 N NaOH, THF, reflux, 0.5 h, see footnote 5. [b] Isolated yield after purification by flash chromatography (SiO_2). [c] GC yield. [d] Cis/trans = 15/85. [e] Determined by ^1H NMR. [f] Cis/trans = 37/63. Determined by GC for trimethylsilylated samples.

(1) Ryu, I.; Suzuki, H.; Murai, S.; Sonoda, N. *Organometallics* **1987**, *6*, 212.

(2) For recent work, see: (a) Brook, M. A.; Hadi, M. A.; Neuy, A. *J. Chem. Soc., Chem. Commun.* **1989**, 957. (b) Li, X.; Stone, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 5586.

(3) BBr_3 (1.0 M solution in CH_2Cl_2) and $BHBr_2{\cdot}SMe_2$ (1.0 M solution in CH_2Cl_2) were purchased from Aldrich Chem. Co. Ltd.

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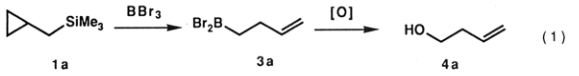
formed in 96% GC yield. Thus, we tested this bromo-

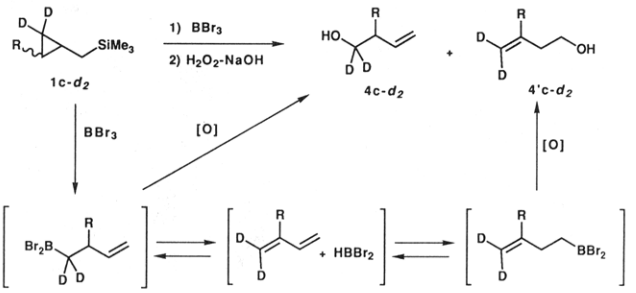


boration/oxidation sequence for several (silylmethyl)-cyclopropanes **1**. The results of one-pot procedure for homoallylic alcohols **4**[5] are listed in Table I. In each case examined, the attack of BBr_3 to **1** was site-selective at the least substituted cyclopropane carbon, yielding **4** bearing a *hydroxymethyl* block. Since one BBr_3 can react with two molecules of **1** to give bis(homoallyl)boranes, the procedure can employ 0.5 molar equiv of BBr_3 without loss of yield (entries 2, 4, and 6).

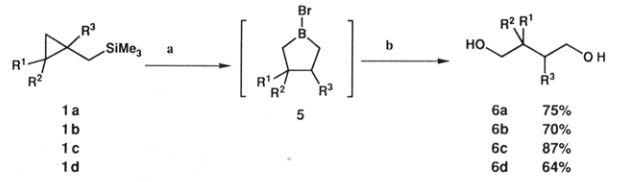
The result with 2-heptyl-substituted substrate **1c** which gave mainly 3-heptylhomoallyl alcohol **4c′** was unanticipated, since we believed the exclusive formation of 2-heptylhomoallyl alcohol **4c**. To elucidate the path for the formation of **4c′**, a *formal 1,2-alkyl rearrangement* product, we examined the reaction of dideuteriocyclopropane **1c**-d_2 in place of **1c**. Two deuteriums in the major product **4c′**-d_2 were at the terminal vinylic position, judging from the ^1H NMR spectrum. Thus, the isomerization was concluded to take place via a dehydroboration/hydroboration sequence (Scheme I).[6]

Next we examined the ring opening reaction of **1** with 1 equiv of dibromoborane ($HBBr_2$), generated in situ from its dimethyl sulfide complex ($HBBr_2$·SMe_2) and BBr_3.[7] As anticipated, the reaction of **1a** with $HBBr_2$ proceeded smoothly to afford boracyclopentane **5a**,[8,9] presumably via haloborative ring opening of **1a** and the subsequent intramolecular hydroboration. When crude **5a** was subjected to oxidation, 1,4-diol **6a** was obtained in 75% yield after isolation by flash chromatography. The results of one-pot conversion of some other (silylmethyl)cyclopropanes **1** to 1,4-diols **6** are summarized in Scheme II. The mode of cyclopropane ring opening was again site-selective between the carbon with silylmethyl group and the least substituted methylene carbon. We have often encountered the formation of δ-silyl alcohols **7** as the byproduct, preparatively; however, they could be easily separated from 1,4-diols **6** by usual column chromatography. The pathway to give

Scheme I

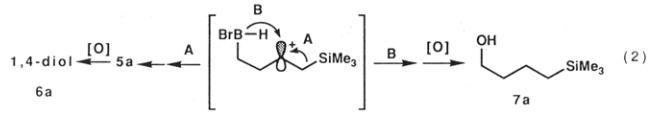


Scheme II.[a] **One-Pot Conversion of (Silylmethyl)cyclopropanes 1 to 1,4-Diol 6**

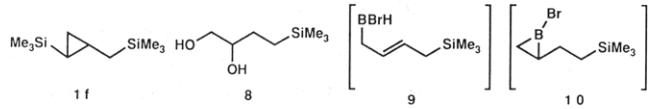


[a] (a) $HBBr_2$ (from $HBBr_2$·SMe_2 and BBr_3), CH_2Cl_2, −78 to 25 °C, 0.5 h; (b) 30% H_2O_2, 3 N NaOH, THF, reflux, 0.5 h.

7 would be the competitive intramolecular hydrogenation from the β-cation intermediate (eq 2).



Interestingly, doubly silyl-functionalized cyclopropane **1f** did not afford 1,4-diol but 1,2-diol **8** (62%), in which one trimethylsilyl group remained intact at the terminal position.[10] This result may be accounted for by the mechanism involving the formation of a β-cation stabilized by two silicon groups, followed by desilylation of the inner silyl group to form (4-silylcrotyl)borane **9**,[11] which then undergoes intramolecular hydroboration leading to **10**.



In summary one-pot conversions of (silylmethyl)cyclopropanes **1** to homoallylic alcohols **4** and 1,4-diols **6** have been achieved on the basis of BBr_3- and $BHBr_2$-induced ring opening of **1**, respectively. Further investigations of metal salts induced opening of silyl-functionalized cyclopropanes are currently ongoing.

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Supplementary Material Available: Listings of spectroscopic and analytical data for all products (4 pages). Ordering information is given on any current masthead page.

(4) **3a′**: ^1H NMR ($CDCl_3$) δ 0.95 (t, J = 7.8 Hz, 2 H), 2.17 (dt, J = 7.6, 7.8 Hz, 2 H), 4.18 (s, 4 H), 4.93 (dd, J = 10.1, 1.8 Hz, 1 H), 4.98 (dd, J = 16.9, 1.8 Hz, 1 H), 5.89 (ddt, J = 16.9, 10.1, 7.6 Hz, 1 H).

(5) Typical procedure for homoallylic alcohol: a solution of BBr_3 (2.0 mL of a 1.0 M in CH_2Cl_2, 2.0 mmol) in 4 mL of CH_2Cl_2 was treated with (silylmethyl)cyclopropane **1d** (0.394 g, 2.0 mmol) under argon atmosphere at −78 °C for 5 min. The reaction mixture was allowed to reach 25 °C slowly, stirred at 25 °C for 30 min, and then treated with 4 mL of THF and 2.5 mL (12 mmol) of 3 N NaOH and 0.7 mL of 30% H_2O_2, and the contents were refluxed for 30 min. After separation from the aqueous layer by saturation using K_2CO_3, the organic layer was dried over $MgSO_4$, filtered, and concentrated. Flash chromatography of the crude product on silica gel using AcOEt–hexane (1:5) as eluent gave pure homoallyl alcohol **4d** (0.100 g) in 72% yield.

(6) For thermal isomerization of organoboranes containing halogens, see: (a) Brown, H. C.; Racherla, U. S. *J. Am. Chem. Soc.* **1983**, *105*, 6506. (b) *J. Org. Chem.* **1983**, *48*, 1389.

(7) Brown, H. C.; Basavaiah, D.; Bhat, N. G. *Organometallics* **1983**, *2*, 1309.

(8) **5a**: ^1H NMR ($CDCl_3$) δ 1.46–1.60 (m, 4 H), 2.56 (dt, J = 3.3, 7.8 Hz, 4 H).

(9) Typical procedure for 1,4-diol: a solution of $BHBr_2$·SMe_2 (2.0 mL of a 1.0 M in CH_2Cl_2, 2.0 mmol) in 4 mL of CH_2Cl_2 was treated with BBr_3 (2.0 mL of a 1.0 M in CH_2Cl_2, 2.0 mmol) under argon atmosphere at 0 °C for 10 min. The reaction mixture was then treated with (silylmethyl)cyclopropane **1d** (0.394 g, 2.0 mmol) at −78 °C for 5 min. The resulting solution was allowed to warm up to 25 °C, stirred at 25 °C for 30, and then treated with 4 mL of THF and 2.5 mL (12 mmol) of 3 N NaOH and 0.7 mL of 30% H_2O_2, and the contents were refluxed for 30 min. After separation from the aqueous layer by saturation using K_2CO_3, the organic layer was dried over $MgSO_4$, filtered, and concentrated. Flash chromatography of the crude product on silica gel using AcOEt–hexane (1:1) as eluent gave pure 1,4-diol **6d** (0.101 g) in 64% yield.

(10) Treatment of **1f** with BBr_3 followed by oxidation with aquous alkaline H_2O_2 gave desilylated homoallylic alcohol **4a** in 74% yield. Formation of **4a** may be consistent with the initial formation of (4-silylcrotyl)dibromoborane and the subsequent acid promoted desilylation to yield homoallylborane as the precursor of **4a**.

(11) Elimination of the inner silyl group in favor of the outer silyl group from a similar cationic intermediate has a precedent, see: Grignon-Dubois, M.; Dunougès, J. *J. Organomet. Chem.* **1986**, *309*, 35. Cf. ref 1.