Organoaluminum-Promoted Rearrangement of Epoxysilanes to α-Silylaldehydes

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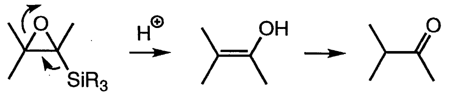
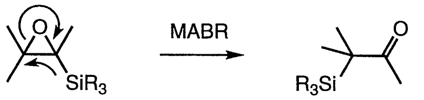
Selective rearrangement of epoxysilanes to α-silylaldehydes has been achieved with high efficiency by using exceptionally bulky oxygenophilic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) as a stoichiometric reagent. Ctalytic use of MABR led to silyl enol ethers in good yield.

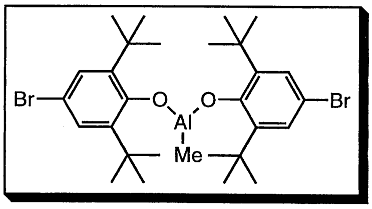
Since Stork and Colvin introduced the transformation of epoxysilanes into carbonyl compounds based on the propensity of suitably substituted organosilanes toward β-elimination in 1971 (eq 1),[1] there has been no precedent for the selective rearrangement of epoxysilanes leading to the corresponding aldehydes or ketones without loss of silyl moieties due to the lack of appropriate Lewis acids.[2] Here we wish to report the successful rearrangement of epoxysilanes to α-silylaldehydes by using the exceptionally bulky oxygenophilic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (abbreviated as MABR) as a stoichiometric and/or catalytic reagent (eq 2).[3] Several examples of this transformation are given in Table 1.



(eq 1)

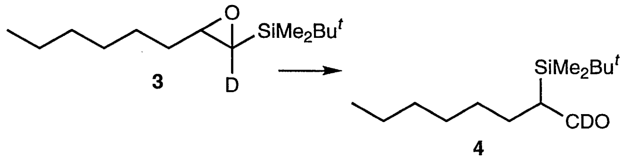
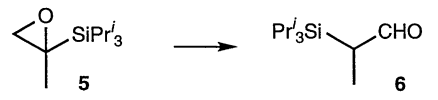
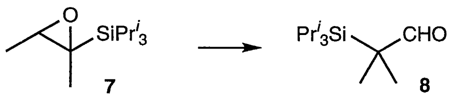
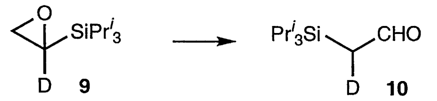


(eq 2)



(MABR)

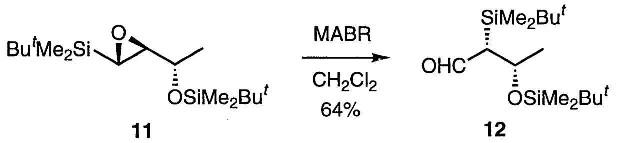
Table 1. Organoaluminum-promoted rearrangement of epoxysilanes [a]

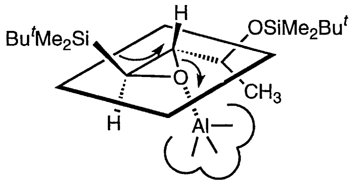
entry		conditions (°C, h)	% yield [b]
			
1	$R = Et$	0, 12	0
2	$R = Ph$	0, 12	13
3	$R = Pr^i$	25, 12	76
4	$R_3 = Me_2Bu^t$	0, 12	79
			
5		0, 12	79
			
6		-78, 3; -40, 1	78
			
7		-78, 0.5; -40, 0.5	94
			
8		25, 12	67

[a] The reaction was carried out in degassed CH_2Cl_2 solvent by using 2 equiv of MABR under the given reaction conditions. [b] Isolated yield of α-silylaldehyde.

When epoxysilanes **1** (R = Pr^i and R_3 = Me_2Bu^t)[4] were treated with 2 equiv of MABR in CH_2Cl_2 at 0~25 °C for 12 h, the corresponding α-silylaldehydes **2** (R = Pr^i and R_3 = Me_2Bu^t) were obtained in 76% and 79% yields, respectively (entries 3 and 4), while reaction of **1** (R = Et and Ph) under similar conditions gave totally unsuccessful results probably because the rearranged aldehydes **2** (R = Et and Ph) were further converted via the acid-catalyzed 1,3-shift of silyl group to the corresponding silyl enol ethers which gradually decomposed *in situ* (entries 1 and 2).[5] The rearrangement of α-deuterated epoxysilane **3** under the influence of MABR afforded the corresponding α-silylaldehyde **4** (79% yield) with the incorporation of a deuterium atom in aldehyde moiety (entry 5), indicating the initial epoxide cleavage at the β position to silicon atom followed by the selective migration of the *tert*-butyldimethylsilyl group.[6] This method represents a potential synthetic equivalent of efficiently converting mono-substituted terminal epoxides to aldehydes (entries 4-6), which is not attainable by conventional methodologies. Epoxysilanes with other substitution patterns of type **5** and **7** underwent epoxide cleavage at the α position to silicon atom and subsequent facile migration of hydride and alkyl groups to give desired α-silylaldehydes **6** and **8**, respectively (entries 6 and 7). This migratory aptitude, which is governed by the stability of cation at the more substituted carbon center,[3] has also been supported with deuterated epoxysilane **9** (entry 8). The superiority of exceptionally bulky MABR was apparent by the reactions of substrate **1** (R_3 = Me_2Bu^t) with other Lewis acids. Attempted use of both less bulky chloromethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide and BF_3•OEt_2 significantly retarded the rate of the rearrangement yielding the desired aldehyde **2** ($R_3 = Me_2Bu^t$) in 55% and 28% yield, respectively.

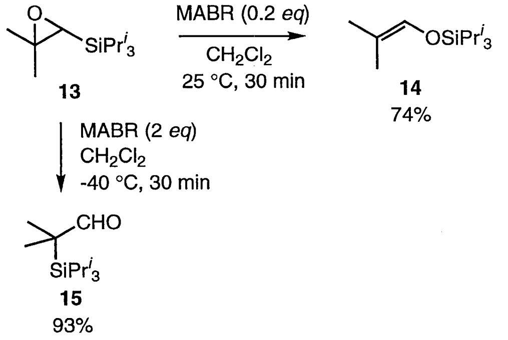
The stereochemical aspect of the MABR-promoted rearrangement of epoxysilanes was also examined with diastereomerically pure epoxysilanes derived from *sec*-allylic alcohols.[7] The essentially pure *erythro*-epoxysilane **11** was smoothly rearranged under the influence of MABR producing the *threo*-α-silylaldehyde **12** exclusively. Hence, this MABR-promoted rearrangement proceeds stereoselectively with rigorous transfer of the chirality of **11**, and the observed stereoselectivity can be interpreted to arise from the *anti* migration of the *tert*-butyldimethylsilyl group to the epoxide moiety as shown in (A).





(A)

The present epoxysilane rearrangement can also be effected by the catalytic amount of MABR. Interestingly, treatment of epoxysilane **13** with 0.2 equiv of MABR facilitated the smooth rearrangement at 25 °C to furnish silyl enol ether **14** in 74% yield, while the reaction of **13** with 2 equiv of MABR at -40 °C gave rise to α-silylaldehyde **15** in 93% yield.[8]



A typical experimental procedure follows (entry 4): A solution of 4-bromo-2,6-di-*tert*-butylphenol (570 mg, 2 mmol) in CH_2Cl_2 (5 mL) was carefully degassed and a 2 M hexane solution of Me_3Al (0.5 mL, 1 mmol) was added at 25 °C under argon. Methane gas evolved immediately. The resulting solution was stirred at 25 °C for 1 h and used as a solution of MABR in CH_2Cl_2 without any purification. After cooling to 0 °C, epoxysilane **1** ($R_3 = Me_2Bu^t$) (116 mg, 0.5 mmol) was added and the resulting mixture was stirred at 0 °C for 12 h. Then the solution was treated with NaF (168 mg, 4 mmol) followed by water (54 μL, 3 mmol). The entire mixture was vigorously stirred at 0 °C for 30 min and filtered with the aid of ether. The filtrate was concentrated and the residual oil was purified by column chromatography on silica gel (ether/hexane = 1:30 as eluants) to give α-silylaldehyde **2** ($R_3 = Me_2Bu^t$) in 79% yield.

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References and Notes

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6 For the β-effect of silicon atom, see: E. W. Colvin, "Silicon Reagents in Organic Synthesis," Academic Press, London (1988).

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8 At the initial stage of the catalytic reaction at -40 °C, we observed the formation of approximately stoichiometric amount of α-silylaldehyde **15** on TLC. Upon warming up to 25 °C, **15** was readily transformed to the correspomding silyl enol ether **14**. This observation indicates that silyl enol ether **14** can be generated *via* the rearrangement of intermediary α-silylaldehyde **15**.