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An Efficient, Catalytic Procedure for Epoxide Rearrangement

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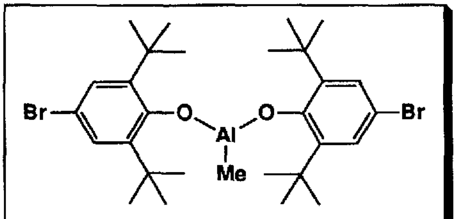
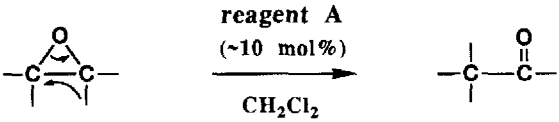
Summary: *Exceptionally bulky, oxygenophilic methylaluminum bis(4-bromo-2,6-di-tert-butylphenoxide) (reagent A) can be utilized as an active catalyst for the transformation of various epoxides to carbonyl compounds with high efficiency and selectivity.*

While the acid-catalyzed rearrangement of epoxides to carbonyl compounds is certainly a well-known transformation, only a few reagents have been employable for this purpose with respect to the efficiency and selectivity of the reaction.[1] In this context, we have recently discovered that the exceptionally bulky, oxygenophilic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (abbreviated to reagent A) can be utilized as a stoichiometric reagent for the transformation of epoxy silyl ethers to β-siloxy aldehydes under mild conditions.[2,3] Here we wish to report that *this aluminum reagent A is an effective catalyst for the rearrangement of various epoxides to carbonyl compounds* as indicated in eq 1.[4] The advantages of the catalytic version are apparent in the areas of economy, ease of large-scale preparation and isolation, and the synthetic potential for *in situ* derivatization of the carbonyl products. Use of an NaF-H_2O workup[5] further simplifies the experimental operation.



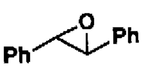
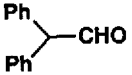
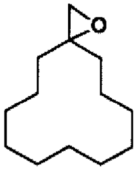
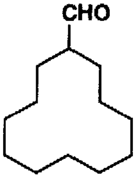
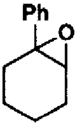
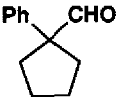
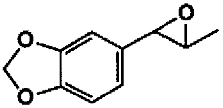
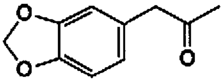
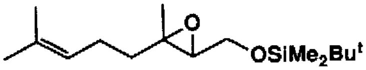
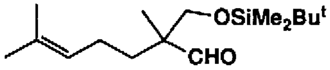
(reagent A)



(eq 1)

Reaction of *trans*-stilbene oxide with reagent A (2 equiv) in CH_2Cl_2 at -78 °C for 10 min gave rise to rearranged diphenylacetaldehyde in 93% yield. In contrast, when this epoxide was treated with the catalytic amount (10 mol%) of reagent A in CH_2Cl_2 at -78 °C, the rearrangement proceeded very slowly and virtually stopped after achieving only low conversion at this temperature.[6] On warming to -20 °C, however, the rate of the reaction was markedly accelerated and was complete within 30 min to furnish the

Table I. Organoaluminum-Catalyzed Rearrangement of Epoxides to Carbonyl Compounds [a]

entry	epoxide	reagent A [b] (mol %)	conditions (°C, h)	product	% yield [c]
1		10	-20, 0.3		95
2		200	-78, 0.5		93
3		20	-20, 0.5		58
4		30	-20, 0.5		77
5		200	-78, 2; -20, 0.3		94
6		5	-20, 1		91
7		10	-20, 1		96
8		200	-78, 0.5		98
9		5	-20, 0.2		84
10		10	-20, 0.5		90
11		200	-78, 0.3		87
12		20	-78, 0.1; 0, 0.3		82
13		200	-78, 1; -20, 0.5		99

[a] The rearrangement was carried out in degassed CH_2Cl_2 by using 0.05~2 equiv of the aluminum reagent A per epoxide under the indicated conditions. The reaction mixture was worked up by the NaF-H_2O method. For experimental details, see text.

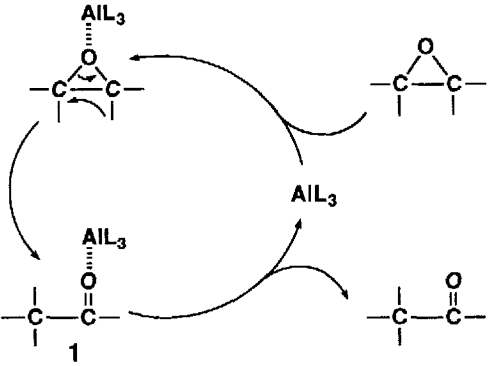
[b] Prepared from Me_3Al and 4-bromo-2,6-di-*tert*-butylphenol (2 equiv) in degassed CH_2Cl_2 at room temperature for 1 h.

[c] Isolated yield by column chromatography.

desired aldehyde in more than 90% yield. Several examples are listed in Table I. The amount of the catalyst varies from 5 to 30 mol% depending on the epoxy substrate. Yields when reagent A is used stoichiometrically are also included for comparison. As revealed in Table I, this catalytic method is applicable to various epoxides with high selectivity.[7] Neither epoxides derived from monosubstituted olefins or internal dialkyl-substituted olefins are employable, however, even with a two-fold quantity of reagent **A**.

The stronger coordination of carbonyl oxygen than epoxide oxygen to an aluminum reagent requires the stoichiometric use of reagent **A** at low temperature. The key element of the present modification is the use of higher reaction temperature (though still at or below 0 °C) than the previously reported conditions[2] in order to induce the dissociation of the aluminum reagent-carbonyl complex **1**, thereby allowing the regeneration of catalyst **A** for further use in the catalytic cycle of the reaction (Scheme 1).[8] The facile dissociation of complex **1** as well as the smooth rearrangement of epoxides is apparently ascribable to the exceptional bulkiness of aluminum reagent **A**. The less bulky methylaluminum bis(4-bromo-2,6-diisopropylphenoxide) was found to be totally ineffective for the rearrangement of *tert*-butyldimethylsilyl ether of epoxy geraniol (cf. entries 12 and 13).[9]

Scheme 1



A typical experimental procedure follows (entry 1). A 0.5 M hexane solution of Me_3Al (0.2 mL, 0.1 mmol) was added to a solution of 4-bromo-2,6-di-*tert*-butylphenol (57 mg, 0.2 mmol) in CH_2Cl_2 (5 mL) at room temperature and the resulting solution was stirred at this temperature for 1 h. Then *trans*-stilbene oxide (196 mg, 1 mmol) in CH_2Cl_2 (0.5 mL) was added at -20 °C. The mixture was stirred at -20 °C for 20 min and treated with NaF (17 mg, 0.4 mmol) followed by water (5.4 μL, 0.3 mmol) at -20 °C. The entire mixture was vigorously stirred at -20 °C for 20 min and filtered with the aid of CH_2Cl_2. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (ether/hexane = 1:10 to 1:5 as eluants) to give diphenylacetaldehyde (186 mg, 95% yield) as a colorless oil.

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References and Notes

1. (a) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737. (b) Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 1693. (c) Milstein, D.; Buchman, O.; Blum, J. *Tetrahedron Lett.* **1974**, 2257. (d) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. (e) Maruoka, K.; Hasegawa, M.; Yamamoto, H.; Suzuki, K.; Shimazaki, M.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1986**, *108*, 3827.
2. Maruoka, K.; Ooi, T.; Yamamto, H. *J. Am. Chem. Soc.*, in press.
3. For other synthetic applications of reagent **A** to the regio- and stereocontrolled Claisen rearrangements, see: (a) Maruoka, K.; Nonoshita, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 7922. (b) Maruoka, K.; Banno, H.; Nonoshita, K.; Yamamoto, H. *Tetrahedron Lett.* **1989**, *30*, 1265.
4. Recent catalytic procedures for the epoxide rearrangement: (a) Isomerization of diene monoepoxide with Pd^0 catalyst: Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623. (b) 1,3-Diketone synthesis from epoxy ketones with Pd^0 catalyst: Suzuki, M.; Watanabe, A.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 2095. (c) Isomerization of diene monoepoxide with Rd^I catalyst: Sato, S.; Matsuda, I.; Izumi, Y. *Tetrahedron Lett.* **1985**, *26*, 1527. (d) Aldol synthesis from epoxy silyl ethers with Me$_3$SiOTf: Suzuki, K.; Miyazawa, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1987**, *28*, 3515.
5. Yamamoto, H.; Maruoka, K. *J. Am. Chem. Soc.* **1981**, *103*, 4186.
6. The reaction was monitored by TLC analysis.
7. Attempted rearrangement of the silyl ether of epoxy geraniol (entries 12 and 13) with a conventional Lewis acid, BF$_3$·OEt$_2$ (2 equiv) gave no desired products.
8. Attempted addition of Me$_3$SiCl or 4A molecular sieves (activated powder from Aldrich Chemical Company Inc.) was not effective to induce the dissociation of the aluminum reagent-carbonyl complex **1** or to capture the *in situ* generated carbonyl compound.
9. Reaction of *tert*-butyldimethylsilyl ether of epoxy geraniol with methylaluminum bis(4-bromo-2,6-diisopropylphenoxide) (2 equiv) at -78 °C for 1.5 h and at -20 °C for 1.5 h yielded (*E*)-1-(*tert*-butyldimethylsiloxy)-3,7-dimethyl-3,6-octadien-2-ol (16% yield) as a major product.

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