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A Facile Workup-Free Catalytic Rearrangement of Epoxides on Immobilized Organoaluminum Columns

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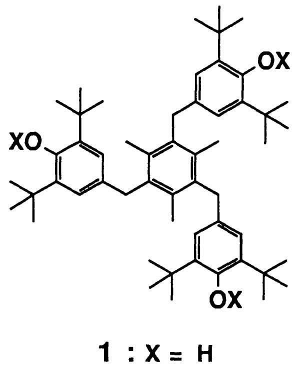
The immobilized organoaluminum columns can be successfully utilized as a workup-free reactor for the catalytic rearrangement of various epoxides to carbonyl compounds.

We recently developed a complexation chromatography1) on the polymeric monomethylaluminum reagent **2** possessing a high recognition ability in complexation with several Lewis-basic substrates.2) Based on the selective Lewis acid-base complex formation, this flow method realized a surprisingly clean separation of structurally very similar ether substrates, which cannot be accomplished by the ordinary silica gel or alumina chromatography.2) During the course of this study, we have also been interested in the potential application of a certain immobilized organoaluminum column as a workup-free reactor to various organoaluminum-mediated reactions. Reported herein is a facile workup-free catalytic rearrangement of epoxides to carbonyl compounds using several immobilized organoaluminum columns.



1 : X = H

2 : X = $-\underset{\text{Me}}{\underset{|}{\text{Al}}}-$

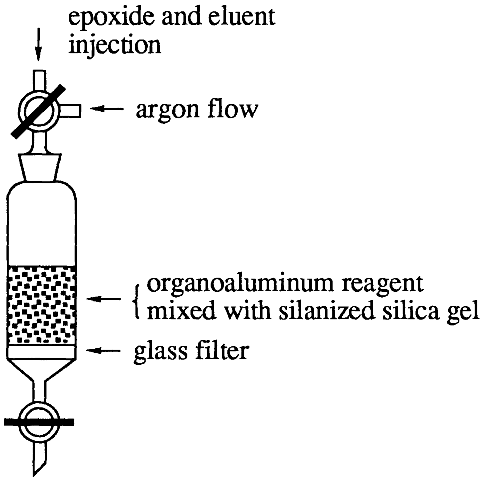
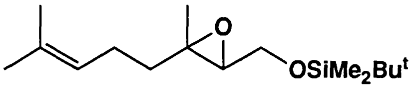
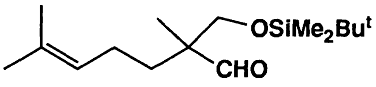
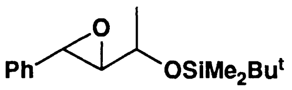
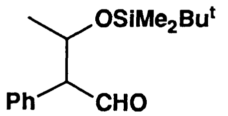
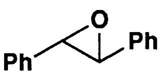
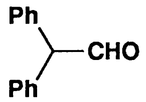
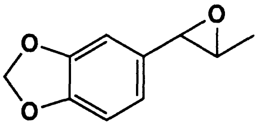
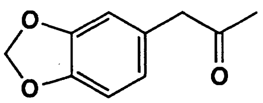
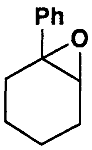
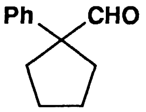


Table 1. Catalytic Rearrangement of Epoxides with Various Organoaluminum Reagents

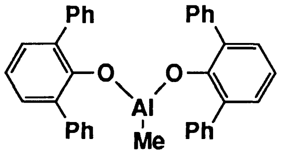
Entry	Epoxide	Conditions[a]	Product	Yield/%[b]
1		2, A		70
2		2, B		67
3		3, A		18
4		4, A		25
5		2, A		58[c,d]
6		2, B		55[c,d]
7		3, A		16[c,d]
8		4, A		33[c,d]
9		2, A		20
10		2, B		35
11		3, A		52
12		3, B		63
13		4, A		70
14		4, B		72
15		2, A		74
16		2, B		90[e]
17		3, A		75
18		3, B		83[e]
19		4, A		81
20		4, B		90[e]
21		2, A		98
22		2, B		85
23		3, A		94
24		3, B		82
25		4, A		94
26		4, B		85

[a] Condition A: In batch method, use of 20 mol% organoaluminum reagents in degassed CH_2Cl_2 at room temperature for 0.1—0.5 h. B: In flow method eluting with degassed hexane (≈200 mL), use of 15—25 mol% organoaluminum reagents at room temperature. For experimental details, see text.

[b] Isolated yield. [c] *Erythro*/*threo* = 3:2 for the starting epoxy silyl ether. [d] The *erythro*/*threo* ratio of the β-siloxy aldehyde is 2:3 by ^{1}H NMR analysis. [e] Eluted with degassed hexane (100 mL) followed by 5% THF in hexane (50 mL).

First, we studied the epoxide rearrangement with the polymeric aluminum reagent **2** (20 mol%) in a conventional batch method as a test of its applicability to the flow method on a column. Treatment of sterically hindered triphenol **1**3) (0.13 mmol) in degassed CH_2Cl_2 (10 mL) with Me_3Al (0.2 mmol) at room temperature for 1 h gave rise to the polymeric aluminum reagent **2**. For example, rearrangement of the *tert*-butyldimethylsilyl ether of epoxy geraniol (1 mmol), which is a challenging substrate due to its susceptibility to various side-reactions,4) at room temperature for 0.1 h yielded after NaF-H_2O workup5) the desired β-siloxy aldehyde in 70% yield, in addition to some by-products with complete consumption of the starting epoxy silyl ether (condition A). By lowering reaction temperature, however, the rearrangement proceeded very slowly with ≈40% recovery of the starting material (53% yield after 0.5 h at -20 °C).6) Hence, the use of room temperature seems appropriate for a flow method.

With these results in hand, we tried the rearrangement of this epoxide in the flow method as follows (condition B): The organoaluminum column for catalytic rearrangement was prepared as described previously with some modification for *in situ* preparation.2) Accordingly, the solution of polymeric aluminum reagent **2** (0.5 mmol) in CH_2Cl_2 (10 mL) was charged on a short-path glass column (15 mm i.d. × 250 mm) packed with silanized silica gel (15 g).7) After evaporation of solvent under vacuum followed by mixing of the residual **2** and silanized silica gel, the stationary phase was washed once with dry, degassed hexane (50 mL) to remove unreacted free triphenol **1** under the pressure of argon (0.3—0.4 kg/cm^2). Under the operating condition, the amount of the immobilized polymeric aluminum reagent **2** as the stationary phase was found to be 0.15—0.25 mmol based on the recovered triphenol **1**. Then, a solution of the *tert*-butyldimethylsilyl ether of epoxy geraniol (1 mmol) in degassed hexane (1 mL) was introduced on to the top of this organoaluminum column at room temperature. Degassed hexane (50 mL) was continuously passed through the column for 10 min, and then ≈150 mL more was rapidly forced through until no further elution of desired aldehyde was observed. Further purification of the concentrated eluates by short-path silica gel chromatography to remove trace triphenol **1** (aluminum ligand) gave the pure β-siloxy aldehyde in 67% yield. It should be noted that the eluate by the flow method contained only a trace of by-products. Presumably, the polar by-products coordinated strongly to the stationary phase, polymeric aluminum reagent **2**. In fact, the remaining by-products could be eluted with 5% THF in hexane.



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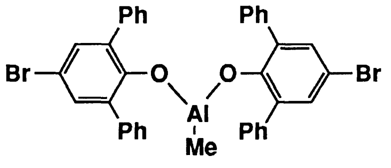

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Other examples of epoxy silyl ethers and simple epoxides are given in Table 1. The yields in the batch method are also included for comparison. Unfortunately, the reaction of the simple epoxide, *trans*-stilbene oxide, afforded the rearranged diphenylacetaldehyde in low yield (entries 9 and 10). Hence, we examined the possibility of using other organoaluminums such as methylaluminum bis(2,6-diphenylphenoxide) (**3**)8) and more Lewis acidic methylaluminum bis(4-bromo-2,6-diphenylphenoxide) (**4**), both of which are nearly insoluble in developing solvents. Indeed, treatment of *trans*-stilbene oxide with **4** (20 mol%) afforded the desired aldehyde in good yield under the same flow condition (entry 14). Furthermore, the organoaluminum reagents, **3** and **4**, were employed successfully for the clean rearrangement of other simple epoxides (entries 18, 20, 24, and 26), though the transformation of epoxy silyl ethers gave less satisfactory results (entries 3, 4, 7, and 8).

References

1) For other complexation chromatography: V. Schrig, *Angew. Chem., Int. Ed. Engl.*, **23**, 747 (1984); V. Schrig and H. Nowotny, *ibid.*, **29**, 939 (1990).
2) K. Maruoka, S. Nagahara, and H. Yamamoto, *J. Am. Chem. Soc.*, **112**, 6115 (1990).
3) Kindly provided by Adeka Argus Chemical Co., Ltd.
4) The rearrangement of this epoxide with several conventional Lewis acids such as $BF_3 \cdot OEt_2$ and $TiCl_4$ gave rise to none of the desired β-siloxy aldehyde, see: K. Maruoka, T. Ooi, and H. Yamamoto, *J. Am. Chem. Soc.*, **111**, 6431 (1989).
5) H. Yamamoto and K. Maruoka, *J. Am. Chem. Soc.*, **103**, 4186 (1981).
6) The catalytic rearrangement of epoxides with methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) at low temperature (-78—0 °C) proceeded with high selectivity, see: K. Maruoka, S. Nagahara, T. Ooi, and H. Yamamoto, *Tetrahedron Lett.*, **30**, 5607 (1989) ; K. Maruoka, T. Ooi, S. Nagahara, and H. Yamamoto, *Tetrahedron* , **47**, 6983 (1991).
7) Silanized silica gel was dried at 120 °C for 1 h and was replaced with argon before use. Mixing of the polymeric aluminum reagent **2** with silanized silica gel is recommended for obtaining efficient rearrangement and reproducibility in this flow method.
8) For other synthetic application of methylaluminum bis(2,6-diphenylphenoxide) (MAPH): K. Maruoka, A. B. Concepcion, N. Hirayama, and H. Yamamoto, *J. Am. Chem. Soc.*, **112**, 7422 (1990).

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