

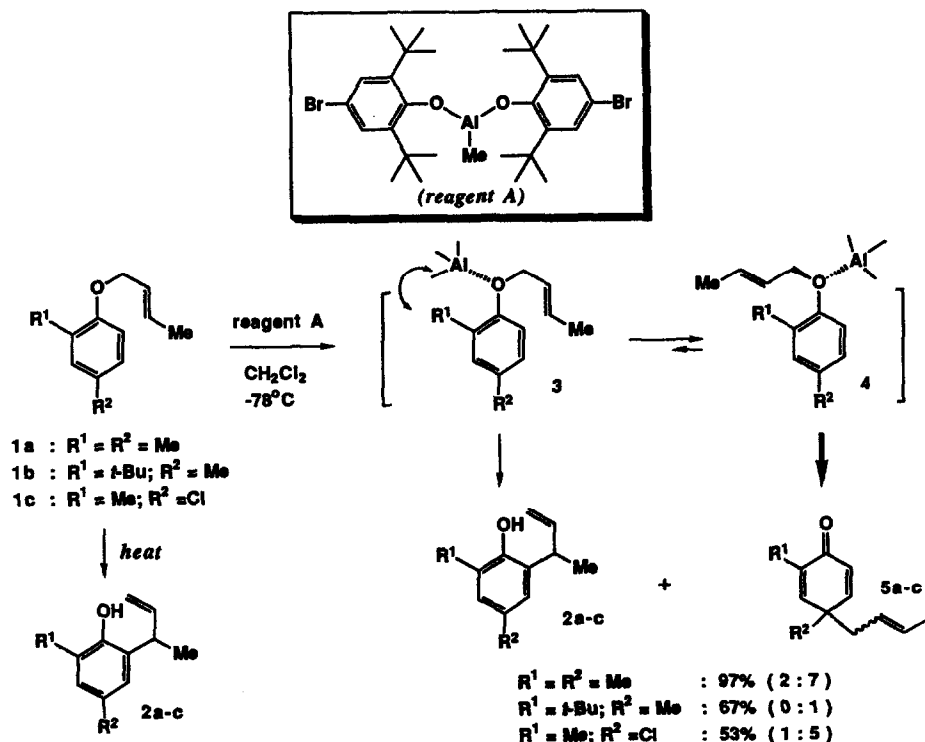
Organoaluminum-Promoted Rearrangement of Allyl Phenyl Ethers

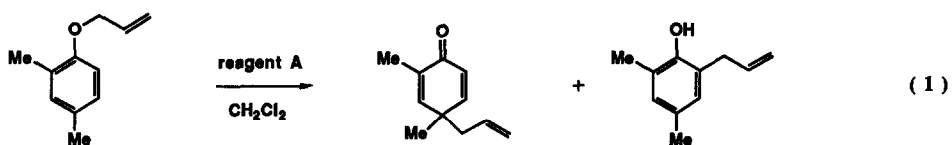
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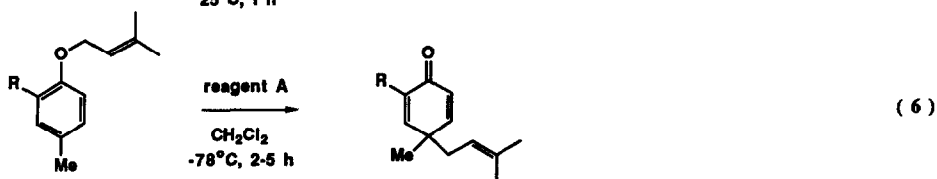
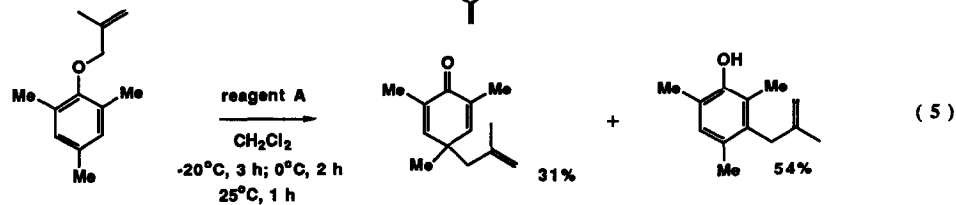
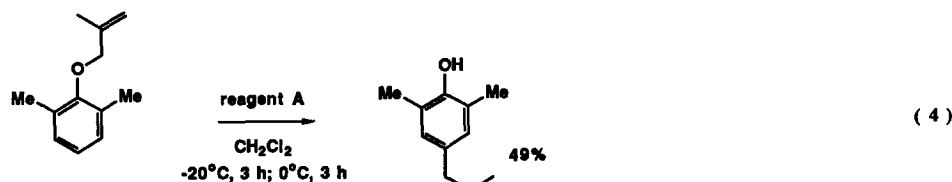
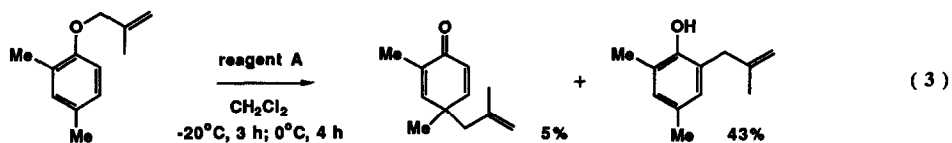
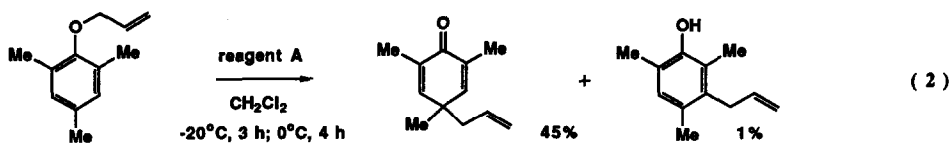
Summary: The Claisen rearrangement of allyl phenyl ethers with exceptionally bulky, oxygenophilic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (reagent A) is found to exhibit an unusual behavior not observable in the ordinary thermal and Lewis acid-induced rearrangement.

The Claisen rearrangement of allyl phenyl ethers (*i.e.*, the aromatic Claisen rearrangement) has been originally effected under thermal conditions (180–200 °C).¹ More recently, a variety of Lewis acids such as BF₃-AcOH, BCl₃, Et₂AlCl, TiCl₄, and (*i*-PrO)₂TiCl₂ have been successfully introduced to accelerate this rearrangement under mild conditions.²⁻⁵ In addition to these procedures, we wish to report an unusual behavior on the aromatic Claisen rearrangement promoted by the exceptionally bulky, oxygenophilic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (abbreviated to reagent A).⁶

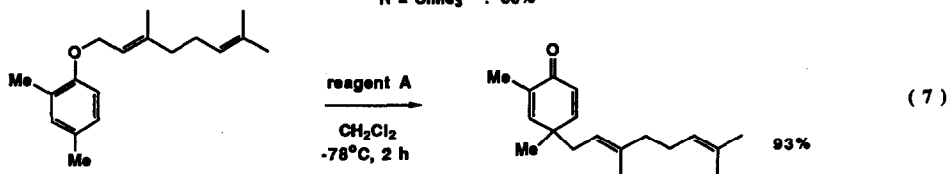




-78°C, 2 h; -40°C, 3 h; -20°C, 1 h : 21% (3 : 4)
 -20°C, 3 h; 0°C, 12 h; RT, 1 h : 92% (1 : 9)



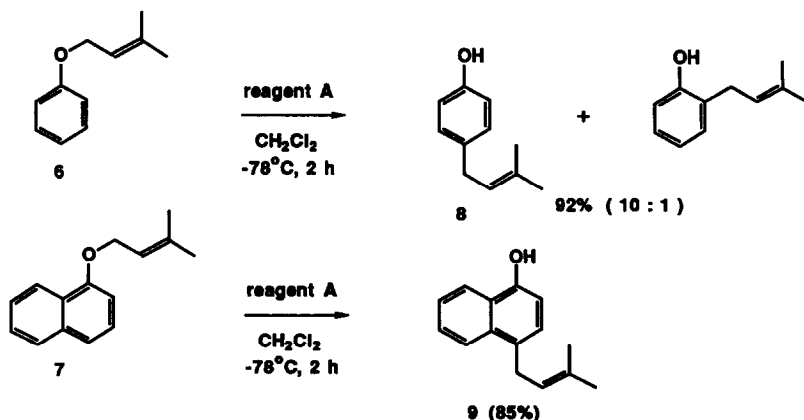
R = Me : 92%
 R = SiMe₃ : 80%



The thermal rearrangement of crotyl 2,4-dimethylphenyl ether (**1a**)⁷ afforded normal Claisen product, 4,6-dimethyl-2-(1-methyl-2-propenyl)phenol (**2a**) exclusively in high yield. In marked contrast, however, treatment of **1a** with bulky aluminum reagent A (2 equiv) in CH₂Cl₂ at -78 °C for 4 h gave rise to 4-crotyl-2,4-dimethyl-2,5-cyclohexadienone (**5a**) (76%; *E/Z* = ~2:1) as a major product accompanied by **2a** (21%).⁸ This result implies that the initial coordination of the allyl phenyl ether **1** to aluminum reagent A yields the sterically more favored complex **4** rather than the alternative **3**, thereby providing the preferred formation of the dienone **5** by remote transfer of crotyl group. In fact, use of the less bulky dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide gave a mixture of **2a** and **5a** (81% combined yield) in a ratio of ~1:1. Furthermore, introduction of bulky *tert*-butyl substituent at the *ortho*-position of phenoxy moiety afforded dienone **5b** (67%; *E/Z* = 5:2) as a sole isolable product. Switching the solvent from CH₂Cl₂ to toluene significantly lowered the rate of the reaction without any affecting the selectivity. This rearrangement exhibits the moderate substituent effect in the aromatic moiety as observed in the rearrangement of **1c**.⁷

With such informations on the organoaluminum-promoted Claisen rearrangement at hand, we have further studied the substituent effect in the allylic as well as phenyl system of the substrates on the course of the rearrangement using other allylic phenyl ether derivatives (eq 1-7). Less substituted allylic systems such as allyl and methallyl groups favored the alkylation at the less substituted *ortho*-position of 2,4-dimethylphenol (eq 1 and 3). 2,6-Dimethylphenyl ether substrate transformed to *para*-allylated phenol exclusively (eq 4). In contrast, 2,4,6-trimethylphenyl ethers favor the formation of dienone products (eq 2 and 5). Use of more substituted allylic systems (e.g., prenyl or geranyl) in the 2,4-dimethylphenyl ethers predominated the dienone formation by stabilization of cationic intermediates (eq 6 and 7). As a whole, *ortho*-alkylated phenols and dienones formation would be interpreted for by a concerted and ionic mechanism, respectively.

Another interesting feature is the organoaluminum-promoted rearrangement of simple allyl phenyl ethers of type **6** and **7**, in which the remote transfer of the prenyl moiety is again observed in view of exceptionally bulky aluminum reagent A to furnish the *para*-substituted phenols **8** and **9** with high selectivity. Notably, the thermal rearrangement of phenyl prenyl ether (**6**) gave rise to a 1:1 mixture of **8** and 2-(1,2-dimethyl-2-propenyl)phenol and the selective formation of **8** has not been attained satisfactorily by the use of conventional Lewis acids.⁵



References and Notes

1. Reviews: (a) Tarbell, D. S. *Org. React.* **1944**, *2*, 1. (b) Jefferson, A.; Scheinmann, F. *Quart. Rev.* **1968**, *22*, 391. (c) Hansen, H. J.; Schmid, H. *Chem. in Britain* **1969**, *5*, 111. (d) Rhoads, S. J.; Raulins, R. N. *Org. React.* **1975**, *22*, 1.
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5. TiCl₄, and (*i*-PrO)₂TiCl₂: Narasaka, K.; Bald, E.; Mukaiyama, T. *Chem. Lett.* **1975**, 1041.
6. For the aliphatic Claisen rearrangement promoted by reagent A, 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. (c) Nonoshita, K.; Banno, H.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.*, in press.
7. The *E/Z* ratios of **1a-c** are 5:1, 4:1, and 5:1, respectively.
8. An experimental procedure for the rearrangement of **1a** with reagent A is as follows: To a solution of 4-bromo-2,6-di-*tert*-butylphenol (570 mg, 2 mmol) in degassed CH₂Cl₂ (5 mL) was added at room temperature a 2 M hexane solution of Me₃Al (0.5 mL, 1 mmol) under an argon atmosphere. The methane gas evolved immediately. The mixture was stirred at this temperature for 1 h and was cooled to -78°C. Then crotyl 2,4-dimethylphenyl ether (**1a**) (88 mg, 0.5 mmol) was added at -78°C. The entire mixture was stirred at this temperature for 4 h. The solution was poured into diluted HCl and extracted with CH₂Cl₂. The combined extracts were dried over Na₂SO₄. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane = 1:5 as eluant) afforded 4-crotyl-2,4-dimethyl-2,5-cyclohexadienone (**5a**) (76% yield) and 4,6-dimethyl-2-(1-methyl-2-propenyl)phenol (**2a**) (21% yield) as colorless oils.

(Received in Japan 13 October 1989)