Tetrahedron Letters,Vol.30,No.10,pp 1265-1266,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

ORGANOALUMINUM-PROMOTED CLAISEN REARRANGEMENT OF BISALLYL VINYL ETHERS

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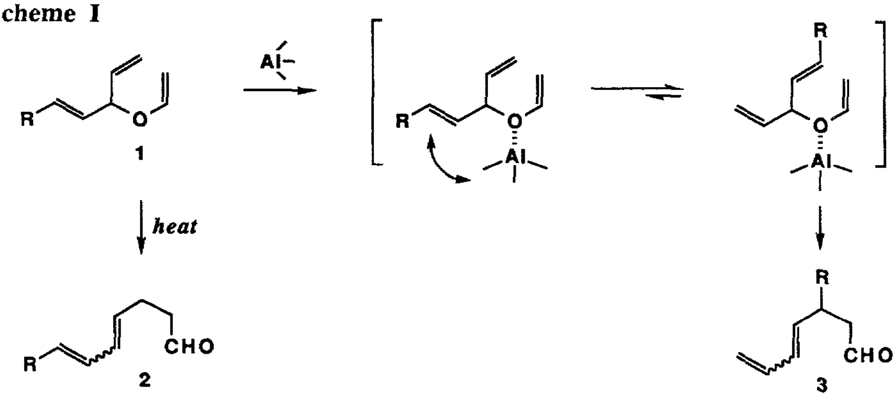
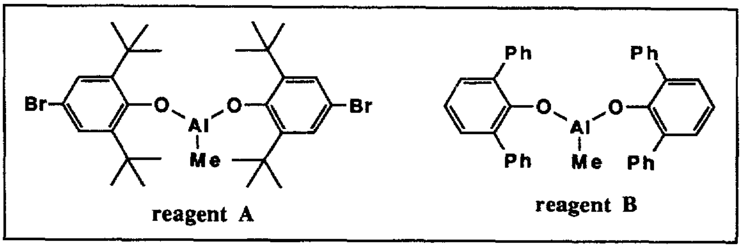
Summary: *The Claisen rearrangement of bisallyl vinyl ethers with exceptionally bulky organoaluminum reagents exhibits unprecedented regiochemical control not observable in the ordinary thermal rearrangement.*

We recently described a highly stereocontrolled Claisen rearrangement of allyl vinyl ethers using modified organoaluminum reagents in which either (*E*) or (*Z*) Claisen products were obtainable under very mild conditions with high stereoselectivity.[1] When alternative allylic systems are available in a substrate, the thermal rearrangement of such a substrate **1** is reported to involve the less substituted allyl system to furnish dienal **2** preferentially.[2] With certain bulky organoaluminum reagents, however, the opposite regioselectivity leading to dienal **3** might be achievable in view of the steric repulsion between the more substituted allylic systems and the bulky Lewis acidic aluminum reagents as illustrated in Scheme I. Here we wish to report the first observation of unusual regiochemical control in the organoaluminum-promoted Claisen rearrangement of bisallyl vinyl ethers.

Scheme I

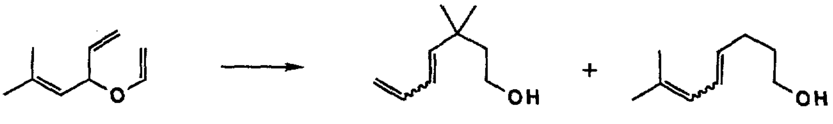




reagent A **reagent B**

In a typical case, bisallyl vinyl ether **1** (R = Bu) was treated with methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (reagent **A**) in CH_2Cl_2 at -78°C to yield a mixture of Claisen products **2** and **3** (R = Bu) in 72% yield.[3] The ratio of **2** and **3** (R = Bu) was determined to be 30:70 by capillary GLC after conversion of the aldehydes to the corresponding alcohols.[4] Use of other solvents exhibited similar regioselectivity so that the intervention of the ionic mechanism seems unlikely. With another bulky methylaluminum bis(2,6-diphenylphenoxide) (reagent **B**) in toluene at -78°C, the product ratio of **2** and **3** (R = Bu) was found to be 31:69.[3] These results are in marked contrast with the thermal rearrangement of **1** (R = Bu) which has resulted in the reversal of regioselectivity (ratio of **2**/**3** = 76:24). The more bulky substrate **1** (R = *t*-Bu) on treatment with the reagent **A** showed somewhat better selectivity (ratio of **2** and **3** (R = *t*-Bu) = 24:76).

As revealed in the following examples, the course of the rearrangement appeared to be highly dependent on the substituent effect in the allylic system of the substrates.[5,6] The bisallyl vinyl ether **4** bearing dimethyl substituents in the γ-positions gave more satisfactory results than its monoalkyl counterpart **1**. The steric difference between vinyl and isopropenyl moieties is even more clear in the second substrate **5** giving the desired Claisen product **6** with high regioselectivity.



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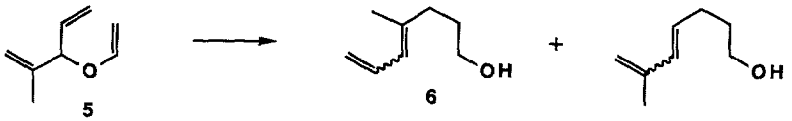
reagent A	:	**83%**	**(76 : 24)**
reagent B	:	**90%**	**(79 : 21)**
heat	:		**(16 : 84)**



5 **6**

reagent A	:	97%	**(89 : 11)**
reagent B	:	79%	**(94 : 6)**
heat	:		**(40 : 60)**

References and Notes

1. Maruoka, K.; Nonoshita, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.*, in press.
2. Cresson, P.; Lacour, L. *Compt. Rend.* **1966**, *262*, 1157.
3. For preparation of the organoaluminum reagents **A** and **B**, see ref 1.
4. The *E*/*Z* ratios of **2** and **3** (R = Bu) were tentatively assigned to be 42:58 and 41:59, respectively.
5. Syntheses of the starting bisallyl vinyl ethers **1** and **5** follow: (i) alkylation of acrolein with alkenyllithium reagents; (ii) transetherification of the resulting bisallyl alcohols with ethyl vinyl ether in the presence of mercury(II) acetate. On the other hand, the substrate **4** was prepared by the alkylation of 3-methyl-2-butenal with vinylmagnesium bromide followed by transetherification of the resulting 5-methyl-1,4-hexadien-3-ol as described above.
6. In view of the easy product isolation, the Claisen products were directly transformed to the corresponding alcohols with $NaBH_4$ in MeOH.

(Received in Japan 24 November 1988)