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Designer Lewis acid based on molecular recognition

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A Lewis acid is an excellent candidate as a proton substitute in man-made organic reactions. The observation that organoaluminum compounds immediately ignite when exposed to air, a reflection of the high affinity of aluminum for oxygen, inspired us to devise a new series of reagents based on that metal. Our goal was to engineer an artificial proton of a special shape, which could be utilized as an effective tool for chemical reactions, by harnessing the high reactivity of the aluminum atom towards oxygen. Such a concept was initially researched by examining the influence of a specially designed organometallic reagent on a typical organic reaction. The successful diastereoface discrimination observed in the alcohol synthesis induced us to examine the more intricate question of enantioface differentiation. Creation of new chirality in a product molecule requires the use of a chiral catalyst. Therefore, an investigation was launched to determine whether a chiral Lewis acid could possibly achieve the desired result.

INTRODUCTION

In the stereocontrolled construction of an organic molecule, Lewis acids play an important role. In fact, most important carbon–carbon bond formation processes are catalysed by Lewis acids. If we were able to design an effective Lewis acid catalyst, we could solve a number of problems in selective organic synthesis.

An effective designer Lewis acid should be based on molecular recognition of a given substrate. Some aspects of the general strategy of molecular recognition for synthetic chemistry are summarized in Figure 1. A specific receptor is synthesized and is used to recognize and interact specifically with a given substrate, and then reach the second level of molecular interaction, the supramolecular level, at which a variety of functions is expected. Molecular recognition in the design of the receptor, therefore, must involve the understanding of many interactions at the molecular level.

Among various receptors of stereospecific reactions, the Lewis acid is certainly the most useful for efficient molecular recognition. Organoaluminum compounds are unique for high reactivity, and co-ordinate with most neutral donor molecules to form stable complexes. Provided the bases do not contain acidic hydrogen atoms, the complexes can, in most cases, be distilled. The stability of such complexes with trimethylaluminum and base molecules is described below.[1]

CASE STUDY 1. DISCRIMINATION OF FUNCTIONAL GROUPS

Discrimination of two different ketones

Our attention has long been focused on the recognition of two different ketones with certain modified organoaluminum reagents, and we introduced exceptionally bulky methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) as a highly efficient Lewis acidic receptor for this purpose.[2]

As revealed by the space-filling model (Fig 3), Lewis acidic MAD provides an exceptionally bulky molecular cleft, which may feature a complementary size, shape, and co-ordination capacity for structurally similar ketonic substrates. First, we examined the recognition ability of MAD for combination with acetophenone and pivalophenone using low-temperature ^{13}C-NMR spectroscopy, since original signals of their carbonyl carbons would shift to lower fields on co-ordination with Lewis acidic MAD. The low-temperature ^{13}C-NMR spectra of ketones and their complexes with MAD in CD_2Cl_2 are indicated in Figure 4. Only signals of the characteristic carbonyl carbons are shown. The top spectrum indicates the signals of free acetophenone carbonyl and pivalophenone carbonyls which appear at δ 198.3 and 208.9, respectively, in a roughly 2:1 ratio. When 0.5 equiv. of MAD was added to an equimolar mixture of acetophenone and pivalophenone, the original signal of acetophenone carbonyl at δ 198.3 decreased and a new signal appeared at δ 213.6. Addition of a further 0.5 equiv. of MAD to this mixture resulted in the complete disappearance of acetophenone carbonyl and the new

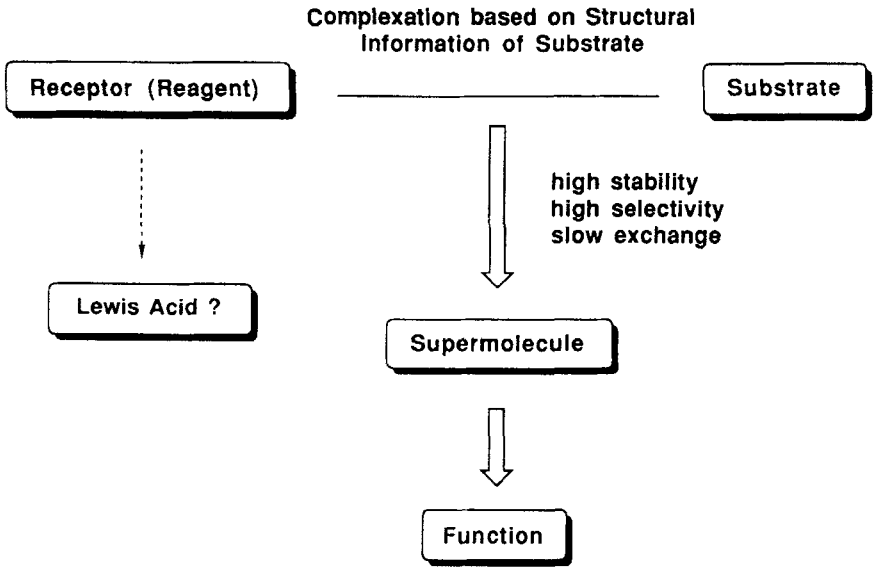
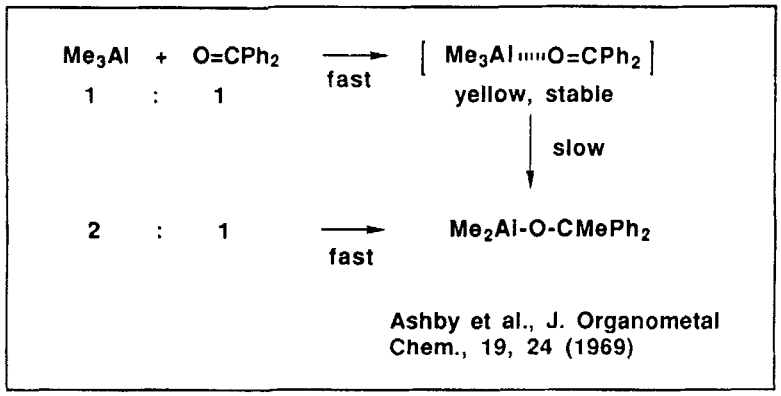


Figure 1 Molecular recognition.



Enthalpies of Formation of Complexes from Trimethylaluminum Monomer

	$-\Delta H_f$ (kcal/mole)
$(Me_2N)_3PO$	32
Et_3N	26
PhCN	25
Ph_3P	18
THF	23
Et_2O	20

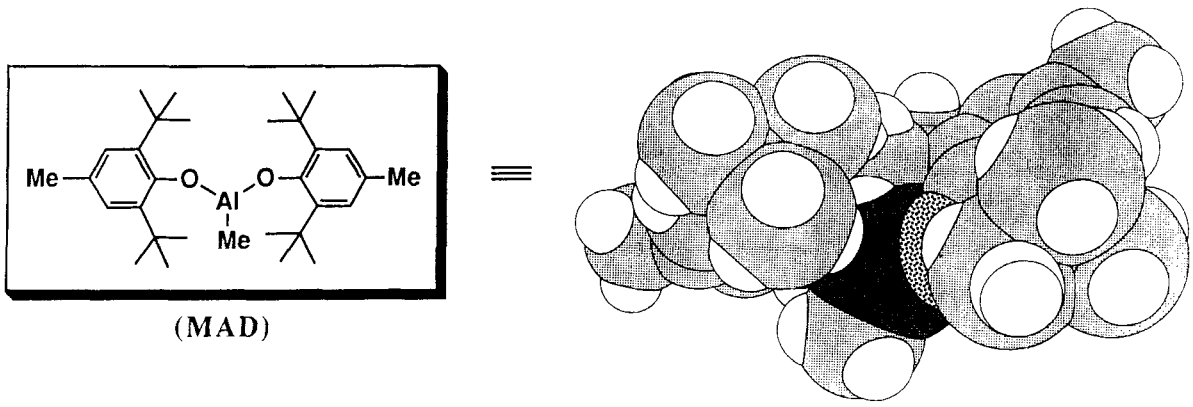
from Organoaluminum Compounds by T. Mole and E. A. Jeffery

Figure 2 Complexation of aluminium reagent with organic substrates.

signal at δ 213.6 became larger, whereas the signal of pivalophenone carbonyl remained unchanged. It should be added that the signal of the pivalophenone–MAD complex appeared at δ 232.6. These results clearly indicate the virtually complete recognition of acetophenone carbonyl by MAD.

Discrimination of two different esters

We further extended our molecular recognition chemistry with Lewis acidic MAD to the selective binding of structurally similar esters.[3] In this case, the recognition sites are in a somewhat remote position, namely, one oxygen away from those of the ketones.



(MAD)

Figure 3 Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD).

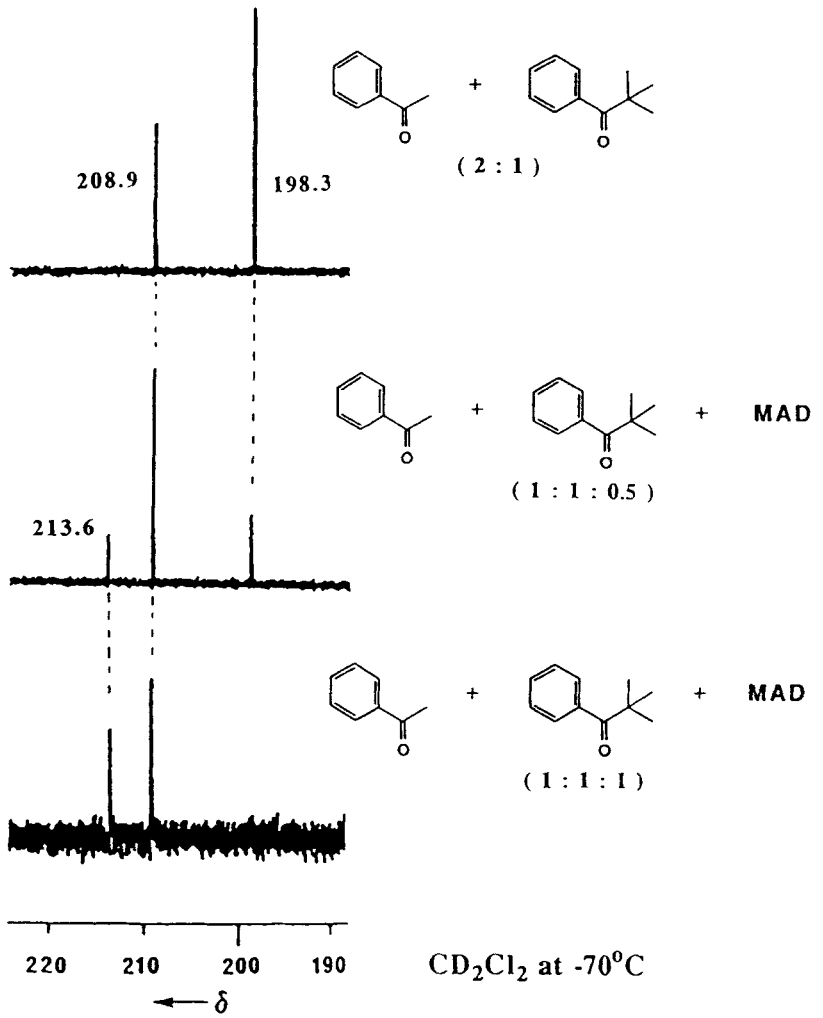


Figure 4 Low temperature ^{13}C-NMR spectra of ketones and their complexes with MAD in CD_2Cl_2.

The 125 MHz ^{13}C-NMR measurement of the *t*-butyl methyl fumarate–MAD complex in $CDCl_3$ at −50°C showed that the original signal of methoxycarbonyl at δ 165.7 shifted downfield to δ 173.3, whereas the signal of *t*-butoxycarbonyl appeared at δ 162.0 rather than at the original peak at δ 164.0 (Fig 5). These assignments are based on the carbonyl carbons of free dimethyl fumarate and di-*t*-butyl fumarate at δ 165.5 and 164.4, respectively; coordinated carbonyl carbons of dimethyl fumarate–MAD and di-*t*-butyl fumarate–MAD complexes appear at δ 173.0 and 172.2, respectively. Further

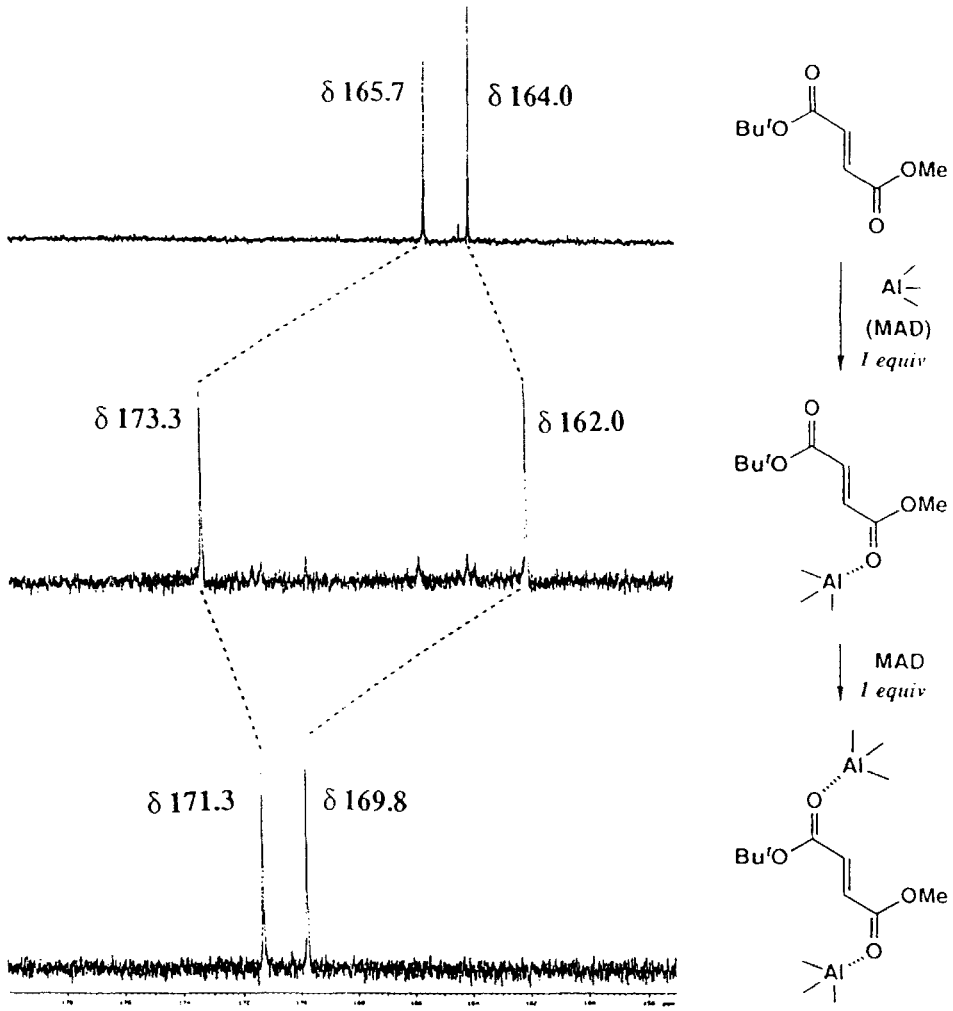


Figure 5 125 MHz ^{13}C-NMR spectra of *t*-butyl methyl fumarate–MAD complex in $CDCl_3$.

addition of one more equiv. of MAD resulted in the shift of the methoxycarbonyl and *t*-butoxycarbonyl signals at δ 173.3 and 162.0 to δ 171.3 and 169.8, respectively.

Discrimination of two different ethers

In contrast to the ketone and ester discrimination, discrimination of two different ethers appears to be more feasible, since in this case the recognition sites are α carbons to co-ordinated oxygens. For example, the low-temperature ^{13}C-NMR spectra of free 3-phenylpropyl methyl and ethyl ethers, and their co-ordination complexes with MAD have been determined (Fig 6); only the characteristic signals of the α-methylene carbons are indicated.[4] The ^{13}C-NMR measurement of a mixture of 1 equiv. each of MAD, methyl and ethyl ethers in $CDCl_3$ at low temperature showed that the original signal of the α-methylene carbon of the methyl ether at δ 72.05 shifted downfield to δ 75.32, whereas the signal of the ethyl ether remained unchanged. This result clearly confirmed the virtually complete recognition of the methyl ether by MAD.

As shown in Figure 7, the remarkable selectivity using exceptionally bulky MAD is apparent by comparison with other Lewis acids. For example, *i*-Bu_3Al and BF_3 gave only 4:1 and 5:3 ratios, respectively. In view of the two exceptionally bulky 2,6-di-*tert*-butyl-4-methylphenoxy ligands, MAD exists as a monomeric species in solution, thereby showing a high oxophilic character even with weak Lewis bases such as ethers. In contrast, less bulky methylaluminum bis(2,6-dimethylphenoxide) and methylaluminum bis(2,6-diisopropylphenoxide) were found not to form any co-ordination complexes with ethers at low temperature, probably due to their strong self-association through electron deficient bonds. In the case of tin tetrachloride, two ethers co-ordinated with tin to give 2:1 complex.

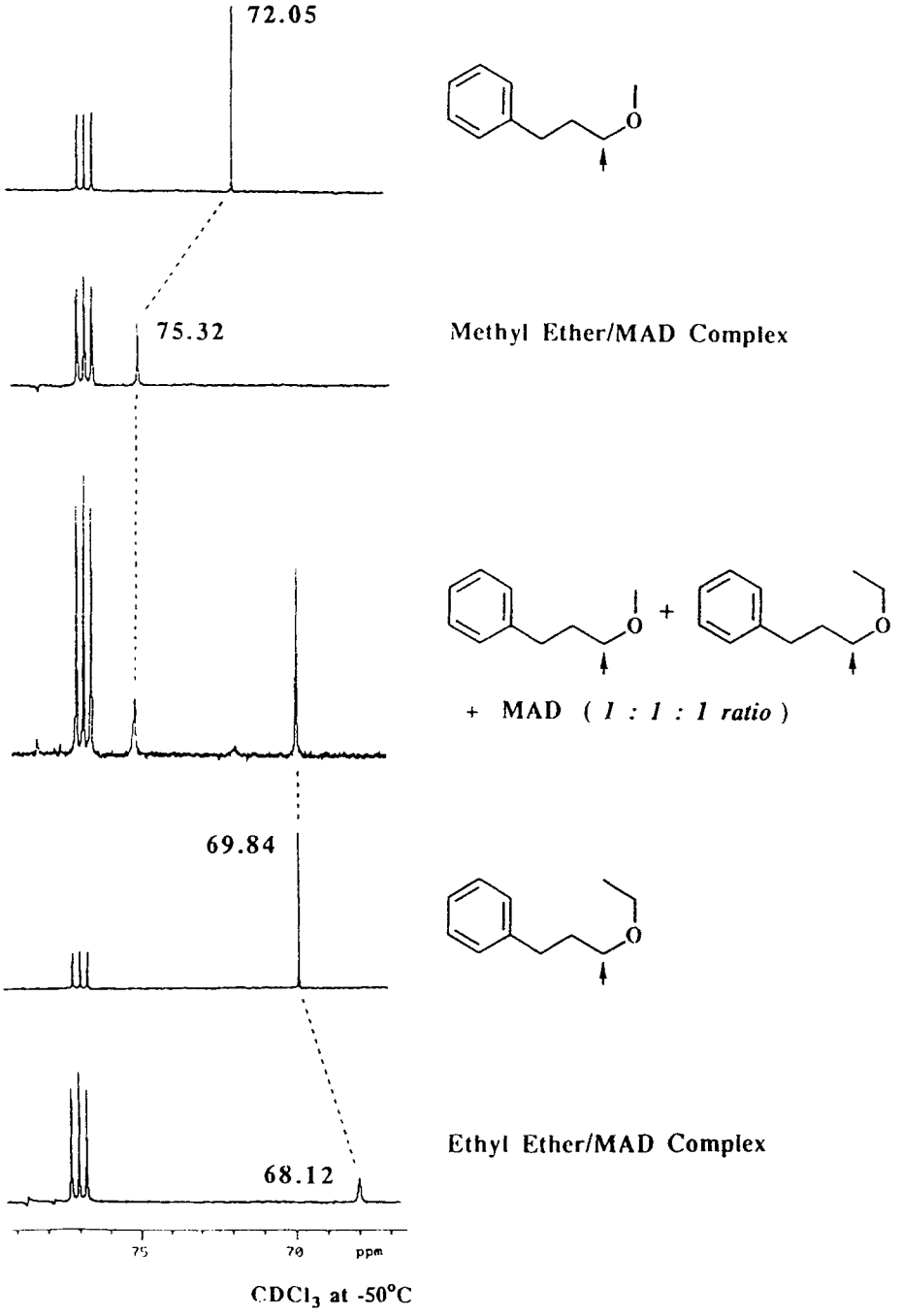
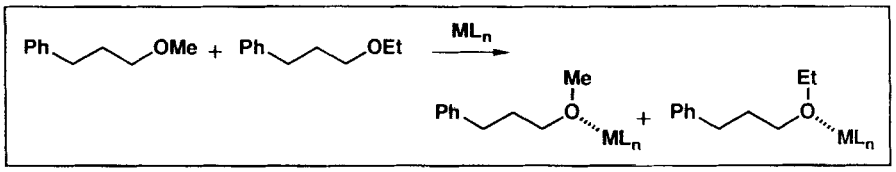
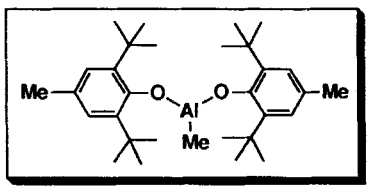


Figure 6 Low temperature ^{13}C-NMR spectra of 3-phenylpropyl methyl and ethyl ethers and their co-ordination complexes with MAD.

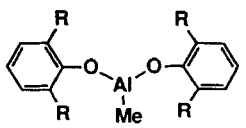
Figure 8 illustrates a simple application of our recognition chemistry to a new type of complexation chromatography.[4] Since various types of hindered polyphenols are readily available as antioxidants, we can make various MAD-type polymeric organoaluminum reagents. For example, reaction of sterically hindered triphenol in CH_2Cl_2 with 1.5 equiv. of Me_3Al at room temperature gave a polymeric monomethylaluminum reagent, and this structure was confirmed by ^{1}H- and ^{13}C-NMR spectroscopies. After removal of solvent, this polymeric aluminum reagent was ground to a powder in an argon box and mixed with equal amounts of silanized silica gel. This was packed in a short-path glass column as a stationary phase and washed once with dry, degassed hexane to remove unreacted free triphenol. Then a solution of 3-phenylpropyl methyl and ethyl ethers in hexane was charged on this column and eluted with the hexane



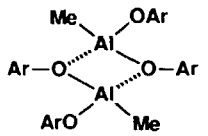


(MAD)

⇨ *Complexation Ratio = 100 : 0*



(R = *i*-Pr, Me)



dimeric structure by self-association

⇨ *No Complexation with Ethers*

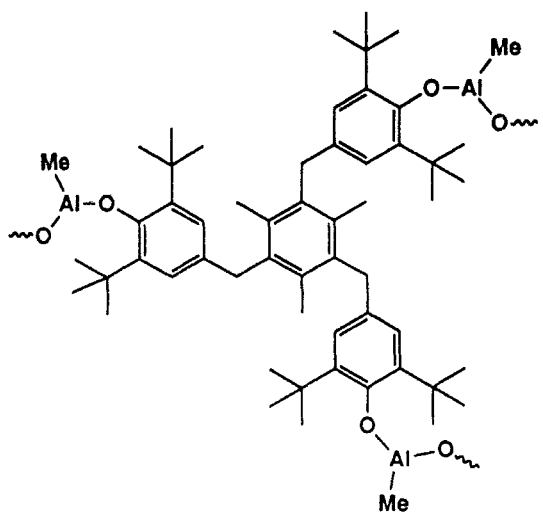
i-Bu_3Al ⇨ *Complexation Ratio = 4 : 1*

$SnCl_4$ ⇨ $(RR'O)_2SnCl_4$ *(2:1 Complex)*

Et_3B ⇨ *No Complexation*

BF_3 ⇨ *Complexation Ratio = 5 : 3*

Figure 7 Recognition ability of various Lewis acids.



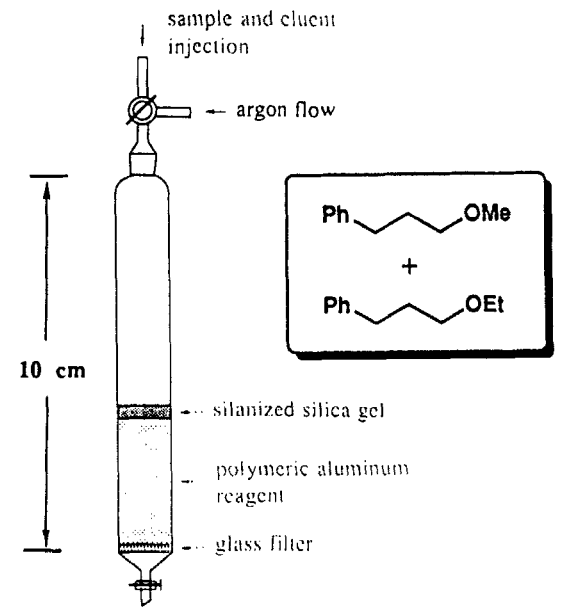


Figure 8 Complexation chromatography.

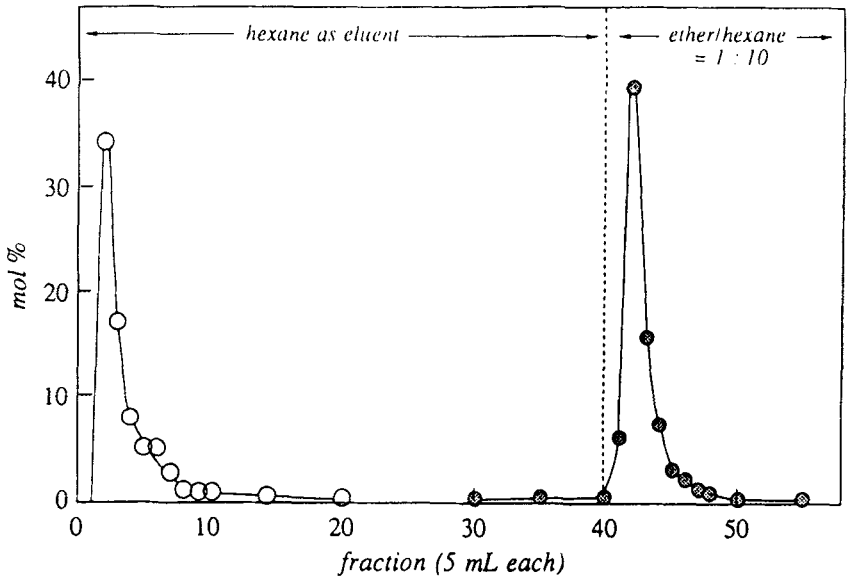


Figure 9 Separation of methyl 3-phenylpropyl ether (●) and ethyl 3-phenylpropyl ether (○) by co-ordination chromatography.

or hexane/ether mixture. The ratio of the two ethers with the aluminum reagent was 1:3. As illustrated in the elution curves of Figure 9, surprisingly clean separation of the methyl and ethyl ethers was realized by this short-path complexation column chromatography.

Stereocontrolled Claisen rearrangement

The rigorous recognition ability of Lewis acidic MAD toward simple methyl and ethyl ethers allows selective organic reactions using various ether substrates. One example is the stereocontrolled Claisen rearrangement of allyl vinyl ethers based on the stereoselective activation of ethereal oxygen by selective co-ordination of one lone pair out of the two lone pairs of electrons of the oxygen atom to aluminum reagent.[5]

In the Claisen rearrangement of allylic vinyl ether **1**, the conformation **2a** (with R equatorial), is thermally stable giving the *E*-olefinic carbonyl compound as a major product (Fig 10). However, on co-ordination to the aluminum reagent, the resulting conformation **5a** is destabilized by the steric repulsion between R and the aluminum ligand (Fig 11). In contrast, the thermally unstable conformation **2b** on co-ordination to the aluminum reagent is more stabilized than **5a**, thereby producing (*Z*)-**6** preferentially. It would be expected that the use of a more bulky aluminum reagent would give higher *Z*-selectivity in view of the increased 1,2-steric interaction between R and the aluminum reagent. Since we have already succeeded in virtually complete recognition of structurally very similar ethers using the exceptionally bulky MAD, it seems logical to utilize such a bulky organoaluminum reagent for stereocontrolled Claisen rearrangement.

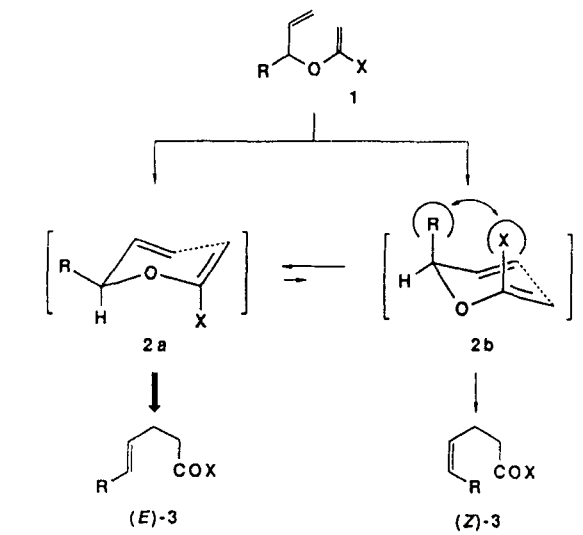


Figure 10 Claisen rearrangement of allylic vinyl ether **1**.

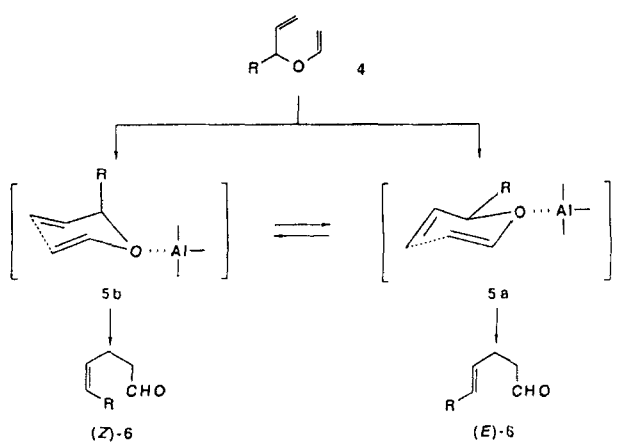


Figure 11 Organoalminum-promoted Claisen rearrangement of allylic vinyl ether 4.

When allyl vinyl ether **4** (R = *i*-Bu) was treated with MAD in CH_2Cl_2 at −78°C, the rearrangement proceeded quite reluctantly to furnish 7-methyl-4-octenal **6** (R = *i*-Bu) in only 43% yield. The *E*/*Z* ratio of **6** (R = *i*-Bu) was determined to be 19:81 by capillary GLC after conversion of the aldehyde to the corresponding alcohol and then to the trimethylsilyl ether. Apparently, the Lewis acidity of MAD, which is effective for the stereoselective activation of carbonyl moieties,[6] is not strong enough to activate the ether substrate **4**. Accordingly, a stronger Lewis acidic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) has been prepared and successfully applied to the rearrangement of **4** (R = *i*-Bu), resulting in clean generation of **6** (R = *i*-Bu) in 64% yield in the *E*/*Z* ratio of 7:93. Clearly, the less likely conformation **2b** (R = *i*-Bu: X = H), when complexed with exceptionally bulky organoaluminum reagents, is more favorable than **5a** as predicted (Fig 11). In fact, when the bulkiness of the aluminum reagent is decreased from MABR to dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide, the *E*/*Z* selectivity in the rearrangement of substrate **4** (R = *i*-Bu) is changed dramatically from 7:93 to 71:29, suggesting that the population of the transition state shifts from **5b** to **5a** with a decrease in the steric size of the aluminum ligands. Surprisingly, treatment of **4** (R = *i*-Bu) in toluene with methylaluminum bis(2,6-diphenylphenoxide) at −20°C gave rise to the *E*-isomer (*E*)-**6** (R = *i*-Bu) almost exclusively (*E*/*Z* = 97:3) in 85% yield. In a space-filling model of MAPH, two phenyl groups of the aluminum ligands are parallel to each other in front of the Lewis acidic aluminum center so that allyl vinyl ether substrates are incorporated in a sterically less demanding manner as a stable chair form of **2a** with the R substituent equatorial, leading to the *E*-isomer (*E*)-**6**.

CASE STUDY 2. DISCRIMINATION OF THE ENANTIOFACE OF CARBONYL GROUPS

Even though considerable progress has been made in recent years, synthetic organic chemists have been much less successful in their attempts to achieve steric control than is commonly found in enzyme-catalysed reactions. To achieve truly stereospecific man-made reactions, the following two controlling factors must be recognized. The first and perhaps the most important is local chirality control (molecular recognition due to bonding interactions, or orbital control). The second is global chirality control (molecular recognition due to non-bonding interactions).

One typical example of local chirality control in organic asymmetric synthesis is Noyori's BINAL-H reduction.[7] The stereochemical results were rationalized with reference to diastereomeric, six-membered cyclic stereocorrelation models. Using acetophenone as a model substrate, it was presumed that A is preferable to B because of the unfavourable interaction of the larger phenyl group with the binaphthyl system in B, resulting in the formation of an alcohol having the observed *R*-configuration (Fig 12).

The very high degree of stereospecificity exhibited in enzymic reactions is attributed to the molecular recognition based on global chirality control. A detailed picture of this stereospecificity, however, in terms of the mechanism of the reactions and the nature of the enzyme–substrate complex, has only begun to unfold over the last few decades. In most cases bonding interaction as a means of controlling the stereospecificity of intermolecular reaction is of minimal use, and the basis of enzymic stereospecificity is non-bonding interaction, i.e. steric control. Similarly, Okamoto's asymmetric polymerization using chiral lithium amide is a unique example of global chirality control.[8]

Although local chirality control is a general means of recognizing the structural features of a given substrate, stereospecificity disappears with structural variations of the substrate. On the other hand, global chirality control is a powerful method by which to recognize the molecule, but the reaction is often too stereospecific and generality may be diminished; thus only one substrate can be used for the receptor. Therefore, we must select certain aspects of local chirality control and global chirality control for man-made reactions which do not result in the loss of either stereospecificity or generality.

The first reliable chiral aluminum reagents of types (*R*)-**7** and (*S*)-**7** were devised for enantioselective activation of carbonyl groups based on the concept of diastereoselective activation of carbonyl moieties with the exceptionally bulky organoaluminum reagents, MAD and MAT.[6] The sterically hindered, optically pure (*R*)-(+)-3,3′-bis(triarylsilyl)binaphthol (*R*)-**8** required for the preparation of (*R*)-**7** can be synthesized in two steps from (*R*)-(+)-3,3′-dibromobinaphthol by bis-triarylsilylation and subsequent intramolecular 1,3-rearrangement of the triarylsilyl groups.[9] Reaction of (*R*)-**8** in toluene with trimethylaluminum produced the chiral organoaluminum reagent (*R*)-**7** quantitatively. Its molecular weight, found cryoscopically in benzene, corresponds closely with the value calculated for the monomeric species **7**. The modified chiral organoaluminum reagents, (*R*)-**7** and (*S*)-**7** were shown to be highly effective as chiral Lewis acid catalysts in the asymmetric hetero-Diels–Alder reaction.[10] Reaction of various aldehydes with activated dienes under the influence of catalytic **7** (5 ~ 10 mol%) at −20°C gave, after exposure of the resulting hetero-Diels–Alder

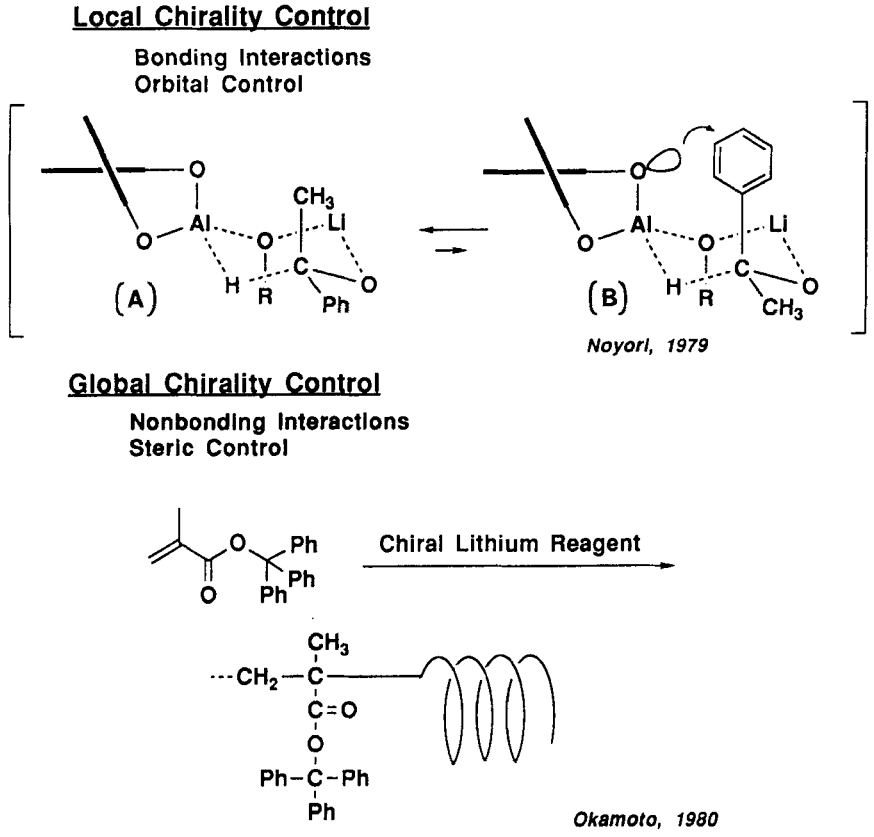


Figure 12 Chiral recognition.

adducts to trifluoroacetic acid, *cis*-dihydropyrones **10** predominantly in high yield with excellent enantioselectivity. The enantioface differentiation of prochiral aldehydes is controllable by the fine tuning of the size of the trialkylsilyl moiety in **7**, thereby allowing the rational designing of the catalyst for asymmetric induction. In fact, switching the triarylsilyl substituent (Ar = Ph or 3,5-Xylyl) to the *tert*-butyldimethylsilyl or trimethylsilyl group led to the eminent loss of enantio- as well as *cis*-selectivity in the hetero-Diels–Alder reaction of benzaldehyde and activated diene **9**. In marked contrast, the chiral organoaluminum reagent derived from trimethylaluminum and (*R*)-(+)-3,3′-dialkyl-binaphthol (alkyl = H, Me, or Ph) was employable only as a stoichiometric reagent and gave less satisfactory results in reactivity and enantioselectivity in the hetero-Diels–Alder reaction (Fig 13).

An interesting preparation method of chiral aluminum reagents has been described.[11] The chiral organoaluminum reagent, (*R*)-**7** or (*S*)-**7**, can be generated *in situ* from the corresponding racemate (±)-**7** by diastereoselective complexation with certain chiral ketones. Among several terpene-derived chiral ketones, 3-bromocamphor is found to be the most satisfactory. The hetero-Diels–Alder reaction of benzaldehyde and 2,4-dimethyl-1-methoxy-3-trimethylsiloxy-1,3-butadiene (**9**) with 0.1 equiv. of (±)-**7** (Ar = Ph) and *d*-bromocamphor at −78°C gave rise to the *cis*-adduct **10** as a major product in 82% ee. Although the extent of asymmetric induction is not yet as satisfactory as that with the optically pure **7** (Ar = Ph) (95% ee), one recrystallization of the *cis*-adduct **10** of 82% ee from hexane gave essentially optically pure **10**, thereby enhancing the practicability of this method. This study demonstrates the future potential for broader applicability of the *in situ* generated chiral catalyst via diastereoselective complexation in asymmetric synthesis (Fig 14).

The enantioselective activation of carbonyl groups with the chiral aluminum reagent, (*R*)-**7** or (*S*)-**7**, also enabled realization of the asymmetric ene reaction of electron-deficient aldehydes with various alkenes.[12] In the presence of powdered 4A molecular sieves, the chiral aluminum reagent, (*R*)-**7** or (*S*)-**7**, can be utilized as a catalyst without any loss of enantioselectivity (Fig 15).

The concept of the enantioselective activation of carbonyl groups with the bulky, chiral aluminum reagents, (*R*)-**7** or (*S*)-**7**, has been further extended to the enantioselective activation of an ether oxygen,

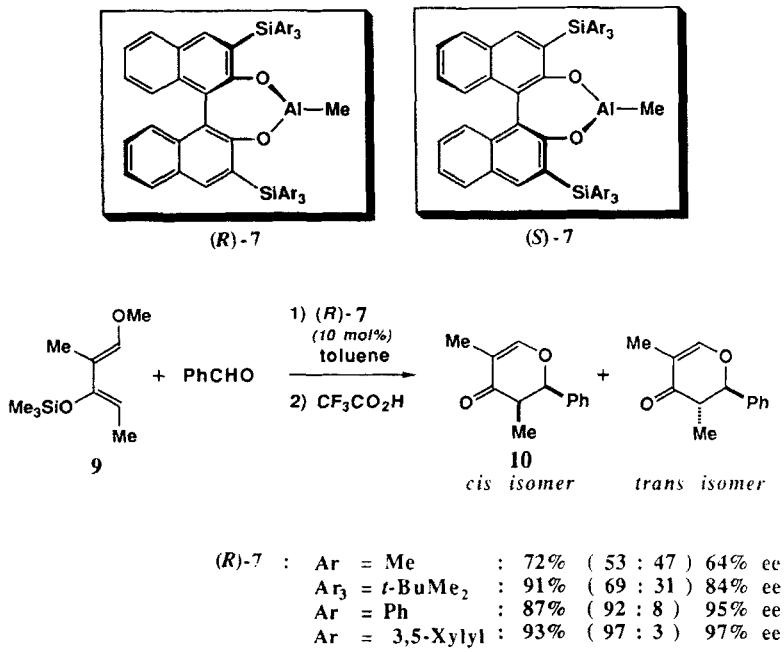


Figure 13 Asymmetric hetero-Diels-Alder reaction.

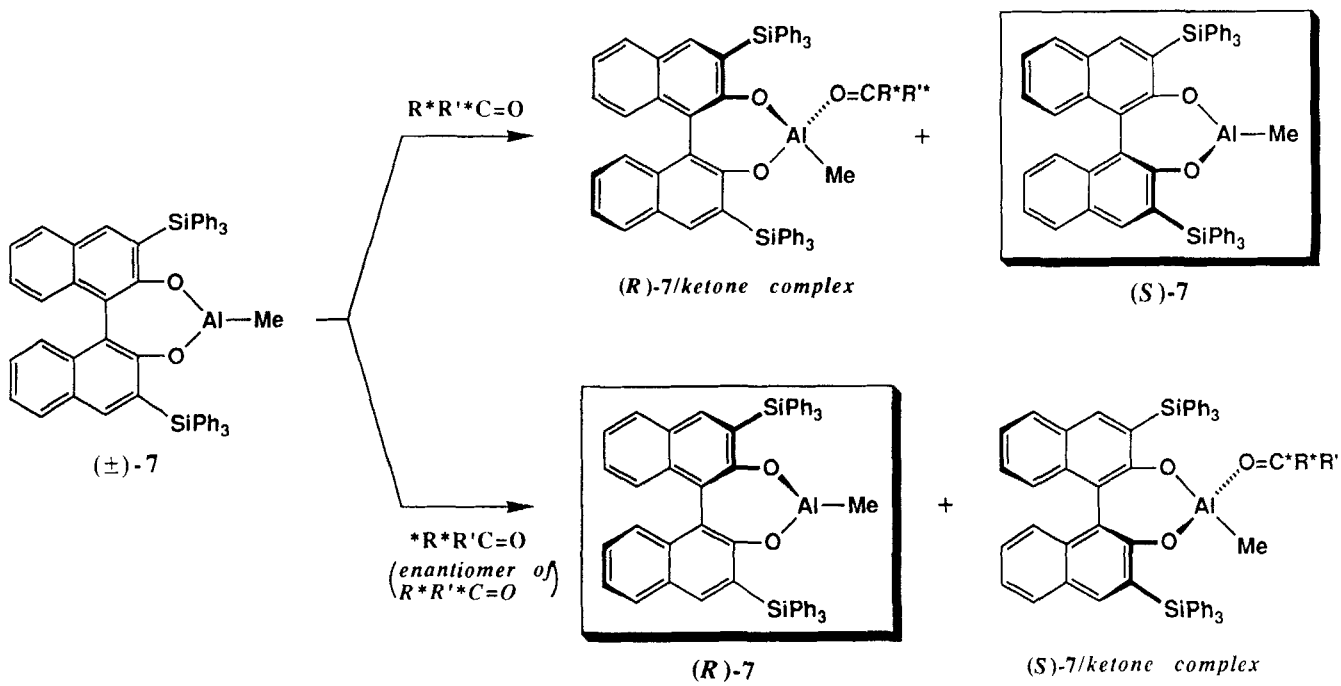


Figure 14 In situ generation of (R)-7 or (S)-7 from the racemate (I)-7.

thereby allowing the first successful example of the asymmetric Claisen rearrangement of allylic vinyl ethers **11** catalysed by (*R*)-**7** or (*S*)-**7** as illustrated in Table 1.[13] This method provides a facile asymmetric synthesis of various acylsilanes **12** or **13** (X = SiR_3) and acylgermanes **12** and **13** (X = $GeMe_3$) with high optical purity. Among various trialkylsilyl substituents of **7**, the more bulky *t*-butyldiphenylsilyl group exhibits the highest enantioselectivity. The conformational analysis of two possible chair-like transition-state structures of an allyl vinyl ether substrate **11** reveals that a chiral organoaluminum reagent **7** can discriminate

Table 1 Asymmetric Claisen rearrangement of allylic vinyl ethers **11**

Allyl vinyl ether	*Catalyst (R)-7*	*Reaction conditions (°C, h)*	*Claisen product*	*Yield (%)*	*% ee*[a]
11 (R = Ph, X = $SiMe_3$)	Ar_3 = Bu^tMe_2	−40, 0.1; −20, 24	**12** (R = Ph, X = $SiMe_3$)	22	14
11 (R = Ph, X = $SiMe_3$)	Ar = Ph	−40, 0.1; −20, 8	**12** (R = Ph, X = $SiMe_3$)	86	80
11 (R = Ph, X = $SiMe_3$)	Ar_3 = Bu^tPh_2	−40, 0.1; −20, 3	**12** (R = Ph, X = $SiMe_3$)	99	88
11 (R = Ph, X = $SiMe_3$)	Ar = Ph[b]	−40, 0.1; −20, 5	**13** (R = Ph, X = $SiMe_3$)	85	80
11 (R = Ph, X = $SiMe_2Ph$)	Ar = Ph	−78, 0.1; −40, 16	**12** (R = Ph, X = $SiMe_2Ph$)	65	85
11 (R = Ph, X = $SiMe_2Ph$)	Ar_3 = Bu^tPh_2	−78, 0.1; −40, 8	**12** (R = Ph, X = $SiMe_2Ph$)	76	90
11 (R = cyclohexyl, X = $SiMe_3$)	Ar = Ph	−40, 0.1; −20, 4	**12** (R = cyclohexyl, X = $SiMe_3$)	79	61
11 (R = cyclohexyl, X = $SiMe_3$)	Ar_3 = Bu^tPh_2	−40, 0.1; −20, 4	**12** (R = cyclohexyl, X = $SiMe_3$)	84	71
11 (R = *trans*-cinnamyl, X = $SiMe_3$)	Ar = Ph	−40, 0.1; −20, 10	**12** (R = *trans*-cinnamyl, X = $SiMe_3$)	40	60
11 (R = Ph, X = $GeMe_3$)	Ar = Ph	−78, 0.1; −40, 15	**12** (R = Ph, X = $GeMe_3$)	73	91
11 (R = Ph, X = $GeMe_3$)	Ar_3 = Bu^tPh_2	−78, 0.1; −40, 16	**12** (R = Ph, X = $GeMe_3$)	68	93

[a] Determined by capillary GLC analysis after conversion to the acetals of (2*R*,3*R*)-butanediol.
[b] Use of (*S*)-**7** as catalyst.

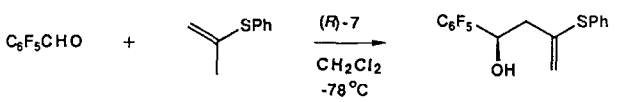


Figure 15 Asymmetric ene reaction.

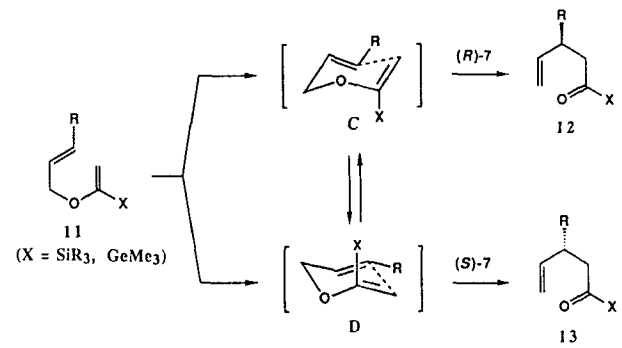


Figure 16 Asymmetric Claisen rearrangement of allylic vinyl ether 11.

between these two conformations, C and D, only by a difference in the orientation of the α-methylene groups of ethers (Fig 16).

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