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ORGANOALUMINUMS IN ORGANIC SYNTHESIS

KEIJI MARUOKA and HISASHI YAMAMOTO

Department of Applied Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan

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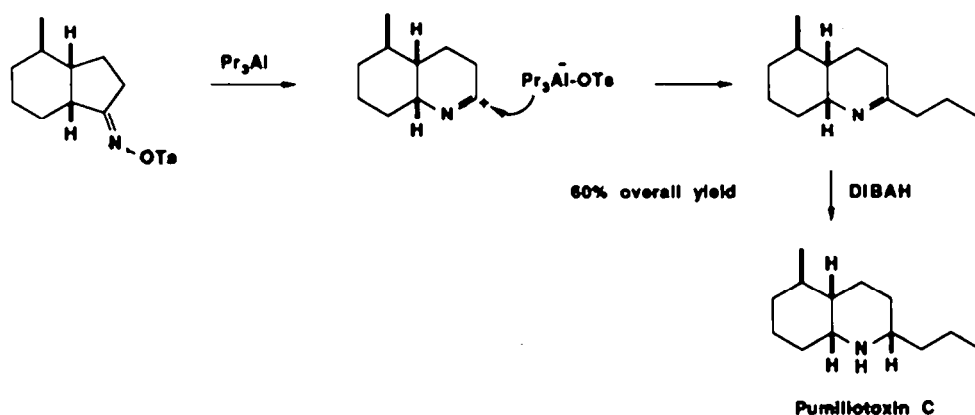
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1. INTRODUCTION

Organoaluminum compounds, little known until the 1950s, have become widely accepted and increasingly important in the field of industry and in the laboratory, particularly after K. Ziegler and colleagues discovered the direct synthesis of trialkylaluminums and their brilliant application to the polymerization of olefins.^{1,2} The chemistry of organoaluminum compounds has been understood in terms of the dynamic nature of the C—Al bond and the high Lewis acidity of their monomeric species. This is directly related to the pronounced tendency of the aluminum atom to build up an octet of electrons. The C—Al bonds exhibit a unique set of properties: (i) their ability to alkylate certain metals and to reduce transition metal salts (ii) their tendency to form bridged complexes containing other metals and organometallics and (iii) their facile reactions with olefins under certain conditions. Organoaluminum compounds also possess a strong affinity for various heteroatoms in organic molecules, particularly oxygen. They generate 1 : 1 coordination complexes even with neutral bases such as ethers. Utilization of this property (heterogenophilicity including oxygenophilicity) in organic synthesis allows facile reactions with hetero atoms particularly oxygen- and carbonyl-containing compounds. However, in sharp contrast to classical Lewis acids such as $\text{BF}_3 \cdot \text{OEt}_2$, AlCl_3 , SnCl_4 , and TiCl_4 , they are endowed with a latent nucleophilic character which can emerge prominently on coordination with a hetero-atom-containing functional group. The aluminum atom serves primarily as the coordination site for the substrate, while the nucleophilic center attached to the aluminum atom can be activated by the formation of the coordination complex facilitating the nucleophilic attack on the substrate as illustrated by the successive Beckmann rearrangement-alkylation sequence using trialkylaluminums (Scheme 1).³ Occasionally the nucleo-

philic center may behave as a proton scavenger. These characteristic features are of great interest to synthetic organic chemists.

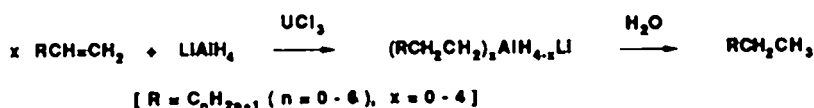


Scheme 1.

A comprehensive review of organoaluminum chemistry appeared in 1972, covering a variety of literature up to late 1971.⁴ Other important review articles have been published since then.⁵⁻¹⁴ It is the aim of this Report to survey the more important recent developments in this area from 1984 with particular emphasis on the synthetic reactions of organoaluminum compounds with organic substrates, arranged by their functional groups. Polymer chemistry using organoaluminums as coordination catalysts will not be discussed here and investigations of a more mechanistic nature on organoaluminum compounds are also excluded.

2. REACTIONS WITH HYDROCARBONS

In view of a weak affinity of the ionic Al—H bond for olefins¹⁵⁻²¹ the hydroalumination of olefins has been studied extensively in the presence of transition metal catalysts. Among these, only Ti and Zr catalysts have proved to be effective for obtaining hydroalumination products and their subsequent functionalization with various electrophiles has been studied.^{22,23} Recently, several other transition metals have been utilized. L  marechal *et al.* found that UCl₃ or UCl₄ is an effective catalyst for the preparation of organoaluminates from terminal olefins and LiAlH₄.²⁴ The active species in this reaction is thought to be U(AlH₄)₃.

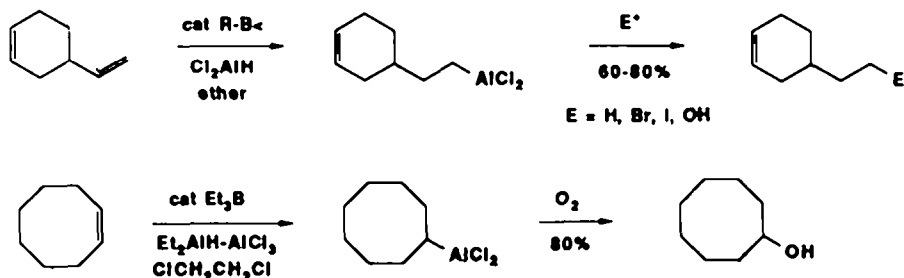


Nickel(0)-olefin complexes such as tris(ethylene)nickel(0) and tris(bicycloheptene)nickel(0) are highly active homogeneous catalysts for the transalkylation of trialkylaluminum with terminal olefins.²⁵ After completion of the reaction the "naked"-nickel(0) can be removed in the form of Ni(CO)₄ by reaction with CO.

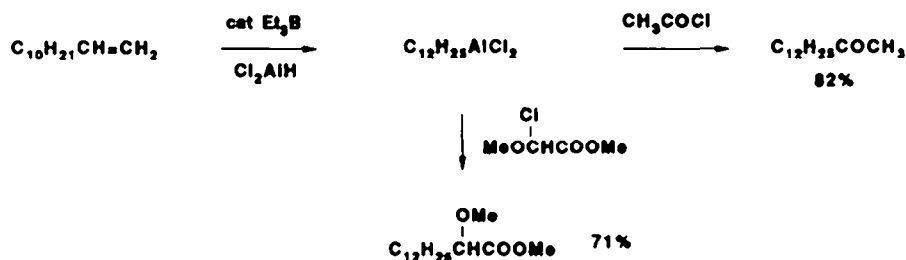


Extensive studies have shown that only terminal olefins can be successfully utilized and hydroalumination of internal olefins proceeds reluctantly even in the presence of transition metal

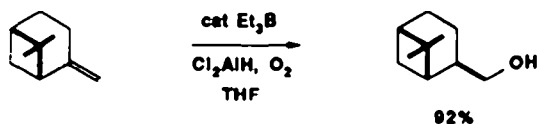
catalysts.^{16,22} In this context the possibility of organoborane-catalyzed hydroalumination has been explored by the authors with consideration for the distinct advantage of hydroboration which is far superior to other hydrometalation reactions. This expectation has been realized by combining the use of catalytic organoboranes and Cl_2AlH as the hydrometalation agent.²⁶ Cl_2AlH (or its synthetic equivalent) can be generated *in situ* from (A) LiAlH_4 and AlCl_3 in ether or (B) R_2AlH ($\text{R} = \text{Et}$ or *i*-Bu) and AlCl_3 in 1,2-dichloroethane. The organoborane-catalyzed hydroalumination using the catalytic $\text{PhB}(\text{OH})_2\text{-Cl}_2\text{AlH}$ or catalytic $\text{Et}_3\text{B-Cl}_2\text{AlH}$ systems in ether (condition A) is applicable to the regio- and chemo-selective functionalization of monosubstituted olefins. Internal olefins as well as terminal olefins are readily hydrometalated with catalytic $\text{Et}_3\text{B-Cl}_2\text{AlH}$ in 1,2-dichloroethane (condition B). Apparently, the coordination of an ethereal oxygen to a Lewis acidic aluminum center under condition A significantly lowers the reactivity of the catalytic system.



A new carbon-carbon bond formation can be realized by the selective coupling between the intermediate alkylaluminum dichloride, generated under the condition B, and certain organic electrophiles.^{26,27}

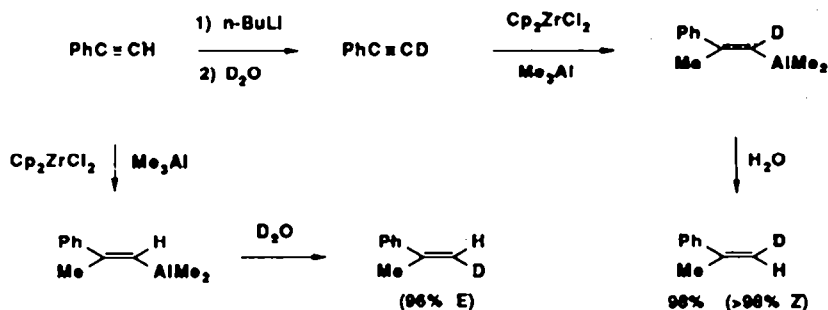


During the course of the investigation on the organoborane-catalyzed hydroalumination, a highly efficient *anti*-Markownikoff hydration of olefins has been found which involves the combination of catalytic organoborane and Cl_2AlH in THF under dry air.²⁸ Organoboranes such as $\text{PhB}(\text{OH})_2$ and Et_3B are active catalysts but inorganic boron catalysts ($\text{BF}_3 \cdot \text{OEt}_2$, $\text{B}(\text{OMe})_3$, $\text{B}(\text{OH})_3$, etc.) gave much less satisfactory results.



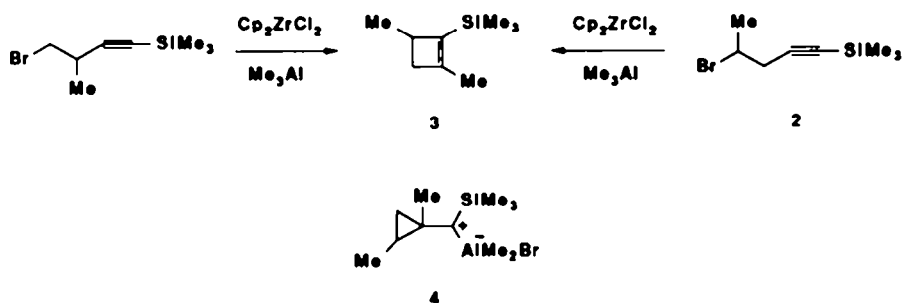
The zirconocene-catalyzed carboalumination reaction of alkynes has been developed by Negishi *et al.* to serve as a new route to stereo- and regio-defined trisubstituted olefins.²⁹ Phenylacetylene and several other alkynes on treatment with $\text{Cp}_2\text{ZrCl}_2\text{-Me}_3\text{Al}$ undergo *cis*-addition to yield the corresponding alkenylaluminums almost exclusively (Scheme 2). Such alkenylaluminums have

already proven to be versatile intermediates for the preparation of a wide variety of trisubstituted olefins. Although the Cp_2ZrCl_2 -catalyzed reaction of alkynes with trialkylaluminum possessing β -hydrogens is complicated by competitive hydrometalation²² and diminished the regioselectivity (70–80%), the hydrometalation can be avoided by using dialkylaluminum chloride in place of trialkylaluminum. Based on the mechanistic studies, they concluded that the Zr-catalyzed carboalumination reaction probably involves the direct Al—C bond addition assisted by Zr.

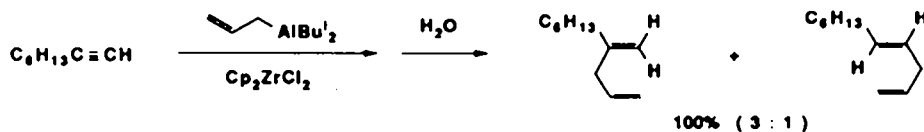


Scheme 2.

Application of the Zr-catalyzed carboalumination to haloalkyl-substituted 1-(trimethylsilyl)-1-alkynes provides a new metal-promoted cyclization reaction.³⁰ The reaction of 4-bromo-3-methyl-1-(trimethylsilyl)-1-butyne (**1**) and its regioisomer **2** with $\text{Cp}_2\text{ZrCl}_2\text{-Me}_2\text{Al}$ gave rise to the same product **3**. The regiochemical results are in good agreement with the intermediary of **4**.

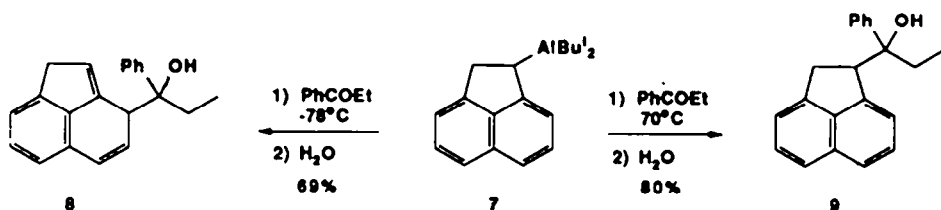


The same group also investigated the Cp_2ZrCl_2 -catalyzed allylaluminumation and benzylaluminumation of alkynes. These reactions are highly stereoselective but are not regioselective.³¹

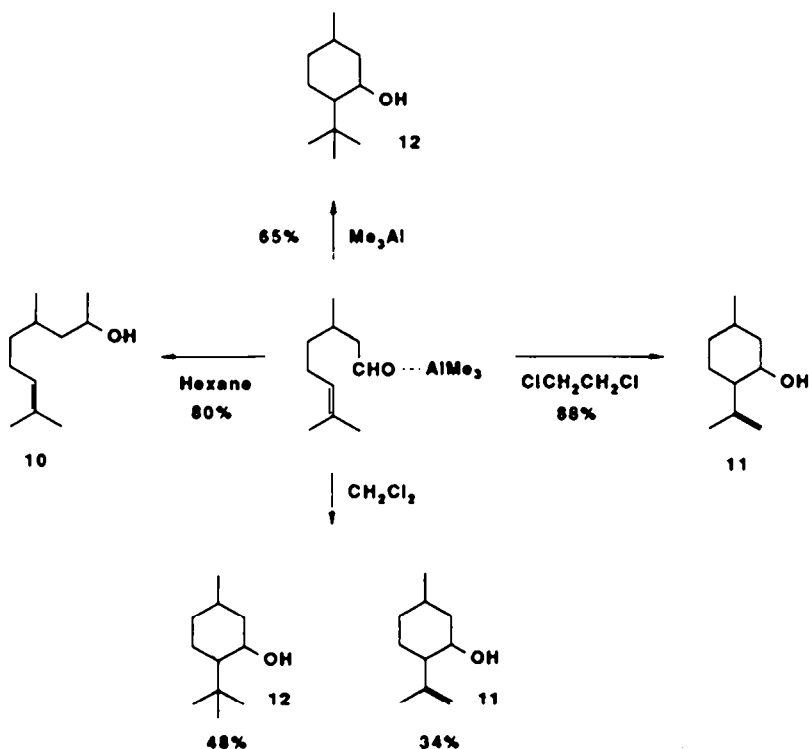


The bimetallic species, $\text{Bu}_2\text{Mg-2Et}_3\text{Al}$ was found by Oshima and Nozaki to be effective for the carboalumination of silylacetylene.³² The compound, $\text{Bu}_2\text{Mg-2Et}_3\text{Al}$ has the bridged structure **5** which is essential for enhancing the reactivity of the C—Al bond. A similar bimetallic bridged species **6** is also involved in the Cp_2ZrCl_2 -catalyzed carboalumination of terminal acetylenes with Me_2Al .³³ The new reaction proceeds in a regiospecific but nonstereoselective manner. However,

propyl)-1,3-dihydroacenaphthene (8). On the other hand, the same reagent at 70°C led to the formation of 1-(1-hydroxy-1-phenyl-1-propyl)acenaphthene (9). In addition, the stereochemically defined adduct of acenaphthylene and diisobutylaluminum deuteride, (*cis*-2-deuterio-1-acenaphthenyl)diisobutylaluminum diethyl etherate, is found to react with ketones at 65°C to yield a 1 : 1 mixture of *cis*- and *trans*-2-deuterio-1-acenaphthenylcarbinols. These findings indicate that electrophilic attack at the ortho position is the kinetically controlled process, while rearrangement to C₁ at higher temperature is thermodynamically favored.

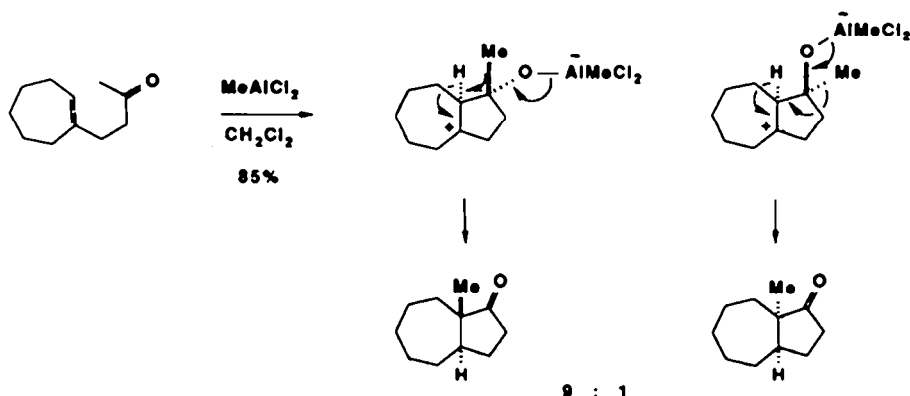


Pronounced solvent as well as temperature effects on the course of trialkylaluminum-induced cyclization of unsaturated aldehydes were observed by the authors.³⁷ Thus, unimolecular decomposition of the 1 : 1 complex of citronellal-Me₃Al at -78°C to room temperature yielded the acyclic compound 10 in hexane, whereas isopregol (11) was produced exclusively in 1,2-dichloroethane. Furthermore, the cyclization-methylation product 12 was formed with high selectivity using excess Me₃Al in CH₂Cl₂ at low temperature (Scheme 4). The 1 : 1 complex of other trialkylaluminum-citronellal decomposed upon warming to room temperature to furnish a reduction product, citronellol as a major product. The reactions of trialkylaluminum with several aliphatic ketones including 2-, 3-alkanones and cyclic ketones have been studied by Nakamura *et al.* to examine the effect of their alkyl substituents on the reaction mode.³⁸



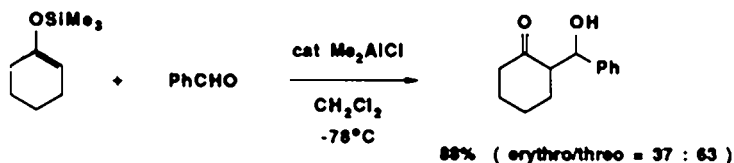
Scheme 4.

Snider and co-workers reported the studies of MeAlCl_2 -induced cyclization of unsaturated ketones. Their results indicate the advantage of alkylaluminum chloride over AlCl_3 in Lewis acid catalyzed reactions, since these reagents are capable of acting as proton scavengers as well as Lewis acids.³⁹ The reaction is interpreted as a MeAlCl_2 -promoted cyclization of the γ,δ -unsaturated ketone followed by the sequential hydride and methyl shift as illustrated in Scheme 5.

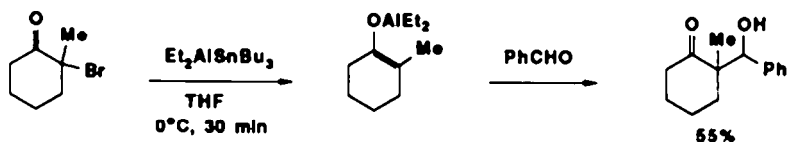


Scheme 5.

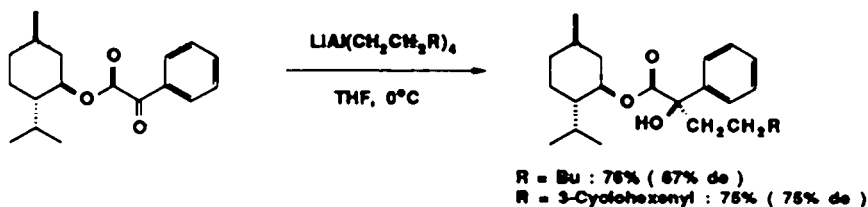
Organoaluminum-catalyzed aldol condensation of aldehydes and silyl enol ethers has been reported.⁴⁰ Me_2AlCl (0.05–0.5 equiv.) is most effective and other organoaluminum reagents such as Me_3Al , EtAlCl_2 , Et_2AlCl , and MeAlCl_2 lowered the yields of aldol products.



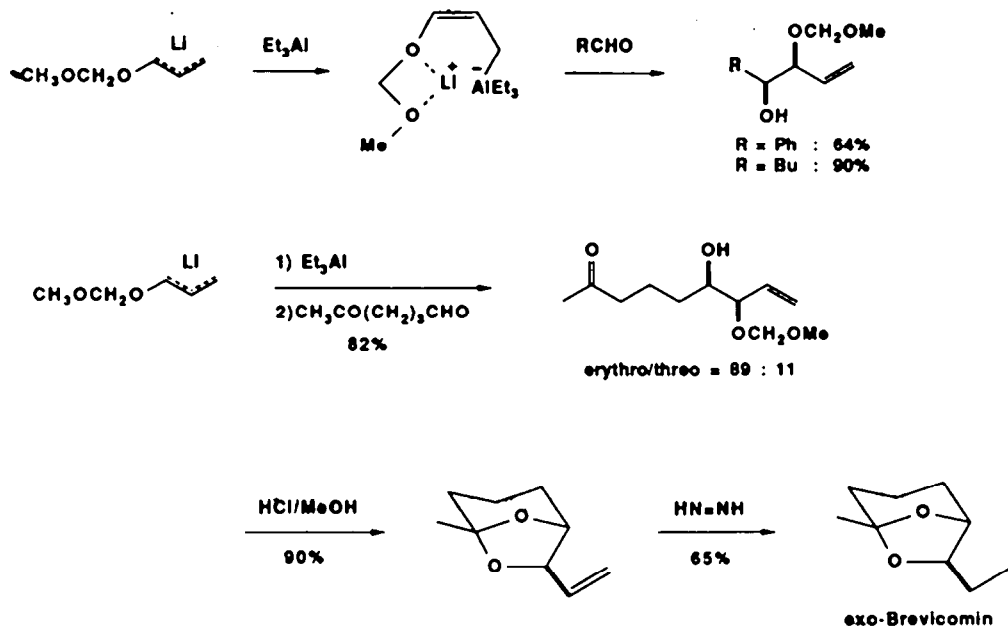
Another aldol reaction has been reported by Oshima and Nozaki.⁴¹ They generated the aluminum enolate regioselectively by treatment of α -halo carbonyl compounds with reagents of the type $\text{Bu}_3\text{SnAlEt}_2$, $\text{Bu}_3\text{PbAlEt}_2$, or $\text{Ph}_3\text{PbAlEt}_2$ and reaction with aldehydes or ketones gave β -hydroxy carbonyl compounds under mild conditions. The following aldol reaction is accelerated by adding catalytic $\text{Pd}(\text{PPh}_3)_4$.



Lithium tetraalkylaluminate prepared by the TiCl_4 -catalyzed hydroalumination of terminal olefins with LiAlH_4 was found to add to (–)-menthyl phenylglyoxylate in a diastereoselective manner.⁴² A variety of α -substituted mandelic acid esters with the absolute configuration of *R* were obtainable in 64–76% dc.

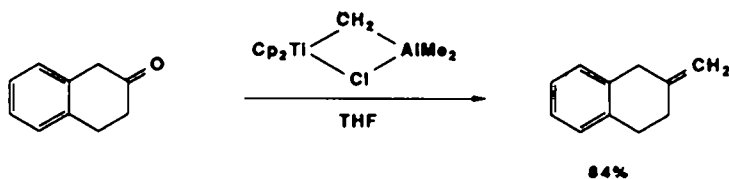


The reaction of hetero-substituted allylic carbanions with carbonyl compounds via allylic aluminum "ate" complex was investigated in detail by Yamamoto and Maruyama.⁴³ Aldehydes reacted with the oxygen-, sulfur-, selenium- and silicon-substituted allylic carbanions at the α -position via ate complexes. In particular, the aluminum ate complex of the allyloxy carbanions gave rise to the *erythro* isomer with very high stereoselectivity. This procedure has been applied to the stereoselective synthesis of *exo*-brevicomine (Scheme 6).

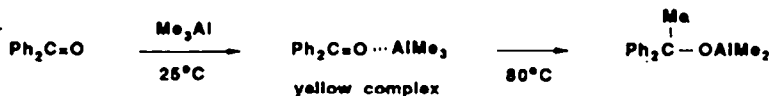


Scheme 6.

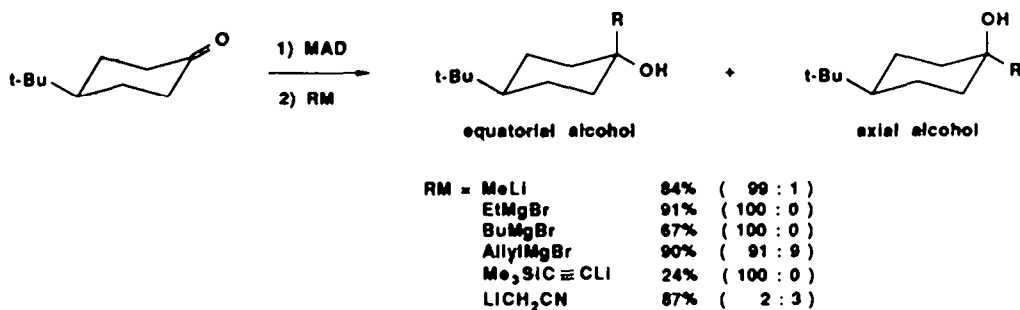
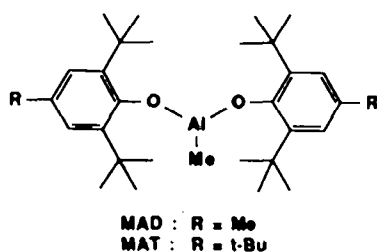
The standard Wittig reagents can function as strong bases and remove the acidic α -protons of carbonyl compounds. With easily enolizable ketones, proton abstraction becomes the dominant reaction. However, Tebbe's reagent, $\text{Cp}_2\text{TiCH}_2 \cdot \text{AlMe}_2\text{Cl}$, which cleanly converted esters and lactones into their corresponding enol ethers⁴⁴ was found to be highly effective for the methylenation of enolizable ketones.⁴⁵ The titanium methylenide fragment $\text{Cp}_2\text{Ti}=\text{CH}_2$ is an active species which reacts chemoselectively with ketones over esters.



Organoaluminum compounds are endowed with high oxygenophilic character and so are capable of forming long-lived monomeric 1 : 1 complexes with carbonyl substrates. For example, the reaction of benzophenone with Me_3Al in a 1 : 1 molar ratio gives a yellow, long-lived monomeric 1 : 1 species which decomposed unimolecularly to dimethylaluminum 1,1-diphenylethoxide during some minutes at 80°C or many hours at 25°C .⁴⁶ This unique property may be utilized for stereo-

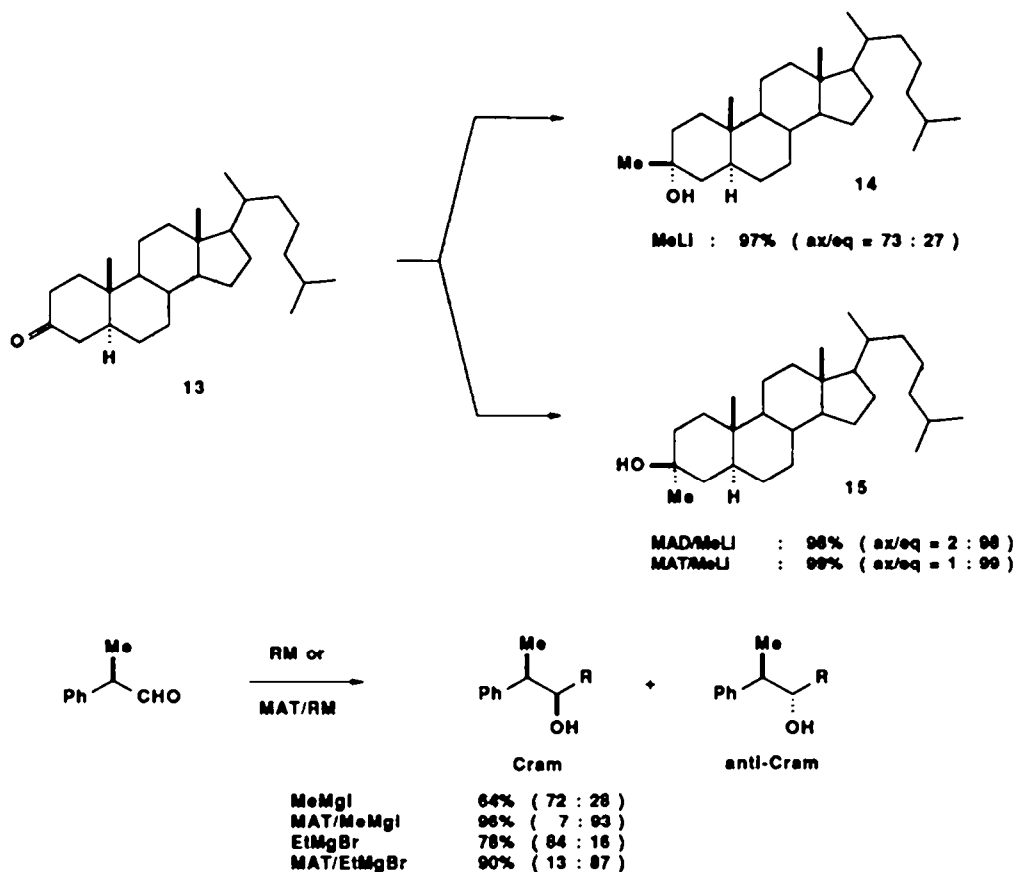


selective activation of the carbonyl group. Among various organoaluminum derivatives which have been examined, exceptionally bulky, oxygenophilic organoaluminum reagents such as methylaluminum bis(2,6-di-*tert*-butyl-4-alkylphenoxide) (MAD and MAT), have shown excellent diastereofacial selectivity in carbonyl alkylation.^{47,48} Thus, treatment of 4-*tert*-butylcyclohexanone with MAD or MAT in toluene produced a 1 : 1 complex which on subsequent treatment with methyl-lithium or Grignard reagents in ether at -78°C afforded the equatorial alcohol almost exclusively. Methyl-lithium or Grignard reagents undergo preferential equatorial attack yielding axial alcohols as the major product. MAD and MAT have played a crucial role in the stereoselective synthesis of hitherto inaccessible equatorial alcohols from cyclohexanones. Interesting results were also obtained for nonsterically demanding nucleophiles such as acetylene and acetonitrile anions which originally provided equatorial alcohols preferentially on reaction with cyclohexanones.⁴⁹ Alkylation of 4-*tert*-butylcyclohexanone with MAD- $\text{Me}_3\text{SiC}\equiv\text{CLi}$ system gave rise to the equatorial alcohol (24%) exclusively with the recovery of unreacted ketone (72%). This result indicates that decomplexation during nucleophilic attack of $\text{Me}_3\text{SiC}\equiv\text{CLi}$ at the aluminum center of the ketone-MAD complex takes precedence over the desired nucleophilic alkylation at the carbonyl group of the ketone-MAD complex. In fact, the ate complex derived from MAD and $\text{Me}_3\text{SiC}\equiv\text{CLi}$ is unreactive to ketones and this results in the recovery of most of the starting ketone. On the other hand, MAD- LiCH_2CN system increases the propensity for equatorial attack of the nucleophile. This suggests the initial ate complex formation by attack of LiCH_2CN upon the MAD followed by alkylation of the ate complex by the ketone.

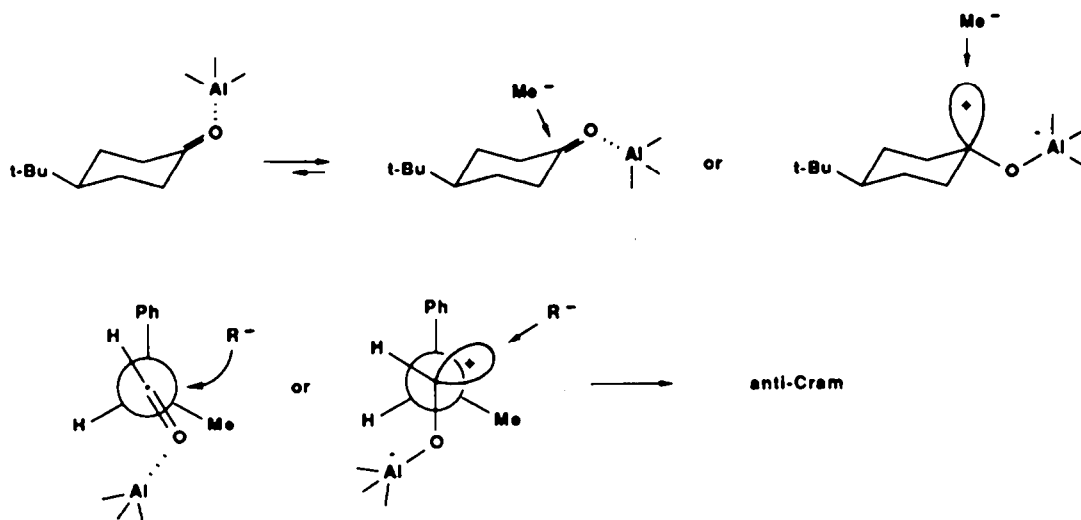


Scheme 7.

This approach has been quite useful in the stereoselective alkylation of steroidal ketones. Reaction of 3-cholestanone (13) with MeLi gave predominantly 3 β -methylcholestan-3 α -ol (axial alcohol) (14), whereas amphiphilic alkylation of the ketone with MAD/MeLi or MAT/MeLi afforded 3 α -methylcholestan-3 β -ol (equatorial alcohol) (15) exclusively. In addition, unprecedented *anti*-Cram selectivity was achievable in the MAD- or MAT-mediated alkylation of α -chiral aldehydes possessing no ability to be chelated. The stereochemical outcome of equatorial and *anti*-Cram selectivity in carbonyl alkylation is best accounted for by nucleophilic addition of carbanions to electrophilically activated carbonyl substrates with MAD or MAT (Scheme 9). In contrast with ordinary carbonyl alkylations, such an amphiphilically activated alkylation would be regarded as a new, as yet unexplored class of alkylation.⁵⁰

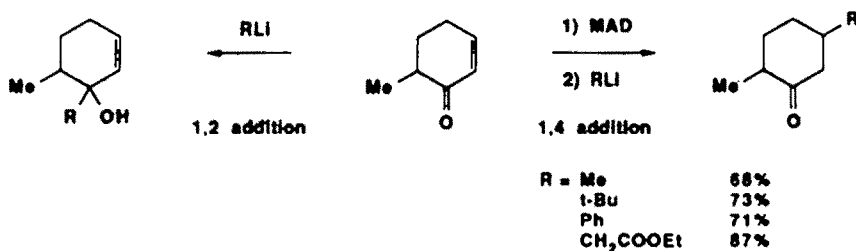


Scheme 8.

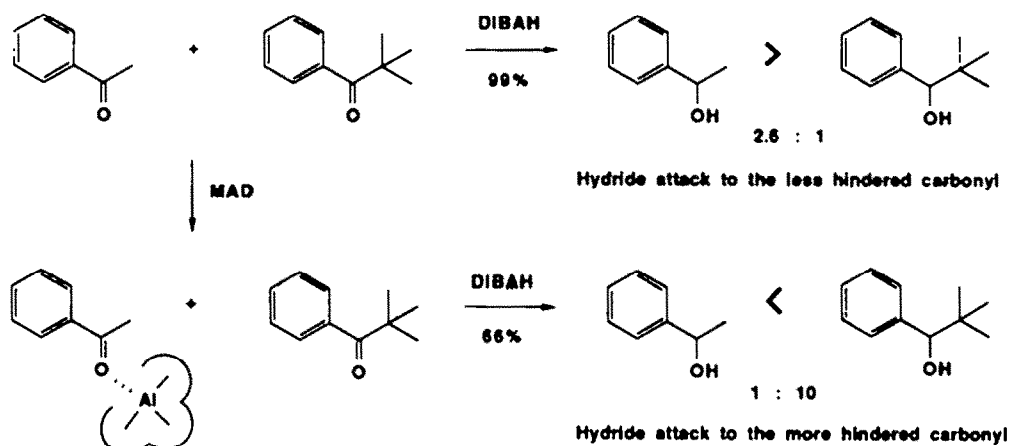


Scheme 9.

Conjugate addition to α,β -unsaturated carbonyl compounds is usually effected by soft organometallics (Cu, Ni, Zr, Zn, Al, etc.). The use of organolithium reagents has never been developed in view of their hard nucleophilic character. However, unusual conjugate addition of organolithium reagents to α,β -unsaturated carbonyl compounds can be accomplished by using the amphiphilic reaction system described above.³¹

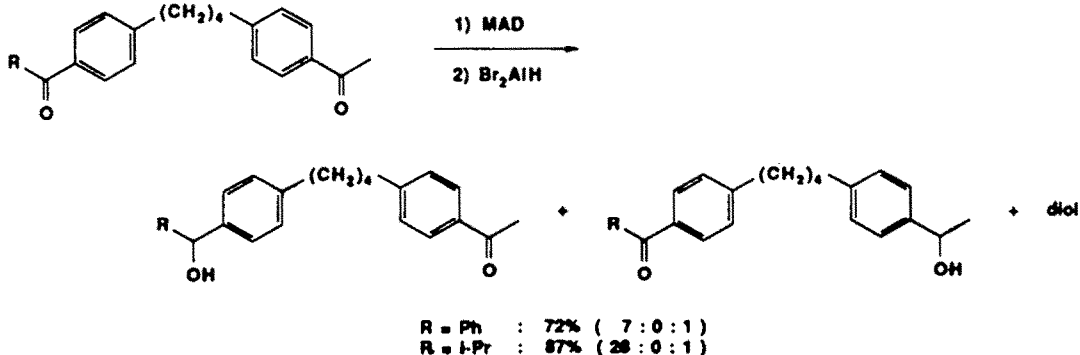


Discrimination of two different carbonyl groups has been successfully carried out by complexing the less hindered carbonyl selectively with MAD.⁵² This observation enabled the selective reduction of sterically more hindered or electronically less polarisable carbonyl substrates. Treatment of an equimolar mixture of acetophenone and pivalophenone in CH₂Cl₂ with MAD (1 equiv.) followed by reduction with DIBAH (1 equiv.) at -78°C yielded the alcohols (66% combined yield) in a ratio of 1:10. The ¹³C NMR measurement of an equimolar mixture of MAD, acetophenone, and pivalophenone in CD₂Cl₂ at -70°C revealed that the original signal of the acetophenone carbonyl at δ 198.3 entirely shifted downfield to δ 213.6, whereas the signal of the pivalophenone carbonyl remained unchanged. From a synthetic point of view, use of each 2 equiv. of MAD and DIBAH seems to be satisfactory in both selectivity and chemical yield (ratio = 1:16; 85% yield). This suggests that decomplexation of the more hindered pivalophenone and MAD occurs during the reaction with DIBAH.



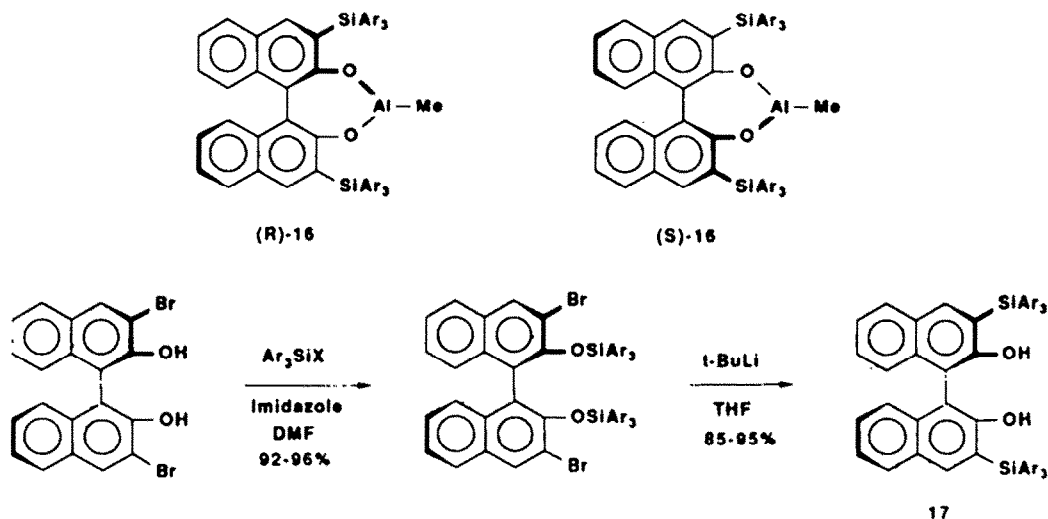
Scheme 10.

This process demonstrates the use of MAD as a temporary protecting group for the normally more reactive functionality of a bifunctional molecule. This is illustrated in Scheme 11.

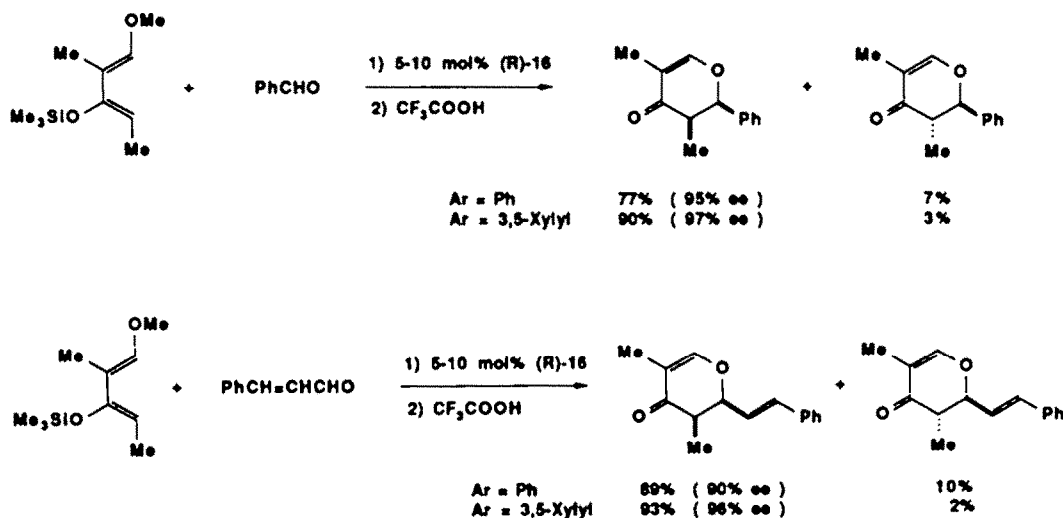


Scheme 11.

Based on the concept of the diastereoselective activation of carbonyl groups with MAD or MAT, the bulky, chiral organoaluminum reagent **16** has been devised for enantioselective activation of carbonyl groups. The sterically hindered, optically pure (*R*)-(+)-3,3'-bis(triarylsilyl)binaphthol (*R*)-**17** required for the preparation of (*R*)-**16** can be synthesized in two steps from (*R*)-(+)-3,3'-dibromobinaphthol by the bis-triarylsilylation and subsequent intramolecular 1,3-rearrangement of

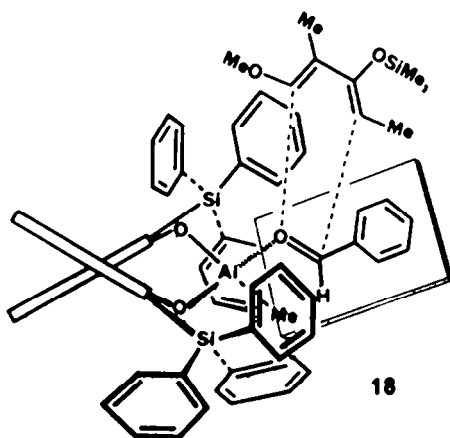


the triarylsilyl group.⁵³ Reaction of (*R*)-**17** in toluene with Me_3Al produced the chiral organoaluminum reagent (*R*)-**16**. Its molecular weight, found cryoscopically in benzene, corresponds closely with the value calculated for the monomeric species **16**. The modified organoaluminum reagent **16** was shown to be employable as a chiral Lewis acid catalyst in the asymmetric hetero-Diels-Alder reaction.⁵⁴ Reaction of various aldehydes with activated dienes under the influence of catalytic **16** (5–10 mol%) at -20°C gave, after exposure of the resulting hetero-Diels-Alder adducts to trifluoroacetic acid, *cis*-dihydropyrone predominantly in high yield with excellent enantioselectivity.

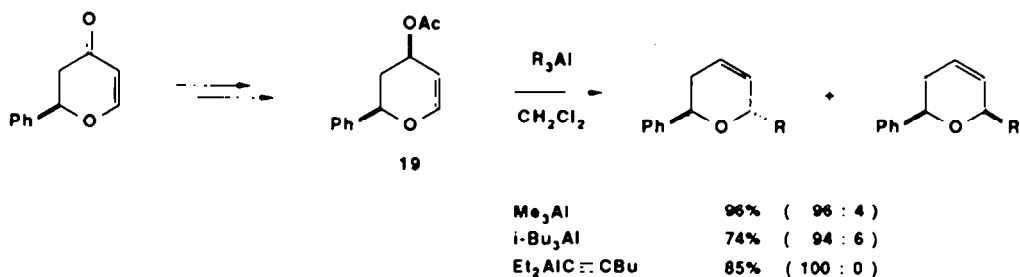


The success of the present asymmetric hetero-Diels-Alder reaction depends upon development of a new method of preparing the optically active disilylbinaphthol **17**. The chiral oxygenophilic

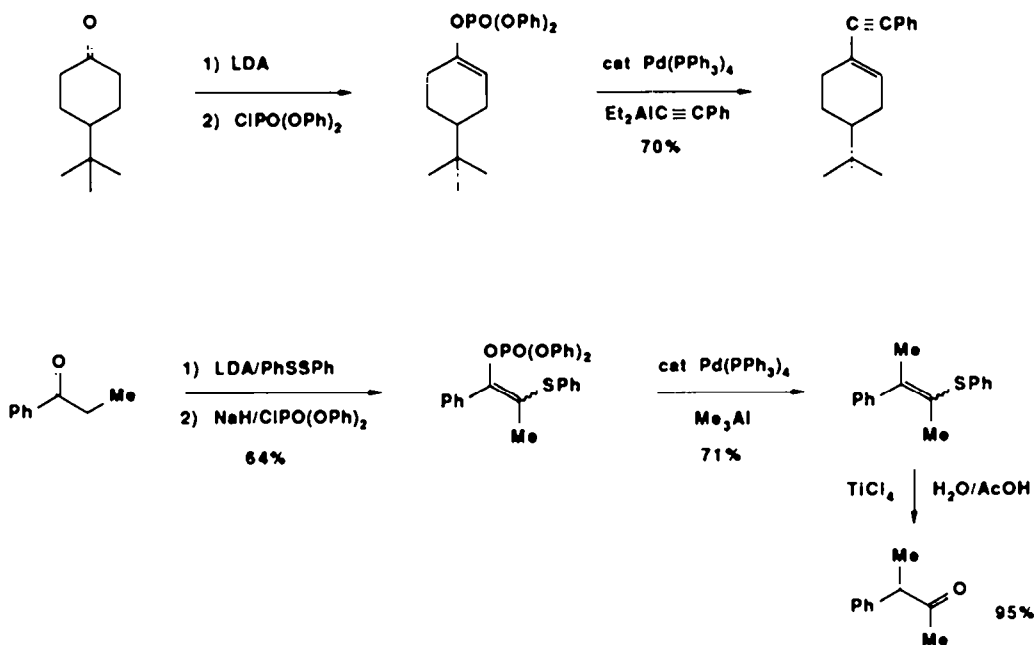
organoaluminum catalyst **16** with its sterically hindered chiral auxiliary may form a stable 1:1 complex with benzaldehyde. This allows the enantioselective activation of the carbonyl group as illustrated in **18**. The diene would then approach benzaldehyde with an endo alignment of the aldehyde phenyl residue and the diene in order to minimize the steric interaction between the incoming diene and the front triarylsilyl moiety, thereby yielding the *cis* adduct predominantly in accord with experimental findings. The hetero-Diels–Alder adduct, once it is formed, then splits off readily from the aluminum center as a result of steric release between the adduct and the aluminum reagent. This results in regeneration of the catalyst **16** for further use in the catalytic cycle of the reaction. In marked contrast, the chiral organoaluminum reagent derived from Me_3Al and (*R*)-(+)-3,3-dialkylbinaphthol (alkyl = H, Me, and Ph) was employable only as a stoichiometric reagent. This gave much less satisfactory results in reactivity and enantioselectivity in the hetero-Diels–Alder reaction.



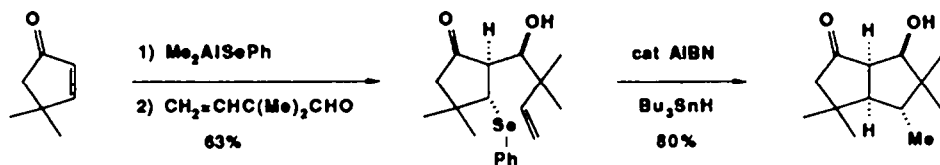
Since the resultant optically active dihydropyrones are readily transformed in a stereoselective way to glycols of the type **19**, the C-glycosidation of glycol **19** with trialkylaluminums has been investigated. Their high synthetic utility as chiral building blocks for the structural elaboration to the concise synthesis of a variety of carbohydrates and polyether antibiotics has been demonstrated by the formation of various C-glycosides which can be obtained with high regio- and stereo-selectivity.⁵⁵



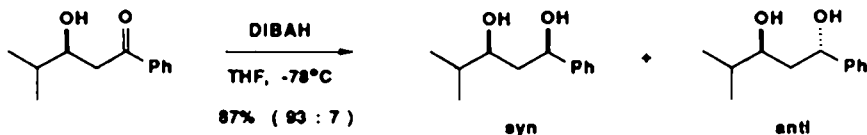
Regioselective olefin formation from ketones has been exploited by Oshima and Nozaki.⁵⁶ Conversion of ketones to the corresponding enol diphenylphosphates and subsequent coupling of enol phosphates by stereospecific C—O bond fission with alkylaluminum in the presence of catalytic $\text{Pd}(\text{PPh}_3)_4$ yields alkenes. In this coupling alkenyl and alkynyl groups are introduced selectively in preference to alkyl substituents. The reaction does not affect a co-existing vinyl sulfide group. This feature enabled 1,2- and 1,3-carbonyl transposition, with or without alkylation, via phenylthio-substituted enol phosphates.



The tandem aldol condensation-radical cyclization sequence for the elaboration of functionalized bicyclo[3.3.0]octane systems has been developed by Leonard and Livinghouse.⁵⁷ Conjugate addition of Me₂AlSePh to dimethylcyclopentenone followed by trapping of the resultant enolate with aldehyde afforded the *trans*, *erythro* aldol predominantly which then underwent radical cyclization with Bu₃SnH and catalytic AIBN yielding the bicyclic ketol stereospecifically. This approach represents a highly convergent method for the annulation of carbocycles leading to the polyquinane sesquiterpenes.

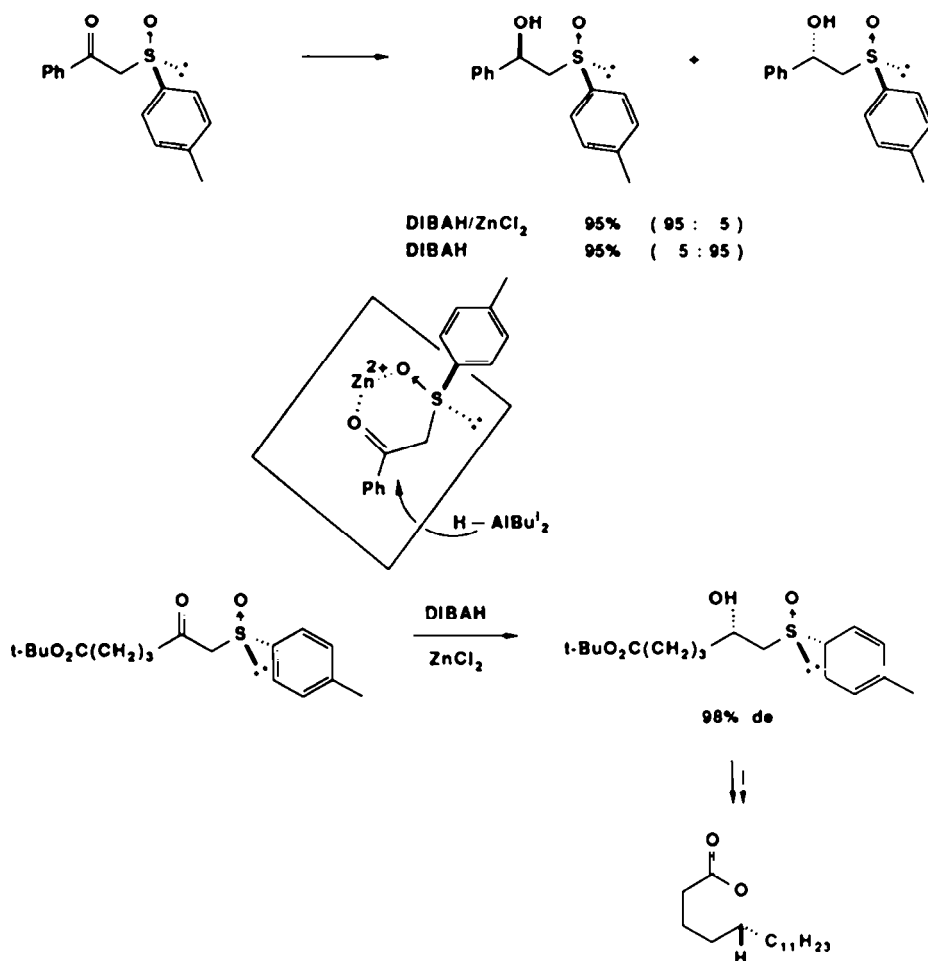


Diisobutylaluminum hydride (DIBAH) is undoubtedly one of the most common reducing agents in organic synthesis and recent interest in the synthetic utility of DIBAH has been directed toward diastereoselective reduction of carbonyl substrates. Kiyooka and coworkers have achieved high 1,3-*syn* diastereoselectivity in the chelation-controlled reduction of β -hydroxy ketones with DIBAH in THF.⁵⁸ The choice of solvents strongly affects the selectivity. Use of CH₂Cl₂ or toluene in place of THF did not show any diastereoselectivity.



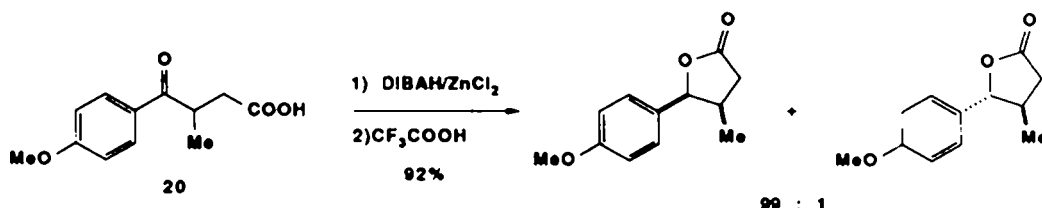
Solladie and Kosugi independently reported the highly diastereoselective reduction of chiral β -keto sulfoxide with DIBAH in the presence of ZnCl₂.⁵⁹⁻⁶² The exclusive formation of the (*R*_c, *R*_c)-

hydroxy sulfoxides is accounted for by the initial complexation of the β -keto sulfoxide with ZnCl_2 and subsequent attack of a hydride from DIBAH on the less hindered site of the chelated species. Interestingly, the sole use of DIBAH resulted in stereochemical reversal, yielding (S_c , S_s)-hydroxy sulfoxides predominantly. The resulting optically active β -hydroxy sulfoxides are readily transformed to a variety of synthetically useful intermediates including chiral allylic alcohols, vicinal triols, and epoxides. This method can be successfully applied to the efficient synthesis of optically pure (R)-(+)-hexadecano-1,5-lactone, the pheromone responsible for some aspects of the social behaviour of the Oriental Hornet, *Vespa orientalis* (Scheme 13).

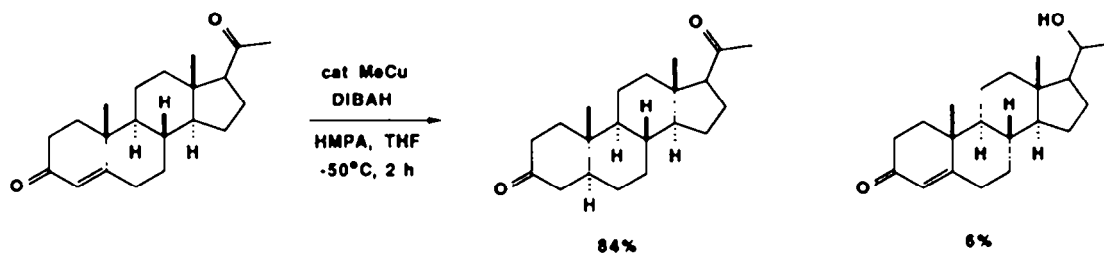


Scheme 13.

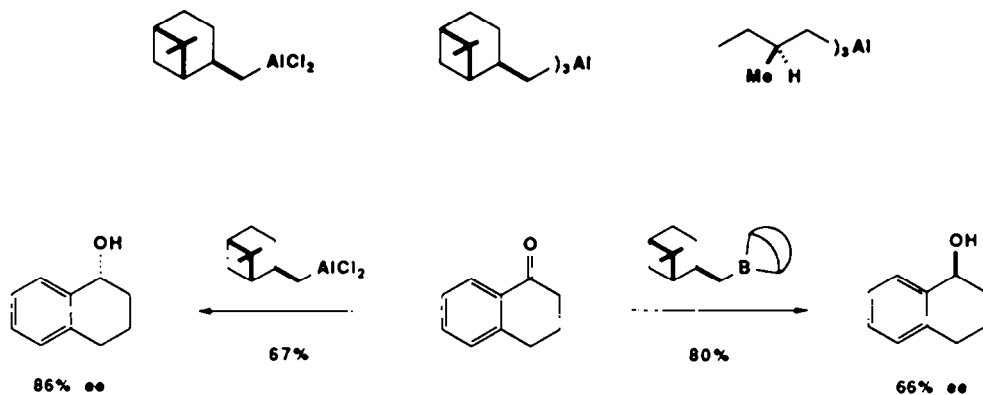
The efficacy of the DIBAH/ ZnCl_2 system in the diastereoselective reduction of carbonyl group has been also demonstrated by Frenette *et al.* for the preparation of important intermediates in the synthesis of selective receptor antagonists of leukotriene D_4 .⁶³ Reduction of keto-acid **20** with DIBAH in the presence of ZnCl_2 proceeded in a highly stereoselective manner giving product ratio of 97:3 to 99:1 in favor of the desired *erythro* products. Hydrosilane-based reduction, zinc borohydride, and L-selectride gave much less satisfactory results.



The reducing reactivity of DIBALH can be dramatically modified by adding a transition-metal compound as exemplified by the methylcopper(II)-catalyzed highly efficient and selective conjugate reduction of α,β -unsaturated carbonyl compounds with DIBALH.⁶⁴ Here, HMPA is an indispensable component for the present conjugate reduction, and it functions as a ligand rather than a cosolvent. The newly developed MeCu/DIBALH/HMPA system exhibits the high chemoselectivity and even in the presence of saturated carbonyl groups, the selective conjugate reduction of α,β -unsaturated carbonyl compounds took place efficiently.

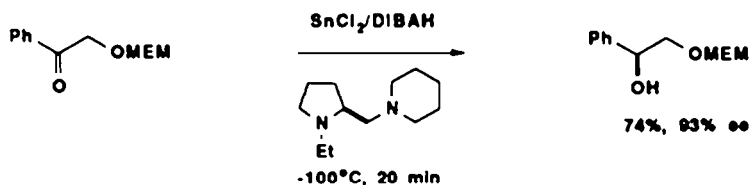


The enantioselective reduction of prochiral ketones with chiral organoaluminum reagents has been studied by several research groups. Giacomelli *et al.* prepared optically active *cis*-myrtanyl-aluminum and (2-methylbutyl)aluminum derivatives.⁶⁵⁻⁶⁷ The extent of enantioselectivity was found to depend heavily on the structure of the ketonic substrate. Midland *et al.* observed that the absolute configuration in the reduction of prochiral ketones with *cis*-myrtanylaluminum dichloride is the opposite of that obtained with a similar organoboron reagent (Scheme 14).⁶⁸



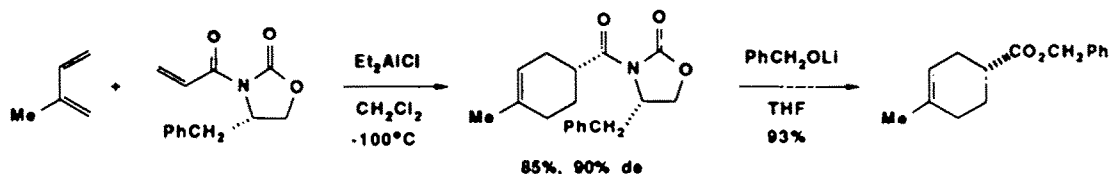
Scheme 14.

Mukaiyama and coworkers reported the asymmetric reduction of prochiral α - and β -hydroxy ketones with a reagent generated from SnCl_2 , a chiral diamine, and DIBALH.⁶⁹ They concluded that use of MEM ethers as a substrate and (*S*)-1-ethyl-2-(piperidinomethyl)pyrrolidine as a chiral ligand is the most effective to achieve high enantioselection.

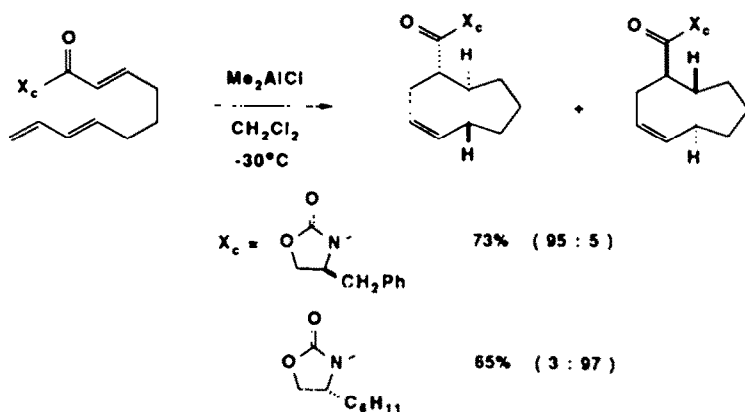


4. ACID DERIVATIVES

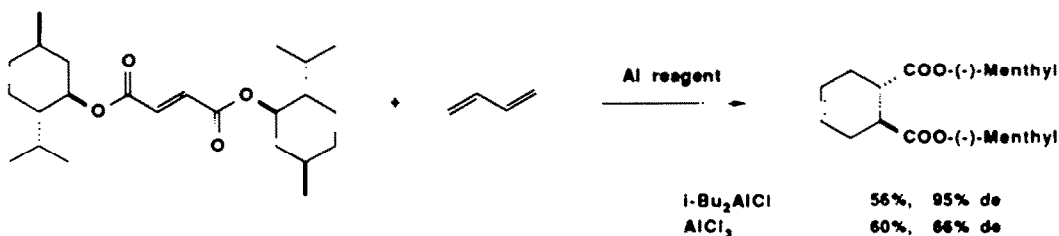
Asymmetric Diels-Alder reactions are little affected by solvent changes. However, the Lewis acids exert a strong catalytic effect and induce higher optical yields. As a consequence of faster rates, increased stereoselectivity, and enhanced regioselectivity, the Lewis acid-catalyzed [4+2] cycloadditions offer many attractive synthetic advantages. Homogeneous alkylaluminum chlorides have now been accepted as most reliable reagents. Evans *et al.* found that chiral α,β -unsaturated N-acyl oxazolidones exhibit high diastereofacial selection in Diels-Alder reactions, particularly those conducted in the presence of Et_2AlCl .⁷⁰ Reaction of the chiral acrylate and crotonate imides with cyclopentadiene furnished *endo*-adducts almost exclusively with diastereoselection of about 95%. The exceptional reactivity of these dienophile Lewis acid complexes allowed the use of less reactive acyclic dienes with high diastereoselectivity (>95% de). The chiral auxiliary is cleaved by transesterification with lithium benzyloxide to the corresponding benzyl ester in 85-95% yield.



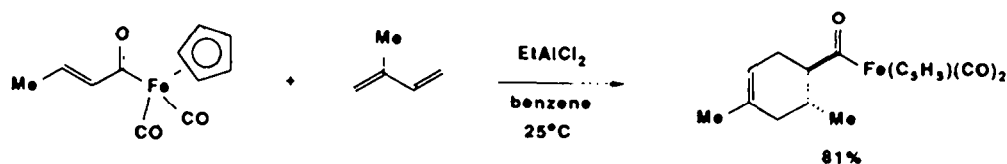
The same group applied this asymmetric Diels-Alder reaction intramolecularly.⁷¹ (*E,E*)-Trienecarboximides derived from chiral oxazolidones undergo Me_2AlCl -catalyzed intramolecular Diels-Alder reactions yielding bicyclic compounds with high *endo*- and diastereoselectivity (*endo/exo* = ~100:1). The stereochemistry is controlled by the stereogenic center at C_4 of the chiral auxiliary.



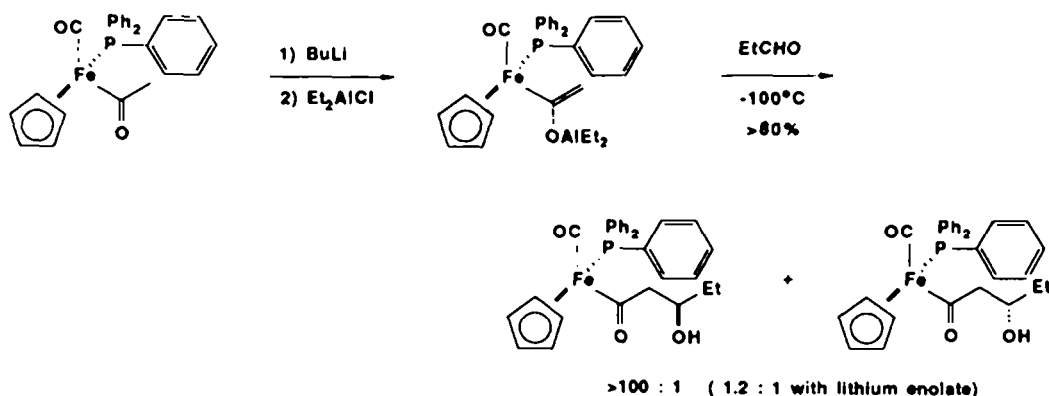
The distinct advantage of homogeneous alkylaluminum chloride over AlCl_3 was clearly demonstrated by the organoaluminum-catalyzed asymmetric Diels-Alder reaction of (–)-dimenthyl fumarate with various cyclic as well as acyclic dienes with remarkably high diastereofacial selectivity.⁷² Here a single reaction species may be responsible for the cycloaddition, since a straight line of the observed enantioselectivity, $\ln (S,S)/(R,R)$ against the reciprocal of the temperature, $1/T$ (in K) was obtained at temperatures ranging from 25 to -40°C .



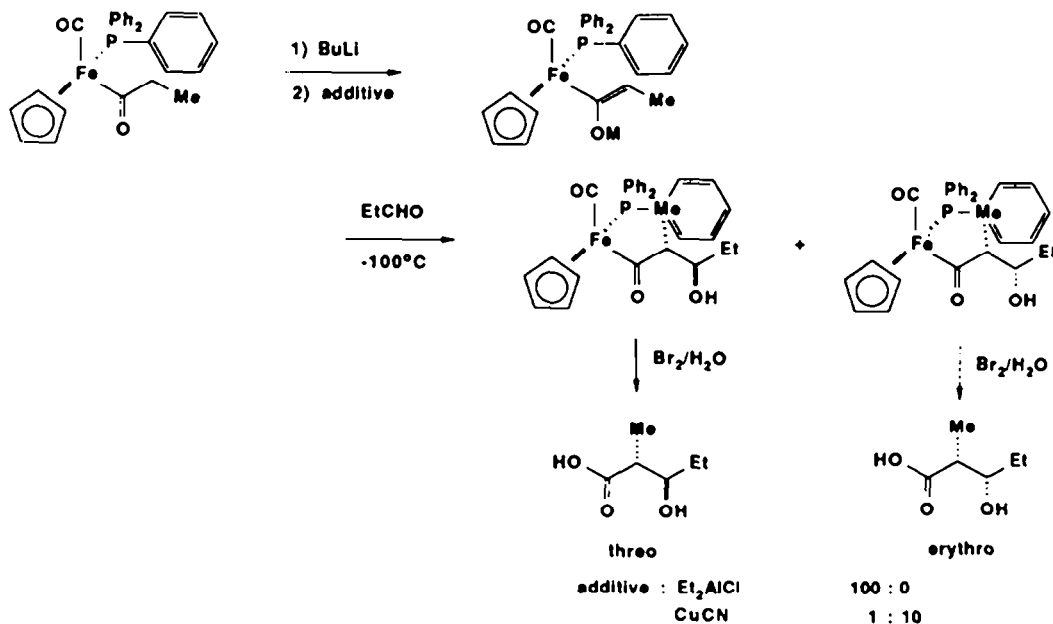
EtAlCl_2 -catalyzed Diels–Alder reactions between alkyl-substituted 1,3-butadienes and $(\eta^1\text{-acryloyl})(\eta^5\text{-cyclopentadienyl})\text{dicarbonyliron(II)}$ complexes have been reported by Herndon.⁷³ In these reactions, the observed regio- and stereo-chemistry were consistent with that generally observed in Diels–Alder reactions. Conventional Lewis acids such as $\text{BF}_3 \cdot \text{OEt}_2$ and TiCl_4 were not effective in promoting the desired cycloaddition.



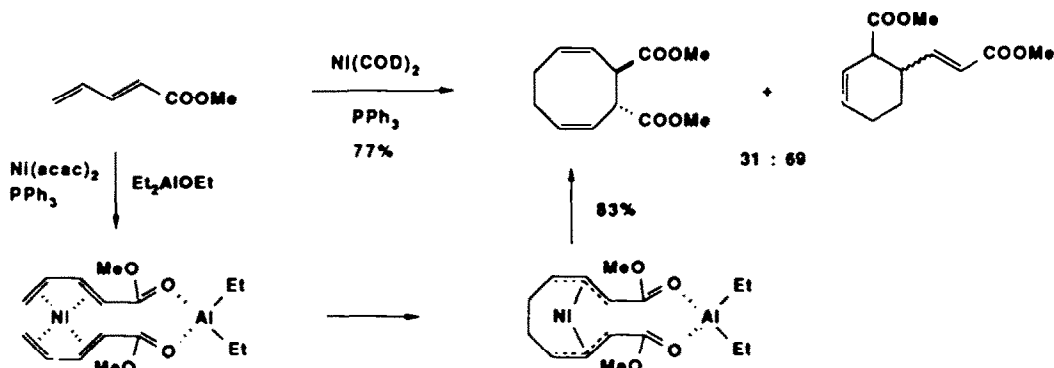
Davies and coworkers studied aldol condensations of the enolate derived from the iron acetyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COMe})$ with aldehydes.^{74,75} Although the lithium enolate did not show any selectivity, the corresponding aluminum enolate by transmetalation with Et_2AlCl exhibited exceptionally high diastereoselectivity ($>99\%$ de). The resultant β -hydroxy acyl complexes are transformed to β -hydroxy acids on decomplexation with Br_2 .



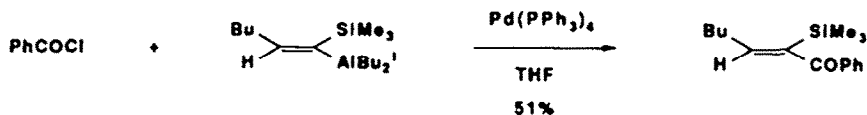
Subsequently they found that the enolates derived from the iron propionyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2\text{CH}_3)$, chiral propionate enolate equivalents, undergo highly stereoselective aldol condensations with aldehydes to yield in the case of the aluminum enolate *threo*- α -methyl- β -hydroxy acids. For the copper enolate, the corresponding *erythro* isomers predominate.⁷⁶



A remarkable directing effect of Et_2AlOEt was observed in the $\text{Ni}(0)$ -catalyzed cyclodimerization reaction.⁷⁷ Treatment of methyl 2,4-pentadienoate with each 5 mol% of $\text{Ni}(\text{COD})_2$ and PPh_3 gave cyclohexene derivatives predominantly whereas in the presence of Et_2AlOEt (10 mol%), cyclooctadiene derivatives can be obtained exclusively. The observed regio- and stereo-chemical control has been ascribed to effective chelation between the ester oxygen atoms and the oxygenophilic organoaluminum reagent as shown in Scheme 15.

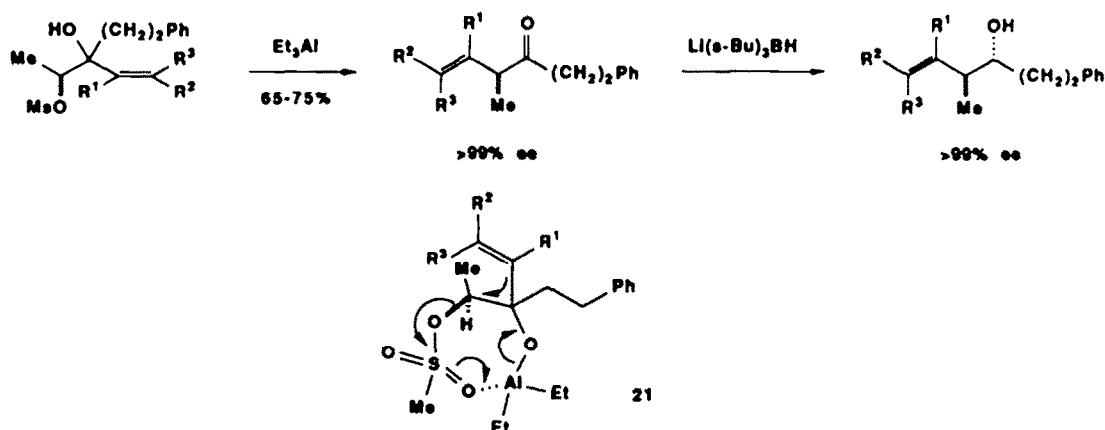


A new ketone synthesis from acyl chlorides was executed by Oshima and Nozaki.⁷⁸ Previously this transformation was accomplished with organometallics containing Cd, Cu, Mg, Mn, etc. In place of these reagents, they utilized trialkylaluminum in THF with a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$. In the case of dialkylalkenylaluminums and dialkylalkynylaluminums, selective transfer of alkenyl and alkynyl groups was observed.

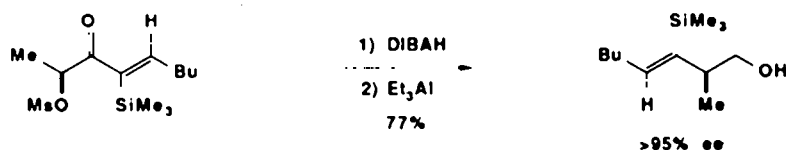


5. ALCOHOL DERIVATIVES

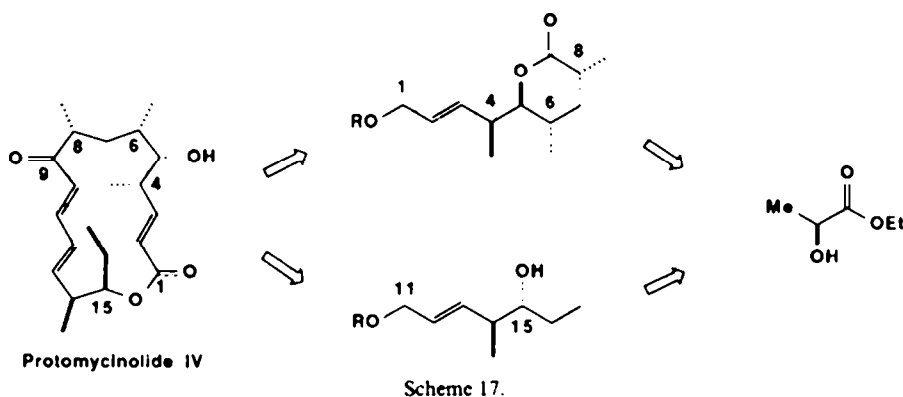
Organoaluminum-promoted asymmetric pinacol-type rearrangements have been studied extensively by Suzuki and Tsuchihashi. First, they found that chiral β -mesyloxy tertiary alcohols, when treated with excess Et_2AlI or Et_3Al , undergo a stereospecific pinacol-type rearrangement as shown in 21 to furnish optically pure α -alkyl, α -alkenyl, or α -aryl ketones.⁷⁹⁻⁸³ The reaction is particularly useful for preparation of optically pure α -methyl- β,γ -unsaturated ketones by migration of an alkenyl group, which occurs with retention of the olefin geometry. The resultant ketones can be reduced by lithium tri-*sec*-butylborohydride with high *threo*-selectivity (Scheme 16).



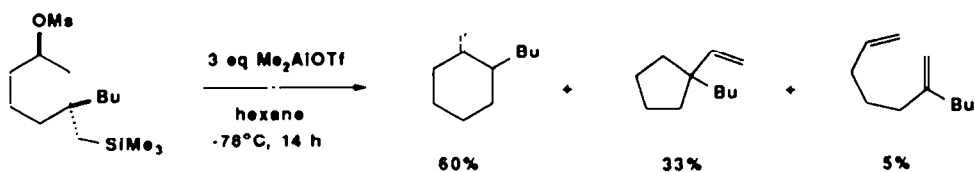
Reductive pinacol-type rearrangement of chiral α -mesyloxy ketones was executed by *in situ* reduction with DIBALH followed by addition of Et_3Al or Et_2AlCl . The resulting aldehyde is reduced as formed to an optically pure 2-aryl- or 2-alkenylpropanol.⁸⁴



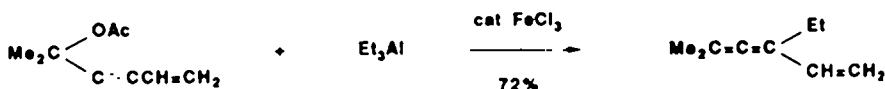
The present pinacol-type 1,2-rearrangement was highlighted by the stereocontrolled asymmetric total synthesis of protomycinolide IV where two chiral fragments, C(1)–C(9) and C(11)–C(17) portions, were constructed from a common chiral starting material, (*S*)-ethyl lactate (Scheme 17).⁸⁵



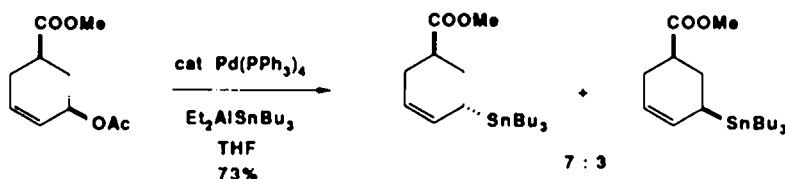
Cationic rearrangement of 3-(trimethylsilyl)methylcyclohexyl mesylates was effected with excess Me_2AlOTf .⁸⁶ In this reaction, the silyl group exhibited a remarkable directing effect to induce successive rearrangement of a hydride and an alkyl group in order to generate a stable β -silyl cationic species which finally afforded the corresponding olefins. As observed in the usual cationic 1,2-rearrangement process, successive migrations of two *anti*-periplanar substituents on axial positions may be greatly favored in these silicon-directing rearrangements.



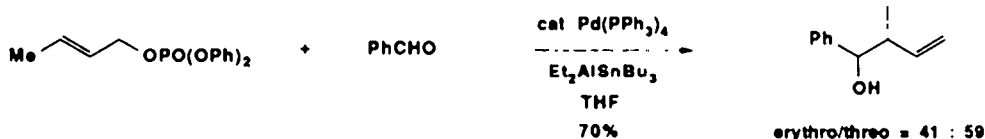
A regio- and stereo-chemical study on the alkylation of several allylic cyclohexenyl esters with Me_3Al and *i*- Bu_3Al has been executed by Gallina.⁸⁷ He concluded that the regio- and stereo-chemical outcome of the reaction is strongly influenced by the nature of the allylic system, leaving group, organoaluminum reagent and by the leaving group orientation. In the case of propargylic acetates, substituted allene was formed according to the acetylene-allene rearrangement upon reaction with organoaluminum reagents in the presence of 3–5 mol% FeCl_3 .⁸⁸



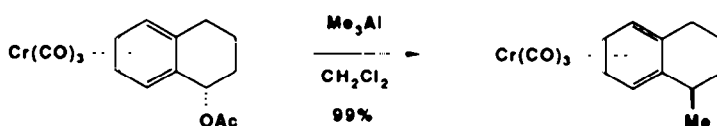
Reaction of allylic derivatives with an aluminum–tin reagent has been reported by two research groups. Trost found a mild and efficient method for the formation of functionalized allylic stannanes from allylic acetates with $\text{Et}_2\text{AlSnBu}_3$ in THF in the presence of catalytic $\text{Pd}(\text{PPh}_3)_4$.⁸⁹ This functional group interconversion represents a net conversion of the electronic nature of the allyl acetate from electrophile to nucleophile. The stannylating agent, which is readily available by reaction of Bu_3SnLi with Et_2AlCl , exhibits a high degree of regioselectivity for the less substituted carbon of the allyl system. The reaction also proceeds with a remarkably high chemoselectivity. Enone, ketone and ester functionalities remain totally intact even in the presence of excess stannyl-aluminum reagent.



Oshima and Nozaki have developed a one-pot synthesis of homoallylic alcohols from allylic phosphates and aldehydes with an aluminum–tin reagent.⁹⁰ Treatment of allylic diphenylphosphate with the reagent prepared from Bu_3SnLi and Et_2AlCl or from SnF_2 and Et_2AlCl in the presence of catalytic $\text{Pd}(\text{PPh}_3)_4$ afforded allylic stannanes which then reacted with aldehydes, by the *in situ* generated $\text{Et}_2\text{AlOPO}(\text{OPh})_2$ as Lewis acid, to produce homoallylic alcohols.

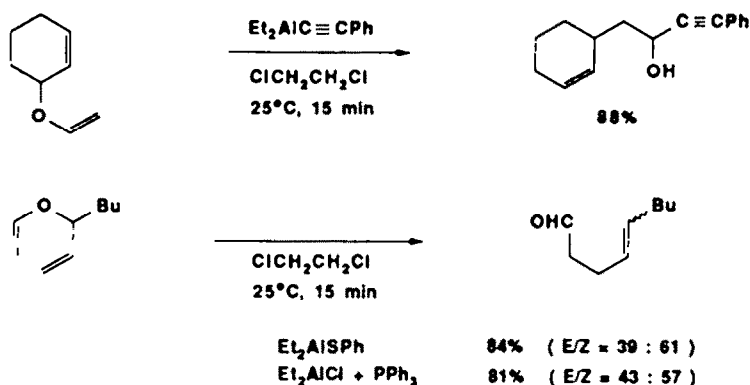


Uemura and coworkers investigated alkylation at the benzylic position of $(\eta^6\text{-arene})\text{tricarbonylchromium}$ complexes.⁹¹ Thus, benzylic acetates and the corresponding free alcohols of $(\eta^6\text{-arene})\text{tricarbonylchromium}$ complexes are alkylated stereoselectively with trialkylaluminums producing *exo*-alkylchromium complexes. The free benzylic hydroxy group could not be replaced by Me_3Al alone, but is smoothly substituted at room temperature in the presence of equimolar TiCl_4 .



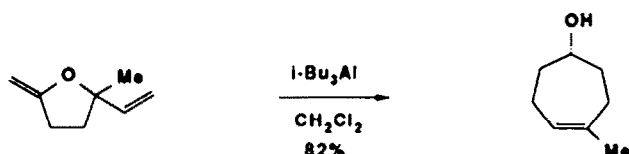
6. ETHERS, EPOXIDES AND ACETALS

Aliphatic Claisen rearrangements have been accomplished by Nozaki's group under very mild conditions in the presence of organoaluminum reagents.⁹² Treatment of simple allyl vinyl ether substrates with trialkylaluminums resulted in the [3,3] sigmatropic rearrangement and subsequent alkylation on the aldehyde carbonyl group. The rearrangement–reduction product was obtained exclusively with *i*- Bu_3Al or DIBALH. The aluminum reagent, Et_2AlSPh or a combination of Et_2AlCl and PPh_3 was effective for the rearrangement providing the normal Claisen products, γ,δ -unsaturated aldehydes, as indicated in Scheme 18.

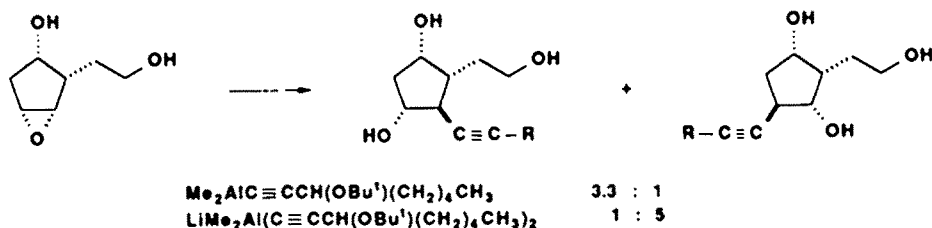


Scheme 18.

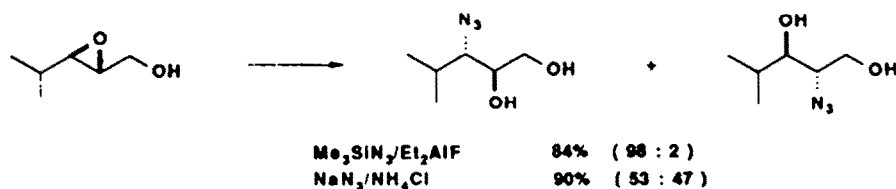
The same group further expanded the organoaluminum-promoted Claisen rearrangement to five-membered ring enol ethers with vinyl substituents.⁹³ Here reaction has proceeded in three different directions: (1) [3,3] sigmatropic rearrangement yielding 7-membered carbocycles, (2) isomerization to vinylcyclopropane derivatives, and (3) $\text{S}_{\text{N}}2'$ type reaction with phenylthio anion via oxolane ring opening.



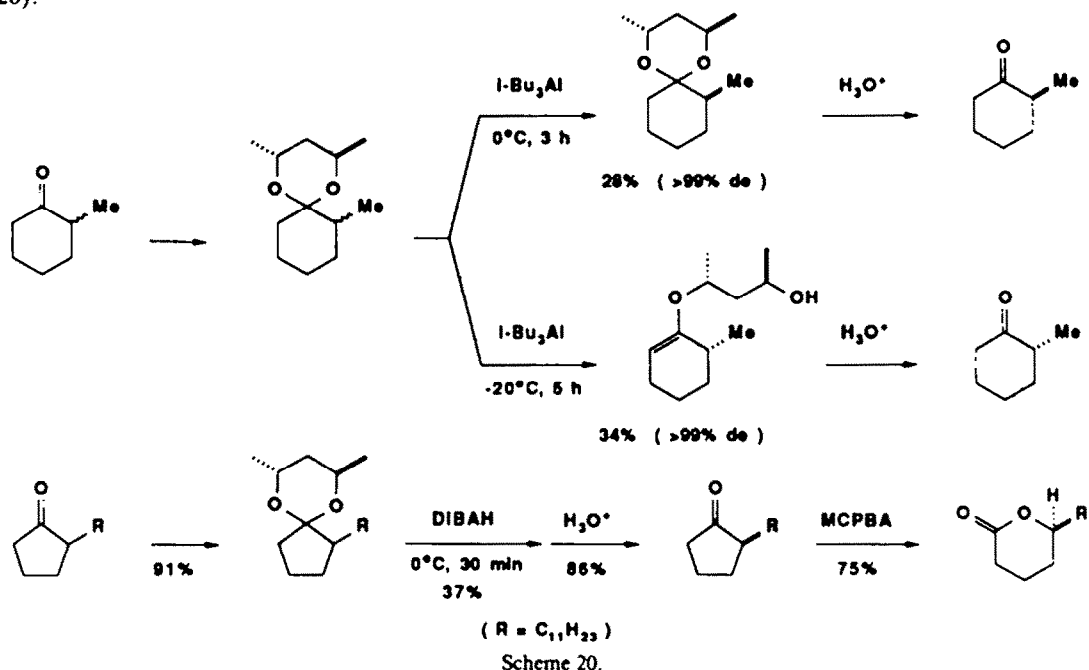
Matthews and Eickhoff studied the regioselectivity of epoxide-opening reactions using alkynyl-aluminum reagents for prostaglandin synthesis.⁹⁴ With two different cyclopentane oxide derivatives, they suggested that the simple substitution of an aluminum ate complex for the usual trialkyl-aluminum can sometimes be useful in achieving desired regioselectivity.



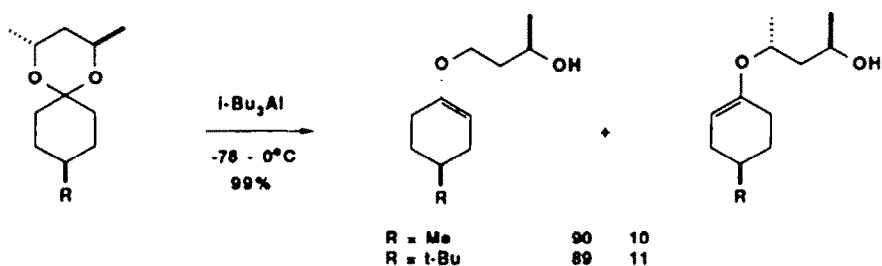
A selective ring-opening of 2,3-epoxy alcohols has been attained with organoaluminum reagents. Previously, two research groups independently reported the regioselective alkylation of epoxy alcohols with trialkylaluminums.^{95,96} More recently, a highly regio- and stereo-selective addition of the azido group to 2,3-epoxy alcohols has been achieved with Me_3SiN_3 - Et_2AlF system.⁹⁷ This method is superior to the conventional one using azide anion which strongly reflects the steric effect of all of the epoxide substituents.



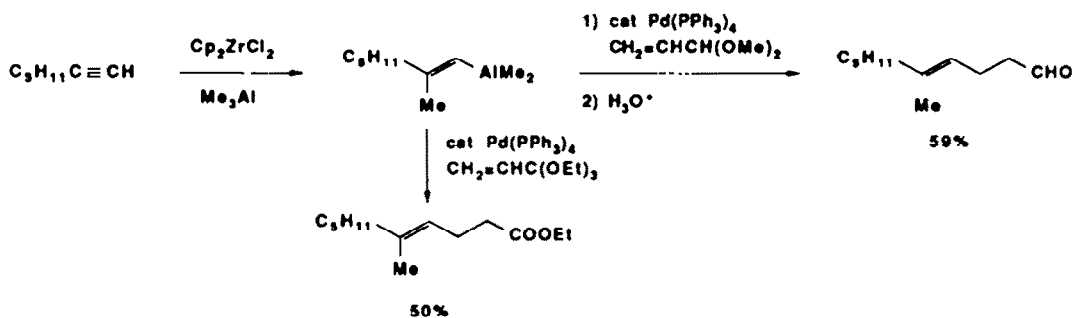
Kinetic resolution of chiral acetals has been effected with certain organoaluminum reagents.¹⁰⁴ When a chiral acetal derived from (2*R*,4*R*)-(-)-pentanediol was treated with *i*-Bu₃Al at room temperature, one diastereoisomer was found to react much faster than the other, and the residual enol ether is transformed to optically pure ketone. The efficiency of this method is demonstrated by a concise synthesis of (*S*)-(-)-5-hexadecano-1,5-lactone, the pheromone of *Vespa orientalis* (Scheme 20).



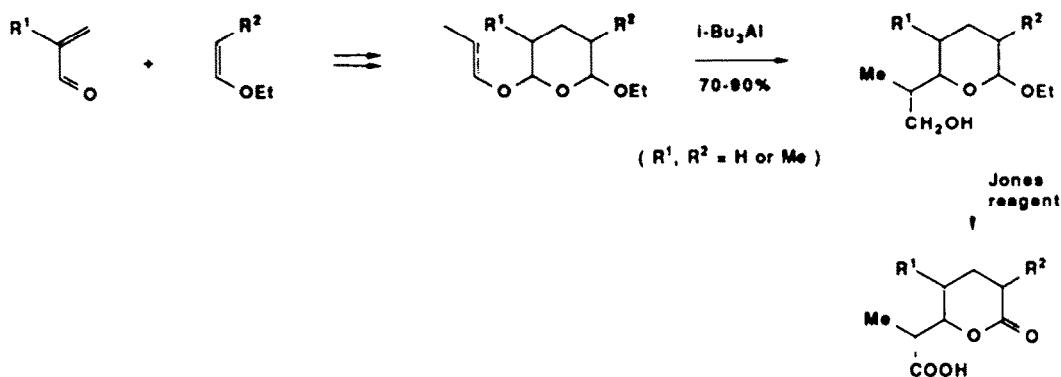
This reaction has been further extended to the asymmetrization of the symmetric acetal with various modified organoaluminum reagents including *i*-Bu₃Al and bulky organoaluminum



Palladium-catalyzed reactions of organoaluminum reagents with α,β -unsaturated acetals and *ortho* esters has been reported by Chatterjee and Negishi.¹⁰⁶ They employed alkenylaluminum reagents which are readily obtainable by the hydroalumination or Cp₂ZrCl₂-catalyzed carboalumination of alkynes with DIBAL or Me₃Al, respectively.

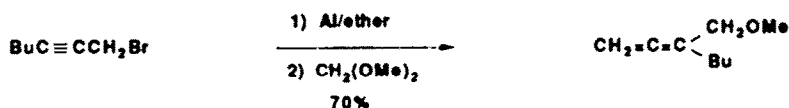


The reductive rearrangement of 2-ethoxy-5-(2-alkenyl)-2H-tetrahydropyran systems with *i*-Bu₃Al has been utilized as the key-step in the synthesis of Prelog-Djerassi related lactones.¹⁰⁷

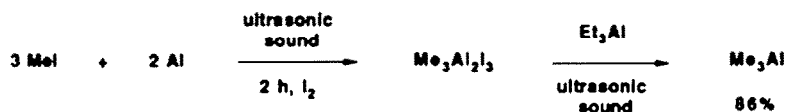


7. HALOHYDROCARBONS

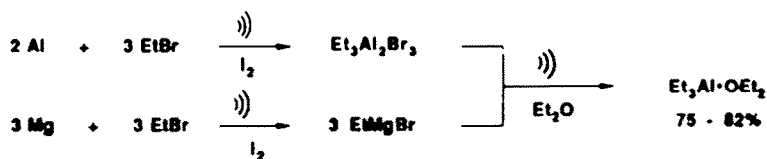
The reaction between alkyl halides and aluminum metal are the basis of the classical and oldest method for the synthesis of organoaluminum compounds. For example, propargylic bromides react with aluminum in ether giving organoaluminum compounds which on treatment with acetals yielded α -allenic ethers solely.¹⁰⁸ However, the method involving simple alkyl halides and aluminum metal requires a long reaction time.



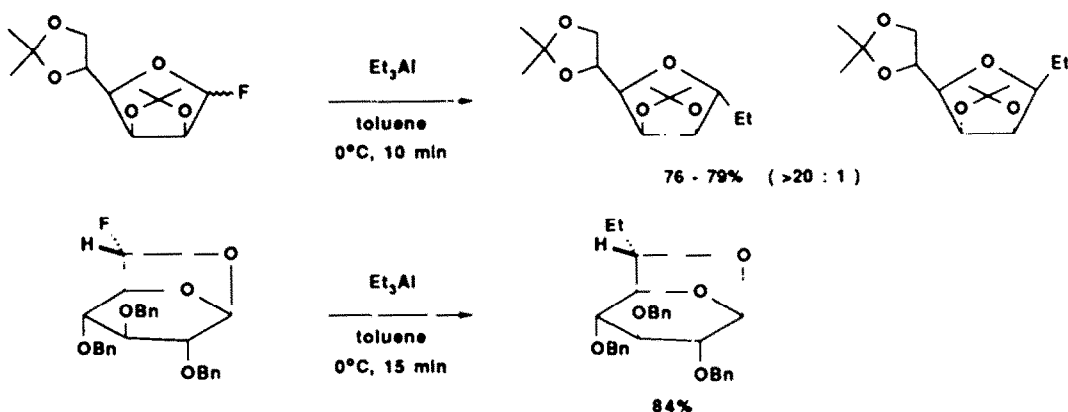
Recently, Lin and coworkers utilized ultrasonic irradiation as a promising method to promote the reaction of methyl iodide with aluminum powder.¹⁰⁹ Methylaluminum sesquiodide was first formed as an intermediate which, without isolation, was then redistributed with Et₃Al to furnish Me₃Al. The first heterogeneous step of the reaction was complete within 2 h at room temperature by ultrasonic irradiation.



They also utilized the ultrasonic irradiation technique for one-pot synthesis of Et₃Al·OEt₂ starting from ethyl bromide, aluminum, and magnesium powders.¹¹⁰

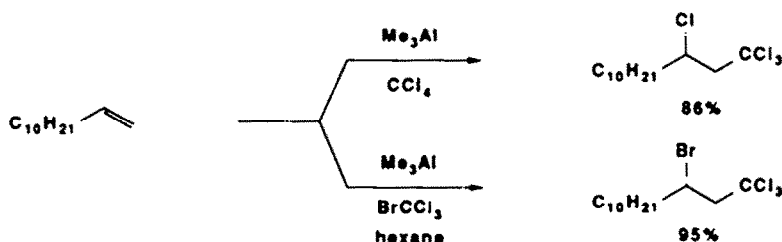


A highly convenient and versatile cyclopropanation method has been recently developed which involves treatment of olefins with various organoaluminum compounds and alkylidene iodide under

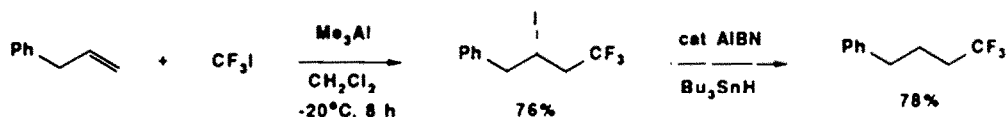


Scheme 21.

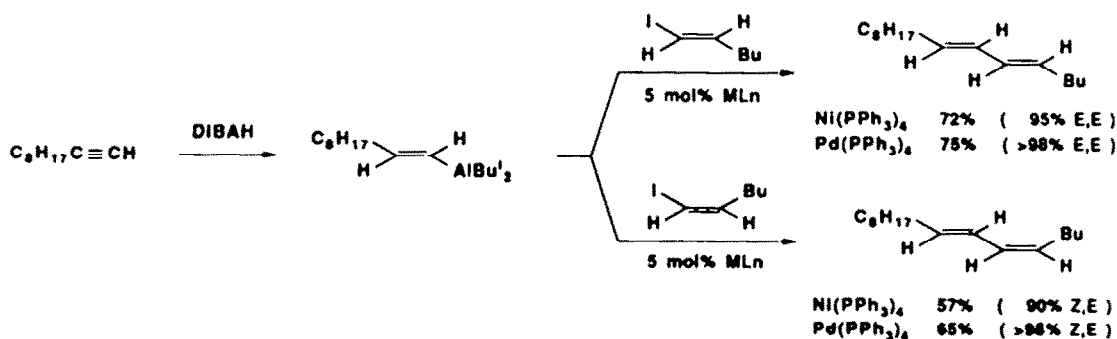
regioselective addition of polyhalomethane to olefins has been developed by the authors.¹¹⁵ Although various organoaluminums were surveyed as initiator for the addition reaction, only Me_3Al was found to be satisfactory.



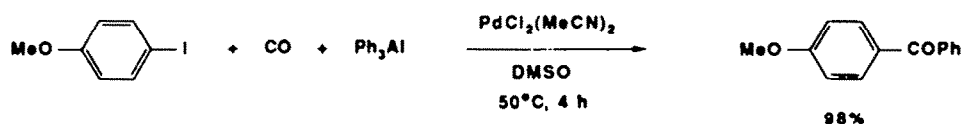
The present organoaluminum-induced addition reaction has been applied to the poly-fluoromethylation of olefins as illustrated below.



The versatility of the coupling reaction was expanded by Negishi *et al.* by the use of transition metal complexes as in the palladium- or nickel-catalyzed reaction of alkenylmetals with unsaturated organic halides as a selective route to arylated alkenes and conjugated dienes.¹¹⁶ Palladium catalysts permit nearly 100% stereospecificity in both alkenyl-aryl and alkenyl-alkenyl coupling reactions, whereas nickel catalysts led to partial stereochemical scrambling in the alkenyl-alkenyl coupling. After the mechanistic study, they concluded that the coupling reaction proceeds by the oxidative addition of $\text{Pd}(0)$ complexes, rate-determining transmetalation involving $\text{Pd}(\text{II})$ complexes, and rapid decomposition of diorganopalladium(II) species to produce the coupling products in one or more subsequent steps.

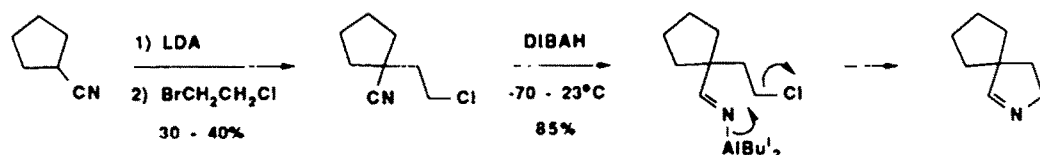


The reaction of organoaluminum compounds with aryl iodide and carbon monoxide in the presence of palladium complex provides a convenient route to the synthesis of various ketones.^{117,118}

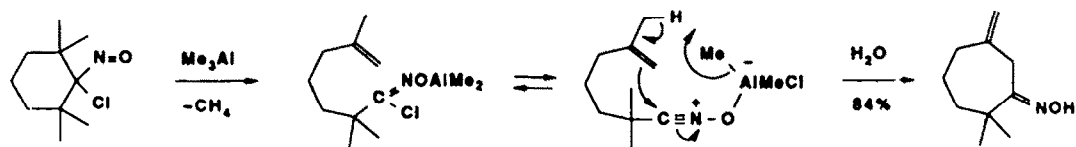


8. NITROGEN COMPOUNDS

DIBAH is a reliable reagent for conversion of nitriles to the corresponding aldehydes via aldimine derivatives.¹¹⁹⁻¹²¹ Recently, the intermediary aldimines were successfully utilized by Overman for preparation of cyclic imines from haloalkynitriles.¹²² Since the starting haloalkynitriles are readily obtainable by the haloalkylation of the nitriles with LDA, the present reaction sequence serves as a new route to 5- and 6-membered azacyclic compounds.

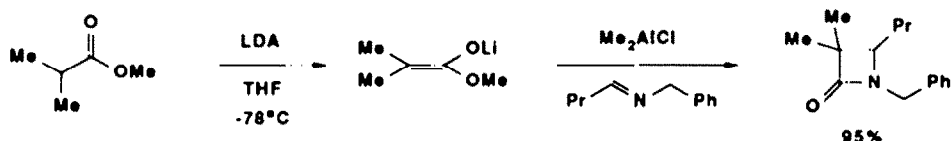


The reaction of sterically hindered α -chloronitroso compounds with Me_3Al was examined by Boer *et al.*¹²³ The conspicuous reaction sequence is interpreted by the initial ring rupture, methane evolution and chlorine migration from carbon to aluminum, intramolecular reaction of the carbon-carbon double bond with the rather electrophilic carbon atom from the nitrile oxide moiety leading to a seven-membered ring having an exocyclic double bond as depicted in Scheme 22. After hydrolysis the corresponding oxime is obtained.



Scheme 22.

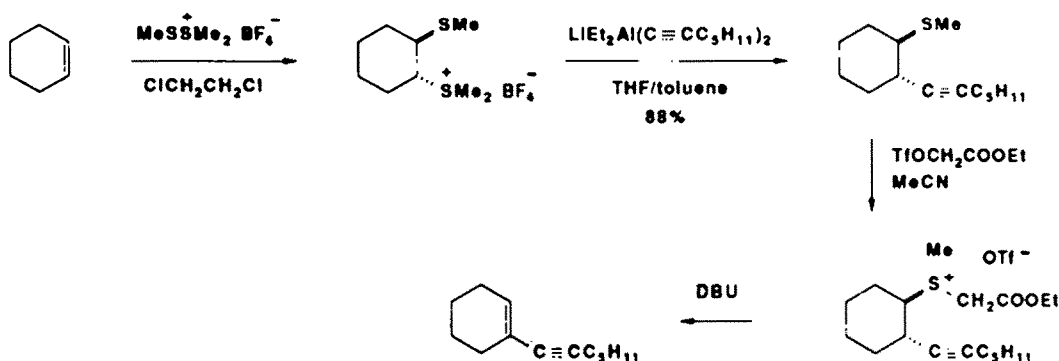
Akiba and coworkers found the efficiency of Me_2AlCl in a new β -lactam synthesis from lithium ester enolates and enolizable aldimines.¹²⁴ In the absence of Me_2AlCl , no β -lactam formation was detected probably because of the proton removal from the enolizable aldimines with lithium ester enolate.



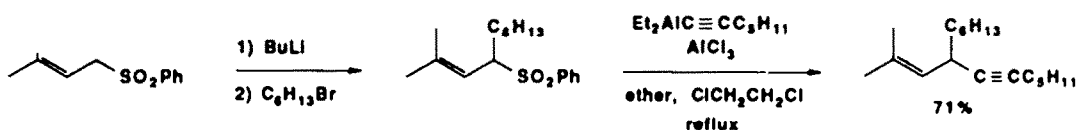
9. SULFUR COMPOUNDS

A novel alkynyl sulfonylation has been developed by Trost.¹²⁵ Alkene forms an adduct with dimethyl(methylthio)sulfonium tetrafluoroborate (DMTSF). Attempted reaction of this adduct

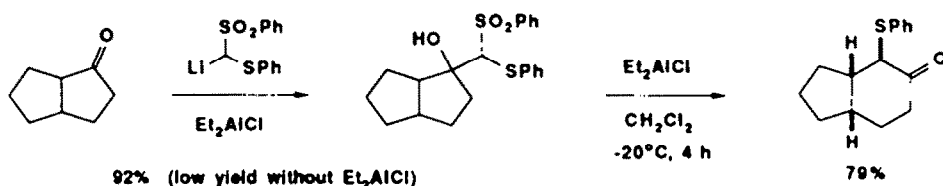
with lithium acetylide failed to react or produced complex mixtures or an allylic sulfide by elimination. However, the aluminum ate complex derived from lithium acetylide and Et_3Al (1 : 1 molar ratio) or Et_2AlCl (2 : 1 molar ratio) has proved to be highly effective for alkynyl sulfenylation with high regio-, chemo- and stereoselectivity. The products were converted into 1,3-enynes by sulfoxide elimination or by alkylation-elimination (Scheme 23).



Trost also found the Lewis acid-initiated alkylation of allylic sulfone with organoaluminum reagents.¹²⁶ Thus, combination of alkenyl- or alkynylaluminum reagents with AlCl_3 promotes the carbon-carbon bond formation of allylic sulfone substrate with removal of sulfonyl group in chemo- regio- and diastereo-selective fashions. The unique advantage of the sulfone as a leaving group stems from the ease of alkylation α to the sulfone prior to the substitution as illustrated in Scheme 24.



The ability of sulfones to be chemical chameleons, that is, to be nucleophiles in the presence of base and electrophiles in the presence of acid, appears to provide great opportunities for designing new reactions. This is demonstrated by a ring expansion to α -phenylthio and α -methoxy ketones.¹²⁷ Although the lithium derivative of (phenylthio)methyl phenyl sulfone, generated with BuLi in THF at -78°C , adds very poorly to ketones, addition of excess Et_2AlCl led to smooth alkylation to the carbonyl group. Subsequent rearrangement proceeds cleanly by treating adduct in CH_2Cl_2 at -78°C with excess Et_2AlCl (6 equiv.).



10. MISCELLANEOUS COMPOUNDS

Nearly 25 years after Ziegler's pioneering work,¹²⁸ DIBAH has secured its place as one of the most common reducing agents in organic synthesis: its popularity has increased considerably, especially after safe and easy-to-handle solutions of DIBAH in toluene and hexane became available.

However, most of the data available are for reactions carried out for preparative purposes, with the concentrations of the reactants, the temperature of the reaction, and the reaction time not specified. Recently, the approximate rates and stoichiometry of the reaction of excess DIBAH with 69 selected organic compounds containing representative functional groups were thoroughly investigated by Yoon and Gyoung under standardized conditions (toluene, 0°C) in order to compare its reducing characteristics with aluminum hydride previously examined and to enlarge the scope of its applicability as a reducing agent.¹²⁹

Kim and Ahn have surveyed the "ate" complex generated from DIBAH and BuLi in an equimolar ratio either in THF-hexane or in toluene-hexane with a series of selected organic compounds containing various functional groups in order to explore the reducing properties and to determine the synthetic utility of the reagent.¹³⁰ This reagent reduces ketones, esters, acid chlorides and acid anhydrides readily, even at -78°C. Consequently, it is useful for selective reduction of these groups in the presence of halide, amide and nitrile groups, which are inert at low temperature. Chemoselective reduction of a ketone in the presence of an ester group has been accomplished with 1 equiv. of the reagent at -78°C.

11. CONCLUDING REMARKS

With the aid of numerous synthetic transformations, the present Report demonstrates that organoaluminum reagents possess a unique set of properties. This makes them highly attractive as versatile reagents in organic synthesis. However, even with these fruitful experimental findings it is difficult to predict how many other chemical properties will emerge in the long-lived organoaluminum chemistry. One may therefore expect that the vast synthetic potential of organoaluminum reagents in selective organic synthesis will continue to be explored in the future.

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