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ALKYLALUMINUM HALIDES

LEWIS ACID CATALYSTS WHICH ARE BRØNSTED BASES

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Abstract—Alkylaluminum halides react with Brønsted acids to liberate an alkane and generate a new Lewis acid. Using these reagents, Lewis acid catalyzed reactions can be run under aprotic conditions, even when acidic protons are produced in the reaction. The use of these reagents for Lewis acid catalyzed ene, Diels–Alder and cycloaddition reactions and Claisen rearrangements is described. These reagents are also useful initiators for cation–olefin addition reactions. In some cases the alkyl groups react as nucleophiles. While this is often undesirable, addition of an alkyl group to carbenium ion intermediates provides novel classes of compounds.

During the past few years we have been examining Lewis acid induced C–C bond forming reactions of alkenes in an attempt to make the readily available double bond a more useful activating group for the elaboration of the carbon skeleton of complex molecules. In exploring both ene[2] and cation–olefin addition reactions,[3] we have found that alkylaluminum halides[4] act as Brønsted bases, as well as Lewis acids, making them valuable reagents. This paper summarizes our experiences and literature reports on the use of these reagents as Lewis acids with the goal of guiding others in their use.

It has long been recognized that pure, anhydrous Lewis acids to not catalyze the polymerization or isomerization of alkenes or the Friedel–Crafts alkylation of aromatics by alkenes. Co-catalysts, such as water, which react with the Lewis acid to produce strong Brønsted acids are necessary.[5] Therefore, use of strictly anhydrous reactants should minimize side reactions in Lewis acid catalyzed ene and Diels–Alder reactions. Unfortunately, it is very difficult to prepare anhydrous, proton-free $AlCl_3$, BF_3, etc.[5] Alkylaluminum halides, on the other hand, are anhydrous and furthermore scavenge any adventitious water, liberating an alkane and generating a new Lewis acid in this process.

Using alkylaluminum halides, Lewis acid catalyzed reactions can now be carried out under aprotic conditions. This can be of value when side reactions are caused by the presence of adventitious protons. It is of especial value when acidic protons are produced by the reaction. In these cases, use of the appropriate alkylaluminum halide in stoichiometric amount gives high yields of products not formed at all with other Lewis acids. Examples of this type of reaction are the ene reaction of aldehydes with alkenes to give homoallylic alcohols which react with Me_2AlCl to give methane and the chloromethylaluminum alkoxide (eqn 1)[6] and the Freidel-Crafts addition of arylsulfinyl halides to alkenes to give allylic sulfoxides and HCl which reacts with $EtAlCl_2$ to give $AlCl_3$ and ethane (eqn 6).[7]

A disadvantage of alkylaluminum compounds as Lewis acids is the nucleophilicity of the alkyl group. This is the price paid for its basicity. While addition of the alkyl group to the reagent-Lewis acid complex is undesirable, addition of the alkyl group to a carbenium ion center in an intermediate may be synthetically useful. The ease of alkyl donation is $R_3Al > R_2AlCl > R_3Al_2Cl_3 > RAlCl_2$. In addition ethylaluminum compounds are more nucleophilic than methylaluminum compounds and can donate a hydride as well as an Et group. Therefore, use of Me_2AlCl may be preferable to use of Et_2AlCl, even though the latter reagent is much cheaper. When the nucleophilicity of the alkyl group is a problem the Lewis acid with next fewer number of alkyl groups should be tried. If its greater acidity is a problem, an additive which is a Lewis base, e.g. ethyl ether, may moderate the reaction.

The alkylaluminum halides cover a wide range of Lewis acidity; replacing chlorines with alkyl groups decreases Lewis acidity. $EtAlCl_2$ is only slightly less acidic than $AlCl_3$, although there are reactions where $AlCl_3$ is necessary. On the other end of the scale, Me_3Al is a very mild Lewis acid, with the sesquichloride and monochloride in between. If no reaction occurs with the Lewis acid chosen a stronger Lewis acid should be tried. If polymerization occurs, a milder Lewis acid should be investigated.

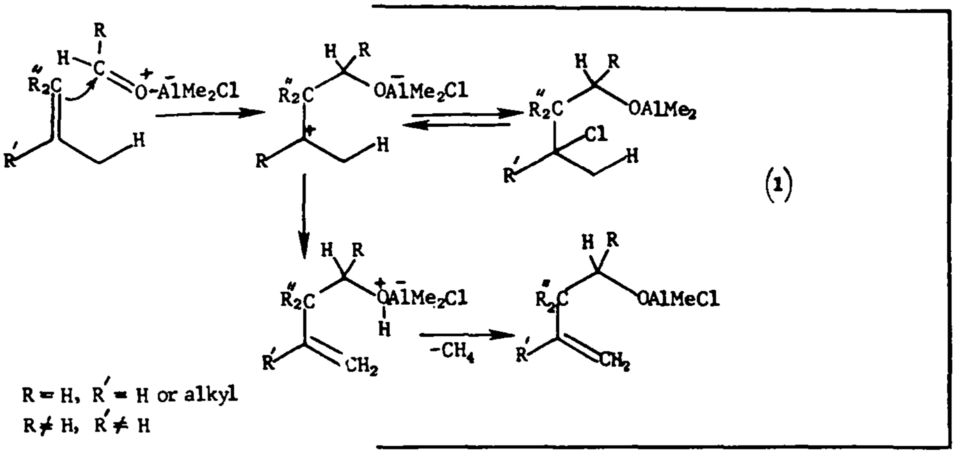
These reagents are easier to use than standard Lewis acids. They are soluble in all organic solvents, including heptane and toluene in which they are commercially available as standardized solutions.[8] In general, heptane solutions are preferred since toluene can undergo Friedel–Crafts reactions. On a laboratory scale, these reagents are transferred by syringe like butyllithium and, unlike anhydrous $AlCl_3$ or $ZnCl_2$, do not require a glove bag or dry box for transfer. Ethylaluminum compounds are available in large quantity at prices of $1–3/lb. Methylaluminum compounds are considerably more expensive.[8]

RESULTS AND DISCUSSION

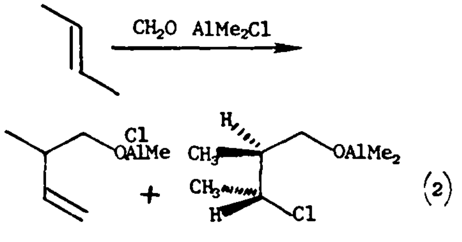
Specific uses of alkylaluminum halides as Lewis acids are detailed below. These reagents have seen enormous use as polymerization, oligomerization and methathesis catalysts, especially with transition metal salt co-catalysts. Until recently, they have seen little use as Lewis acid catalysts, even in the extensively investigated Friedel–Crafts reaction.[9]

Ene reactions

Alkylaluminum halides are clearly valuable in controlling the Prins type reaction of aldehydes with alkenes so that ene adducts are obtained in high yield. Using $\mathrm{Me_2AlCl}$ in stoichiometric amounts, formaldehyde reacts with all types of alkenes to give ene adducts. Aliphatic and aromatic aldehydes, which had never been successfully used as enophiles, given ene adducts with alkenes containing at least one disubstituted vinylic carbon (eqn 1).[6] Our studies have shown that these are Prins reactions,[10] proceeding through carbenium ion intermediates. Loss of methane from the $\mathrm{Me_2AlCl}$·alcohol complex prevents proton catalyzed side reactions or solvolysis of the homoallylic alcohol.



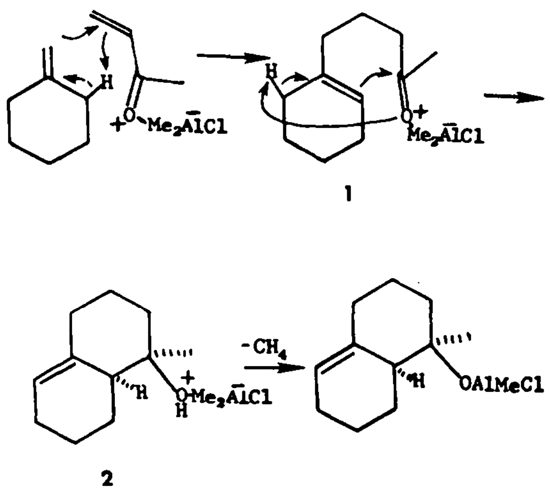
Due to the absence of nucleophiles in the medium, these reactions are cleaner than typical Prins reactions, usually giving only ene adduct. *m*-Dioxanes, a common product of the Prins reaction, are not formed because the aldehyde cannot act as a nucleophile since it is fully complexed to $\mathrm{Me_2AlCl}$. The only nucleophiles present are the ligands on the aluminum. The methyl group of $\mathrm{Me_2AlCl}$ is not sufficiently nucleophilic to add to the carbenium ion. ($\mathrm{Me_3Al}$ is quite different, *vide infra.*) The chloride does add to the carbenium ion. Tertiary chlorides are not observed, although they may be formed reversibly. Secondary chlorides are formed with the stereospecifically *cis* addition of $\mathrm{CH_2OH}$ and Cl across the double bone (eqn 2). These can be isolated in varying amoungs if 1 eq of $\mathrm{Me_2AlCl}$ is used. If an excess of $\mathrm{Me_2AlCl}$ is used, Lewis acid assisted solvolysis of the chloride regenerates the carbenium ion intermediate.



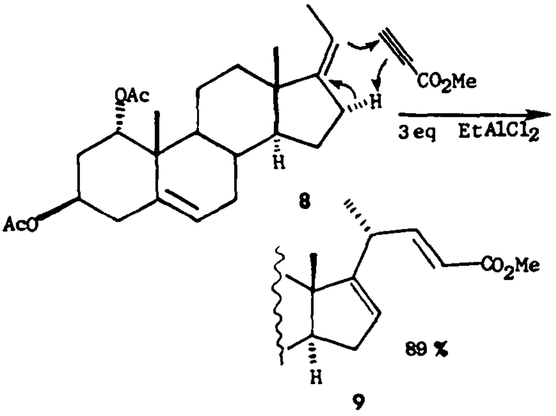
Reactions run with 1.5 eq of $\mathrm{Me_2AlCl}$ for 1–2 hr give only ene adduct since its formation is made irreversible by loss of methane. Loss of alkane can conceivably be used to drive Lewis acid catalyzed reactions is which the equilibrium constant is unfavorable.

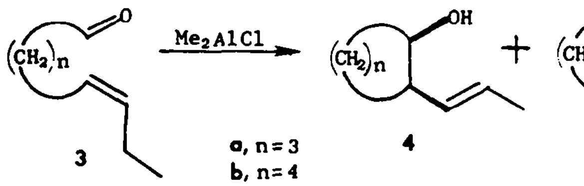
It is remarkable that alkenes are more nucleophilic toward an aldehyde than the methyl groups of $\mathrm{Me_2AlCl}$. Clearly, as the alkene is made less nucleophilic, or the alkyl group more nucleophilic, alkyl addition to the aldehyde will be more of a problem. For this reason $\mathrm{Et_2AlCl}$ which has more nucleophilic alkyl groups, and can act as a hydride donor, is not a suitable reagent. With alkyl and aryl substituted aldehydes, addition of a methyl group from $\mathrm{Me_2AlCl}$ to the aldehyde competes with the ene reaction even with nucleophilic alkenes. This addition is the exclusive reaction with less nucleophilic mono- and 1,2-disubstituted alkenes. Addition of a methyl group to formaldehyde is not a serious problem except with the least nucleophilic alkenes, such as compounds with monosubstituted double bonds further deactivated by complexation of $\mathrm{Me_2AlCl}$ to a basic site elsewhere in the molecule. In these cases, use of $\mathrm{Me_3Al_2Cl_3}$ or $\mathrm{EtAlCl_2}$ often gives good results.

Alkylaluminum halides are useful catalysts for the intramolecular ene reactions of unsaturated carbonyl compounds. The MVK·$\mathrm{Me_2AlCl}$ complex reacts with methylene–cyclohexane at −20° to give the expected ene adduct **1** in 60% yield.[11] If the reaction mixture is allowed to warm to 25°, an intramolecular ene reaction, with the ketone functioning as the enophile, occurs to give **2**. Normally a tertiary alcohol is unstable in the presence of a Lewis acid, undergoing solvolysis to give a tertiary carbenium ion. Here the alcohol–$\mathrm{Me_2AlCl}$ complex loses methane to give a methylchloroaluminum alkoxide which does not solvolyze. Dichloroaluminum t-alkoxides, formed from $\mathrm{RAlCl_2}$ and tertiary alcohols do solvolyze.



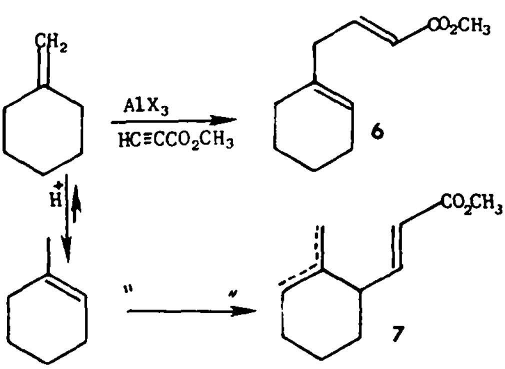
Using Me_2AlCl, the less nucleophilic 1,2-disubstituted double bond can be used as an ene component in intramolecular ene reactions of aldehydes for the first time. Treatment of **3a** or **3b** with Me_2AlCl gives the expected ene adduct **4** and the alcohol **5** in varying proportions.[3b] Synthesis of **4** is optimized by working at high dilution and high temperature for reasons which are obvious from mechanistic considerations. Ene reaction is a unimolecular reaction of the aldehyde–Me_2AlCl complex. Methyl addition is a bimolecular reaction involving the above complex and a second molecule of Me_2AlCl. The unimolecular reaction is favored at lower concentrations. The bimolecular reaction is favored at low temperatures where its larger negative entropy of activation is less important. Excess Me_2AlCl also favors methyl addition.





	conc, M	% yield	% yield
a	0.4	37	48
a	0.04	66	24
b	0.4	75	17
b	0.04	93	2

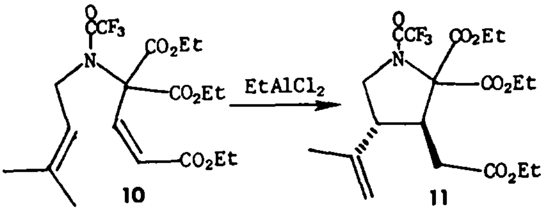
We have found that $EtAlCl_2$ is preferable to $AlCl_3$ as a catalyst for the ene reactions of α,β-unsaturated esters.[2,12] Although these reactions do not produce acidic protons, adventitious water causes problems in $AlCl_3$ catalyzed reactions. Reaction of methylenecyclohexane with methyl propiolate and $AlCl_3$ gives the desired ene adduct **6** contaminated with 10–25% of the ene adduct **7** formed from 1-methylcyclohexene, produced by proton catalyzed isomerization of methylenecyclohexene (eqn 3). With $EtAlCl_2$, only **6** is formed. $EtAlCl_2$ is also the preferred catalyst for use with methyl chloropropiolate, dimethyl acetylenedicarboxylate and methyl α-substituted acrylates.



(3)

Use of alkylaluminum halides is especially desirable when more than one equivalent of Lewis acid must be used, e.g. when basic sites are present in the ene component. A precursor to 1,25-dihydroxycholesterol, **9**, has been constructed in 89% yield by an ene reaction of **8** with methyl propiolate using 3 equivalents of $EtAlCl_2$.[13] (One equivalent for each acetate and one for methyl propiolate.) No **9** is obtained using 3 equivalents of $AlCl_3$ because of competing protonation of the double bond followed by Wagner–Meerwein rearrangements. Dauben and Brookhart have carried out a similar series of transformations using Et_2AlCl.[14]

Oppolzer has used Et_2AlCl to catalyze the ene reaction of **10** to give exclusively the *trans* isomer **11**.[15] This reaction is instantaneous with 30 equiv. of Et_2AlCl at −78° and requires 30 min with 3 equiv of Et_2AlCl at −35°. It is unlikely that **10** would tolerate 30 equiv of other Lewis acids.

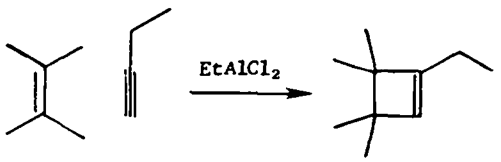


Diels–Alder reactions

Alkylaluminum halides have been used sporadically as catalysts for Diels–Alder reactions. While their proton scavenging ability may be of some value here, it is not clear that these reagents are preferable to standard Lewis acids for these reactions. Robinson, in the initial work on Lewis acid catalyzed Diels–Alder reactions used $TiCl_4$–Et_2AlCl for the reaction of butadiene with acrolein.[16] Miyajima and Inukai found that $EtAlCl_2$ gave better yields than $AlCl_3$ or Et_2AlCl for the same reaction.[17] Kuran *et al.* found $AlCl_3$ or BCl_3 to be superior to $EtAlCl_2$ for the Diels–Alder reaction of butadiene with acrylonitrile, methacrylonitrile, methyl acrylate or methyl methacrylate.[18] The Diels–Alder reaction of methylcyclopentadiene with a variety of dienophiles is efficiently catalyzed by $EtAlCl_2$.[19] Roush has found alkylaluminum halides to be useful catalysts for intramolecular Diels–Alder reactions with α,β-unsaturated esters as dienophiles.[20]

[2 + 2] *Cycloadditions*

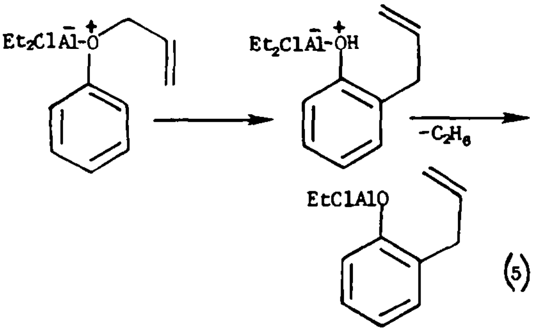
Lukas *et al.* have reported that Lewis acids catalyze the cycloaddition of acetylenes or allenes with olefins to give cyclobutenes or alkylidenecyclobutanes, respectively.[21] The proposed mechanism involves addition of the Lewis acid to the acetylene or allene to give a vinyl cation which adds to the olefin (eqn 4). $EtAlCl_2$ is the optimal catalyst for this reaction, probably because it prevents proton catalyzed side reactions. $EtAlCl_2$ is also useful for the cycloaddition of methyl 2,3-butadienoate with olefins[22] and methyl propiolate with 1,2-disubstituted alkenes.[12] In these reactions the Lewis acid is coordinated to the ester.



(4)

Claisen rearrangements

Sonnenberg reported that Et_2AlCl catalyzes the Claisen rearrangement of allyl phenyl ethers to give *o*-allyphenols in 89–96% yield.[23] The initially formed phenol·Et_2AlCl complex loses ethane to give the aluminum phenoxide, thereby preventing further reactions of the type common with other Lewis acid catalyzed Claisen rearrangements (eqn 5). This approach to catalysis of the Claisen rearrangement deserves further study.



(5)

Friedel–Crafts reactions

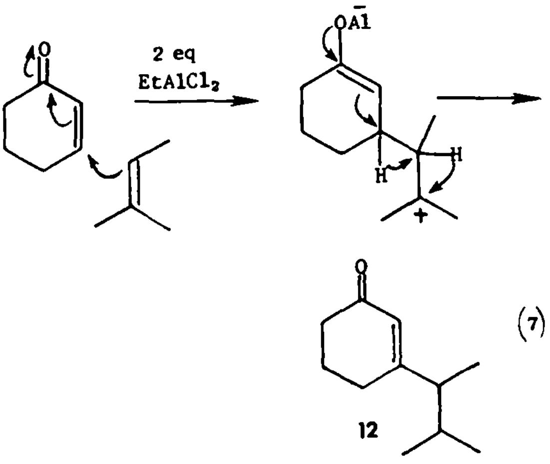
Friedel–Crafts reactions of acid chlorides or anhydrides with aromatics or alkenes proceed with the production of an equivalent of protic acid. These reactions should work better with alkylaluminum halides as Lewis acids,[9] especially aliphatic Friedel–Crafts reactions in which the alkene is susceptible to rearrangement via protonation–deprotonation. In the one system we have looked at, this has been the case. Treatment of alkenes with toluenesulfinyl chloride and 1 eq of $EtAlCl_2$ in ether gives good yields of the corresponding allylic sulfoxide as its $AlCl_3$ complex, with loss of ethane (eqn 6).[7] Only with the least nucleophilic terminal alkenes is formation of ethyl tolyl sulfoxide a significant side reaction. Me_2AlCl cannot be used because of the increased nucleophilicity of the alkyl groups. Since $EtAlCl_2$ is a stronger Lewis acid than desired, ether is used as a solvent to moderate the reaction. Use of $ZnCl_2$ or $AlCl_3$ as the Lewis acid leads to proton induced side reactions.

Cation–olefin addition reactions

Alkylaluminum halides are useful initiators for cation–olefin addition reactions. In some cases an alkyl group on the aluminum reacts with a carbenium ion intermediate in a synthetically useful manner.

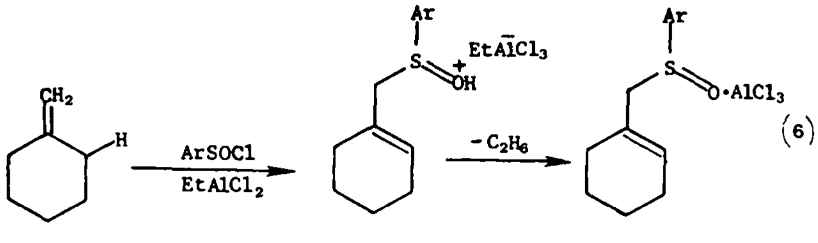
We have found that cyclohexenone (or other β-monosubstituted enones or enals) reacts with alkenes in the presence of >1 eq of $EtAlCl_2$ to give a zwitterion which undergoes two 1,2-hydride shifts to generate a new α,β-unsaturated carbonyl compound **12** (eqn 7).[3a] Although this reaction may not be unique to $EtAlCl_2$, no **12** is formed if $AlCl_3$, $BF_3{\cdot}OEt_2$ or $TiCl_4$ is used. Related intramolecular reactions also proceed best with $EtAlCl_2$ although other Lewis acids can be used. No reaction occurs if ≤ 1 eq of $EtAlCl_2$ is used. Kinetic studies have shown that the initial rate of reaction with 1.1, 1.2 and 1.3 equiv of $EtAlCl_2$ is proportional to the excess of Lewis acid present.

The reaction of cyclohexenone with 2 eq of $EtAlCl_2$ should produce cyclohexenone·$AlCl_3$ and Et_2AlCl.[24,25] The olefin may react with this enone·$AlCl_3$ complex with Et_2AlCl simply functioning as an efficient proton scavenger. It is tantalizing to speculate that the alkene adds to small amounts of cyclohexenone-$AlEt_2^+AlCl_4^-$ present in equilibrium with cyclohexenone·$AlCl_3$ and Et_2AlCl. This hypothesis is consistent with the special role of $EtAlCl_2$; the Et groups will help stabilize the very electrophilic cation and the chlorides will stabilize the anion.



(7)

The reactions of $CH_2O{\cdot}Me_3Al$ with alkenes are quite different than those of $CH_2O{\cdot}Me_2AlCl$ which give homoallylic alcohols by a two-step ene reaction (eqn 1). With Me_3Al the allylic alcohol **13** and saturated alcohol **14** are formed in varying ratios along with small amounts of ene adduct. The zwitterionic intermediate formed in this case reacts by transfer of the more nucleophilic Me group to give **14** and conceivably by a 1,5-proton shift to the more basic Me group to give **13**.



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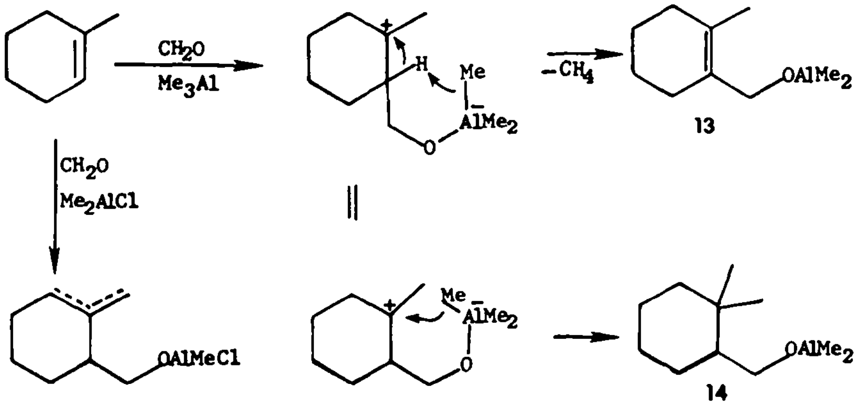
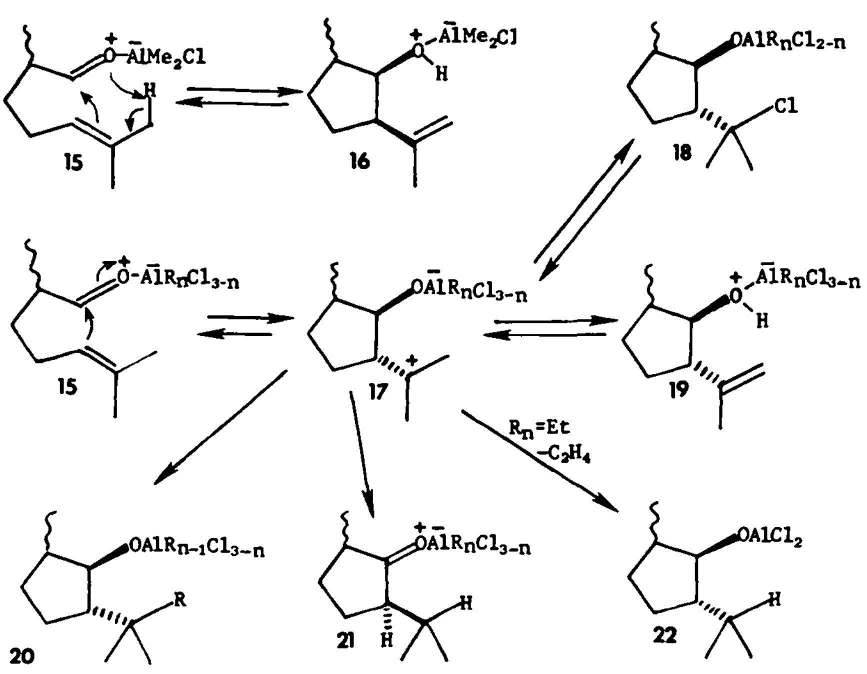


Our studies of 2,6-dimethyl-5-heptenal (**15**) have indicated the effect of acid strength, temperature, alkyl group and number of eq of Lewis acid on the nature of the reaction.[3b] With 1 eq of Me_2AlCl at −80°, a concerted Lewis acid catalyzed ene reaction gives **16**. With 2 eq of Me_2AlCl a more electrophilic complex is formed so that formation of **17** by a more rapid reaction becomes the major process. At −80°, a high yield of chloroalcohol **18** is formed. At 0°, formation of **18** is reversible so that products obtained from **17** by three competing irreversible reactions are obtained. A 1,5-Me shift gives **20**, a 1,5-proton shift gives **19** which loses methane, and two 1,2-hydride shifts give **21**. Treatment of **15** with 2 eq of $MeAlCl_2$ at −80° gives mainly **21**. Due to the greater acidity of $MeAlCl_2$, chloro alkoxide **18** is unstable, reverting to **17**. Since the Me group is less basic and nucleophilic than that of Me_2AlCl, **19** reverts to **15** faster than it loses CH_4 and **20** is not formed. With 2 eq of $EtAlCl_2$ at −80°, a reductive cyclization to give **22** is the major process. Apparently the zwitterion reacts via hydride delivery from the β-hydrogen of the Et group.

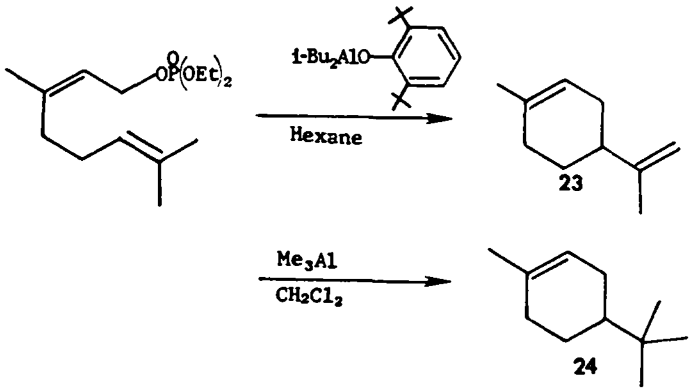
Yamamoto and Nozaki have explored the use of organoaluminum reagents for the initiation of cation-olefin cyclization by the heterolysis of terpenoid allylic phosphates.[26] They have shown that choice of solvent and ligands on the aluminum has a remarkable effect on the reaction. For instance, treatment of neryl diethyl phosphate with diisobutylaluminum 2,6-di-t-butylphenoxide gives almost exclusively limonene (**23**). On the other hand, reaction with Me_3Al in CH_2Cl_2 gives mainly **24** (eqn 8).

Quasi-intramolecular reactions

The reaction of an alkylalunimum halide with a dienol liberates an alkane and generates a new Lewis acid which can complex to a dienophile. The resulting complex undergoes a Lewis acid catalyzed Diels–Alder reaction which we term quasi-intramolecular since the diene is covalently bonded to the aluminum and the dienophile is complexed to it. This reaction has been used in a model study for the synthesis of pseudomonic acid in which the diene is generated by a Me_2AlCl catalyzed ene

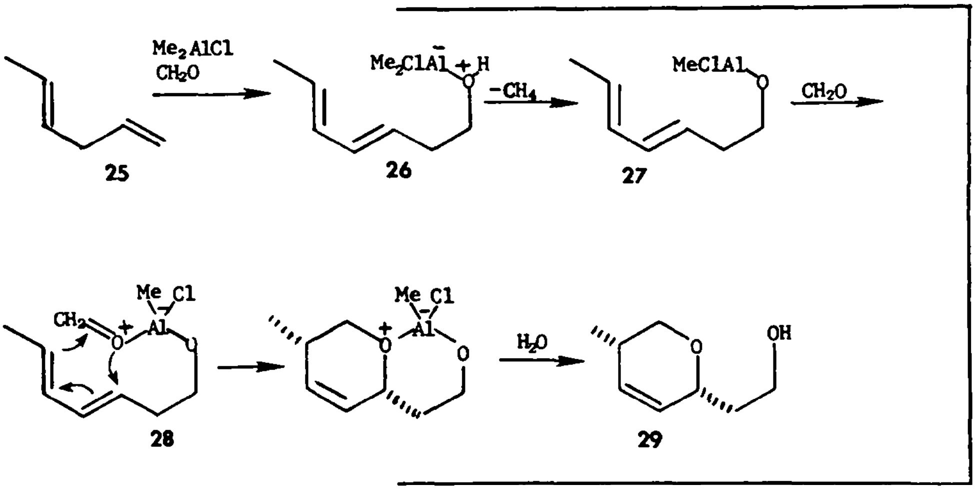


a, αMe **b**, βMe



(8)

reaction of formaldehyde. Treatment of **25** with CH_2O and Me_2AlCl gives mainly **26** which loses CH_4 to give a new Lewis acid **27**. Complexation of **27** with CH_2O gives **28** which undergoes a quasi-intramolecular Lewis acid catalyzed Diels–Alder reaction to give **29** in 35% yield from **25**. Quasi-intramolecular reactions, which depend on the ability of alkylaluminum halides to react with proton acids to generate a new Lewis acid, have broad synthetic potential.



Alternatives

It has long been recognized that Brønsted acids can cause problems in Lewis acid catalyzed reactions. Mukaiyama has explored bases which are compatible with $TiCl_4$.[27] He has found that $Ti(OCH(CH_3)_2)_4$ is often useful. $TiCl_4$ alone is not suitable for the catalysis of the Claisen rearrangement of allyl phenyl ethers, since 2-(2-chloropropyl)phenols are formed even at −78°. However, if trimethylsilylacetanilide is added as a proton scavenger, good yields of 2-allylphenols are obtained at 0°.[28] We have found that 2,6-di-t-butylpyridine, which Brown has shown will not complex to Lewis acids,[29] prevents side reactions in $AlCl_3$ catalyzed ene reactions with methyl propiolate.[12]

CONCLUSION

From the above results, it is clear that organoaluminum compounds, due to their ability to act as proton scavengers and alkyl donors, have an efficacy as Lewis acids that is just beginning to be appreciated. The nucleophilicity of the alkyl groups is sometimes a problem, but can also be synthetically useful.

EXPERIMENTAL

General information. Me_2AlCl was purchased from Texas Alkyls as a 14.6% w/w soln in heptane (d = 0.724, 1.14 M). $EtAlCl_2$ was purchased from Texas Alkyls as a 25.1% w/w soln in heptane (d = 0.772, 1.53 M). Me_3Al was purchased from Alfa as a 25% w/w soln in hexane (d = 0.679, 2.35 M). $MeAlCl_2$ was made by refluxing Me_2AlCl and $AlCl_3$ in heptane. All experiments were conducted in anhyd solvents under N_2 in flame dried glassware.

Reaction of limonene with isovaleraldehyde·Me_2AlCl. Me_2AlCl (6.0 mL of 1.13 M, 6.78 mmol) was added to a soln of isovaleraldehyde (0.39 g, 4.54 mmol) and limonene (0.68 g, 5.00 mmol) in 15 mL CH_2Cl_2 at 0°. The soln was allowed to warm to 25°, and stirred for 2 hr. The reaction was quenched by slow addition of 5 mL of sat NaH_2PO_4 soln. Ether was added and precipitated Al-salts were dissolved by dropwise addition of 10% HCl. The organic layer was separated. The aqueous layer was washed three times with ether. The combined organic layers were dried ($MgSO_4$) and evaporated to give crude product. Evaporative distillation (96°, 0.025 torr) gave 0.69 g (69%) of 4-methyl-γ-methylene-α-(2-methylpropyl)-3-cyclohexene-1-propanol: NMR (CCl_4) δ 5.40(m, 1), 4.88(m, 1), 4.72(m, 1), 3.77(m, 1), 2.92–1.07(m, 13), 1.77(br s, 3) and 0.93(br d, 6, J = 7 Hz); IR (neat) 3490, 1640 and 888 cm^{-1}.

Reaction of 1-pentene with formaldehyde·Me_2AlCl. Me_2AlCl (6.0 mL of 1.13 M, 6.78 mmol) was added to a soln of paraformaldehyde (0.14 g, 4.54 mmol of CH_2O), and 1-pentene (0.35 g, 5.00 mmol) in 15 mL of CH_2Cl_2 at 0°. The reaction was stirred 2.5 hr at 25° and worked up as described above to give, after evaporative distillation, 0.36 g (78%) of a 9:1 mixture of *trans*- and *cis*-3-hexen-1-ol: NMR (CCl_4) δ 5.53(m, 2), 4.80(m, 1, OH), 3.63(br t, 2, J = 7 Hz), 2.18–1.48(m, 4) and 1.00(br t, 3, J = 7 Hz); IR (neat) 3440 and 968 cm^{-1}.

Reaction of methylenecyclohexane with methyl vinyl ketone. Methyl vinyl ketone (0.35 g, 5 mmol) was added to a soln of Me_2AlCl (4.16 mL, 1.14 M, 4.75 mmol) in 25 mL CH_2Cl_2 at −20°.

Methylene cyclohexane (0.53 g, 5.5 mmol) was added immediately. The reaction was stirred for 2 hr at −20°, quenched with water and extracted 3 times with ether which was dried and evaporated giving 0.646 g (78%) of crude **1**. Chromatography of 0.423 g on silica gel (7:1 petroleum ether–ether) gave 0.212 g (39%) of pure **1**: NMR (CCl_4) δ 5.38(br, 1), 2.31(t, 2, J = 7 Hz), 2.06(s, 3), 2.0–1.0(m, 12); ^{13}C NMR (C_6D_6) 206.1, 137.3, 121.7, 42.9, 37.8, 29.4, 28.4, 25.6, 23.4, 23.0 and 22.1; IR (neat) 3050, 1720 and 1670 cm^{-1}. Anal: C, H.

The reaction was repeated as described above for 6 hr at 25°. Workup gave 0.936 g of which 0.836 g was chromatographed as described above giving 0.045 g (6%) of **1** and 0.387 g (52%) of **2**: NMR ($CDCl_3$) δ 5.7(br s, 1) 2.6–1.3(m, 14) and 1.20(s, 3); ^{13}C NMR ($CDCl_3$) 137.0, 124.6, 72.2, 46.3, 40.4, 35.2, 26.8, 25.2, 23.1, 22.5 and 22.0; IR (neat) 3490, 1670 and 1110 cm^{-1}. Anal: C, H.

Cyclization of Z-6-*nonenal with* Me_2AlCl. A soln of *Z*-6-nonenal (**3b**) (0.184 g, 1.3 mmol), 92% **3b**, 8% *E*-isomer) in 4.0 mL of CH_2Cl_2 was cooled to 0° and treated with Me_2AlCl (1.7 mL of 1.14 M in heptane, 1.9 mmol). The soln was stirred for 2.5 hr at 0° and worked up to give 0.180 g of material which was shown by GC to be 75% **4b**, 17% **5b** and 4% of the *trans*-isomer of **4b** obtained from the *E*-isomer. Chromatography on silica gel (4:1 petroleum ether–ether) gave 80 mg (44%) of **4b** and 35 mg (17%) of **5b**. The spectral data for **4b** follow: NMR ($CDCl_3$) δ 5.55(m, 2), 3.81(br, 1), 2.18(br, 1), 1.72(m, 3, virtually coupled), and 1.2–1.9(m, 9); IR (neat) 3400, 3030, 1060, 1040 and 965 cm^{-1}. Mol. Wt. Calcd for $C_9H_{16}O$: 140.1201. Found: 140.1206.

Repetition of the reaction in 40 mL of CH_2Cl_2 at 25° for 2 hr gave 181 mg which was shown by GC to be 90% **4b**, 1–2% **5b** and 6% of the *trans*-isomer of **4b** from the *E*-isomer.

Reaction of methylenecyclohexane with p-*toluenesulfinyl chloride and* $EtAlCl_2$. $EtAlCl_2$ (1.8 mL of 1.57 M in heptane, 2.8 mmol, 1.4 eq) was added to a soln of methylenecylcohexane (0.192 g, 2 mmol) and *p*-toluenesulfinyl chloride (0.349 g, 2 mmol) in 5 mL anhyd ether at 0°. The soln was stirred 30 min at 0° and 1 hr at 25° and quenched by addition of water and more ether. The precipitated Al salts were dissolved by addition of 10% HCl. The aqueous layer was extracted 3 times with ether. The combined organic layers were washed with 10% NaOH, brine, dried ($MgSO_4$) and evaporated to give 512 mg. Chromatography on silica gel (1:1 hexane-EtOAc) gave 296 mg of 1-cyclohexen-1-ylmethyl *p*-tolyl sulfoxide m.p. 61–66°. An analytical sample was prepared by recrystallization from hexane: m.p. 67–69°; NMR ($CDCl_3$) δ 7.5(d, 2, J = 8 Hz), 7.28(d, 2, J = 8 Hz), 5.52(br s, 1), 3.47(d, 1, J = 12 Hz), 3.26(d, 1, J = 12 Hz), 2.4(s, 3), 2.0(m, 4) and 1.55(m, 4); IR(KBr) 1640 and 1040 cm^{-1}. Anal. C, H, S.

Reaction of 1-*methylcyclohexene with formaldehyde and trimethylaluminum*. Trimethylaluminum (1.75 mL, 2.35 M in hexane, 4.0 mmol) was added to 1-methylcyclohexene (0.19 g, 2.0 mmol) and paraformaldehyde (0.090 g, 3 mmol) in 10 mL of CH_2Cl_2. After 15 min, 10 mL of water was added followed by 10 mL of 10% HCl to dissolve the alumina. Normal workup gave 0.15 g (60%) of a colorless oil which GC showed to consist of 8% ene adducts, 24% of **13** and 64% of **14**. Pure samples of **13** and **14** were isolated by preparative GC.

The data for **13** follow: NMR ($CDCl_3$) δ 4.11(s, 2), 2.18(s, 1, OH), 2.1–1.8(m, 4), 1.75(br s, 3) and 1.8–1.1(m, 4); IR ($CDCl_3$) 3620; MS *m*/*e*(rel intensity) 126(M^+, 42), 111(71), 108(37), 97(31), 95(46), 93(84), 67(96) and 55(80).

The data for **14** follow: NMR ($CDCl_3$) δ 3.84(dd, 1, J = 10.5, 3.4 Hz), 3.30(dd, 1, J = 10.5, 8.1 Hz), 2.17(s, 1, OH), 1.8–1.0(m, 9), 0.97(s, 3) and 0.80(s, 3); ^{13}C NMR($CDCl_3$) δ 64.4, 49.1, 42.0, 32.3, 30.7, 26.1, 25.6, 22.4 and 20.4; IR($CDCl_3$) 3630, 1365, 1030, 1010 and 980 cm^{-1}; MS *m*/*e* (rel intensity) 142(M^+, 0.4), 127(1), 124(16), 111(17), 110(6), 109(31), 96(7), 95(12), 82(28), 81(31), 69(82), 68(24), 67(47), 55(55) and 41(100).

Cyclization of **15** *with* 2 eq *of* Me_2AlCl *at* −78° Me_2AlCl (2.7 mL of 1.14 M in heptane, 3.1 mmol) was added to a soln of **15** (0.212 g, 1.51 mmol) in 4.5 mL of CH_2Cl_2 at −78°. The reaction was stirred 4 hr at −78° and worked up to give 0.22 g which NMR showed to be mainly **18a**. Chromatography on silica gel (4:1 pentane–ether) gave 144 mg (54%) of **18a** (some decomposition to **15** and **20** occurred on chromatography): NMR ($CDCl_3$) δ 3.60(dd, 1, J = 7.3, 7.3 Hz), 2.31(s, 1, OH), 1.5–2.1(m, 6), 1.62(s, 3), 1.54(s, 3) and 1.02(d, 3, J = 6.2 Hz); ^{13}C NMR($CDCl_3$) 81.7, 74.5, 58.7, 42.9, 31.8, 30.5, 30.3, 25.5, and 17.3; IR(neat) 3400 and 1110 cm^{-1}; MS *m*/*e* 140, 125, 123, 122 and 109. Calc. for $C_9H_{17}ClO$: C, 61.18; H, 9.70; Cl, 20.07%) (Found: C, 59.15; H, 9.11; Cl, 19.26.)

Cyclization of **15** *with* 2 *eq of* $EtAlCl_2$ *at* −78°. $EtAlCl_2$ (1.7 mL of 1.17 M in pentane, 1.99 mmol) was added to a soln of **15** (0.148 g, 1.05 mmol) in 3 mL of CH_2Cl_2 at −78°. The reaction was stirred for 2 hr at −78° and worked up to give 0.145 g which GC showed consisted of 73% of **22a**, 11% of **21a** and 14% of **20a**. Chromatography on silica gel (2:1 pentane–ether) gave 77 mg (51%) of **22a**: NMR ($CDCl_3$) 3.28 (dd, 1, J = 7.0, 7.0 Hz), 1.77 (s, OH), 1.4–1.9 (m, 3), 1.1–1.4 (m, 4), 1.01 (d, 3, J = 6.2 Hz), 0.96 (d, 3, J = 6.2 Hz) and 0.86 (d, 3, J = 6.4 Hz); IR (neat) 3340 and 1080 cm^{-1}; MS *m*/*e* (rel intensity) 142 (M^+, 67), 127(35), 124(22), 109(64), 99(27), 95(36), 85(60), 82(70), 81(78) and 71(100). Mol. Wt. Calc. for $C_9H_{18}O$: 142.1358. Found: 142.1354.

Reaction of **25** *with formaldehyde and* Me_2AlCl. Me_2AlCl (13.2 mL of 1.14 M, in heptane, 15 mmol) was added to a soln of paraformaldehyde (0.45 g, 15 mmol) and *trans*-**25** (0.41 g, 5.00 mmol) in 15 mL of CH_2Cl_2. The soln was stirred for 1 hr at 0° and worked up to give 0.5 g which was chromatographed on silica gel (2:1 petroleum ether–ether) to give 0.18 g (32%) of several minor products which are probably 1:1 adducts, followed by 0.135 g (19%) of **29**: NMR ($CDCl_3$)δ 5.84(br d, 1, J = 10, 2.5, 4.5 Hz), 5.56(br d, 1, J = 10, 1, 2 Hz), 4.31(m, 1), 3.98–3.50(m, 4), 3.0(br s, 1, OH), 2.18(m, 1), 1.79(dt, 2, J = 7, 7 Hz) and 1.08(d, 3, J = 7 Hz); ^{13}C NMR 131.0, 128.6, 73.5, 68.8, 60.4, 36.8, 29.3 and 18.4; IR 3400, 3055, and 1655 cm^{-1}. Anal. C, H.

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