of ketone II. Why enolization is greater for the cyclohexoxy derivative compared to the other hydrides is not clear, especially in its comparison to $LiMgH_2OPh$. One explanation is that the amount of axial alcohol produced in the reaction of every ketone with $LiMgH_2OPh$ is very nearly the same as that observed for MgH_2. Thus if MgH_2 is the reducing agent for $LiMgH_2OPh$ and MgH_2 gives 100% yield in each case, it is not surprising that those hydride reagents that disproportionate to MgH_2 give no enolization as is observed in the case of MgH_2.

It was desired to determine if the degree of stereoselectivity was higher in the initial stages of the reaction than after equilibrium had a chance to take place. In this connection, 4-*tert*-butylcyclohexanone was allowed to react with a 100% excess of lithium (2,2,6,6-tetrabenzylcyclohexoxy)dihydridomagnesiate. The results are given in Table VI. As can be seen from the data, the lower the temperature, the greater the observed enolization to reduction ratio. At −25 °C, for example, the major product (64%) after quenching is the starting ketone, 4-*tert*-butylcyclohexanone. It should also be noted that the initial reaction is very fast and that after 30 s little more than 5% change was observed in the yield of product. Also between 30 and 18000 s, less than 5% change was observed in the ratio of alcohols. The thermodynamic product is the equatorial alcohol, and if 4-*tert*-butylcyclohexanone is allowed to react under the equilibrium conditions inherent for Meerwein–Ponndorf–Verley or Birch reductions, the equatorial alcohol is produced in 98–99% yield. For lithium alkoxymagnesium hydride reductions, never less than 86% of the axial alcohol is observed; therefore, if equilibration is taking place, it is taking place very slowly.

Table VII (expt 64–68) lists the results of the reactions of ketones I, II, III, and IV with lithium dialkoxymagnesium hydrides prepared according to eq 5. The most selective reagents were the bis(tetramethylcyclohexoxy) and bis(tetrabenzylcyclohexoxy) hydrides (expt 67 and 68) which reduced ketone I to provide 89 and 85% axial alcohol, respectively. However, a large amount of enolization accompanied the reactions (70 and 63%, respectively). On the other hand, expt 65 shows that the bis di-*tert*-butyl derivative enolized only 20% of the ketone while reducing the ketone to 81% of the axial alcohol. The sodium reagent (expt 66) not only produced a 55:45 axial to equatorial alcohol ratio but also enolized 90% of the ketone. When LiH and LiOR were allowed to react under similar conditions (expt 64), a 74:26 ratio of axial to equatorial alcohol was observed, but 72% of the ketone was enolized.

When ketones II, III, and IV were allowed to react with these reagents, lesser amounts of enolization were observed with very stereoselective results. All the reagents studied produced 99 and 100% axial alcohol when allowed to react with ketones II and III, respectively. The reactions with camphor (ketone IV) produced greater than 90% exo alcohol with little enolization except for expt 64 and 66 which produced 70 and 64%, respectively, of the starting ketone. These reagents represent a method of using lithium and sodium hydride for reduction which has not been previously reported.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. MPS 7504127), Union Camp, and Alcoa for financial support of this work.

Registry No. $LiMgH_2(OCH_3)$, 72749-25-8; $LiMgH_2$(O-*i*-Pr), 72749-26-9; $LiMgH_2$(O-*t*-Bu), 72749-27-0; $LiMgH_2(OCH_2$-*t*-Bu), 72749-28-1; $LiMgH_2(OCHPh_2)$, 72749-12-3; $LiMgH_2$(O-c-C_6H_{11}), 72749-13-4; $LiMgH_2$(OPh), 72749-14-5; lithium [(2-methylcyclohexyl)oxy]magnesium hydride, 72749-15-6; lithium (2,6-diisopropylphenoxy)magnesium hydride, 72749-16-7; lithium (2,6-di-*tert*-butylphenoxy)magnesium hydride, 72749-17-8; lithium [(2,2,6,6-tetramethylcyclohexyl)oxy]magnesium hydride, 72749-18-9; lithium [(2,2,6,6-tetrabenzylcyclohexyl)oxy]magnesium hydride, 72749-19-0; lithium methoxide, 865-34-9; lithium isopropoxide, 2388-10-5; lithium *tert*-butoxide, 1907-33-1; lithium 2,2-dimethylpropoxide, 3710-27-8; lithium diphenylmethoxide, 2036-66-0; lithium cyclohexyl oxide, 4111-51-7; lithium phenoxide, 555-24-8; lithium 2-methylcyclohexyl oxide, 72727-48-1; lithium 2,6-diisopropylphenoxide, 72727-49-2; lithium 2,6-di-*tert*-butylphenoxide, 55894-67-2; lithium 2,2,6,6-tetramethylcyclohexyl oxide, 72727-50-5; lithium 2,2,6,6-tetrabenzylcyclohexyl oxide, 72727-51-6; magnesium hydride, 7693-27-8; *cis*-4-*tert*-butylcyclohexanol, 937-05-3; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; *cis*-3,3,5-trimethylcyclohexanol, 933-48-2; *trans*-3,3,5-trimethylcyclohexanol, 767-54-4; 2,2,6,6-tetrabenzylcyclohexanol, 3849-12-5; *cis*-2-methylcyclohexanol, 7443-70-1; *trans*-2-methylcyclohexanol, 7443-52-9; *endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 507-70-0; *exo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 124-76-5; [(2,2,6,6-tetramethylcyclohexyl)oxy]magnesium hydride, 72727-52-7; lithium bis[(2,2,6,6-tetramethylcyclohexyl)oxy]magnesium hydride, 72749-24-7; 2,2,6,6-tetramethylcyclohexanone, 1195-93-3; 2,2,6,6-tetrabenzylcyclohexanone, 7382-13-0; 2,2,6,6-tetramethylcyclohexanol, 6948-41-0.

Hydrometalation. 5. Hydroalumination of Alkenes and Alkynes with Complex Metal Hydrides of Aluminum in the Presence of Cp_2TiCl_2

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Terminal alkenes and internal alkynes are reduced rapidly and in high yield by reaction with $LiAlH_4$, $NaAlH_4$, $LiAlMe_3H$, $NaAlMe_3H$, $LiAlH_2(NR_2)_2$, $NaAlH_2(NR_2)_2$, or Vitride [$NaAlH_2(OCH_2CH_2OCH_3)_2$] in the presence of a catalytic amount of Cp_2TiCl_2 in THF at room temperature. When these reactions were quenched with D_2O or I_2, quantitative yields of the corresponding deuterium or iodine compounds were obtained in most cases. This method provides a convenient and high-yield route to alkyl- and vinylaluminum compounds as intermediates in organic synthesis.

Considerable interest in recent years has been directed toward the development of carbometalation and hydrometalation reactions involving alkenes and alkynes. The reasons for this interest are clear: first, alkenes and alkynes are very fundamental and economic building blocks for more complex organic compounds, and second, carbometalation and hydrometalation provide routes to form carbon–metal bonds which can then be functionalized

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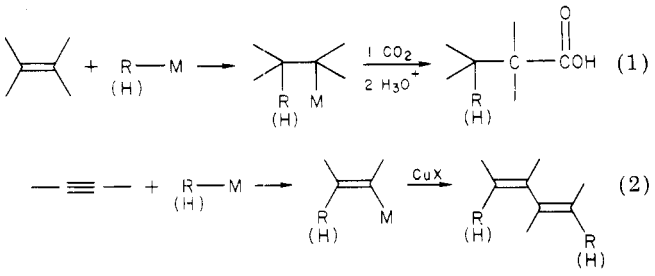
(eq 1 and 2) to form numerous classes of compounds.



Carbometalation reactions have evolved significantly in just the last few years due to the efforts of numerous workers; however, hydrometalation reactions have received much less attention. The work of Brown[1] in the development of hydroboration as a synthetic tool in organic chemistry stands alone in terms of the degree of development of the method and in terms of its utility. However, the product of hydroboration (R_3B) contains C–B bonds which are not easily functionalized compared to C–Mg or C–Al bonds. In addition, diborane is quite expensive, thus providing sufficient impetus to develop other hydrometalation reactions, particularly those that can form more active C–M bonds and whose metal hydride reagent is not so expensive.

Recently, Schwartz and co-workers have developed a hydrometalation reaction involving the addition of $Cp_2Zr(H)Cl$ to alkenes and alkynes.[2] The reaction proceeds well for terminal alkenes and uses stoichiometric amounts of catalyst. In addition, Sato and co-workers[3] have effected the reduction of alkenes and alkynes with $LiAlH_4$ in the presence of transition-metal halides. Although one might assume that hydrometalation products are produced as intermediates, deuterolysis of the reaction mixture shows that only $TiCl_4$ and $TiCl_3$ catalysts produce a deuterium-incorporated product.

Some time ago we reported the direct synthesis of $NaAlH_4$ (eq 3) and a convenient synthesis for $LiAlH_4$ (eq 4).[4] It is clear that these complex metal hydrides, espe-

$$Na + Al + 2H_2 \xrightarrow[2000\ psi]{140\ °C} NaAlH_4 \quad (3)$$

$$NaAlH_4 + LiCl \xrightarrow[25\ °C]{Et_2O} LiAlH_4 + NaCl \quad (4)$$

cially $NaAlH_4$, should be a most inexpensive source of soluble metal–hydrogen compound. In addition, if all four hydrogens can be made to react with olefin, $NaAlH_4$ should indeed represent the least expensive source of soluble or insoluble metal hydride available for hydrometalation reactions (eq 5). It has been known for some time that

$$NaAlH_4 + 4RHC{=}CH_2 \rightarrow NaAl(CH_2CH_2R)_4 \quad (5)$$

$NaAlR_4$ compounds react much like R_3Al compounds and are easily functionalized. However, it should be noted that the ease of functionalization for the alkyl groups is best for the first group and progressively more difficult for the remaining ones.

Bis(dialkylamino)alanes are produced in nearly quantitative yield and in a high state of purity by the reaction of Al, H_2, and R_2NH compounds and are also readily available, inexpensive, and reactive metal hydrides. We reported earlier that bis(dialkylamino)alanes add to olefins and alkynes in the presence of catalytic amounts of Cp_2TiCl_2 in benzene solution in high yield (eq 6). We have

$$HAl(NR_2)_2 + RHC{=}CH_2 \xrightarrow{Cp_2TiCl_2} RCH_2CH_2Al(NR_2)_2 \quad (6)$$

just reported the details of $HAl(NR_2)_2$ hydroalumination of alkenes[6] and now we wish to report our latest results in hydroalumination of alkenes and alkynes with $NaAlH_4$, $LiAlH_4$, and some of their derivatives.

Experimental Section

Apparatus. All reactions were performed under nitrogen or argon at the bench by using Schlenk-tube techniques or in a glovebox equipped with a recirculating system to remove oxygen and solvent vapors.[7] Calibrated syringes equipped with stainless-steel needles were used to transfer reagents. All glassware and syringes were heated in an oven and cooled under a flow of nitrogen or argon. All inorganic and organic compounds, including internal standards for GLC, were prepared by weighing the reagent in a tared volumetric flask and diluting with the appropriate solvent.

Proton NMR spectra were obtained by using a Varian Model A-60 60-MHz spectrometer or a JEOL Model PFT-100 100-MHz Fourier transform spectrometer. All chemical shift values are expressed in parts per million (δ values) relative to Me_4Si as the internal standard. All mass spectra were obtained by using a Hitachi RMU-7 mass spectrometer. GLC analyses were obtained by using an F&M Model 720 gas chromatograph. IR spectra were obtained by using a Perkin-Elmer Model 621 IR spectrometer. High-pressure reactions were carried out by using an autoclave rated to 15 000 psi obtained from the Superpressure Division of the American Instrument Co.

Analytical Methods. Gas analyses were carried out by hydrolyzing samples with 0.1 M HCl on a standard vacuum line equipped with a Toepler pump.[7] Aluminum was determined by adding excess standard EDTA solution to hydrolyzed samples and then back-titrating with standard zinc acetate solution at pH 4 with dithizone as an indicator. Amines were analyzed by injecting hydrolyzed samples with an internal standard on the gas chromatograph. Carbon and hydrogen analyses were carried out by Atlantic Microlab, Inc.

All products arising from the quenching of reactions of hydrides and alkynes with H_2O, D_2O, I_2, or CO_2 were identified by GLC and compared to authentic samples obtained commercially or synthesized by known methods. All NMR spectra were obtained in $CDCl_3$ or benzene-d_6.

Lithium and sodium trimethylaluminohydrides were prepared by the equimolar addition of a benzene, diethyl ether, or THF solution of trimethylaluminum (obtained from Ethyl Corp. and distilled under vacuum in a drybox) to a lithium or sodium hydride slurry in the appropriate solvent. The addition was carried out in a one-necked round-bottomed flask equipped with a magnetic stirring bar and a pressure-equalizing addition funnel while being cooled with an ice–water bath. The addition funnel was fitted with a rubber serum cap which was attached to an argon-filled manifold connected to a mineral oil filled bubbler by a syringe needle. After the addition and stirring (usually 10 min) the reaction mixture became a clear, pale brown solution which was analyzed for aluminum by EDTA titration and for lithium and sodium by flame-ionization photometry.

Sodium bis(2-methoxyethoxy)aluminohydride (Vitride T) was obtained as a 70% toluene solution from Matheson Coleman and Bell.

Lithium and sodium bis(diethylamino)- and bis(diisopropylamino)aluminohydride were prepared by adding, with stirring at 0 °C, a stoichiometric amount of diethylamine or diisopropylamine to a THF solution of lithium or sodium aluminum hydride.

(1) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, 1962.
(2) D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, **96**, 8115 (1974).
(3) F. Sato, S. Sato, and M. Sato, *J. Organomet. Chem.*, **131**, C26 (1977); *ibid.*, **122**, C25 (1976); F. Sato, S. Sato, H. Kodema, and M. Sato, *ibid.*, **142**, 71 (1977).
(4) E. C. Ashby, G. Brendel, and H. E. Redman, *Inorg. Chem.*, **2**, 499 (1963).
(5) E. C. Ashby and S. Noding, *Tetrahedron Lett.*, 4579 (1977).
(6) E. C. Ashby and S. Noding, *J. Org. Chem.*, **44**, 4364 (1979).
(7) F. W. Walker and E. C. Ashby, *J. Chem. Educ.*, **45**, 654 (1968).

Additionally these compounds were prepared by adding a stoichiometric amount of bis(diethylamino)- or bis(diisopropylamino)alane to activated lithium or sodium hydride. The clear, pale yellow-brown THF solutions were analyzed for lithium, aluminum, and hydrogen by the standard methods described. If benzene solutions were desired, the THF was removed under vacuum and replaced by freshly distilled benzene. This procedure was repeated three times. The amount of THF which remained according to GLC was ≤5%.

Activated LiH was prepared by the hydrogenation of *tert*-butyllithium using Me_4Si as the internal standard.

Materials. Solvents. Fisher reagent-grade benzene and hexane were stirred over concentrated H_2SO_4, washed with Na_2CO_3 and then distilled water, dried over anhydrous $MgSO_4$, and then distilled from $NaAlH_4$ under nitrogen. The catalyst Cp_2TiCl_2 was obtained from Alfa Inorganics.

Alkenes. 1-Octene (bp 122–123 °C), 1-methyl-1-cyclohexene (bp 110–111 °C), styrene (bp 145–146 °C), *cis*-2-hexene (bp 67–68 °C), *trans*-2-hexene (bp 107–103 °C), 2-ethyl-1-hexene (bp 119–120 °C), cyclohexene (bp 82–83 °C), 3,3-dimethyl-1-butene (neohexene) (bp 40–41 °C), and methylenecyclohexane (bp 102–103 °C) were obtained from Chemical Samples Co. or Aldrich Chemical Co. and distilled and stored over 4A molecular sieves.

Alkynes. 2-Hexyne (bp 83–84 °C), 4-octyne (bp 132–133 °C), 1-phenyl-1-propyne (bp 185–186 °C), 1-octyne (bp 124–125 °C), and phenylethyne (bp 170 °C at 19 mm) were obtained from Chemical Samples Co. or Aldrich Chemical Co. and distilled and stored over 4A molecular sieves.

1-(Trimethylsilyl)-1-octyne was prepared as discussed in ref 6. Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.23; H, 12.13.

Preparation of Complex Aluminohydrides. $LiAlH_4$ (Alfa Inorganics) solutions in THF or diethyl ether and $NaAlH_4$ (Alfa Inorganics) solutions in THF were prepared by refluxing $LiAlH_4$ and $NaAlH_4$ in the appropriate solvent for at least 24 h followed by filtration through a fritted-glass filter funnel in the drybox. The resulting clear solutions were standardized for aluminum content by EDTA and for hydrogen by standard vaccum-line techniques.[8] Activated LiH was prepared by the hydrogenation of *tert*-butyllithium or *n*-butyllithium at 4000 psi of hydrogen for 12 h at room temperature in hexane. The resulting LiH slurry was removed via syringe under an argon atmosphere or in a drybox.

Sodium hydride as a 50% oil dispersion was obtained from Alfa Inorganics. The oil was removed by repeated washing and decantation using freshly distilled hexane.

General Reactions of Alkenes and Alkynes with Complex Metal Hydrides. A 10 × 18 mm test tube with a Teflon-coated magnetic stirring bar was flamed and cooled under a flow of argon or nitrogen. A saturated solution of Cp_2TiCl_2 in THF (0.125 M) was prepared (the solutions had to be made fresh each day). One or two milliliters of the Cp_2TiCl_2–THF solution was introduced into the vessel and then the alkene or alkyne added. Immediately after addition, a violet color developed but diminished in intensity with time. Then the reaction mixture was stirred at room temperature or at higher temperatures, depending upon the reactants, for up to 40 h in some cases. In general, the reactions involving internal alkynes were complete in 20 min. The reactions were quenched by various means (see General Quenching Techniques section) and worked up by the regular method (addition of water, extraction with diethyl ether or hexane, and drying over $MgSO_4$). Most products were separated by GLC using a 6 ft, 10% Apiezon L 60-80 column with a helium flow rate of 45 mL/min: 1-octene (110 °C, oven temperature), 1-methyl-1-cyclohexene (50 °C), 2-ethyl-1-hexene (50 °C), and cyclohexene (50 °C). A 20-ft, 10% TCEP column with a helium flow rate of 45 mL/min was used for 1-hexene, *cis*-2-hexene, *trans*-2-hexene, neohexene (45 °C, flow rate 25 mL/min), 2-hexyne (70 °C), 1-octyne (70 °C), 1-(trimethylsilyl)-1-octyne (100 °C), and diphenyl-1-propyne (125 °C). A 10-ft, 5% Carbowax 20M column was used for diphenylethyne (200 °C, flow rate 60 mL/min). The yield was calculated by using a suitable hydrocarbon internal standard for each case (n-$C_{12}H_{26}$, n-$C_{14}H_{30}$, or n-$C_{16}H_{34}$), and the products were identified by comparing the retention times of authentic samples with those of the products under similar conditions and/or by coinjection of products and authentic samples obtained commercially or synthesized by known methods.

General Quenching Techniques. Quenching with H_2O. After the desired reaction time for the catalytic hydrometalation reaction described above, the reaction was quenched with water or a saturated solution of ammonium chloride to produce the protonated species. The amounts of recovered starting material and products were determined by the methods described above.

Quenching with D_2O. The same procedure used for quenching with H_2O was followed. The amounts of recovered starting material and products were determined by the GLC methods and conditions described above. Each product was collected from the gas chromatograph and submitted for mass spectral analysis. The corrected percent of deuterium incorporation for the product was calculated by comparing the mass spectrum of the protonated species with the mass spectrum of the deuterated species and by subtracting the contributions of naturally occurring isotopic components from each molecular ion peak. This procedure was followed for all unsaturated substrates observed under these reaction conditions.

The regioselectivity of reactions was monitored by the use of NMR for 1-phenyl-1-propyne and 1-(trimethylsilyl)-1-octyne after the products were isolated by preparative GLC. For 1-phenyl-1-propyne, 95% of the major product, *cis*-1-phenyl-1-propene, was deuterated, with 90% of the deuterium located on C-1 as indicated by a quartet of triplets at 5.78 ppm (J = 7 Hz, 1 H) and a doublet at 1.89 ppm (J = 7 Hz, 3 H). The other isomer (deuterium located on C-2) showed a singlet at 1.89 ppm and a multiplet at 6.36–6.54 ppm. No *trans*-1-phenyl-1-propene was observed. However the two major products, 1-phenylpropene (15%) and 3-phenyl-1-propene (15%) contained 55 and 85% deuterium, respectively. The deuterium in the 3-phenyl-1-propene was located on C-3 as indicated by a multiplet at 4.4–5.8 ppm (3 H).

The products from the reduction of 1-(trimethylsilyl)-1-octyne were prepared independently.[9] *cis*-1-(Trimethylsilyl)-1-octene was prepared by the hydrogenation of 1-(trimethylsilyl)-1-octyne with 5% Pd/C in 95% ethanol and the reaction monitored until the desired amount of hydrogen was absorbed. The cis isomer was collected and purified via GLC under the aforementioned conditions. The trans isomer was also detected by GLC. The cis isomer, when coinjected under GLC conditions with the product of the hydroalumination reaction, showed a trace characteristic of only the cis isomer. The trans isomer obtained from the hydrogenation reaction had a retention time identical with that of the minor product from the hydroalumination reaction.

The following data were obtained for *cis*-1-(trimethylsilyl)-1-octene: IR (neat, film) 2960 (s), 2940 (s), 2860 (m), 1600 (m), 1470 (m), 1260 [for octene: IR (neat, film) 2960 (s), 2860 (m), 1600 (m), 1470 (m), 1260 (s), 850 (br, s)]; NMR (CCl_4, Me_4Si) δ 0.14 (s, 9 H), 0.74–2.66 (m, 11 H), 2.15 (q, 2 H, J = 8 Hz), 5.49 (d, 1 H, J = 13.0 Hz), 6.33 (dt, 1 H, J = 14 and 7 Hz); mass spectrum, m/e (relative intensity) 184 (M^+, 2), 170 (13), 169 (70), 141 (4), 125 (4), 114 (23), 109 (13), 99 (26), 85 (15), 73 (100), 67 (9), 59 (91), 44 (21), 41 (14). Anal. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12. Found: C, 71.54; H, 13.14.

The NMR spectrum of the trans isomer matched the spectrum found in the literature:[10] NMR (CCl_4, Me_4Si) δ 0.16 (s, 9 H), 0.6–1.6 (m, 11 H), 2.1 (m, 2 H), 5.6 (d, 1 H, J = 18 Hz), 6.0 (dt, 1 H, J = 18 and 6 Hz).

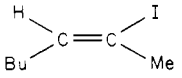
Quenching with I_2. A known concentration of iodine in benzene was prepared, and a stoichiometric amount was added to the catalytic hydroalumination reaction after the desired time. This mixture was then allowed to stir at room temperature for 1 h. Afterward, water was added followed by a saturated sodium thiosulfate solution. The organic layer was then separated and dried over sodium sulfate and analyzed by GLC or NMR. This procedure was followed for 2-hexyne. The iodoalkenes were identified by NMR in the following way. When the catalytic hydroalumination reaction of 2-hexyne was quenched with D_2O,

(8) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, 1969.

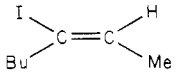
(9) R. A. Walker and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).

(10) F. A. Carey and J. R. Toler, *J. Org. Chem.*, **41**, 1966 (1976).

the products were the cis alkenes which were confirmed by co-injection of authentic samples in the gas chromatograph. From Zweifel's work,[11] it is known that hydroaluminated compounds quenched with iodine maintain their regiochemistry. Therefore, the iodoalkene obtained from the quenching with I_2 of the reaction involving 2-hexyne was 2- and 3-iodo-*cis*-2-hexene. NMR was used to distinguish between the two isomers:



methyl singlet at 2.36 ppm



methyl doublet at 1.63 ppm, $J = 7$ Hz

Anal. Calcd for $C_6H_{11}I$: C, 34.30; H, 5.28. Found: C, 34.51; H, 5.25.

Results and Discussion

Sato and co-workers[3] reported that titanium tetrachloride and zirconium tetrachloride catalyze the addition of $LiAlH_4$ to olefinic double bonds to produce the corresponding lithium organoaluminate. They reported, for example, that 1-hexene produced 99% *n*-hexane when allowed to react with $LiAlH_4$ in THF at room temperature for 30 min in the presence of 2 mol % of $TiCl_4$ followed by hydrolysis (eq 7). However, the reactions were not

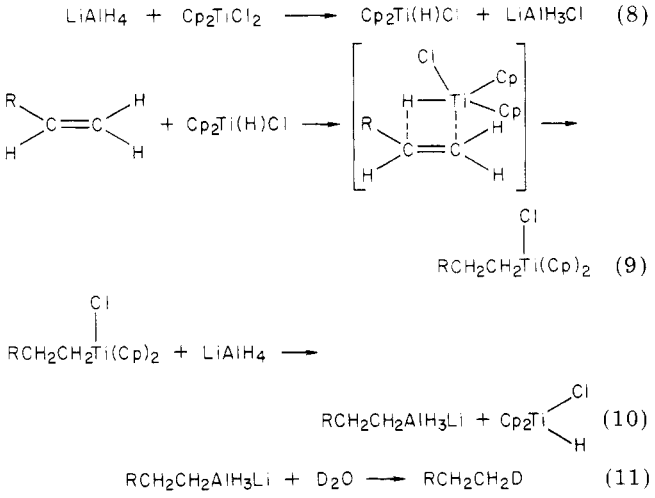
$$C_4H_9CH{=}CH_2 + LiAlH_4 \xrightarrow[\text{or } ZrCl_4]{TiCl_4} \xrightarrow{H_2O} C_6H_{14} \quad (7)$$

quenched with D_2O which in effect monitors the production of the hydrometalated intermediate. When these reactions were quenched with bromine, only 70% of the corresponding bromide was obtained in most cases. Therefore, the product obtained from the quenching of the reaction with H_2O could be misleading in terms of the formation of the intermediate hydrometalated product. We have recently reported that the reaction of $LiAlH_4$ with olefins in the presence of $NiCl_2$ results in the formation of the reduction product in quantitative yield in almost every case; however, addition of D_2O to the reaction mixture resulted resulted in very low deuterium incorporation in the product.[12]

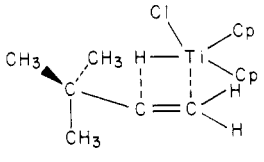
Since previous work has not definitely shown the presence of a hydrometalation intermediate in the reduction of olefins with complex metal hydrides, we investigated the hydrometalation reaction of unsaturated molecules in more detail, particularly looking for a different hydride and/or catalyst that would give a higher percentage of hydrometalated intermediate as evidenced by deuterium incorporation in the product. Lithium and sodium aluminum hydride, lithium and sodium trimethylaluminohydride, lithium and sodium bis(dialkylamino)aluminohydride, and Vitride [sodium bis(2-methoxyethoxy)-aluminohydride] were allowed to react with a series of alkenes and alkynes in a 1:1 ratio in the presence of 5 mol % of Cp_2TiCl_2 in THF. The results are presented in Tables I and II. Titanocene dichloride was chosen as the catalyst because it worked so well in the previously studied hydrometalation reaction with bis(dialkylamino)alanes,[6] and since then Sato[3] has investigated other catalysts.

The results of Tables I and II show that all of the hydrides behaved similarly. When allowed to react with terminal alkenes, the reactions were over in 10 min at room

Scheme I. Proposed Mechanism of Hydrometalation of Olefins by $LiAlH_4$ in the Presence of Cp_2TiCl_2



temperature. After quenching with D_2O, each product was analyzed via mass spectrometry and the mass spectrum of the product compared to the mass spectrum of the deuterated species obtained from quenching the corresponding Grignard reagent with D_2O. The percent deuterium incorporation in the product was considered an indication of the intermediate formation of hydrometalated species. All terminal alkenes, i.e., 1-octene, 1-hexene, styrene, methylenecyclohexane, and 2-ethyl-1-hexene (except neohexene), provided high yields of deuterium incorporation product (95–100%). A mechanism for this reaction is proposed in Scheme I. The low yield of deuterium incorporation product (55%) in the case of neohexene is undoubtedly due to the steric influence of a *tert*-butyl group attached to the C=C double bond (I).



I

Another observation in this study which parallels the bis(dialkylamino)alane alumination reaction is that the overall yield of the alkane decreased in the following manner: octane (98%) ≈ hexane (99%) > ethylbenzene (85%) > methylcyclohexane (70%) ≈ 2-ethylhexane (70%) > neohexane (60%).

The internal alkenes (*cis*-2-octene, *cis*-2-hexene, and *trans*-2-hexene) were not as readily hydrometalated as the terminal alkenes. In all cases only low yields (1–5%) of the corresponding alkanes were observed. The reactions were carried out as described for the terminal alkenes except the reaction time was increased to 36 h. In addition, the reaction temperature was increased to 60 °C, but to no avail. Sato[3] found that internal alkenes could be hydroaluminated if the reactions were carried out for 120 h at 60 °C in the presence of $TiCl_4$ or $ZrCl_4$. We were hoping that Cp_2TiCl_2 would allow the reaction to take place under milder conditions, but unfortunately this did not happen.

For terminal alkynes (1-octyne and phenylethyne), results similar to those observed for the hydroalumination reactions with $[(i\text{-Pr})_2N]_2AlH$ were realized, namely, deprotonation of the acetylenic proton followed by addition to the unsaturated linkage. Only small amounts of alkenes (3–10%) and alkanes (4–13%) were observed. The starting alkyne showed a large amount (85%) of deuterium incorporation at the terminal carbon atom when the reaction

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(12) E. C. Ashby and J. J. Lin, *Tetrahedron Lett.*, 51, 4481 (1977).

Table I. Reactions of Complex Aluminum Hydrides with Alkenes and Alkynes in the Presence of 5 mol % of Cp_2TiCl_2[a]

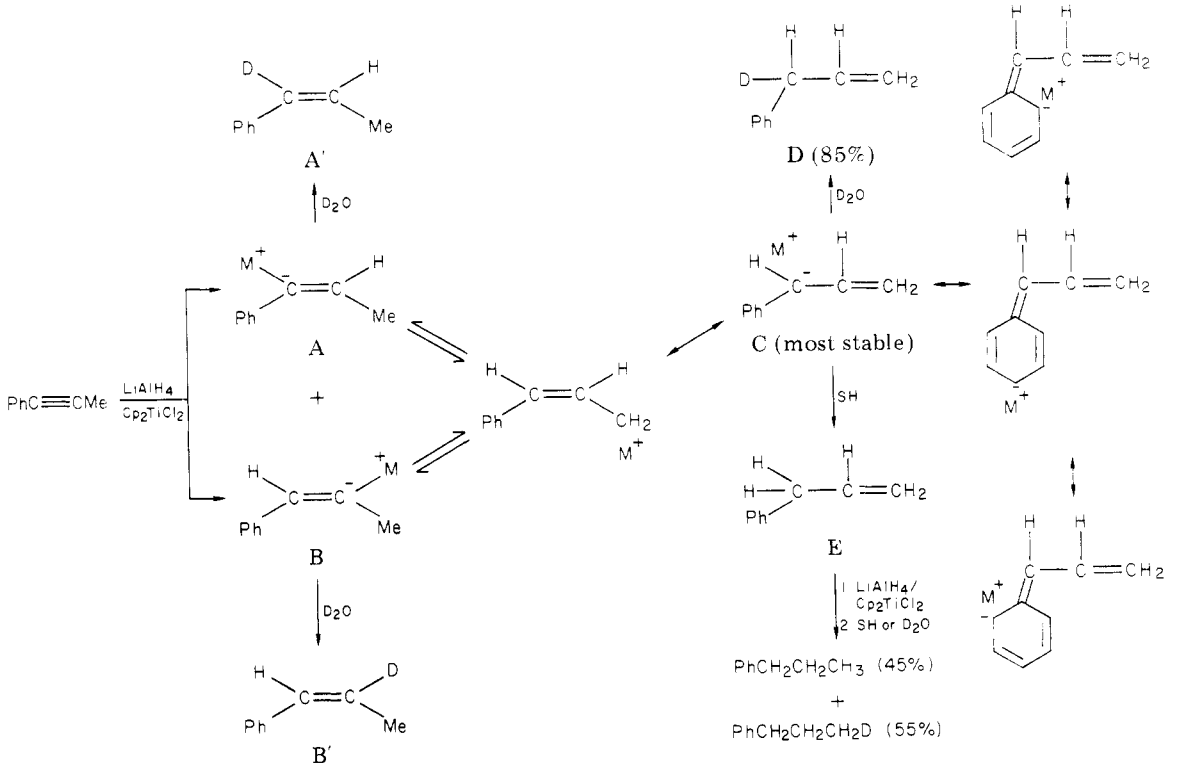
		$LiAlH_4$		$NaAlH_4$		$LiAlMe_3H$		$NaAlMe_3H$		$NaAl(OCH_2CH_2OCH_3)_2H_2$	
alkene or alkyne	product	product yield, %[b]	D incorp, %	product yield, %[b]	D incorp, %	product yield, %[b]	D incorp, %	product yield, %[b]	D incorp, %	product yield, %[b]	D incorp, %
1-octene[c]	octane	98	99	99	100	98	100	100	100	100	100
1-hexene	hexane	99	100	99	100	98	100	99	100	100	100
styrene[d]	ethylbenzene	70	100	75	97	73	94	71	98	72	99
methylene-cyclohexane	methylcyclohexane	70	95	71	94	69	94	69	93	70	94
2-ethyl-1-hexene	2-ethylhexane	70	95	71	91	71	95	70	93	69	93
neohexene	2,2-dimethylbutane	60	55	62	56	58	53	58	53	59	51
cis-2-hexene	hexane	5		5		6		3		2	
trans-2-hexene	hexane	5		5		5		3		2	
cyclohexene	cyclohexane	3		1		0		0		0	
1-methyl-1-cyclohexene	methylcyclohexane	0		0		0		0		0	
1-octyne	octane	4		4		2		6		5	
	1-octene	3		3		5		6		6	
phenyl-ethyne	ethylbenzene	13		15		11		10		10	
	styrene	10		11		9		9		11	
4-octyne	*cis*-4-octene	99	100	99	100	100	100	99	100	99	100
2-hexyne[e]	*cis*-2-hexene	99	100	98	100	99	100	100	99	100	100
1-phenyl-1-propyne	1-phenylpropane	15	55	8	50	17	51	13	51	14	50
	1-deuterio-*cis*-1-phenyl-1-oropene (90)	70	95	(90)	94	(90)	97	(90)	96	(90)	93
	2-deuterio-*cis*-1-phenyl-1-propene (10)			75 (10)		70 (10)		68 (10)		69 (10)	
	3-phenyl-1-propene	15	85	17	82	13	83	19	86	17	82
1-(trimethylsilyl)-1-octyne	1-(trimethylsilyl)-octane	15	20	18	18	13	19	17	20	18	16
	cis-1-(trimethylsilyl)-1-octene	35	65	39	67	34	65	30	68	35	61

[a] All reactions were carried out in THF at room temperature for 2 h in a 1:1 molar ratio of complex aluminohydride to alkene or alkyne. [b] Yields were determined by GLC based on internal standards. [c] When the reaction was quenched with a solution of I_2 in benzene, a 95% yield of only 1-iodooctane was obtained. [d] 90% $PhCH(D)CH_3$ formed. [e] When the reaction was quenched with a solution of I_2 in benzene, a 95% yield of a 51:49 ratio of 2-iodo- to 3-iodo-*cis*-2-hexene was obtained.

was quenched with D_2O, indicating the formation of the alkynylalane as a result of deprotonation. When the temperature was lowered or raised, no major effect was observed except that the rate was affected in the expected way. Normally, all reactions were conducted at room temperature for 2 h in a reagent to alkyne ratio of 1:1 in the presence of 5 mol % of Cp_2TiCl_2. The temperature was lowered to 0 °C, and after 2 h, only a trace of alkene or alkane was observed; however, after 12 h, 10% (the same amount observed at room temperature) alkene and alkane were observed. Longer reaction times showed little improvement in the formation of alkene. By raising the temperature to 50 °C, the amount of alkane increased to 30% after 30 min. After 2 h, 40% octane and 45% octene were observed; however, when the reaction was quenched with D_2O, the product showed only 50% deuterium incorporation. We reported earlier that 1-octyne and phenylethyne could be reduced to 1-octene (99%) and styrene (94%) in high yield by $LiAlH_4$ in the presence of a catalytic amount of $NiCl_2$.[12] However, when the reaction was carried out for 48 h at room temperature in THF, the amount of deuterium incorporation in the product was only 15%. Thus, although $NiCl_2$ is an excellent catalyst for the $LiAlH_4$ reduction of terminal alkynes, the desired intermediate vinylalane is not formed as the major product.

The internal alkynes, (i.e., 4-octyne, 2-hexyne, 1-phenyl-1-propyne, and 1-(trimethylsilyl)-1-octyne) were allowed to react with the series of complex aluminohydrides under the conditions stated in Tables I and II. 4-Octyne and 2-hexyne produced 99 and 100% *cis*-4-octene and *cis*-2-hexene, respectively, with 100% deuterium incorporation in both products. The NMR spectrum of the product from 2-hexyne showed a 53:47 ratio of 2-deuterio- to 3-deuterio-*cis*-2-hexene. In the case of the reaction with 1-phenyl-1-propyne (eq 12, Scheme II), 15% 1-phenylpropane, 70% *cis*-1-phenyl-1-propene, and 15% 3-phenyl-1-propene were obtained under these same conditions. When the reaction was quenched with D_2O, the products, 1-phenylpropane, *cis*-1-phenyl-1-propene, and 3-phenyl-1-propene, incorporated 55, 95, and 85% deuterium, respectively. The NMR spectrum showed a 90:10 ratio of 1-deuterio-*cis*-1-phenyl-1-propene (A′, eq 12) to 2-deuterio-*cis*-1-phenyl-1-propene (B′, eq 12). According to Scheme I, eq 9, the formation of the titanocene hydridochloride–alkyne complex determines the regiochemistry of the products. In this case, the titanium hydridochloride catalyst is complexed to the π cloud of the phenyl ring with the titanium closer to the carbon holding the

Scheme II



(12)

Table II. Reactions of Selected Alkenes and Alkynes with Complex (Dialkylamino)aluminohydrides in the Presence of 5 mol % Cp_2TiCl_2[a]

complex aluminum hydride	alkene or alkyne	product	yield, %	D incorp, %
$LiAlH_2(NEt_2)_2$	1-octene	octane	96	98
	1-octyne	1-octene	10	
		octane	11	
	4-octyne	4-octene	95	97
	cis-2-octene	octane	5	
$LiAlH_2(N\text{-}i\text{-}Pr_2)_2$	1-octene	octane	92	96
	1-octyne	1-octene	12	
		octane	11	
	4-octyne	4-octene	97	97
	cis-2-octene	octane	2	
$NaAlH_2(NEt_2)_2$	1-octene	octane	15	
	1-octyne	1-octene	15	
		octane	13	
	4-octyne	4-octene	93	
	cis-2-octyne	octane	trace	
$NaAlH_2(N\text{-}i\text{-}Pr_2)_2$	1-octene	octane	95	96
	1-octyne	1-octene	10	
		octane	13	
	4-octyne	4-octene	91	93
	cis-2-octene	octane	2	

[a] The reactions were carried out in THF at room temperature for 2 h in a 1:1 molar ratio of complex aluminohydride to alkene or alkyne.

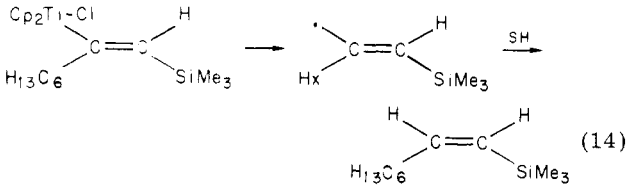
phenyl ring. Also, the bulky cyclopentadienyl groups on the titanium can adapt a staggered arrangement with the phenyl group if the titanium is closer to the number one carbon, whereas this kind of arrangement would be more difficult and would involve the methyl group if the arrangement were on the opposite side. Therefore, the least hindered position would be the one where the titanium would be located closer to the number one rather than the number two carbon. Once A and B form, hydrogen migration can take place, resulting in the formation of an intermediate with C being the most stable resonance contributor. Intermediate C can then undergo the transmetalation step (Scheme I) with $[(i\text{-Pr})_2N]_2AlH$ following the β-hydride addition to yield D on quenching with D_2O or abstract hydrogen from the solvent to form E. Once E, a terminal alkene, is formed, it may also undergo catalytic hydrometalation to yield, after similar steps, the protonated or deuterated 1-phenylpropane. In all cases, it is probably most likely that the protonated products result from a homolytic cleavage of the intermediate titanium species before the transmetalation step takes place. Therefore, the hydroalumination of internal alkynes shows great promise for the formation of vinylaluminates which are known to undergo further reaction with CO_2, cyanogen, and halogens to form α,β-unsaturated carboxylic acids, nitriles, and vinyl halides.[11]

As noted earlier, the terminal octyne reactions were not clean. Therefore, 1-(trimethylsilyl)-1-octyne was prepared by the reaction of 1-octynyllithium with chlorotrimethylsilane (eq 13). When this alkyne was allowed to

$$C_6H_{13}C{\equiv}CH + n\text{-BuLi} \xrightarrow[-C_4H_{10}]{} C_6H_{13}C{\equiv}CLi \xrightarrow[\text{LiCl}]{Me_3SiCl} C_6H_{13}C{\equiv}CSiMe_3 \quad (13)$$

react under the conditions stated in Tables I and II, the reaction was slow even at 60 °C. The best results obtained showed a 35% yield of *cis*-1-(trimethylsilyl)-1-octene (65% deuterium incorporation) and a 15% yield of 1-(trimethylsilyl)hexane (20% deuterium incorporation). Presumably because of the bulkiness of the trimethylsilyl group, some homolysis of the intermediate alkenyl titanium compound takes place, resulting in hydrogen abstraction from solvent, causing poor deuterium incorporation of the product when D_2O is added (eq 14).

In conclusion, hydroalumination reactions using complex aluminohydrides work extremely well for terminal alkenes and internal alkynes but do not work well for internal alkenes and terminal alkynes. An interesting observation which is a result of this work is that the regiochemistry



(14)

involved for both the bis(dialkylamino)alane[4] and the aluminate reactions is approximately the same. This indicates that the regiospecific step must be the same for both reactions. We suggest that the complexation of the intermediate titanium hydrido compound or the formation of the alkyltitanium compound is the rate-determining step, after which the subsequent steps of Scheme I follow.

Acknowledgment. We are indebted to the National Science Foundation (Grant No. MPS 7504127), Union Camp Corp., and the Alcoa Foundation for financial support of this work.

Registry No. 1-Octene, 111-66-0; octane, 111-65-9; 1-hexene, 592-41-6; hexane, 110-54-3; styrene, 100-42-5; ethylbenzene, 100-41-4; methylenecyclohexane, 1192-37-6; methylcyclohexane, 108-87-2; 2-ethyl-1-hexene, 1632-16-2; 2-ethylhexane, 589-81-1; neohexene, 558-37-2; 2,2-dimethylbutane, 75-83-2; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7; cyclohexene, 110-83-8; cyclohexane, 110-82-7; 1-methyl-1-cyclohexene, 591-49-1; 1-octyne, 629-05-0; phenylethyne, 536-74-3; 4-octyne, 1942-45-6; *cis*-4-octene, 7642-15-1; 2-hexyne, 764-35-2; 1-phenyl-1-propyne, 673-32-5; 1-phenylpropane, 103-65-1; 1-deuterio-*cis*-1-phenyl-1-propene, 72087-52-6; 2-deuterio-*cis*-1-phenyl-1-propene, 72090-05-2; 3-phenyl-1-propene, 300-57-2; 1-(trimethylsilyl)-1-octyne, 15719-55-8; 1-(trimethylsilyl)octane, 3429-76-3; *cis*-1-(trimethylsilyl)-1-octene, 57365-48-7; 1-iodooctane, 629-27-6; 2-iodo-*cis*-2-hexene, 72087-50-4; 3-iodo-*cis*-2-hexene, 72087-51-5; Cp_2TiCl_2, 1271-19-8; $LiAlH_4$, 16853-85-3; $NaAlH_4$, 13770-96-2; $LiAlMe_3H$, 62816-22-2; $NaAlMe_3H$, 66484-08-0; $NaAl(OCH_2CH_2OCH_3)_2H_2$, 22722-98-1; *cis*-2-octene, 7642-04-8; $LiAlH_2(NEt_2)_2$, 72749-21-4; $LiAlH_2(N\text{-}i\text{-}Pr_2)_2$, 72749-22-5; $NaAlH_2(NEt_2)_2$, 62259-84-1; $NaAlH_2(N\text{-}i\text{-}Pr_2)_2$, 72749-23-6.

Hydrometalation. 6. Evaluation of Lithium Hydride as a Reducing Agent and Hydrometalation Agent

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The reactions of activated lithium hydride with carbonyl compounds (aldehydes, ketones, esters, and enones), alkenes, and alkynes in the presence of transition-metal halides were investigated. Significant reaction involving the above substrates was accomplished only when an equimolar amount of VCl_3 was used in conjunction with the lithium hydride. Aldehydes were reduced to their corresponding alcohols in high yield (95–97%), and esters were also reduced to their corresponding alcohols in high yield (93–95%) with a small amount (5–7%) of the corresponding aldehyde (of the carboxylic acid portion) formed. Reductions of cyclohexanones were highly stereoselective. In this connection, 4-*tert*-butylcyclohexanone was reduced to the axial alcohol in 96% yield and with 82% stereoselectivity. The only enone to be reduced was cinnamaldehyde, which gave the 1,2-reduction product in 90% yield. Terminal olefins were reduced to alkanes whereas internal olefins were completely unreactive. In this connection, 1-octene was reduced to octane in 95% yield. In this example, 30% deuterium incorporation of the product was observed when hydrolysis was effected with D_2O. Such a result indicates formation of the intermediate octyllithium in 30% yield. Since alkynes and internal olefins are not reduced at all with LiH and VCl_3 and terminal olefins are, reduction of enynes and dienes with LiH and VCl_3 could serve as a selective reduction method for the reduction of a terminal double bond in the presence of a triple bond and also for the selective reduction of a terminal double bond in the presence of an internal double bond.

Lithium, sodium, and potassium hydrides have been widely used as bases in synthetic organic chemistry, but have not been used as reducing agents. Some time ago we developed a simple method for the preparation of a very active form of lithium hydride.[1] This method involves the room-temperature hydrogenolysis of *tert*-butyllithium (eq 1). The resulting white solid is easily filtered from the

$$t\text{-}C_4H_9Li + H_2 \xrightarrow[1000\ \text{psi}]{\text{room temp}} i\text{-}C_4H_{10} + LiH \qquad (1)$$

reaction mixture but is most conveniently used as a slurry due to its high degree of pyrophoricity. This form of lithium hydride appears to be much more reactive than the lithium hydride that is commercially available and which is prepared at about 450 °C. A preliminary experiment[2] showed that benzophenone is reduced to benzhydrol in 6% yield when stirred with activated lithium hydride for 2 h, whereas no trace of benzhydrol was found when commercial lithium hydride was used under the same conditions.

Recently Caubere and co-workers showed that the reagent NaH–RONa–MX_n is capable of reducing halides,[3,4] ketones, alkenes, and alkynes.[5,6] Although these reactions were not catalytic, they did provide a 75–95% yield of the corresponding alkanes, alcohols, alkanes, and alkenes, respectively.

In our continuing search for new stereoselective reducing agents and new hydride systems to effect hydrometalation of alkenes and alkynes, we investigated the reactions of activated LiH with various carbonyl compounds, alkenes, and alkynes in the absence and presence of catalysts. The

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