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LITHIUM ALUMINUM HYDRIDE, A HOMOGENEOUS HYDROGENATION CATALYST

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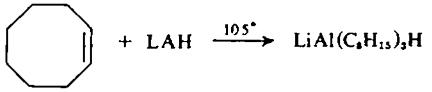
Abstract—Lithium aluminum hydride is a homogeneous catalyst for the selective hydrogenation of 2-pentyne and conjugated dienes to monoolefins. Deuterium tracer experiments involving 1,3-pentadiene have shown that the metal hydride and gaseous hydrogen each donate one hydrogen atom to the diene. LAH adds to 2-pentyne in a *trans* manner. The mechanism of the hydrogenation reaction is discussed.

Lithium aluminum hydride will reduce certain carbon–carbon double bonds which are either conjugated with other functional groups[1,2] or are located near a group which apparently activates the hydride reagent.[3] Other investigators have observed the reduction of triple bonds to double bonds in the LAH reduction of, for example, α,β-acetylenic acids and esters[4] or compounds containing the 1-hydroxy-2-acetylenic group ($R_2COCH{\equiv}C{-}$).[4b,6] However, isolated triple bonds are resistant to hydride attack at room temperature.[4b,6]

The above reductions presumably occur by an addition of the hydride to the unsaturated systems followed by hydrolysis of the resulting Al–N, Al–O or Al–C bonds during workup of the products. Under more severe conditions (110–140°), LAH will add slowly to isolated double bonds of hydrocarbons and lead to saturation of the linkage upon hydrolysis (e.g., Eqs 1 and 2).[7]



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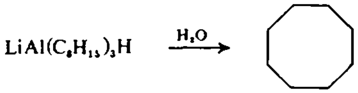


(2)

[1a] R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.* **69**, 1197, 2548 (1947); [b] F. A. Hochstein and W. G. Brown, *Ibid.* **70**, 3484 (1948); [c] A. Uffer and E. Schittler, *Helv. Chim. Acta* **31**, 1254 (1964); [d] W. J. Bailey and M. E. Hermes, *J. Org. Chem.* **29**, 1254 (1964).

[2a] K. E. Hamlin and A. W. Weston, *J. Amer. Chem. Soc.* **71**, 2210 (1949); [b] R. T. Gilsdorf and F. F. Nord, *Ibid.* **74**, 1837 (1952).

[3] B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.* **87**, 3423 (1965).

[4a] G. E. Benedict and R. R. Russell, *J. Amer. Chem. Soc.* **73**, 5444 (1951); [b] For a review on the reduction of triple bonds with LAH, see V. M. Micovic and M. L. Mihailovic, *Lithium Aluminum Hydride in Organic Chemistry* Monograph Vol. 237 of the Serbian Acadamy of Sciences (1955).

[5] E. B. Bates, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.* 1854 (1959); J. D. Chanley and H. Sobotka, *J. Amer. Chem. Soc.* **71**, 4140 (1949).

[6] J. Colonge and R. Gelin, *C. R. Acad. Sci., Paris* **236**, 2074 (1953); B. L. Shaw and M. C. Whiting, *Chem. & Ind.* 409 (1953); B. L. Shaw and M. C. Whiting, *J. Chem. Soc.* 3217 (1954).

[7] K. Ziegler, H. G. Gellert, H. Martin, K. Nagel and J. Schneider, *Liebigs Ann.* **589**, 91 (1954).

Aluminum-carbon bonds will undergo hydrogenolysis (e.g., Eq 3).[8]

$$\mathrm{Na(i\text{-}Bu_3AlH) + H_2\,(220\,atm) \xrightarrow[Pt_2O]{150^\circ,\ 8{\cdot}5\,hr} Na(i\text{-}Bu_2AlH_2) + CH_3CH(CH_3)CH_3} \qquad (3)$$

Therefore, one reasonably might expect LAH to function as a hydrogenation catalyst *via* a succession of addition and hydrogenolysis steps.

Using *cis*-2-pentene, 1,3-pentadiene, 1,3-cyclooctadiene, 1,5-cyclooctadiene and 2-pentyne as substrates, we have investigated the catalytic properties of LAH for the hydrogenation of olefins and acetylenes. Part of the results obtained are listed in Table 1. Generally, filtered anhydrous tetrahydrofuran (THF) solutions of LAH were employed.

The hydride in THF exhibited very low activity at 190° for the hydrogenation of the unconjugated double bonds of either *cis*-2-pentene (Expt 1) or 1,5-cyclooctadiene

TABLE 1. HYDROGENATIONS
Solvent: Tetrahydrofuran, 40 ml
Temp: 190°
H_2 Pressure: 800–1400 psig

Expt No.	Unsaturated Substrate,[b] mmoles	Catalyst, mmoles	Rxn Time, Hr	Conversion of Substrate, %	Product Composition (No-Loss Basis)[a,b]				
					n-C_5H_{12}	1-C_5H_{10}	*cis*-2-C_5H_{10}	*trans*-2-C_5H_{10}	C_{10} (Dimers)
1	*cis*-2-C_5H_{10} 100	LAH 20	1·5	1·1	1·1	0	98·9	0	0
2	1,3-C_5H_8 90	LAH 20	0·1–0·3	100	0	8·2	10·4	57·1	24·3
3	1,3-C_5H_8	None	1	16	—	—	—	—	100
4	2-Pentyne 73	LAH 26	5·0	95[c]	0	0	9·0	91·0	0
5	2-Pentyne 200	LAH 20	10	84[d]	4·3	3·7	32·8	59·2	0
6	2-Pentyne 9	LAD 24	<0·1	80·4	0	0	3[i]	97[i]	0
7	2-Pentyne 90	Dec[e] LAH	0·1	29	3·9	2·5	88·8	4·8	0
8	1,5-COD[f] 95	LAH 20	6	0	—	—	—	—	—
9	1,3-COD[g] 95	L AH 20	4	48·6[h]	—	—	—	—	—

[a] Analyses were not made for products having mol. wts greater than that of C_{10} (dimers) hydrocarbons. Since the material balances were generally high, such compounds would be minor products.

[b] All C_5 reactants and products are straight chain compounds.

[c] The conversion from the hydrogenation was ~50%. Part of the olefin was formed during the workup of the product. See the text for further discussion.

[d] A minor part of the conversion may have been for the reason given in footnote *c* of this Table.

[e] The heterogeneous material obtained by pyrolyzing 30 mmoles of LAH in THF.

[f] 1,5-Cyclooctadiene.

[g] 1,3-Cyclooctadiene.

[h] The product composition was 96% cyclooctene and 4% unidentified.

[i] See Experimental for the deuterium content.

[8] Admittedly, rather high temperatures and a catalyst have been employed. H. E. Podall, H. E. Petree and J. R. Zietz, *J. Org. Chem.* **24**, 1222 (1959).

(Expt 8). Apparently, there was little interaction between LAH and the double bonds since neither positional nor configurational isomerization of the latter occurred. On the other hand, 1,3-pentadiene was hydrogenated selectively to a mixture of pentenes (Expt 2). Although the hydrogenation occurs at 150°, a higher temperature ($\sim$180–190°) is preferable because of the more convenient reaction rate. In addition to monoolefins, dimeric compounds (C_{10}) also are produced. They are thought to be, at least in part, Diels-Alder adducts that form from 1,3-pentadiene at 190° in the absence of LAH (Expt 3). The rate of hydrogenation of 1,3-cyclooctadiene mainly to cyclooctene is slower. While only a 10 to 20-minute period was required for the hydrogenation of 1,3-pentadiene, a 4-hr period was insufficient to hydrogenate a comparable amount of 1,3-cyclooctadiene (Expt 9). The hydrogenation of 2-pentyne to mainly 2-pentene also is slow at 190° (Expts 4 and 5).

Relatively large quantities of LAH have been used for the hydrogenations. For example, 20–26 mmoles of LAH for 73–100 mmoles of substrate is typical. When a lower catalyst–substrate molar ratios was employed, a longer reaction period was required and the catalyst appeared to lose activity with time (Expt 5). The loss of activity likely is due to a slow reaction between THF and the hydride at the elevated temperatures required for the hydrogenation.

LAH may function as a catalyst by adding to triple bonds or conjugated dienes to form intermediate metal alkyls which subsequently undergo hydrogenolysis, e.g.:

$$CH_2{=}CHCH{=}CHCH_3 + LAH \longrightarrow (n\text{-}C_5H_9)LiAlH_3 \xrightarrow{n\text{-}C_5H_8} (n\text{-}C_5H_9)_2LiAlH_2, \text{ etc.} \quad (4)$$

$$(n\text{-}C_5H_9)LiAlH_3 + H_2 \longrightarrow n\text{-}C_5H_{10} + LAH \quad (5)$$

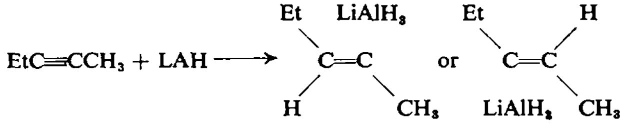
To test this possibility, 1,3-pentadiene (48 mmoles) was hydrogenated ($\sim$145 mmoles H_2 present initially) for 50 minutes at 190° in the presence of LAD (48 mmoles).[9] A 50% yield of pentene was obtained which consisted of 3% pentene-d_0, 93·5% pentene-d_1, and 3·5% pentene-d_2. A similar experiment (75 minutes reaction time) with LAH ($\sim$50 mmoles) and D_2 (55–65 mmoles) gave a pentene product consisting of $<$24% pentene-d_0, $>$75% pentene-d_1, and $\sim$1% pentene-d_2. The preponderance of monodeuterated pentene in the products supports the proposed mechanism and precludes the possibility that both hydrogen atoms in the olefin product came from the same reactant, i.e., either the gaseous hydrogen or the metal hydride. The reverse of eq 4 must be slow compared to the hydrogenolysis step (Eq 5). If it were not so, deuterated 1,3-pentadiene would have been formed from addition-elimination reactions between LAD and the diene, and, consequently, considerable quantities of polydeuterated pentenes would have resulted.

Similar experiments with 2-pentyne, LAD and H_2 were not definitive because a much longer reaction time (5–7 hr) was required and extensive exchange between LAD and H_2 occurred. Although some exchange occurred in the above experiments that involved 1,3-pentadiene, it was not sufficient to invalidate the results obtained and the conclusions made.

In further support of the proposed mechanism of hydrogenation, evidence that LAH will add to 2-pentyne has been obtained *via* the following deuterium labeling

[9] A high LAD–substrate molar ratio was employed to minimize the introduction of hydrogen into the product from the catalytic action of $LiAlD_3H$, $LiAlD_2H_2$, etc. which are formed in successive regenerations of the catalyst as shown in Eq 5.

experiments. A solution of 2-pentyne (9 mmoles) and LAD (24 mmoles) was heated to 190° in a H_2 atmosphere for 5 minutes,[10] then cooled and quenched with H_2O. The resulting 2-pentene was 97% *trans* and 3% *cis* and consisted of 2·5% pentene-d_0, 97·3% pentene-d_1, and 0·2% pentene-d_2 (Expt 6). In an analogous experiment, a THF solution of 2-pentyne (73 mmoles) and LAH (26 mmoles) was heated at 190° in a H_2 atmosphere for <20 minutes, then cooled and quenched with excess D_2O. A partial conversion of the 2-pentyne resulted. The 2-pentene was 95% *trans* and 5% *cis* and consisted of 8% pentene-d_0, 91% pentene-d_1, and 1% pentene-d_2. The high selectivity for monodeuterated pentene formation indicates that an intermediate adduct, lithium alkenylaluminum hydride, was formed which upon solvolysis produced 2-pentene. The addition is rapid and stereospecifically *trans*. Inherent in the conclusion that LAH adds in a *trans* manner (Eq 6) is the assumption that the geometry of the double bond is not altered during the solvolysis of the intermediate adduct (Eq 7).



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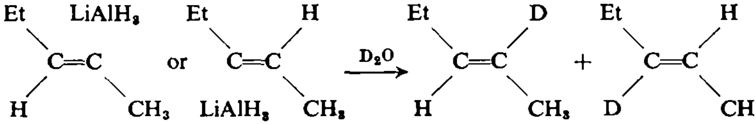

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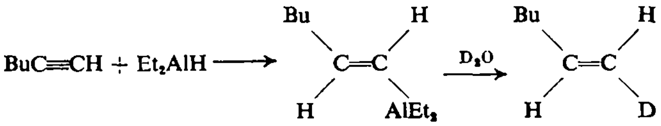
The *trans* addition of LAH to triple bonds followed by solvolysis provides a convenient method for the obtaining of *trans* olefins with or without the incorporation of deuterium. The scope of this reaction will be reported later.

The observed *trans* addition is particularly noteworthy since dialkylaluminum hydrides (R_2AlH) add to triple bonds exclusively in a *cis* manner, e.g.[11,12]



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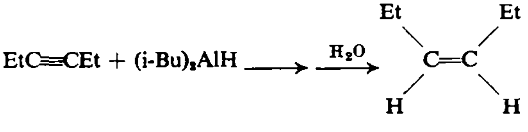

(9)[12]

This would indicate a difference in mechanism for the two addition reactions. The LAH reduction of compounds having a 1-hydroxy-2-acetylenic group also gives

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[10] No detectable pressure decline was observed which indicates that little hydrogenation occurred in this brief period before the solution was quenched with water. Exchange between LAD and H_2 was negligible.

[11] G. Wilke and H. Müller, *Liebigs Ann.* 618 (1958); P. S. Skell and P. K. Freeman, *J. Org. Chem.* 29, 2524 (1958).

[12] G. Wilke and H. Müller, *Chem. Ber.* 89, 444 (1956).

trans-ethylenic products.[13] However, the hydroxyl group may control the stereochemistry of these conversions.[1b,14]

Presumably, the LAH-catalyzed hydrogenation of 2-pentyne should produce *trans*-2-pentene since the hydrogenolysis, like the above hydrolysis, of the intermediate lithium alkenylaluminum hydride (Eq 5) would be expected to occur without altering the geometry of the double bond. There are indications that the hydrogenation does proceed initially in a *trans* manner. For example, 2-pentyne was hydrogenated for 5 hr and then the solution was quenched with excess D_2O. The total conversion of the 2-pentene was ~95%. From the amount of hydrogen absorbed and from the amount of 2-pentene-d_1 found in the product, it appears that about half of the 2-pentene was formed *via* the hydrogenation reaction and the other half resulted from the solvolysis with D_2O of some intermediate adduct. The isolated pentene consisted of 91% *trans*-2-pentene and 9% *cis*-2-pentene (Expt 4). Assuming that the 2-pentene from the reaction of D_2O with the adduct was 97% *trans* and 3% *cis* (*vide supra*), the 2-pentene from the hydrogenation reaction would have to be ~85% *trans* and ~15% *cis* in order for the final product to have the composition indicated above. The stereochemistry of the hydrogenation supports our conviction that LAH is functioning as a homogeneous catalyst.[15] Usually heterogeneous catalysts promote the hydrogenation of acetylenes predominantly to *cis*-olefins.[16]

When a long reaction time (10 hr) was required for the hydrogenation of 2-pentyne, the 2-pentene product contained considerable amounts of the *cis* isomer (Expt 5). Since LAH is a poor double bond isomerization catalyst (*vide supra*), these results indicate that another substance is slowly formed which can either promote the isomerization of double bonds or catalyze the hydrogenation of 2-pentene to *cis*-2-pentene. To see if a second catalyst species can be formed from LAH which will produce mainly the *cis* isomer, the mental hydride was deliberately decomposed by heating a THF solution of the reagent at 190–200° in the absence of hydrogen. A gray solid was obtained which catalyzed the hydrogenation of 2-pentyne at 190° to 95% *cis*-2-pentene and only 5% *trans*-2-pentene (Expt 7).

EXPERIMENTAL

Reagents. LAH and LAD were purchased from Metal Hydrides, Incorporated and powdered in a dry, inert atmosphere. Tetrahydrofuran solutions of LAH were prepared and filtered in a dry box filled with N_2. An emission spectrographic analysis of the purchased LAH showed it to be free of transition metal contaminants. The 1,3-pentadiene, obtained from Phillips Petroleum Co., consisted of a mixture of the *cis* and *trans* isomers. Ten per cent cyclopentene also was present; however, it was inert under the present experimental conditions. High-purity *cis*-2-pentene and 2-pentyne were purchased from Phillips Petroleum Co. and Columbia Organic Chemicals Co., Inc., respectively. 1,3-Cyclooctadiene and 1,5-cyclooctadiene were obtained from City Services, Research and Development Co. Anhydrous THF was obtained from Du Pont Co. All unsaturated substrates and the THF solvent were distilled from LAH before they were used. Deuterium gas of >99% purity was purchased from BIO·RAD laboratories.

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[13] E. B. Bates, E. R. H. Jones, M. C. Whiting, *J. Chem. Soc.* 1854 (1954). See also Ref. 4*b*, p. 126.

[14] J. Attenburrow, A. F. B. Cameron, J. F. Chapman, R. M. Evans, B. A. Herns, A. B. A. Jansen and T. Walker, *J. Chem. Soc.* 1094 (1952).

[15] Possibly, other hydride species such, as $LiAlH_2$, may be formed under the reaction conditions. The participation of these species as catalysts in the present system has not been determined.

[16] D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.* **78**, 2518 (1956); E. F. Meyer and R. L. Burwell, *Ibid.* **85**, 2877 (1963); G. Webb and P. B. Wells, *Trans. Faraday Soc.* **61**, 1232 (1965).

Hydrogenation procedure. An 80-ml, stainless steel autoclave was used for all of the hydrogenation experiments. Stirring was provided by a bar magnetic (sheathed with stainless steel) placed inside the autoclave which was rotated by an external magnetic stirrer. The autoclave was loaded in a N_2-filled dry box with the solvent, LAH (or LAD) and substrate to be hydrogenated. H_2 (or D_2) was introduced into the assembled autoclave and the system heated to the desired temp. The progress of the hydrogenation was followed by the decrease in the press. as measured by a suitable transducer and a Daystrom-Weston recorder. With the exception of the experiments below, the reaction conditions, quantities of reagents and yields of products for each experiment are listed in Table 1 or the text.

The product compositions were determined quantitatively by GLC with either a polyphenyl ether–Carbowax or a Ucon Polar–Firebrick column (Wilkins Instrument Co.). Frequently, the organic products were extracted from the THF into decane before they were analyzed by GLC techniques. To do this, the THF solutions were placed in a separatory funnel along with decane. Water and finally 5% HCl were added slowly to decompose the excess hydride reagent. Combined hydrocarbon extracts were washed several times with ice water and dried over K_2CO_3.

The individual components of the various products were identified by the coincidence of their GLC emergence times with those of authentic materials. Also each compound was individually trapped by GLC techniques and further analyzed by comparing their IR spectra and/or their mass spectrometric cracking patterns with those of authentic compounds.

Addition of LAD *to 2-pentyne.* A THF solution (20 ml) of 2-pentyne (8·8 mmoles) and LAD (24 mmoles) was heated for 5 min at 190° in a H_2 atm. (~500 psig). No press. drop occurred. The solution was cooled, quenched with cold water and extracted with decane. The 2-pentyne was 80·4% converted to 2-pentene. The isomer distribution of the latter was 97% *trans* and 3% *cis*. A mass spectrometric analysis of the pentene product indicated the following composition: C_5H_{10}, 2·5%; C_5H_9D, 97·3%; $C_5H_8D_2$, 0·2%. The recovered H_2 had the following composition, as indicated by mass spectrometric analysis: H_2, 97·6%; HD, 2·1%; D_2, 0·3%. These results indicate that only 1–2% of the deuterium atoms in LAD exchanged with the gaseous H_2.

A similar experiment involving LAH, 2-pentyne and D_2 was performed in an analogous manner. See the text for the results.

Limited hydrogenation of 2-pentyne. 2-Pentyne (73 mmoles) in 40 ml of THF which contained 26 mmoles of LAH was hydrogenated (1200 psig) for 4·5 hr. During this period, a pressure decrease occurred equivalent to ~33 mmoles H_2 which would indicate that ~45% of the 2-pentyne had been hydrogenated to pentenes. Excess D_2O was added to the cold THF solution and the product extracted into decane. The resulting pentenes (69 mmoles) consisted of 59% pentene-d_0, 40% pentene-d_1 and <1% pentene-d_2. These latter results indicate that 59% of the 2-pentene resulted from the hydrogenation and that 40% resulted from the solvolysis with D_2O of an adduct of 2-pentyne and LAH. For the purpose of discussion (see text), an intermediate value of ~50% is taken as the amount of 2-pentyne hydrogenated. The isomeric composition of the isolated 2-pentyne was 91% *trans* and 9% *cis*.

Deuterium labeling-hydrogenation of 1,3-pentadiene. 1,3-Pentadiene (48 mmoles) in 40 ml of THF which contained 48 mmoles (2 g) of LAD was hydrogenated (1500 psig of H_2) for 50 min at 190° according to the general procedure described above. Approximately 50% of the diene was converted to pentene whose composition, as determined by mass spectrometric analysis, was: C_5H_{10}, 3·0%; C_5H_9D, 93·5%; $C_5H_8D_2$, 3·5%.

In a similar experiment, 1,3-pentadiene (48 mmoles) in 40 ml of THF which contained 50 mmoles of LAH was treated with D_2 (400 psig or ~55–65 mmoles of D_2) for 75 min at 190°. The pentene obtained consisted of <24% pentene-d_0, >75% pentene-d_1 and 1% pentene-d_2.

Decomposition of LAH. A filtered THF solution (125 ml) of LAH (5 g; 130 mmoles) was placed in an autoclave and heated in a N_2 atm. at 190° for 6 hr. The gray precipitate was isolated by filtration which was performed inside a N_2-filled dry box. About 25% of the solid (equivalent to ~30 mmoles of LAH), 90 mmoles of 1,3-pentadiene and 30 ml of THF were placed in an 85 ml autoclave, H_2 introduced and the hydrogenation of the diene performed as described above (see Expt 7, Table 1).

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