Tetrahedron Vol 23, pp 4509 to 4515 Pergamon Press Ltd. 1967 Printed in Great Britain

REDUCTION OF ACETYLENES AND CONJUGATED DIOLEFINS BY LITHIUM ALUMINUM HYDRIDE

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(*Received in USA* 16 *February* 1967; *accepted for publication* 21 *March* 1967)

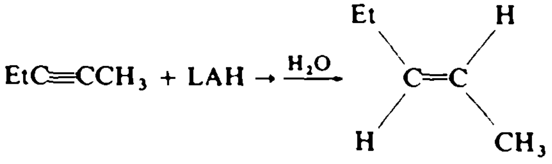
Abstract—A convenient method is described for the stereospecific reduction of acetylenes by LAH. For example, 2-pentyne, 3-hexyne, 1-phenylpropyne and diphenylethyne in an ether solvent have been reduced to the corresponding *trans* olefin in high yield. 2,4-Hexadiene was reduced in a similar manner to give a mixture of 2- and 3-hexenes. With toluene as the solvent, the main products from acetylenes are the saturated hydrocarbons. Whereas a *trans* addition of the hydride to the triple bond occurs in ether solvents, it appears that *cis* addition occurs in toluene.

LITHIUM aluminum hydride (LAH) has been shown[1] to be an effective homogeneous catalyst for the selective hydrogenation of alkynes and conjugated diolefins to monoolefins. Deuterium tracer experiments showed that LAH functions as a catalyst by adding to the unsaturated system to form intermediate metal alkyls which subsequently undergo hydrogenolysis, e.g.,

$$CH_2{=}CHCH{=}CHCH_3 + LAH \rightarrow (C_5H_9)LiAlH_3 \xrightarrow{n\text{-}C_5H_8} (C_5H_9)_2LiAlH_2, \text{etc.} \qquad (1)$$

$$(C_5H_9)LiAlH_3 + H_2 \rightarrow n\text{-}C_5H_{10} + LAH \qquad (2)$$

Interestingly, 2-pentyne in tetrahydrofuran (THF) was converted mainly to *trans*-2-pentene when treated consecutively with LAH and water. Apparently, the LAH added *trans* to the triple bond (Eq 3),[1] which is in contrast to the *cis* addition which occurs with dialkylaluminum hydrides in neat or hydrocarbon media (Eqs 4–6).[2–4]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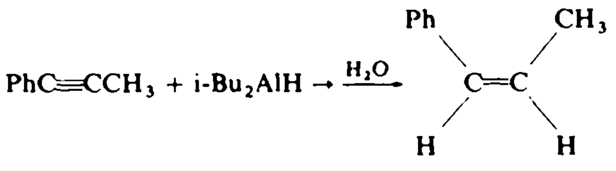
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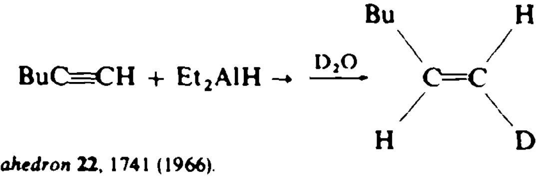
(5)[3]

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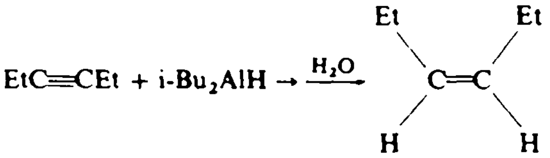
[1] L. H. Slaugh, *Tetrahedron* **22**, 1741 (1966).

[2] J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.* **88**, 2213 (1966).

[3] G. Wilke and H. Müller, *Liebigs Ann.* **618**, 267 (1958); P. S. Skell and P. K. Freeman, *J. Org. Chem.* **29**, 2524 (1958).

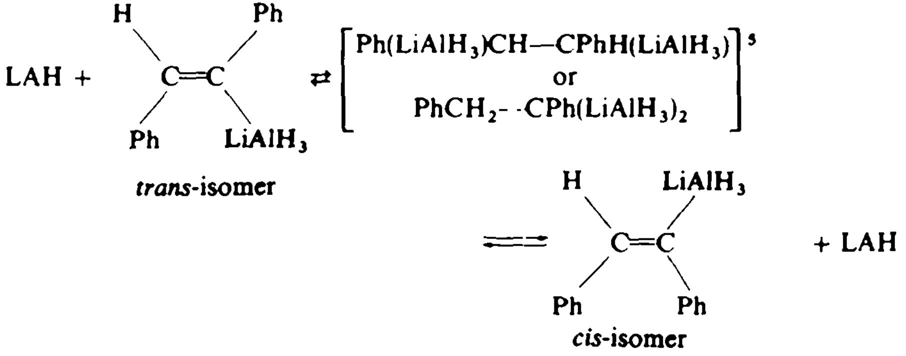
[4] G. Wilke and H. Müller, *Chem. Ber.* **89**, 444 (1956).



$$\mathrm{EtC{\equiv}CEt + i\text{-}Bu_2AlH \rightarrow \xrightarrow{H_2O} \overset{Et}{\underset{H}{}}C{=}C\overset{Et}{\underset{H}{}}} \qquad (6)^{4}$$

The above *trans* addition of LAH to triple bonds followed by hydrolysis is an attractive method for the preparation of *trans* olefins. However, the experimental conditions (autoclave pressured with hydrogen) are rather inconvenient. Further investigation has shown that stereospecific reduction of isolated triple bonds to *trans* olefins can be achieved conveniently with LAH in an ether solvent under nitrogen at atmospheric pressure (Table 1). For example, olefinic products that contain $\geq 96\%$ *trans* olefin have been prepared from 3-hexyne (Expt 2 and 3), 1-phenylpropyne (Expt 8 and 9) and diphenylethyne (Expt 7). The substrates were heated in an appropriate refluxing solvent with an excess of LAH and the reaction mixtures were then cooled and hydrolyzed. In a similar manner, a conjugated diolefin, 2,4-hexadiene, was reduced to a mixture of monoolefins (Expt 12). Because of the high volatility of 2-pentyne, at the temperature necessary to attain a reasonable rate of hydride addition, the use of an autoclave (autogenic pressures, nitrogen atmosphere) was required for the reduction of the substrate to *trans*-2-pentene (Expt 4 and 5). These reductions can be accomplished with solutions of LAH which have been filtered to remove the insoluble impurities or simply with crude commercial LAH added to the solvent (not filtered). Either technique gives essentially the same results (compare Expt 2 and 3, 4 and 5 or 8 and 9).

3-Hexyne reacts slowly with LAH in refluxing THF ($\sim 66°$): 53% conversion occurred in ~ 100 hr. However, when a mixed solvent, THF/bis(2-methoxyethyl) ether (diglyme), of higher refluxing temperature (117–150°) was used, a 96% conversion was obtained in a relatively short time, 4·5 hr (Expt 2). Aryl substituted acetylenes are more easily reduced than are alkyl substituted acetylenes. 1-Phenylpropyne was 98–99% reduced in 12–13 hr in refluxing THF to mainly *trans*-1-phenylpropene (Expt 8 and 9). Under similar conditions, diphenylethyne was 100% converted in < 2 hr to *trans*-stilbene (Expt 7). A longer reaction period before hydrolysis, 14 hr, gave a product containing 76% *trans*- and 24% *cis*-stilbene. The metal hydrides present apparently promoted the isomerization of the initially formed *trans*-vinylaluminum adduct. This probably occurs *via* an addition-elimination reaction, e.g.,



$$\mathrm{LAH} + \overset{H\qquad Ph}{\underset{Ph\qquad LiAlH_3}{C{=}C}} \rightleftarrows \left[\begin{array}{c}\mathrm{Ph(LiAlH_3)CH{-}CPhH(LiAlH_3)}\\ \text{or}\\ \mathrm{PhCH_2{-}CPh(LiAlH_3)_2}\end{array}\right]^{5} \rightleftarrows \overset{H\qquad LiAlH_3}{\underset{Ph\qquad Ph}{C{=}C}} + \mathrm{LAH} \qquad (7)$$

trans-isomer

cis-isomer

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[5] In THF the concentration of these diadducts must be very low because 1,2-diphenylethane was not detected in the hydrolyzed product.

TABLE 1[a] LITHIUM ALUMINUM HYDRIDE REDUCTIONS

Expt No	Unsaturated substrate	Solution of LAH[b]	Temp, °C	Time, Hr	Conversion of substrate, %	Product composition[c]		
						trans Olefin	*cis* Olefin	Saturated hydrocarbon
1 (A)	$EtC\equiv CEt$	THF, filtered	125	1·7	66[d]	~100	Trace	0
2	$EtC\equiv CEt$	THF/diglyme,[e] filtered	117 150	4·5	96·5	96·1	3·9	0
3	$EtC\equiv CEt$	THF/diglyme,[f] unfiltered	108–138	10	91·1	98·4	1·6	0
4 (A)	$MeC\equiv CEt$	THF, filtered	125–130	2·3	92	~100	Trace	0
5 (A)	$MeC\equiv CEt$	THF, unfiltered	125–138	1·3	89·4	~100	Trace	0
6 (A)	$MeC\equiv CEt$	Toluene, unfiltered	125	30	100	1·2	1·2	97·6[g]
7	$PhC\equiv CPh$	THF, filtered	~66	< 2[h]	100	96·8	3·2	0
8	$PhC\equiv CMe$	THF, filtered	~66	13	99	>99·8	Trace	0
9	$PhC\equiv CMe$	THF, unfiltered	~66	12	98·3	97·6	2·4	0
10	$PhC\equiv CMe$	Toluene, unfiltered	~111	6	58·2	4·7	27·7	67·6
11	$PhC\equiv CMe$	Toluene, unfiltered	~111	41	100	8·7	8·9	82·4
12	$MeCH{=}CH{-}CH{=}CHMe$	THF/diglyme,[f] unfiltered	112 131	14	82	← 99[i] →		1

[a] Quantities of reagents: unsaturated substrate, ~50 mmoles; LAH, 74–97 mmoles; total solvent, 50–60 ml. Where indicated by (A) the reaction was carried out in an autoclave. Conventional glassware was used for the other experiments.

[b] As indicated, certain LAH solutions were filtered to remove insoluble impurities present in the crude hydride reagent.

[c] The double bond is in the same position as was the triple bond in the reactant substrate.

[d] In another experiment where refluxing THF (~66°) at atmospheric pressure was employed, only a 53% conversion was obtained in 103 hr.

[e] Diglyme is bis(2-methoxyethyl) ether. A THF solution of LAH was added to diglyme and most of the THF removed by distillation.

[f] Diglyme, THF and LAH were mixed and most of the THF removed by distillation.

[g] During the experiment, the pressure within the autoclave increased. This indicates that the LAH underwent decomposition with the liberation of hydrogen. Therefore, it is possible that part of the *n*-pentane resulted from a catalyzed hydrogenation of the substrate.[1]

[h] A longer reaction period before hydrolysis, 14 hr, gave a product containing 75·7% *trans*-stilbene and 24·3% *cis*-stilbene.

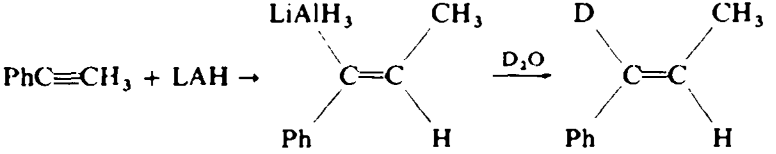
[i] *trans*-3-Hexene, 35%; *cis*-3-hexene, 15%; *trans*-2-hexene, 24%; *cis*-2-hexene, 25%.

(Eq 7). Although considered less likely, it is conceivable that the initial adduct dissociates to produce a vinyl carbanion that subsequently isomerizes. It is noteworthy that a similar isomerization occurs when certain acetylenic compounds are treated with diisobutylaluminum hydride.[2]

An unexpected result was obtained when 1-phenylpropyne was reduced in refluxing toluene (compare Expt 9 with 10 and 11). Considerable n-propylbenzene (67·6% of the reduced material) was formed even with a limited conversion of the reactant. Intermediate adducts containing two carbon-metal bonds per substrate must have been formed since decomposition of the mixture with D_2O produced the saturated hydrocarbon containing 94·5% n-propylbenzene-d_2 and 4·5% n-propylbenzene-d_1. Mass spectrometric analysis indicated that ~75% of the deuterium in the saturated hydrocarbon was located in the *alpha* position.[6] The reduced product also contained 27·7% *cis*-1-phenylpropene and 4·7% *trans*-1-phenylpropene. The deuterium content of the olefinic material was 90·1% d_1 and 9·1% d_0 for the *cis* isomer and 59·7% d_1 and 39·5% d_0 for the *trans* isomer. These results indicate that most of the olefin resulted from the addition of LAH to the triple bond to form a vinylaluminum adduct which subsequently was solvolyzed with D_2O. The undeuterated 1-phenylpropene (4·3% of the total olefin product) was formed *via* an undetermined route where both hydrogens came from the LAH reagent.

Nearly 86% of the 1-phenylpropene formed in toluene consisted of the *cis* isomer. This result differs markedly from the essentially all *trans* reduction which occurs in THF (Expt 9). Conceivably, a *trans*-vinylaluminum adduct (phenyl and methyl groups are *trans* to each other) was formed initially which then isomerized to the *cis*-vinylaluminum adduct *via* an addition-elimination mechanism similar to that shown in Eq 7.[8] However, this seems unlikely since a longer reaction time and a deeper conversion of the reactant substrate produced an olefinic product containing less of the *cis* isomer (~50%) and more of the *trans* isomer (Expt 11). It appears, therefore, that mainly the *cis* adduct, rather than the *trans* adduct, is formed initially.[9] The former may isomerize slowly to the latter.[10] The reason why LAH adds *cis* to 1-phenylpropyne in toluene, rather than *trans* as it does in THF, may be a consequence of the relative solubilities of the hydride in the two solvents. In toluene where LAH is essentially insoluble, the vinylaluminum adduct may be formed on the surface of the metal hydride, in which case a *cis* addition of the reagent likely is favored.

Deuterolysis of the adduct formed from LAH and 1-phenylpropyne in THF produced *trans*-1-phenylpropene-d_1 containing ≥90% of the deuterium in the *alpha* vinyl position (Eq 8).



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[6] In a similar case, it has been shown[7] that solvolysis with D_2O appears to label C–Al bonds reliably.

[7] J. J. Eisch and G. R. Husk, *J. Organometal. Chem.* **4**, 415 (1965).

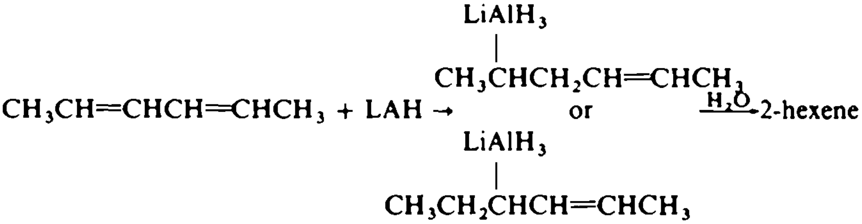
[8] It is assumed that the geometry of the double bond is not altered during the subsequent solvolysis of the adducts.

[9] If one considers only the monodeuterated olefin product as being indicative, the ratio of *cis*:*trans* addition of LAH to 1-phenylpropyne is ~93:7.

[10] The equilibrium concentrations of the two adduct isomers is unknown.

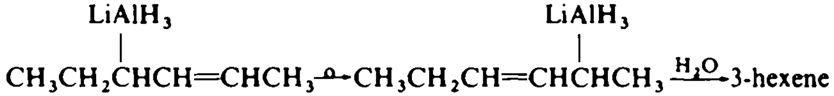
The orientation of the addition of LAH in THF is analogous to that found for a similar addition with diisobutylaluminum hydride in neat or hydrocarbon media[2] which, however, led to *cis*-1-phenylpropene.

The LAH reduction of 2,4-hexadiene produced a mixture of olefins: *trans*-2-hexene, 24%; *cis*-2-hexene, 25%; *trans*-3-hexene, 35%; *cis*-3-hexene, 15% (Expt 12). 2-Hexene formation probably involves a 1,2-addition of the hydride to one of the double bonds (Eq 9).



$$CH_3CH{=}CHCH{=}CHCH_3 + LAH \rightarrow \begin{array}{c} CH_3\overset{LiAlH_3}{\overset{|}{C}}HCH_2CH{=}CHCH_3 \\ \text{or} \\ CH_3CH_2\overset{LiAlH_3}{\overset{|}{C}}HCH{=}CHCH_3 \end{array} \xrightarrow{H_2O} 2\text{-hexene} \qquad (9)$$

The formation of 3-hexene may be rationalized by a 1,4-addition of LAH to the diene or by a rearrangement of an allylaluminum adduct (Eq 10).



$$CH_3CH_2\overset{LiAlH_3}{\overset{|}{C}}HCH{=}CHCH_3 \xrightarrow{\Delta} CH_3CH_2CH{=}CH\overset{LiAlH_3}{\overset{|}{C}}HCH_3 \xrightarrow{H_2O} 3\text{-hexene} \qquad (10)$$

In support of the latter possibility, allylic rearrangements involving the migration of a R_2Al group were shown to occur when diisobutylaluminum hydride was added to conjugated diolefins[7] and when an allyldialkylalane was formed by the reaction of vinylaluminum compounds with diazomethane.[11]

EXPERIMENTAL

LAH, obtained from Hydrides Inc., Beverly, Massachusetts, was either used as purchased or dissolved in THF and the residual gray solid removed by filtration under a N_2 atm. THF and diglyme were dried by refluxing them over CaH_2 for several hr prior to distillation. The high purity acetylenic and olefinic reactants were treated with alumina before use. The solvents and unsaturated substrates were stored under N_2. D_2O was used as purchased from Columbia Organic Chemical Company.

The preferred and most convenient method to be used for the reduction of alkyl substituted acetylenes or conjugated dienes boiling at least as high as the hexynes or hexadienes uses a mixed solvent with crude LAH (unfiltered soln) as illustrated below for 3-hexyne. The reduction of lower boiling acetylenes should be carried out in a simple pressure reactor. Because of their greater reactivity, aryl substituted acetylenes can be reduced by LAH in refluxing THF. Dimers apparently are not formed in significant amounts since

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[11] H. Hoberg, *Angew. Chem.* 78, 493 (1966).

high temp GLC analyses of several of the products failed to reveal their presence. The results of the GLC analyses were therefore normalized with respect to the substrate, the olefinic products, and the saturated products. The individual organic products obtained in the experiments described below were identified by the coincidences of their GLC emergence times, IR spectra and/or mass spectrometric fragmentation patterns with those of authentic compounds. All manipulations involving air sensitive compounds were carried out under a N_2 atm.

Reduction of 3-hexyne with an unfiltered solution of LAH (Expt 3). A mixture of 50 ml diglyme, 10 ml dry THF and 2·8 g (74 mmoles) LAH was heated and low boiling distillate removed (~3 ml) until the flask temp was ~125°. The mixture was cooled to room temp under a N_2 atm, 4·4 g (54 mmoles) 3-hexyne added, and the mixture heated to reflux. The temp of the flask contents rose from 108° to 138° during a 10-hr period. The reaction mixture was cooled and slowly hydrolyzed with ice-cold water. The aqueous slurry was extracted with 50 ml of n-octane, neutralized with dil HCl and extracted once more with n-octane. The combined organic material was washed twice with water and dried over $CaCl_2$. GLC analysis (85°, 20 ft × ⅛ in. column packed with 5% poly-*meta*-phenyl ether, 6 ring, on 60/80 mesh Chromosorb W; Model 600B Hy Fl, Wilkins Instrument and Research, Inc., Walnut Creek, California) of the reaction product showed a 91·1% conversion of the hexyne to hexenes. Further GLC analyses of the hexene fraction over a 20 ft dimethyl sulfolane column and a 10 ft tris(cyanoethoxy)propane column showed it to be 98·4% *trans*-3-hexene and 1·6% *cis*-3-hexene. No other isomeric hexene was detected.

Reduction of 3-hexyne with a filtered solution of LAH (Expt 2). A clear, filtered THF soln (50 ml) containing ~85 mmoles LAH and 50 ml diglyme were combined and heated until ~50 ml of lower boiling liquid was removed. The flask temp at this point was 138°. The system was cooled and 4·1 g (50 mmoles) 3-hexyne added. The soln was refluxed for 4·5 hr during which time the temp of the flask contents increased from 117° to 150°. n-Octane was added, the soln cooled and the mixture hydrolyzed with dil 6N HCl. n-Octane extracts of the hydrolyzed soln were combined, washed, and dried over $CaCl_2$. GLC analyses indicated that 96·5% of the 3-hexyne had been converted to n-hexenes consisting of 96·1% *trans*-3-hexene and 3·9% *cis*-3-hexene.

Reduction of 2,4-hexadiene with an unfiltered solution of LAH (Expt 12). The same procedure as given above for the reduction of 3-hexyne with an unfiltered LAH soln was employed. The reaction mixture was refluxed 14 hr at 112–131°. GLC analyses of the hydrolyzed product showed that the hexadiene had been 82% converted to a mixture containing *trans*-3-hexene, 35%; *cis*-3-hexene, 15%; *trans*-2-hexene, 24%; *cis*-2-hexene, 25%; n-hexane, 1%.

Reduction of 2-pentyne with an unfiltered solution of LAH (Expt 5). Crude LAH (3·7 g, ~97 mmoles), 3·7 g (54 mmoles) 2-pentyne and 50 ml THF were combined in an 85-ml magnetically stirred autoclave and heated under a N_2 atm at 125–138° for 1·3 hr. After it was cooled, the mixture was hydrolyzed and worked up as described above. GLC analysis (30°, 20 ft × ¼ in column packed with 20% SF-96 on Firebrick, 40/60 mesh) showed a conversion of 89·4% and that the pentene product was nearly all *trans*-2-pentene with only a trace of *cis*-2-pentene being present.

Reduction of 1-phenylpropyne and diphenylethyne (Expt 7–11). These aryl substituted acetylenes were reduced by heating them in one of the following: filtered LAH-THF solns, unfiltered THF solns containing crude LAH or an unfiltered toluene-LAH mixture. The resultant mixtures were hydrolyzed with either dil HCl or water and worked up as described above for the reduction of 3-hexyne. The reaction conditions and results are listed in Table 1.

In two instances (Expt 8 and 10), the resultant mixture from the reaction of LAH with 1-phenylpropyne was solvolyzed with D_2O. The *trans*-1-phenylpropene product from Expt 8 was shown by mass spectrometric analysis to be >99·8% monodeuterated and <0·2% dideuterated. The analysis also indicated that none of the deuterium was located in the methyl group. The methyl group NMR spectrum of a sample of *trans*-1-phenylpropene-d_1 consists of a strong doublet with a splitting of 6·5 c/s surrounding some weak unresolved fine structure. The splitting of 6·5 c/s is indicative of a single hydrogen on the carbon atom adjacent to the methyl group and is taken as proof of dominant deuterium substitution in the position *alpha* to the ring. The unresolved fine structure between the lines of the doublet can be accounted for by deuterium in the *beta* position. From a comparison of relative intensities, we estimate the *trans*-1-phenylpropene to be >90% *trans*-1-phenylpropene-αd_1. The n-propylbenzene from Expt 10 was 4·5% monodeuterated, 94·5% dideuterated and 1% trideuterated. On the basis of the distribution of the tropylium ions (mass spectrometric analyses) at masses 93, 92 and 91, ~80% of the n-propylbenzene-d_2 was α,α-dideutero-n-propylbenzene, ~15% was α,β- or α,γ-dideutero-n-propylbenzene and ~5% was dideutero-n-propylbenzene with no deuterium located in the *alpha* position.

Acknowledgements– Appreciation is expressed to C. H. Holm for the NMR analyses and to R. E. Thorpe for the mass spectrometric analyses.