In very dilute carbon tetrachloride solution **9a** showed absorption at 3591 cm^{-1} in the infrared. The nmr spectrum in carbon tetrachloride solution (*ca.* 10 mole %) showed the following: five aromatic hydrogens, 7.22 ppm; 2-*endo*-hydrogen, 3.58 ppm; 7-*anti*-hydrogen, 2.90 ppm; 1- and 4-bridgehead hydrogens, 2.67 ppm; remaining alkane hydrogens, 1.0–1.8 ppm; and hydroxyl hydrogen, 0.67 ppm.

The *p*-nitrobenzoate (**9b**) was prepared in the usual manner. Recrystallization from ethanol gave mp 139–140°. *Anal.* Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68. Found: C, 70.99; H, 5.66.

The tosylate (**9c**) was prepared in the usual manner[6] and gave mp 106–107°. *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.16; H, 6.48. Found: C, 70.37; H, 6.62.

7-*anti*-Phenyl-2-*exo*-norbornanol (10a).—The reaction sequence was the same as that employed for the preparation and isolation of **9a**. From 37.0 g (0.108 mole) of 3-*endo*-phenyl-2-*exo*-norbornyl tosylate (**3c**), 21.2 g (0.200 mole) of sodium carbonate, and 500 ml of glacial acetic acid stirred under reflux for 3 hr was obtained *ca.* 23.0 g of colorless oil. Reduction of this oil with 3.8 g (0.18 mole) of lithium aluminum hydride in 500 ml of ether gave 21.8 g of colorless oil.

Chromatography of this oil on F-20 alumina with ligroin and ligroin–ether solvent mixtures gave 3-phenylnortricyclene, **9a**, **3a**, and then 6.3 g (38%) of **10a**, mp 89–90° after recrystallization from ligroin.[20] *Anal.* Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.83; H, 8.57.

In very dilute carbon tetrachloride solution **10a** showed absorption at 3620 cm^{-1} in the infrared region. The nmr spectrum in carbon tetrachloride solution (*ca.* 10 mole %) showed the following: five aromatic hydrogens, 7.13 ppm; 2-*endo*-hydrogen, 3.78 ppm; hydroxyl hydrogen, 3.67 ppm; 7-*syn*-hydrogen, 3.26 ppm; 1- and 4-bridgehead hydrogens, 2.48 ppm; and remaining alkane hydrogens, 0.8–1.8 ppm.

The *p*-nitrobenzoate (**10b**) gave mp 89–90°. *Anal.* Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68. Found: C, 70.92; H, 5.77.

The tosylate (**10c**) gave mp 98–99°. *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.16; H, 6.48. Found: C, 70.19; H, 6.43.

Registry No.—**1a**, 497-37-0; **1b**, 10472-43-2; **2a**, 497-36-9; **2b**, 10472-51-2; **3b**, 10561-83-8; **3c**, 10561-82-7; **4b**, 10472-59-0; **4c**, 10472-58-9; **5b**, 10561-86-1; **5c**, 10561-85-0; **6b**, 10472-44-3; **6c**, 10472-63-6; **7a**, 14182-93-5; **7b**, 14182-94-6; **7c**, 14182-95-7; **8a**, 14182-96-8; **8b**, 14182-97-9; **8c**, 14182-98-0; **9a**, 14181-14-7; **9b**, 14271-39-7; **9c**, 14181-15-8; **10a**, 14181-16-9; **10b** 14181-17-0; **10c**, 14181-18-1.

Acknowledgment.—We are indebted to Mr. Louis Joris, Chemistry Department, Princeton University, for the determination of the O–H-stretching vibrations in dilute carbon tetrachloride solutions for **9a** and **10a**. Also we are grateful to Mr. Charles Harding for the preparation of *exo*- and *endo*-norbornyl *p*-nitrobenzoates.

Stereochemistry and Mechanism of Carbon–Carbon Double-Bond Reduction in Methyl Cinnamate by Lithium Aluminum Hydride[1]

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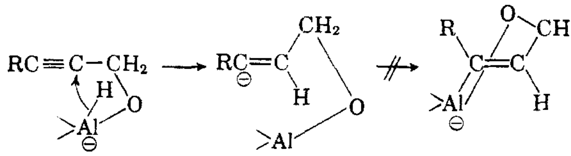
The reduction of the double bond in methyl cinnamate by lithium aluminum deuteride is shown to lead, after deuteronolysis, to an approximately equimolar mixture of *erythro-* and *threo*-$C_6H_5CHDCHDCD_2OH$. Olefin reduction can be completely avoided by using hydrocarbons as the reaction medium. A self-consistent hypothesis is advanced to account for the observed lack of stereospecificity in reduction and for effects of various solvents on the course of hydride reductions.

Although reduction of olefinic bonds by lithium aluminum hydride has been known for some time, especially in the case of α,β-unsaturated carbonyl systems, there seem to be only two contradictory studies of its stereochemistry. Reduction of some acetylenic alcohols and glycols are reported[2] to yield only the *trans* olefins, which implies a stereospecific *trans* reduction. On the other hand, reduction[3] of 7-substituted norbornadienes by $LiAlD_4$ followed by deuteronolysis by D_2O results in *anti*-7-substituted norbornenes in which both deuteriums at carbons 5 and 6 are *exo*, which implies a stereospecific *cis* reduction. Although these results appear contradictory both are reasonable if one considers that in each case it is the constraints of the unsaturated system which determine the over-all stereochemistry. In the case of the acetylenic systems *cis* reduction would require the formation of a structure analogous to a *trans*-cyclopentene (eq 1).[4] Since such geometry is forbidden by the constraints of the test substance an alternative path is followed and the over-all addition occurs *trans* (eq 2). In the case of 7-substituted norbornadienes the intramolecular nature[3] of the reaction requires *exo* hydride transfer, ultimately leading to *cis* reduction (eq 3).[4] Note that *trans* reduction would require an intermediate of type I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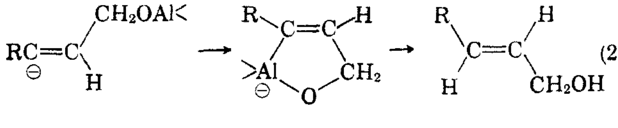
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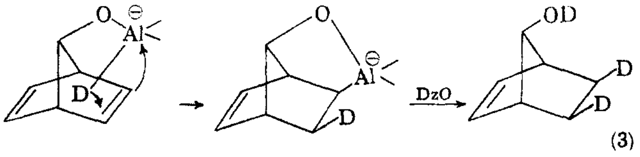
(3)

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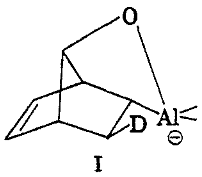
[1] (a) This work was supported in part by a National Science Foundation Grant GP-5061. Exploratory work was supported by the University of Connecticut Research Foundation. (b) Presented in part before the Division of Organic Chemistry at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954).

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

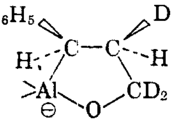
[4] We assume that protonolysis of the carbon-aluminum bond occurs with retention of configuration (*vide infra*).



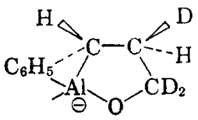
I

which again is prohibited by the steric constraints of the test substance.

To gain more general information on the stereochemistry of olefin reduction by hydride we have investigated reduction of methyl cinnamate by $LiAlD_4$ followed by deuteronolysis. The constraints of this system are minimal. Both intermediates and products are diastereomeric because of the substitution of deuterium for hydrogen, and should be of about the same energy. Interconversion of intermediates such



IIa



IIb

as IIa and b, regardless of the exact nature of the carbon–aluminum bond, is then kinetically controlled in that the thermodynamic properties of the system do not significantly favor formation of one of the diastereomers. The stereochemistry of the product, $C_6H_5CHDCHDCD_2OH$, is conveniently determined by its nmr spectrum. The aliphatic protons of the undeuterated counterpart, $C_6H_5CH_2CH_2CD_2OH$, form an AA′BB′ spectral system where $J_{AB} \neq J_{AB'}$. *If the reduction occurs stereospecifically* then the nmr spectrum of the aliphatic protons will consist of a *single AB pattern*. Whether the product is *erythro* or *threo* could be established by independent synthesis, although in principle one could predict which of the couplings, $J_{erythro}$ or J_{threo}, is the larger from a knowledge of the conformer distribution in the product. *If the reduction occurs nonstereospecifically*, then the nmr spectrum of the aliphatic protons will consist of *two distinct AB patterns*, and the ratio of integrated intensities reflects the partitioning between the two stereochemical paths.

Note that this method is but a variant of the classical use of *erythro,threo* isomers in determining stereochemistry, but that it has the important property that the diastereomeric products, and most intermediates and transition states preceding them, are of approximately the same free energy.[5]

Experimental Section

Vapor phase chromatography was performed on a Wilkens Aerograph Hy-Fi Model 600 (flame ionization detector), using either a 6-ft 10% diethylene glycol succinate (*ca.* 150°) column, a 10-ft 20% DC silicone grease (*ca.* 165°) column, or a 6-ft 10% Carbowax 20M (*ca.* 135°) on Chromosorb W, 80/100 column. The detector response was calibrated using mixtures of known composition of cinnamyl and hydrocinnamyl alcohol. Nmr spectra were obtained on an A-60 spectrometer system using an NMR Specialties HD-60A spin decoupler. Since sweep widths are uncalibrated, the reported couplings are accurate to only ±5%. Methyl cinnamate was a commercial product (EKWL) usually used without further purification.

Hydride Reductions.—The following method is representative of that used in other experiments. To a mechanically stirred suspension of 0.7 g (0.021 mole) of lithium aluminum hydride (LAH) in *ca.* 30 ml of absolute ether was added a solution of 2.9 g (0.020 mole) of methyl cinnamate (**1**) in *ca.* 20 ml of absolute ether. After being stirred for 4 hr at ambient temperature the mixture was decomposed[6] by consecutive, cautious addition of 0.7 ml of water, 0.7 ml of 15% NaOH, and 2.1 ml of water. The mixture was filtered and solvent was evaporated at reduced pressure to afford 2.6 g of an oil whose infrared spectrum was superimposable on that of hydrocinnamyl alcohol. Examination by vpc showed a peak with a retention time equal to that of hydrocinnamyl alcohol and with an area greater than 99% of the total.

Reductions performed at −25° for 4 hr afforded only cinnamyl alcohol, although reduction at 0° for 24 hr gave only hydrocinnamyl alcohol.

A.—Lithium aluminum deuteride (LAD) was used in place of LAH; reaction time at ambient temperature was 5.5 hr, and decomposition was effected by adding 3.5 ml of D_2O. After the mixture was processed as described above the residue was distilled, bp 79° (1 mm), to give 1.28 g of alcohol. The extent of deuterium incorporated was determined by nmr on a 30% CCl_4 solution. No signal was observed at the resonance position of the $-CH_2O-$ group. Using a normal sample of $C_6H_5CH_2CH_2CH_2OH$ as standard and assuming no deuterium incorporation into the aromatic ring by this experiment, we determined the number of protons remaining at the benzylic and internal methylenic positions by measuring their integrals relative to the aromatic resonance and comparing these integrated intensities with those obtained in the standard. The sample was found to contain 1.03 and 1.06 protons per molecule at the benzylic and methylenic positions, respectively, corresponding to 97 and 94% monodeuteration. The deuterium-irradiated nmr spectrum clearly shows two AB patterns whose integrated intensities are equal to within 5%, $J_{AB} = 6.3$ cps and $J_{AB'} = 9.0$ cps. In some experiments decomposition was effected by CH_3OD,[7] to ensure greater homogeneity, without affecting the experimental observations relative to decompositions with D_2O.

B.—The reduction was performed as above for 5 hr. Decomposition was effected at −71° by slow addition of CH_3OD (3 ml) followed by D_2O. Processing afforded 1.22 g of product whose deuterium-irradiated nmr spectrum again showed two AB patterns of *ca.* equal intensity.

C.—A slurry of 0.7 g (0.021 mole) of LAH in pentane (50 ml) containing 3.0 g (0.019 mole) of **1** was mechanically stirred at ambient temperature for 21 hr, then decomposed by successive addition of CH_3OH (5 ml) and H_2O (2 ml) and processed as above to yield 0.25 g of product. The filter cake was dissolved in HCl and extracted with pentane to afford another 0.56 g of alcohol (total yield 29%). The nmr spectrum of the product is that of cinnamyl alcohol, with no trace of hydrocinnamyl alcohol.

D.—A slurry of LAH (0.7 g), **1** (2.9 g), and 50 ml of reagent-grade hexane was heated at 60 ± 1° for 16.5 hr. After addition of 5 ml of CH_3OH and 2 ml of H_2O, most inorganic material was solubilized by addition of 25 ml of 5% hydrochloric acid. The filtered acid layer was extracted with $CHCl_3$ (25 ml) and the usual processing afforded 1.58 g of product (59%) whose nmr spectrum was that of cinnamyl alcohol; vpc examination showed the absence (<1%) of hydrocinnamyl alcohol, with the area of cinnamyl alcohol being >96.5% of the total.

E.—A slurry of LAH (0.7 g) and **1** (2.9 g) in 45 ml of benzene was maintained at 59–60° for 14.5 hr and processed as above to give 1.95 g of product (73%). Examination by vpc (silicone grease) showed the absence of hydrocinnamyl alcohol, the presence of cinnamyl alcohol (96% of total area), and two other components with retention times of about 1 min less than that of the latter (retention time of 6 min).

F.—A slurry of 0.4 g (0.012 mole) of LAH and 1.8 g of (0.011 mole) **1** in 30 ml of anisole was stirred at ambient temperature for 20 hr, and was then decomposed with 2.5 ml of CH_3OH.

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[5] An earlier version of this paper commented extensively on the use of this technique in determining the stereochemistry of reactions at primary carbon atoms and on its potential as an operational criterion for the concertedness of certain types of reactions. These sections have been deleted at the suggestion of the referees, but additional examples demonstrating the versatility of the technique will be published shortly.

[6] V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

[7] A. Streitwieser, L. Verbit, and P. Stang, *ibid.*, **29**, 370 (1964).

The mixture was poured into 25 ml of 5% hydrochloric acid and the organic phase was extracted with another 25 ml of 5% acid. Examination of the dried ($MgSO_4$) anisole solution showed the mixture to be 34:66 of hydrocinnamyl–cinnamyl alcohol, although resolution was made difficult by the effect of solvent. Anisole was evaporated at 1 mm to afford 1.03 g of product whose composition by vpc was 28:72 of hydrocinnamyl–cinnamyl alcohol. Assuming a 30:70 ratio the total yield of alcohols is 61%.

When the reaction was performed at 59–60° for 12.5 hr, cinnamyl alcohol accounted for less than 2% of the total alcohols present in the crude reaction mixture.

G.—When a slurry of 0.7 g of LAD and 2.9 g of **1** in 40 ml of anisole was stirred at room temperature for 45 hr, cinnamyl alcohol was the only alcohol identified on vpc examination. A similar mixture was maintained at 60 ± 2° for 3 hr and decomposed with 5 ml of CH_3OD and processed as above. Evaporation of solvent at ambient temperature at 1 mm gave 2.05 g (76%) of product whose composition (vpc) was 4.3% hydrocinnamyl alcohol, 95.7% cinnamyl alcohol. The crude product was enriched to 8% hydrocinnamyl alcohol by distilling a portion through a Kragen tube at 0.4 mm. The nmr spectrum of this material showed two AB quartets of comparable intensity.

H.—A slurry of 0.2 g of LAD and 0.8 g of **1** in 15 ml of *t*-butyl ethyl ether was stirred at ambient temperature for 24 hr, then decomposed with 3 ml of CH_3OD. After the usual processing, vpc examination of the solution showed a 13:87 ratio of hydrocinnamyl–cinnamyl alcohol. Several small peaks, which may arise from solvent, also were apparent.

Attempted Nmr Examination of the Intermediate.—To a stoppered serum vial containing 0.5 g of LAD in 5 ml of absolute ether was added 1.00 g of recrystallized **1** in about 1 ml of ether. The vial was immersed in an ice bath for 24 hr, then centrifuged at 2000 rpm for 1 hr. The clear supernatant liquid was transferred by means of a gas-tight syringe to an nmr tube flushed with, and maintained in, a dry argon atmosphere (all transfer operations were done under a strong argon purge), and the tube was sealed. Examination by nmr showed only resonances of diethyl ether and a broad, diffuse band in the aromatic region (~350 cps, from CH_3 of ether), although the spectrum was carefully scanned at high gain from −2000 to +500 cps, relative to TMS.

Results and Discussion

Reduction of methyl cinnamate (**1**) in diethyl ether using LAD followed by hydrolysis with D_2O or CH_3OD afforded $C_6H_5CHDCHDCD_2OH$ (**2**). Nmr analysis (see Experimental Section) indicated 97 and 94% monodeuteration at the positions α and β to the aromatic ring, respectively. When the protons were spin-decoupled from the deuterons, the aliphatic protons gave rise to *two AB patterns of equal intensity* (to within 5%). This observation shows unequivocally that an approximately equimolar mixture of *erythro*- and *threo*-$C_6H_5CHDCHDCD_2OH$ was formed. Consequently, *olefinic reduction by hydride occurs nonstereospecifically* and is random to within the error limits of our experimental method.

The lack of stereospecificity could arise in at least two distinct ways. (1) The carbon–aluminum bond of an intermediate might possess sufficient ionic character that the resulting carbonionic center would be effectively planar. Subsequent reaction would occur with equal probability at either face of the carbon. (2) Protonolysis of the C–Al bond might occur with equal probability of retention or inversion of configuration. The latter possibility does not seem likely based on what is currently known. Thus, ". . . electrophilic cleavage of vinylic carbon–metal bonds proceeds with retention of configuration . . ."[8] Less complete information is known for alkyl metals. Protonolysis of the carbon bond to boron (also in Group IIIA) is thought to proceed with retention;[9] carbonation of the more ionic alkyl lithiums under appropriate conditions leads to the product with predominant retention of configuration;[10] recently it has been shown that the carbonation products of the norbornyl Grignard were formed in the same ratio as that of the *exo,endo* Grignard reagents themselves;[11] current speculation is that electrophilic substitution at saturated carbon–metal bonds occurs *via* retention except as modified by ionization processes.[12] Protonolysis of the vinyl C–Al bond occurs with retention,[13] as does protonolysis of the alkyl C–Al bond in the norbornyl systems.[3] Nevertheless, the possibility of a nonstereospecific protonolysis was probed experimentally by conducting the hydride reduction at room temperature followed by methanolysis at −71°. Since the literature citations above suggest a strong steric preference in cleavage of carbon–metal bonds, it was reasoned that, if the stereochemical outcome was a result of protonolysis, then protonolysis at a low temperature could demonstrate, at the very least, increased stereospecificity relative to that at room temperature. However, the experimental results of low temperature protonolysis were indistinguishable from those cited above! We interpret this to mean that the lack of stereospecificity should be attributed to the ionic character of the carbon–aluminum bond.

When we turned to poor Lewis bases (pentane, hexane, benzene) in the hopes of effecting stereospecific reduction, cinnamyl alcohol (**3**) was the only product identified. (In some experiments it was demonstrated that 0.4% hydrocinnamyl alcohol would have been detected readily.) This result shows that hydride transfer from aluminum to an olefinic carbon is facilitated by Lewis bases, presumably through coordination with aluminum.

The practical consequences of the above results are obvious. Hydride reduction of C=O without concomitant reduction of a conjugated olefinic group frequently is possible in ether only at low temperatures. A search for a more convenient method of accomplishing this same end has led to the introduction of AlH_3, which seems to leave C=C linkages unaffected in all cases studied.[14] On the basis of our results we suggest that hydride reduction of functional groups can be accomplished even more conveniently, in good yield, and without accompanying olefinic double-bond reduction by using benzene (and other hydrocarbons) as the solvent and at temperatures at least as high as 60°. This should prove to be a valuable synthetic procedure. Our observation also suggests that solvents might modify the course of hydride reductions of other functional groups.

We next turned to ethers known to be weaker Lewis bases (at least toward the proton) than diethyl ether in the expectation that some degree of stereospecificity would be observed. When anisole (pK_a of the con-

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[8] H. G. Kuivila, W. Rahman, and R. H. Fish, *J. Am. Chem. Soc.*, **87**, 2835 (1965).

[9] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, Chapter 8.

[10] D. Y. Curtin and W. J. Koehl, Jr., *Chem. Comm.*, 262 (1960).

[11] F. R. Jensen and K. L. Nakamaye, *J. Am. Chem. Soc.*, **88**, 3437 (1966).

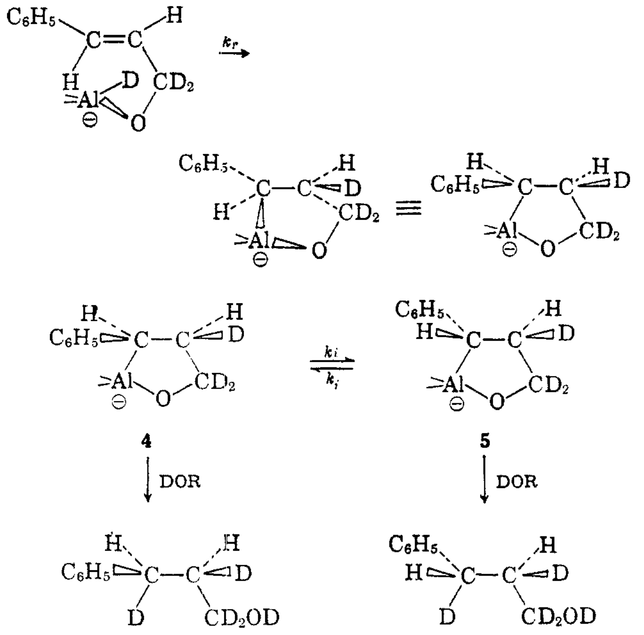
[12] F. R. Jensen and L. H. Gale, *ibid.*, **82**, 148 (1960).

[13] J. J. Eisch and W. C. Kaska, *ibid.*, **88**, 2213 (1966).

[14] M. J. Jorgenson, *Tetrahedron Letters*, 559 (1962); H. C. Brown and N. M. Yoon, *J. Am. Chem. Soc.*, **88**, 1464 (1966).

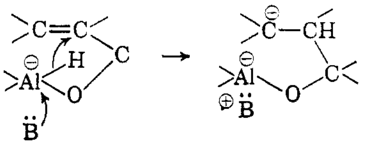
jugate acid = −6.54[15]) was used as the solvent, reduction with LAH at 60° for 12.5 hr afforded alcohol containing over 98% of **2**, but reaction at ambient temperature for 20 hr gave a mixture with the ratio of saturated (**2**) to unsaturated (**3**) product being 30:70. When this same reaction was conducted with LAD at ambient temperature for 45 hr, no carbon–carbon double-bond reduction occurred! This difference between LAH and LAD exhibited in the course of (abnormal) hydride reactions is reminiscent of a previous experience where 7-t-butoxynorbornadiene was reduced by LAH in tetrahydrofuran, but was not reduced by LAD until $AlCl_3$ was added.[3] When the reaction between **1** and LAD was conducted at 60° for 3 hr there was isolated alcohol (75% yield) which contained only 4.3% saturated alcohol. When the deuterium spin-decoupled nmr spectrum of this sample was examined, the aliphatic protons appeared as *two AB quartets of approximately equal intensity.*

Our results do not permit a definitive statement of mechanism. We have adopted the one below as a working postulate,[16] but recognize that several variants, differing in the precise timing of steps and in the cyclic or acyclic nature of intermediates, are admissible. Isomerization **4** ⇄ **5** presumably occurs *via* an inversion–rotation sequence at a carbanionic benzylic carbon. If sufficient delocalization occurs to give a planar center, rotation alone suffices to effect the transformation **4** ⇄ **5**. An attempt to detect and identify the organoaluminum species present was unsuccessful (see Experimental Section).



The lack of olefinic bond reduction in hydrocarbons suggests that k_r is a function of solvent Lewis base strength. The formation of a random mixture (to within the limits of our experimental error) of *erythro-* and *threo-*$C_6H_5CHDCHDCD_2OH$ upon low-temperature protonolysis suggests that k_i is "large," at least in diethyl ether at ambient temperature. That **2** is formed nonstereospecifically in the early stages of reaction in anisole (4% of **2**, 96% of **3**) shows $k_i \gg k_r$ under the conditions employed.

Our results and some seemingly unrelated ones can be explained within a single self-consistent framework. We postulate that hydride transfer from Al to C is facilitated by coordination of Al with a Lewis base. We can view this at the limit as a concerted reaction (eq 4). The greater is the coordination, the more facile is the hydride transfer; hence k_r increases with Lewis base strength. However, if the hydride is not transferred until coordination is relatively strong, then the C–Al bond will have an effectively high ionic character and k_i will be relatively large. Hence one encounters the dilemma that when olefinic reduction by the hydride becomes feasible it will be nonstereospecific, *provided the constraints of the system being reduced do not affect k_i.*[2,3]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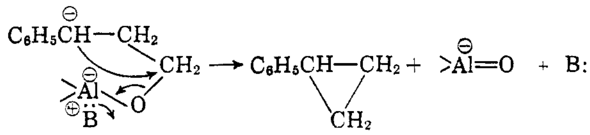
Others have recently noted that LAH reduction of the cinnamate system in THF led to cyclopropane formation.[17] Since THF is a stronger Lewis base than diethyl ether, this observation is understandable on the basis of an effectively larger ionic character of the C–Al bond in THF. In the limit of a completely ionic bond one would have an excellent nucleophile (the carbanion) participating in an intramolecular, S_N2 reaction with a rather good leaving group at the γ carbon (eq 5). This reaction is reminiscent of a curious solvent-sensitive rearrangement we had reported earlier[18] and which we had rationalized by consideration of the Lewis base properties of the solvent (eq 6). It is important to note that the entire gamut of reactivity (C=O reduction without C=C reduction; C=O reduction with C=C reduction; C=O and C=C reduction and cyclopropane formation) is run over a relatively narrow span of base strength (pK_a of conjugate acids are −6.54 ($C_6H_5OCH_3$), −3.59 (Et_2O), −2.08 (THF)).[15,19–21]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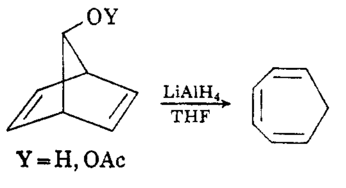
(6)

Registry No.—**1**, 103-26-4; lithium aluminum hydride, 1302-30-3; lithium aluminum deuteride, 14128-54-2.

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[15] E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **84**, 1680 (1962).

[16] F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

[17] M. J. Jorgenson and A. W. Friend, *ibid.*, **87**, 1815 (1965); R. T. Vyeda and D. J. Cram, *J. Org. Chem.*, **30**, 2083 (1965).

[18] B. Franzus and E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 3902 (1963).

[19] E. M. Arnett and C. Y. Wu, *ibid.*, 1684 **84**, (1962).

[20] At least some of the difference in reactivity between THF and diethyl ether may arise from the difference in temperature used in the reaction leading to cyclopropanes. However, no such difference was present in our study of the rearrangement leading to tropilidene.

[21] The importance of coordination of external species with metals in affecting organometallic reactions has previously been explicitly recognized by Dessy (*J. Am. Chem. Soc.*, **85**, 1812 (1963)).