

# The Mechanism of Lithium Aluminum Hydride Double-Bond Reductions in the 7-Substituted Norbornadienes and *syn*-7-Substituted Norbornenes<sup>1</sup>

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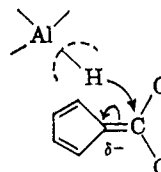
The driving force for double-bond reduction (by lithium aluminum hydride) in 7-substituted norbornadienes and *syn*-7-substituted norbornenes resides in a very favorable geometry for hydride addition to the double bond. The reaction product from 7-acetoxynorbornadiene or 7-hydroxynorbornadiene with lithium aluminum hydride is anti-7-norbornenol (*syn* reduction). Results from deuterium-labeling experiments have indicated *exo* deuteride addition followed by formation of an *exo* aluminum-carbon bond. Deuterolysis of this intermediate results in *exo,exo*-dideuterio-anti-7-hydroxynorbornene. Double-bond reduction (with lithium aluminum hydride) occurs with *syn*-7-norbornenol and *syn*-7-acetoxynorbornene (*syn* reduction) but not with anti-7-acetoxynorbornene. The difference in behavior between the *syn* and *anti* isomers points to intramolecular reduction, the minimal importance of strain as a driving force for double-bond reduction, and the important role of geometric configuration in facilitating double-bond reduction. 7-*t*-Butoxynorbornadiene does not react with lithium aluminum hydride unless catalyzed by a trace of aluminum chloride. The product from this reduction is anti-7-*t*-butoxynorbornene, and again results of deuterium labeling experiments point to *exo* deuterium and *exo* aluminum addition. A mechanism for reduction is postulated which involves a geometrically favorable transition state in which hydride hydrogen is positioned at an internuclear distance almost equal to that of the final product. Calculations were made in order to determine if these internuclear distances for the transition state were indeed plausible.

## Introduction

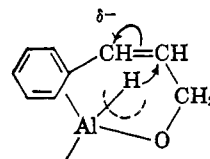
The addition of lithium aluminum hydride to double bonds was first observed by Nystrom and Brown.<sup>2</sup> In a subsequent publication Hochstein and Brown<sup>3</sup> inferred from deuterium-labeling experiments that reduction of compounds such as cinnamaldehyde to hydrocinnamyl alcohol occurred in two successive stages, with the attack upon the double bond (second stage) occurring more slowly than the reduction of the carbonyl group (first stage).

Since Brown's classic work, other investigators have observed the reduction of acetylenic bonds to olefinic bonds in the reduction of acetylenic alcohols with lithium aluminum hydride<sup>4</sup> and reduction of a triple

bond to a double bond in the lithium aluminum hydride reduction of acetylenic acids to olefinic alcohols.<sup>5</sup> Similarly, the lithium aluminum hydride reduction of unsaturated nitro compounds ( $\text{ArCH}=\text{CHNO}_2$ ) to saturated amines<sup>6a</sup> and saturated nitroethanes ( $\text{ArCH}_2\text{CH}_2\text{NO}_2$ )<sup>6b,c</sup> plus the lithium aluminum hydride reduction of  $\alpha$ -ethylcrotonic acid amide to  $\alpha$ -ethylbutylamine<sup>7</sup> represent other examples of double-bond reduction. Double- and triple-bond reductions with lithium aluminum hydride appear to be quite facile in those compounds in which an O-Al or N-Al bond close to the unsaturated center is formed first,<sup>8</sup> the reduction proceeding quite readily at room temperature. In contrast, lithium aluminum hydride reduction of aromatics such as anthracene<sup>9,10</sup> proceeds only at temperatures over 220°. Although the temperatures required for lithium aluminum hydride reduction of aromatics appear to be excessive, the reaction of  $\alpha$ -olefins with lithium aluminum hydride (in ether) proceeds quite readily at temperatures slightly over 100°. Indeed, dimethylfulvene and presumably other fulvenes react with lithium aluminum hydride in the cold.<sup>11</sup> This is not surprising when one considers that the driving force for this reaction is probably the formation of an (incipient) cyclopentadienyl anion.



The probable driving force for the double-bond reductions in compounds such as cinnamaldehyde<sup>2,3</sup> would be the formation of an (incipient) benzyl carbanion.



(1) Presented before the Division of Organic Chemistry at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug.-Sept. 1964.

(2) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197, 2548 (1947).

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

(4) E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954); J. D. Chanley and H. Sobotka, *J. Am. Chem. Soc.*, **71**, 4140 (1949).

(5) V. M. Mitchovitch and M. L. Mihailovic, *Compt. rend.*, **231**, 1238 (1950); G. E. Benedict and R. R. Russell, *J. Am. Chem. Soc.*, **73**, 5444 (1951).

(6) (a) K. E. Hamlin and A. W. Weston, *ibid.*, **71**, 2210 (1949); (b) R. T. Gilsdorf and F. F. Nord, *ibid.*, **74**, 1837 (1952); (c) cf. also W. J. Bailey and M. E. Hermes, *J. Org. Chem.*, **29**, 1254 (1964).

(7) A. Uffer and E. Schittler, *Helv. Chim. Acta.*, **31**, 1397 (1948).

(8) In reality, the reducing agent is no longer lithium aluminum hydride but is, instead, a derivative such as lithium alkoxy aluminum hydride.

(9) S. L. Sampey and S. M. Cox, *J. Am. Chem. Soc.*, **71**, 1507 (1949).

(10) I. Goodman, *J. Chem. Soc.*, 846 (1951).

(11) K. Ziegler, H. Gellert, H. Martin, K. Nage, and J. Schneider, *Ann.*, **589**, 91 (1954).

The *only* driving force for double-bond reduction cannot be carbanion stabilization of an intermediate or transition state since such stabilization cannot be realized in triple-bond reductions of certain aliphatic acetylenic alcohols<sup>4</sup> and acids.<sup>5</sup> One could, on the other hand, argue that triple-bond reduction is probably more facile than double-bond reduction. Reduction of *anti*-7-benznorbornadienyl acetate to *anti*-7-benznorbornenol<sup>12</sup> demonstrates that double-bond reduction *via* lithium aluminum hydride can be facile even though no apparent stable carbanion can be invoked as the driving force for the reaction.

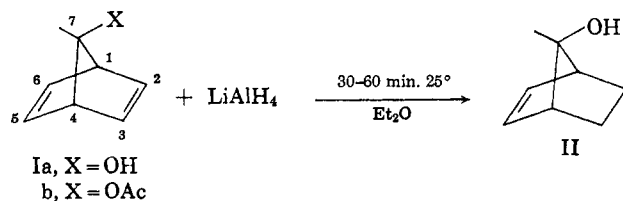
The presence of the benzene ring in the above compounds is not essential for reduction to occur since Story has observed the same type of reduction for 7-acetoxynorbornadiene (Ib) to *anti*-7-norbornenol (II).<sup>13</sup>

We decided to investigate 7-substituted norbornadienes and 7-substituted norbornenes as model systems for studying double-bond reductions by lithium aluminum hydride. Our selection of this system was based, in part, on the fact that in this system a stable carbanion could not be invoked as the driving force for reduction. As an added bonus, this system was amenable to facile identification of *syn*- and *anti*-7-substituted norbornenols (the reduction products of diene reduction) by n.m.r. spectroscopy<sup>14</sup>; we were also able to determine the direction of hydride approach (*exo* or *endo*) to the double bond by utilizing deuterium labeling and n.m.r. spectroscopy.<sup>14,15</sup>

## Results

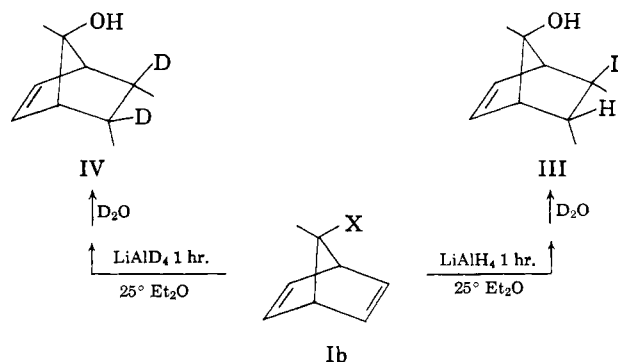
In order to offer a reasonable explanation for the double-bond reduction in the 7-substituted norbornadiene (and norbornene) system, we felt that it behooved us to obtain (if possible) answers to the following questions. (1) What was the role of the bridge substituent in facilitating reduction of the double bond? (2) Was the reduction intra- or intermolecular? (3) Was the driving force for double-bond reduction relief of strain of the norbornadienyl system<sup>16</sup> or favorable geometry for facile reduction?

Both 7-acetoxynorbornadiene (Ib) and the corresponding alcohol (Ia) reacted with lithium aluminum hydride (LiAlH<sub>4</sub>) to form *anti*-7-norbornenol (II). Since the structures of *syn*-7-norbornenol<sup>17</sup> (V) and *anti*-7-norbornenol<sup>18</sup> (II) have been well characterized,

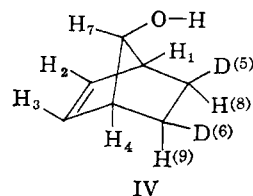


we were able to determine easily (quantitatively) the course of reduction by n.m.r. spectroscopy<sup>14</sup>

and v.p.c. Reduction of Ib by lithium aluminum hydride followed by D<sub>2</sub>O decomposition resulted in *anti*-7-norbornenol with one deuterium in the *exo* position (III). Reduction of Ib with lithium aluminum deuteride (LiAlD<sub>4</sub>) followed by D<sub>2</sub>O decomposition resulted in *anti*-7-norbornenol with two deuteriums in the *exo* position (IV).



The assignment of configuration to *exo,exo*-5,6-dideuterio-*anti*-7-hydroxynorbornene (IV) was based on its n.m.r. spectrum (Figure 1). The chemical



shift for the *endo* hydrogens of 7-substituted norbornenes occurs at 55–60 c.p.s. from TMS (tetramethylsilane) at 60 Mc.<sup>14,15</sup>; furthermore, since  $J_{18} = J_{49} \cong 0$  (but  $J_{46} = J_{15} \neq 0$ ), one would anticipate that the *endo* hydrogens H-8 and H-9 would appear as a singlet between 55 and 60 c.p.s. (A<sub>2</sub> system). Reference to Figure 1 shows a singlet at 58 c.p.s., in precise agreement with that expected for IV. The configuration corresponding to two *exo* hydrogens (*endo* deuteriums) should have a multiplet (A<sub>2</sub>B<sub>2</sub> because of coupling with the bridgehead protons) at about 110 c.p.s. Similarly, the assignment of structure III was based on the observation that the area of the *endo* hydrogens (at about 55 c.p.s.) was twice that of the *exo* hydrogens (at about 110 c.p.s.). Story has noted similar results.<sup>19</sup>

If we assume that the reduction is intramolecular (*vide infra*), a plausible mechanism for reduction would consist of (1) formation of an oxygen–aluminum bond at C-7, (2) hydride (or deuteride) transfer to C-2, and (3) formation of an aluminum–carbon bond (Al–C<sub>3</sub>), either *concomitantly* or *subsequently*. The driving force for the above reduction cannot be attributed solely to strain energy since norbornadiene and lithium aluminum hydride in refluxing tetrahydrofuran underwent no reaction. Similarly, 7-*t*-butoxynorbornadiene was left unchanged under the same experimental conditions experienced by Ia and Ib.

The reaction of *syn*-<sup>20</sup> and *anti*-7-substituted norbornenes with lithium aluminum hydride were run in order to more critically differentiate between strain

(12) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

(13) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(14) E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

(15) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962); P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

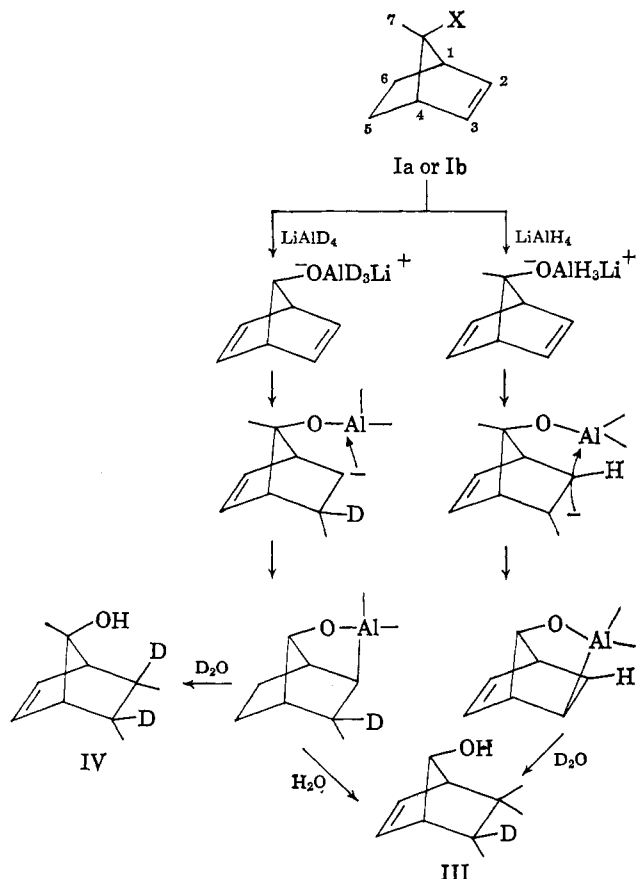
(16) R. B. Turner, W. R. Meador, and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

(17) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

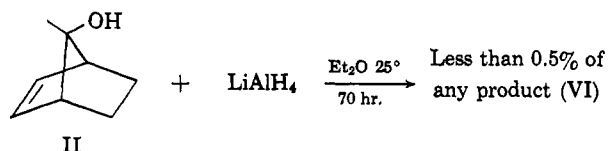
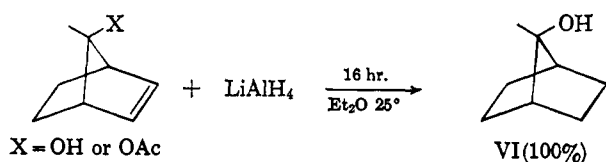
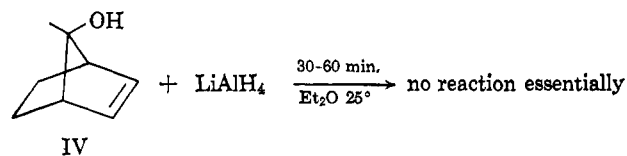
(18) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(19) P. R. Story, *ibid.*, **83**, 3347 (1961), footnote 8.

(20) We wish to express our appreciation to Dr. W. C. Baird, Jr., of these laboratories for a generous gift of *syn*-7-norbornenol.



energy and geometric factors as the driving force for the reduction. Using v.p.c. with an internal standard, we were able to determine the presence of as little as 0.5% 7-norbornanol (VI). Although reaction rates were slower in the 7-norbornenyl system than in the 7-norbornadienyl system, there is no doubt that *syn*-7-substituted norbornenes reduced totally to 7-norbornanol (VI), whereas *anti*-7-substituted norbornenes, under even more severe conditions, underwent less than 0.5% double-bond reduction.



If the relative reduction rates of the *syn* to *anti* isomers (>200) were translated wholly into strain energy, this would amount to greater than 3 kcal., which is approximately the strain energy difference between norbornadiene and norbornene<sup>16</sup> (or between norbornene and norbornane<sup>16</sup>). However, the dif-

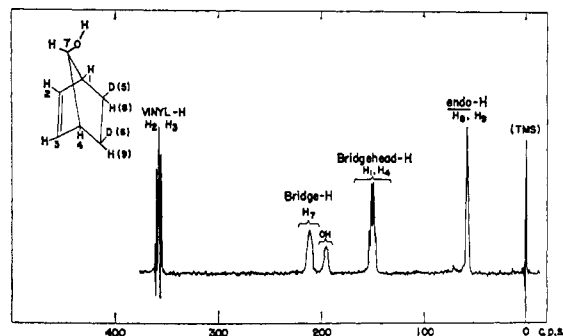
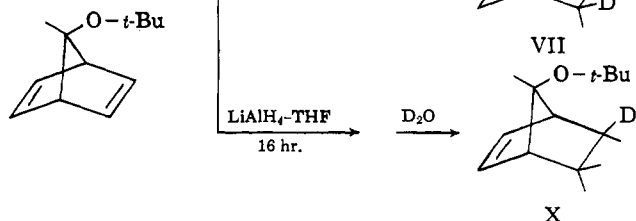
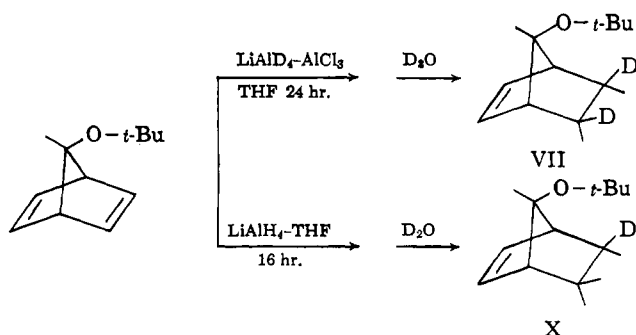
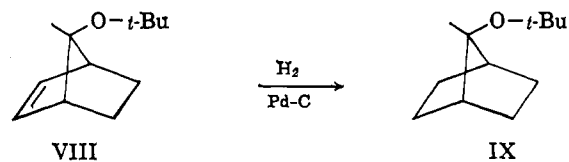
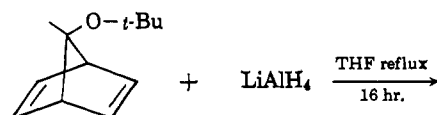


Figure 1. N.m.r. spectrum of *exo,exo*-5,6-dideuterio-*anti*-7-hydroxynorbornene.

ference in steric strain between the *syn* and *anti* isomers should be negligible so that, if double-bond reduction were intermolecular and the driving force for reduction was relief of strain, then one would anticipate that both the *syn* and *anti* isomers would reduce at approximately equal rates. Since the experimental difference in rate between *syn* and *anti* isomers cannot be interpreted in terms of strain energy, the difference in ease of reduction must be rationalized in terms of favorable geometric requirements, which, of necessity, requires that reduction is intramolecular. One can now realize that parts of questions (2) and (3) have been answered; e.g., reduction is intramolecular and at relatively constant strain the main driving force for reduction is favorable geometric requirements.

Because the foregoing arguments ascribe a critical role in double-bond reductions to the bridge oxygen, we investigated in greater detail the reduction of 7-*t*-butoxynorbornadiene with lithium aluminum hydride. Heating 7-*t*-butoxynorbornadiene with lithium aluminum deuteride in refluxing tetrahydrofuran for 44 hr. afforded no sign of reduction. However, addition of traces of aluminum chloride led smoothly to double-bond reduction and the formation (after  $\text{D}_2\text{O}$  decomposition) of *exo,exo*-5,6-dideuterio-*anti*-7-*t*-butoxynorbornene (VII). Apparently there is enough alu-

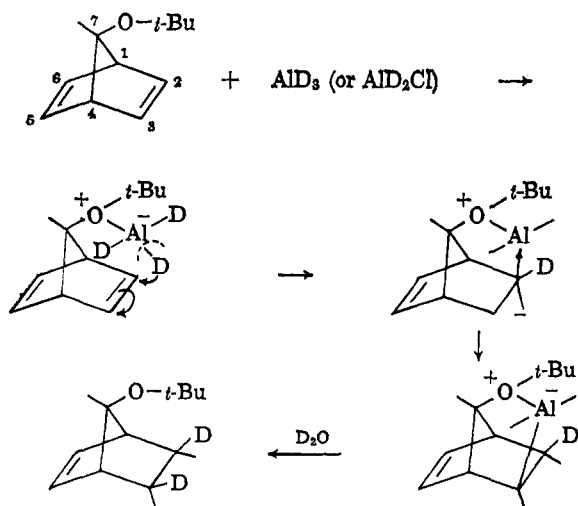


minum halide (or similar catalytic impurity) in ordinary lithium aluminum hydride to allow reduction of the double bond without further addition of aluminum chloride as a catalyst. Such reductions were carried out in tetrahydrofuran at reflux overnight. The only product, isolated in almost quantitative yields, was *anti*-7-*t*-butoxynorbornene (VIII). Its structure was assigned on the basis of elemental analysis, its n.m.r. spectrum, and catalytic hydrogenation (0.95 mole of H<sub>2</sub> absorbed) to 7-*t*-butoxynorbornane (IX). The latter had the correct elemental analysis for IX and showed no vinyl hydrogens in the n.m.r. When the reaction mixture was decomposed by D<sub>2</sub>O one deuterium was incorporated into the *exo* position to give X.

As was the case previously, all the evidence again points to some mechanism involving (i) the oxygen-aluminum bond, (ii) deuteride or hydride transfer to carbon (C-2), and (iii) formation of an aluminum-carbon bond (Al-C<sub>3</sub>) which, on decomposition by D<sub>2</sub>O, gives rise to a deuterium in the *exo* configuration.

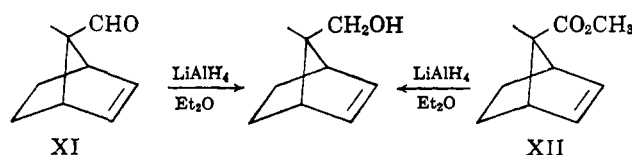
### Discussion

In all cases studied reduction of the ring carbon-carbon double bond occurs *syn* to the 7-substituent, even when the 7-substituent is the very bulky *t*-butoxy group. Since steric repulsions would favor *exo* attack on the ring *anti*- to the 7-substituent, *a fortiori*, so for the large *t*-butoxy group, our results demonstrate the relative unimportance of steric effects. Since all substituents bear an oxygen at the 7-position, our results show that oxygen assumes the specific role in double-bond reduction of constraining the reducing species to remain in the environment of the olefinic center which is attacked. For all compounds studied other than 7-*t*-butoxynorbornadiene, covalent oxygen-aluminum bond formation assures such constraint. In the case of the ether, lack of reaction with "pure" LiAlD<sub>4</sub> but facile reduction after the addition of traces of AlCl<sub>3</sub> permits the postulate that the ether oxygen coordinates with aluminum hydride or chloroaluminum hydride,<sup>21</sup> again affording constraint. The formation

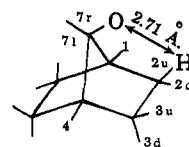


(21) E. A. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947); see also E. L. Eliel and T. J. Brett, *J. Org. Chem.*, **28**, 1923 (1963); see also J. H. Brewster and H. O. Bayer, *ibid.*, **29**, 105 (1964), footnote 17.

of an oxygen-aluminum bond, whether covalent or coordinated, permits a facile addition of hydride or deuteride to the double bond (at C-2) followed by aluminum-carbon bond formation (Al-C<sub>3</sub>). The lack of LiAlD<sub>4</sub> reaction, AlCl<sub>3</sub> catalysis, *syn* reduction (formation of *anti* isomer), and *exo* addition are all consistent with the mechanism shown. The geometric requirements of the bridge oxygen take on added significance when one considers that compounds XI and XII when treated with lithium aluminum hydride<sup>22</sup> in refluxing diethyl ether underwent the usual carbonyl reduction with apparently no double-bond reduction. These reaction conditions, although not identical with conditions used in the reduction of *syn*-7-acetoxynorbornene to 7-norbornanol, are sufficiently rigorous that one would anticipate some double-bond reduction if a favorable reaction path were available. The contrasting reactivities of the *syn*-7-hydroxy- and 7-hydroxymethylnorbornenes thus place limits on the transition state leading to C=C reduction.



We have calculated the distance between the bridge oxygen and the *exo* hydrogen (at C-2) by assuming that in the *syn*-7-substituted norbornenyl system a hydride ion has been added to C-2 and a carbanion formed at C-3. Since this model has essentially the same geome-



Al(diameter) = 2.52 Å.

For symbols 1, r, u, and d, see ref. 24.

try as the norbornane skeleton, we have utilized the elegant method and model of Wilcox in determining internuclear distances.<sup>23</sup> Together with Pauling's covalent radii<sup>24</sup> we evaluated the internuclear distance between the bridge oxygen (7r) and the *exo*-hydrogen (2u) to be 2.7 Å. Since the diameter of a tetrahedral aluminum atom (2.52 Å.) occupies nearly all of the space between these two atoms, our calculations strongly support our contention that in the reactive species hydrogen is situated quite favorably for facile hydride transfer to the double bond. This calculation shows us that the hydrogen of the aluminum is less than 0.2 Å. from the position of the H in the final product (2.71 Å. - 2.52 Å.).

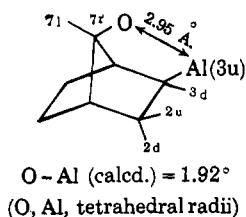
We can use these same methods to determine the distance between an aluminum atom at C-3 (3u) and the bridge oxygen (7r).

Such calculations lead to a distance of 2.95 Å. vs. a distance of 1.92 Å. for the O-Al bond calculated from tetrahedral radii. Formation of the intermediate alkoxyalkylaluminum hydride must then involve some

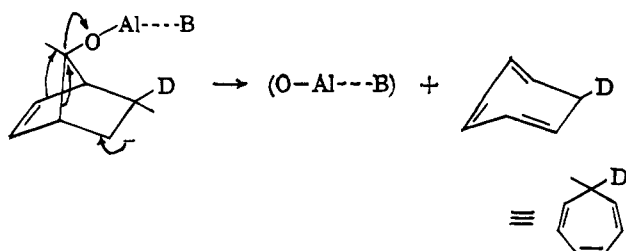
(22) R. K. Bly and R. S. Bly, *ibid.*, **28**, 3165 (1963).

(23) C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

(24) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.



distortion of bond angles to accommodate the normal oxygen-aluminum distance of 1.92 Å. This bond distortion takes some energy, so if a stepwise process obtains in double-bond reduction, aluminum-carbon bond formation might encounter a small but finite free energy of activation. This could account, in part, for the fact that in coordinating solvents (B) rearrangement of the carbanion (formed from hydride or deuteride transfer to the double bond of a 7-substituted norbornadiene) to cycloheptatriene occurs before formation of the aluminum-carbon bond.<sup>25</sup>



Certainly the driving force for the lithium aluminum hydride double-bond reduction in 7-substituted norbornadienes and *syn*-7-substituted norbornenes appears to be a very favorable geometric arrangement of the atoms. The reaction is intramolecular, with the bridge oxygen serving as the focal point of an alkoxy-aluminum hydride system capable of facile hydride addition to the double bond.

## Experimental

All melting points were taken in sealed capillaries and were uncorrected. Infrared spectra were determined using a Beckman IR-5 spectrophotometer and a Baird Model 4-55 recording spectrophotometer. V.p.c. analysis was carried out on a Perkin-Elmer Model 154-D and a modified 154-A vapor fractometer. Preparative gas chromatography was done on an Aerograph Autoprep Model A-700. N.m.r. spectra were determined with a Varian Associates A-60 spectrometer. Elemental analyses were performed by both the Analytical Research Division of Esso Research and Engineering Co. and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Both ethyl ether and tetrahydrofuran were dried prior to use by distillation from lithium aluminum hydride. Reductions were run under an atmosphere of nitrogen with magnetic stirring throughout.

**Preparation of anti-7-Norbornenol (II) and exo-5-Deuterio-anti-7-norbornenol (III).**<sup>13</sup> To a stirred mixture of 3.5 g. (0.092 mole) of lithium aluminum hydride in about 250 ml. of ether was added, over 40 min., 10.1 g. (0.067 mole) of 7-acetoxynorbornadiene<sup>13</sup> in 200 ml. of ether. Complete reduction occurs in 30-60 min. V.p.c. analysis at 80° on a 5% polypropylene glycol (on Chromosorb P) column at 90

cc./min. helium flow shows complete disappearance of the dienyl acetate (8.8-9.0 min. from air) and the formation of the *anti* alcohol (9.4-9.8 min. from air). This mixture was allowed to stand overnight. Part (~15%) was decomposed with D<sub>2</sub>O (3.0 ml., 0.15 mole) using a paste of sodium sulfate and D<sub>2</sub>O and finishing decomposition of the intermediate with 2.0 ml. of D<sub>2</sub>O (0.20 mole). The remainder was decomposed in the same way using H<sub>2</sub>O. In each of the fractions the ether layers were decanted, the solids were washed with ether, and the ether extracts were washed with water and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave *anti* alcohol<sup>13</sup> as a white solid. From the water decomposition fraction was obtained 5.35 g. (0.0495 mole) and from the D<sub>2</sub>O decomposition we obtained 0.90 g. (0.0083 mole), for a total yield of 86%. The *anti* alcohol from the D<sub>2</sub>O decomposition was further purified by sublimation at 60° and ~100 mm. The sublimate was dissolved in CDCl<sub>3</sub> and the n.m.r. spectrum was obtained. (See Table I.)

Table I<sup>a</sup>

Assignment	Internal TMS, c.p.s.	$\tau$	Area, %	
			Found	Calcd. for 1 <i>exo</i> -D
Vinyl	360	5.99	21.3	22.2
Bridge	215	3.58	10.5	11.1
OH	169	2.81	10.5	11.1
Bridgehead	152	2.53	21.9	22.2
<i>exo</i>	~109	~1.82	12.0	11.1
<i>endo</i>	~60	~1.00	23.7	22.2

<sup>a</sup> Ratio *endo*:*exo* (calcd.) = 2.0:1, (found) = 1.98:1.

**Reaction of 7-Norbornadienol (Ia) with Lithium Aluminum Hydride.** Using the same technique as described above, 0.264 g. (0.0069 mole) of LiAlH<sub>4</sub> was treated with 0.500 g. (0.0046 mole) of 7-norbornadienol.<sup>13</sup> After addition of the alcohol, the reaction mixture was stirred for 1 hr. at room temperature and then the reaction mixture was decomposed with 0.25 ml. of water, 0.25 ml. of 15% NaOH, and 0.8 ml. of water. After extraction of the decomposed reaction mixture with ether, drying of the ether (anhydrous MgSO<sub>4</sub>), and concentration of the *anti* alcohol by distillation of the ether, v.p.c. (5% polypropylene glycol on Chromosorb P at 80° and 90 cc./min. of helium) showed no 7-norbornadienol (2.9 min. from air) and the formation of *anti*-7-norbornenol (4.4 min. from air).

**Preparation of exo,exo-5,6-Dideuterio-anti-7-hydroxy-norbornene (IV).** To a slurry of 0.509 g. (0.012 mole) of LiAlD<sub>4</sub> in about 20 ml. of dry ether was added 1.003 g. (0.0067 mole) of 7-acetoxynorbornadiene in 20 ml. of dry ether. Addition was complete in 15 min. and stirring was continued for 30 min. Excess deuteride was decomposed by a paste made from 3.0 ml. of D<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub>, followed by 2.0 ml. of D<sub>2</sub>O. After remaining overnight, the reaction mixture was filtered, the solid was washed with ether, and the ether extracts were combined and dried over anhydrous magnesium sulfate. After distillation of the ether, the remaining solid was sublimed and resublimed at 80° and 15 mm. to give 0.230 g. (0.0021 mole) of pure *exo,exo*-dideu-

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

terated *anti* alcohol (IV). The n.m.r. spectra of IV has been discussed in detail elsewhere.<sup>14</sup>

**Control Runs of Norbornadiene and 7-*t*-Butoxynorbornadiene with Lithium Aluminum Hydride.** A mixture of 0.8174 g. (0.0215 mole) of LiAlH<sub>4</sub> and 0.9176 g. (0.0099 mole) of norbornadiene in 25 ml. of tetrahydrofuran was stirred at reflux for 16 hr. After decomposition of excess hydride with aqueous base and extraction with *n*-pentane, v.p.c. analysis on a 2-m. Perkin-Elmer "R" column at 56° (conditions known to differentiate between norbornene, norbornane, and norbornadiene) showed *only* unreacted norbornadiene.

To 0.1337 g. (0.0035 mole) of LiAlH<sub>4</sub> in 5 ml. of dry ether was added 0.327 g. (0.002 mole) of 7-*t*-butoxynorbornadiene<sup>13</sup> in 5.0 ml. of dry ether. The solution was stirred at room temperature for 1 hr. and the excess hydride was decomposed with wet sodium sulfate. The ether solution was filtered from the salts and dried over anhydrous magnesium sulfate. Most of the ether was removed under vacuum using a rotary evaporator. V.p.c. analysis (5% polypropylene glycol column at 80°) on a concentrated ether solution showed only one peak at 4.4 min. from air both before and after treatment with lithium aluminum hydride. Evaporation of the rest of the solvent gave a liquid residue (0.270 g.) whose infrared spectrum and n.m.r. spectrum<sup>14</sup> were identical with those of the starting diene.

**Reaction of *syn*-7-Norbornenol (V) with Lithium Aluminum Hydride.** Lithium aluminum hydride (0.1252 g., 3.3 mmoles) in 7.0 ml. of ether was treated with 0.1067 g. (0.97 mmole) of *syn*-7-norbornenol<sup>20</sup> dissolved in 4.0 ml. of ether. After 45 min. at room temperature a 2.0-ml. sample was removed and decomposed with water, the ether was decanted, and the sample was dried over anhydrous magnesium sulfate. Analysis by v.p.c. (5% polypropylene glycol on Chromosorb P at 80°) showed *only syn*-7-norbornenol (4.0 min. from air). The rest of the reaction mixture was stirred 17.5 hr. at room temperature. A 2.0-ml. sample was again analyzed by v.p.c., but this time no starting *syn* alcohol was present and only a peak corresponding to 7-norbornanol (VI) (10.6 min. from air) was present by v.p.c. analysis. The remainder of the reaction mixture was decomposed with wet sodium sulfate and worked up as described above. After evaporation of the ethyl ether, the solid remaining (0.0562 g.) was sublimed at 70° and 200 mm. to give material, m.p. 149–150° (lit.<sup>18</sup> m.p. 150–151°). The infrared spectrum (0.5% KBr pellet) of this solid was identical with that of 7-norbornanol formed from catalytic hydrogenation of 7-hydroxynorbornadiene.

**Reaction of *anti*-7-Norbornenol (II) with Lithium Aluminum Hydride.** Lithium aluminum hydride (0.1284 g., 3.38 mmoles), and 0.1088 g. (0.98 mmole) of *anti*-7-norbornenol<sup>13</sup> in 11 ml. of ether were stirred at room temperature. After 5 and 21.5 hr., 2.0-ml. samples were worked up as described for the *syn* alcohol and analyzed by v.p.c. Only *anti*-7-norbornenol was detected (4.4 min. from air); no 7-norbornanol (VI) was detected (10.6 min. from air). After 70 hr. v.p.c. again showed *no* reaction and the sublimed product (0.0588 g.) had an infrared spectrum identical with starting *anti*-7-norbornenol.

**Preparation of *exo,exo*-5,6-Dideuterio-*anti*-7-*t*-bu-**

**toxinorbornene (VII).** To 0.1748 g. (4.1 mmoles) of lithium aluminum deuteride (98%) was added 0.3238 g. (1.97 mmoles) of 7-*t*-butoxynorbornadiene in 7 ml. of dry tetrahydrofuran. The reaction mixture was stirred at reflux for 16.5 hr. Analysis of a sample decomposed with D<sub>2</sub>O showed, by vapor phase chromatography (Perkin-Elmer 2-m. "R" column at 126°), the reaction mixture to contain about 3% of reduced material (VII) (13.4 min. from air), with the remainder mostly 7-*t*-butoxynorbornadiene (18.1 min. from air). A trace of aluminum chloride was added to the above reaction mixture; after 7 and 24 hr. at reflux, v.p.c. showed 36.7 and 100% reaction, respectively. The reaction mixture was treated with 2.0 ml. of D<sub>2</sub>O at room temperature for 7 hr. with stirring. Methylene chloride and water were added to the reaction mixture and the methylene chloride then was filtered from the precipitate and dried over anhydrous magnesium sulfate. Evaporation of solvent on a rotary evaporator gave 169 mg. of material. The 13.4-min. v.p.c. peak was trapped on an analytical v.p.c. column for n.m.r. analysis. A series of electronic integrations gave the relative areas for compound VII as shown in Table II.

Table II

Assignment	TMS internal, c.p.s.	$\tau$	Calcd.	Found
Vinyl	355 (triplet)	5.92	2.00	2.03
Bridge	195 (broad singlet)	3.25	1.00	0.97
Bridgehead	142 (multiplet)	2.37	2.00	2.01
<i>exo</i>	...	...	0.00	0.15 ± 0.05
<i>endo</i>	51 (singlet)	0.85	2.00	2.10
Methyl (from O- <i>t</i> - Bu group)	67 (singlet)	1.12		

The n.m.r. spectrum (Figure 2) shows a singlet at 51 c.p.s.; the arguments for this spectrum strongly supporting structure VII are completely analogous to those given for IV. The assignment of *anti* configuration resides in the observation that the vinyl proton resonance at 355 c.p.s. approximates a triplet (*syn* bridge hydrogen) and *not* a doublet of triplets as would be anticipated for the *syn* isomer (*anti* bridge hydrogen).<sup>14,26</sup>

**Preparation of *anti*-7-Butoxynorbornene (VIII).** A mixture of 45 ml. of tetrahydrofuran, 1.26 g. (0.033 mole) of LiAlH<sub>4</sub>, and 2.50 g. (0.0152 mole) of 7-*t*-butoxynorbornadiene<sup>13</sup> was stirred at reflux overnight. Decomposition of the excess hydride and intermediates was accomplished by adding 1.3 ml. of H<sub>2</sub>O, 1.3 ml. of 3 *N* NaOH, and 3.8 ml. of water. A precipitate was formed on boiling. The solids were filtered, washed with pentane, and dissolved in NaOH solution, and the solution was extracted with pentane. The combined pentane extracts were washed with four 75-ml. portions of water and dried over anhydrous magnesium sulfate. Evaporation of the pentane on a

(26) As shown in ref. 14, the *anti* bridge hydrogen (*syn* isomer) splits the vinyl proton resonance into a doublet of triplets (doublet separation ~0.8 c.p.s.). We have prepared some *syn*-7-*t*-butoxynorbornene by catalytic hydrogenation of the diene (coupled with preparative gas chromatography) and indeed have observed this doublet of triplets characteristic of the *syn* isomers.<sup>14</sup> We will report on the stereochemistry of catalytic hydrogenations of the norbornadienyl system in a forthcoming publication.

rotary evaporator under vacuum left 2.49 g. of crude product (95% crude yield). V.p.c. on a 2-m. Perkin-Elmer "R" column at 126° indicated that of the four v.p.c. peaks 72.5% consisted of compound VIII (13.4 min. from air), leading to an over-all yield of VIII of 69%. The other v.p.c. peaks have not been identified. The *anti*-7-*t*-butoxynorbornene was purified by preparative gas chromatography using a 12 ft.  $\times$   $\frac{3}{8}$  in. Ucon nonpolar on acid-washed Chromosorb column at 132° with a 200 cc./min. helium flow. This material was further purified by trapping from a 2-m. Perkin-Elmer "R" column at 126°. The n.m.r. of this compound shows the vinyl triplet characteristic of *anti*-7-substituted norbornenes.

Anal. Calcd. for  $C_{11}H_{16}O$ : C, 79.46; H, 10.91. Found: C, 79.67; 79.64; H, 10.69, 10.43.

**Preparation of 7-*t*-Butoxynorbornane (IX).** Catalytic hydrogenation of 0.255 g. (1.54 mmoles) of *anti*-7-*t*-butoxynorbornene (VIII) in 5.0 ml. of ethanol on 10% palladium on carbon resulted in uptake of 35.4 ml. of hydrogen (after 1.5 hr.) at 767 mm. at 25° (95% of theory). The product (after filtration from catalyst and concentration on a rotary evaporator) weighed 0.129 g., and v.p.c. on a Perkin-Elmer "R" column at 126° showed only a single peak (15.7 min. from air). Distillation through a Kragen tube at 10 mm. (pot temperature 80°) gave a product free from vinyl hydrogen (n.m.r.) with a v.p.c. identical in retention time (15.7 min.) with the product obtained from catalytic hydrogenation of 7-*t*-butoxynorbornadiene.

Anal. Calcd. for  $C_{11}H_{20}O$ : C, 78.5; H, 11.98. Found: C, 78.33; H, 12.08.

**Preparation of *exo*-5-Deuterio-*anti*-7-*t*-butoxynorbornene (X).** A mixture of 0.1658 g. (4.36 mmoles) of  $LiAlH_4$  and 0.3158 g. (1.93 mmoles) of 7-*t*-butoxynorbornadiene in 7 ml. of tetrahydrofuran was stirred at reflux overnight. Excess hydride was decomposed with  $D_2O$  and the reaction mixture was worked up in the same manner as that used for compound VI. The crude yield was 0.231 g. Preparative gas chromatography was used to purify compound X, using the same conditions used with compound VIII. N.m.r. analysis of X for area integration was done by assuming the sum of the vinyl, bridge, and bridgehead hydrogens is 5.00. On this assumption there are 1.21 *exo* hydrogens and 2.04 *endo* hydrogens. Thus compound X is at least 69.5% monodeuterated in the *exo* position.

**Calculation of Internuclear Distances.** Wilcox's method and model<sup>23</sup> of bicyclo[2.2.1]heptane was used for calculation of internuclear distances between the C-2 and C-7 positions. The coordinates of C-2 and

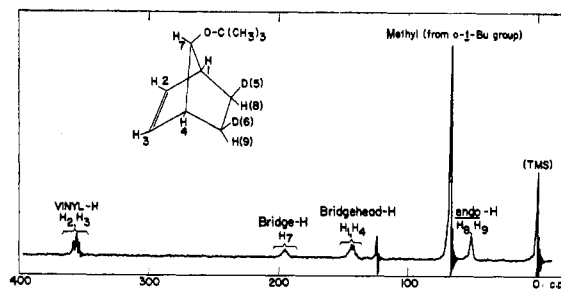


Figure 2. N.m.r. spectrum of *exo,exo*-5,6-dideuterio-*anti*-7-*t*-butoxynorbornene (VII).

C-7 from Wilcox's work are shown in Table III. Similarly, the unit vectors for an *exo* atom at C-2 (2u) and an atom to the right on C-7 (7r) are shown in Table IV. Using a C-H bond distance of 1.09 Å.<sup>24</sup> we could get coordinates of an *exo* hydrogen at C-2; calling this the  $x_2, y_2, z_2$  coordinate, we obtained this coordinate in the following manner:  $x_2 = 0.770 + 0.349 \times 1.09 = 1.150$ ,  $y_2 = 1.217 + 0.842 \times 1.09 = 2.135$ , and  $z_2 = -0.868 + 0.414 \times 1.09 = -0.417$ .

Table III

	x	y	z
C-2	0.770	1.217	-0.868
C-7	0.000	0.000	1.032

Table IV

	$i(x)$	$j(y)$	$k(z)$
2u	0.349	0.842	0.414
7r	0.000	0.824	0.566

Similarly, using a C-O bond distance of 1.43 Å.<sup>24</sup> we were able to determine the coordinates of an oxygen atom at C-7 (7r) to the right ( $x_1, y_1, z_1$ ). We were then able to calculate the distance ( $d$ ) between the oxygen at C-7 and the *exo* hydrogen at C-2. The

$$d = [(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2]^{1/2}$$

calculations for the *exo* aluminum (3u) and bridge oxygen (7r) were done in an analogous manner.

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