lution was then added dropwise to a suspension of 0.5 g of $LiAlH_4$ in 50 mL of THF contained in a 100-mL flask. Vigorous stirring and cooling (0 °C) were maintained throughout the addition. The resulting mixture was refluxed for 24 h. The residual $LiAlH_4$ was cautiously destroyed and the reaction mixture poured into ice water and extracted with three 50-mL portions of ether. The combined extracts were dried ($MgSO_4$) and concentrated on a steam bath. GLC analysis on a 24 ft × 0.125 in. Hi-Pak SE-30 indicated two components in a 5:95 ratio (in order of increasing retention times). These peaks had identical retention times with those of the two components obtained from the reduction of camphene with hydrogen, the observed ratio in this instance being (in order of increasing retention times) 28:72. The latter peak to elute is, therefore, assigned as *endo*-2,2,3-trimethylnorbornane (**15**), and the former peak as *exo*-2,2,3-trimethylnorbornane.

Preparation of Authentic *exo*-1 and *endo*-1. *exo*-2-Norbornanecarboxylic acid[16] was converted to the corresponding acid chloride [bp 80–81 °C (10 Torr), lit.[17] 84 °C (15 Torr)] by treatment with thionyl chloride.

exo-2-Norbornanecarboxylic acid chloride (12.2 g, 77.0 mmol) was placed in a 1-L, three-necked, flame-dried flask equipped with an addition funnel, reflux condenser, and Teflon-coated magnetic stirrer bar. Dry ether (200 mL) was added. The addition funnel was charged with 200 mL (0.260 mol) of a solution of methyllithium in ether, which was added under a static head of nitrogen at a rate sufficient to maintain a gentle reflux. At the completion of addition the resulting mixture was refluxed for 45 min, then cautiously hydrolyzed with 50 mL of water followed by 50 mL of 6 M HCl. The layers were separated, and the aqueous layer extracted with three 125-mL portions of ether. The combined organic layers were washed with 250 mL of a saturated aqueous solution of $NaHCO_3$, dried ($MgSO_4$), and concentrated under reduced pressure to give 12.4 g of a dark brown, viscous oil. This material was subjected to chromatography through a 2.3 × 48.5 cm column of alumina (neutral, Fischer chromatography grade). Elution was achieved by treatment with 200 mL of petroleum ether followed by elution with 200 mL of a 1:9 (v/v) mixture of diethyl ether–petroleum ether and finally by 200 mL of diethyl ether. The material of interest eluted with the diethyl ether containing fractions. These were collected and concentrated under reduced pressure. The residual viscous oil (5.6 g) was distilled [bp 93–95 °C (13 Torr)] to give 3.8 g (32%) of material with the empirical formula $C_{10}H_{18}O$: IR (neat) 3450 (br, OH), 2940 cm^{-1}.

The ^1H NMR spectrum of this material in CCl_4, observed in the presence of the shift-inducing reagent $Eu(fod)_3$, revealed two isomers, one of which moved considerably more rapidly downfield than the other upon sequential addition of $Eu(fod)_3$. A comparison of these spectra with that of the *endo*-1 isolated from the reaction of norbornylmagnesium bromide with acetone established that one component was in fact *endo*-1, which we conclude formed as a result of epimerization in the course of the reaction of *exo*-2-norbornanecarboxylic acid chloride with methyllithium. The remaining component is, by exclusion, assigned the structure *exo*-1. Component analysis can also be achieved on 24 ft × 0.125 in. Hi-Pak Carbowax column (Hewlett-Packard). Under these conditions the endo isomer elutes first.

Registry No.—*endo*-1, 61723-39-5; *exo*-1, 61723-40-8; *endo*-3, 13058-87-2; **4**, 61723-41-9; **7**, 640-54-0; **8**, 23887-56-1; *endo*-**9**, 61723-42-0; *exo*-**9**, 61723-43-1; **11**, 4696-14-4; **12**, 28871-71-8; **12a**, 18310-60-6; **13**, 1873-09-2; **14**, 18310-62-8; **14** ditosylate, 61723-44-2; *p*-toluenesulfonyl chloride, 98-59-9; acetone, 67-64-1; *exo*-2-norbornanecarboxylic acid chloride, 1195-11-5.

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Reduction of Some 7-Norbornenols with Lithium Aluminum Hydride–Aluminum Chloride

Donald C. Kleinfelter* and George Sanzero

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

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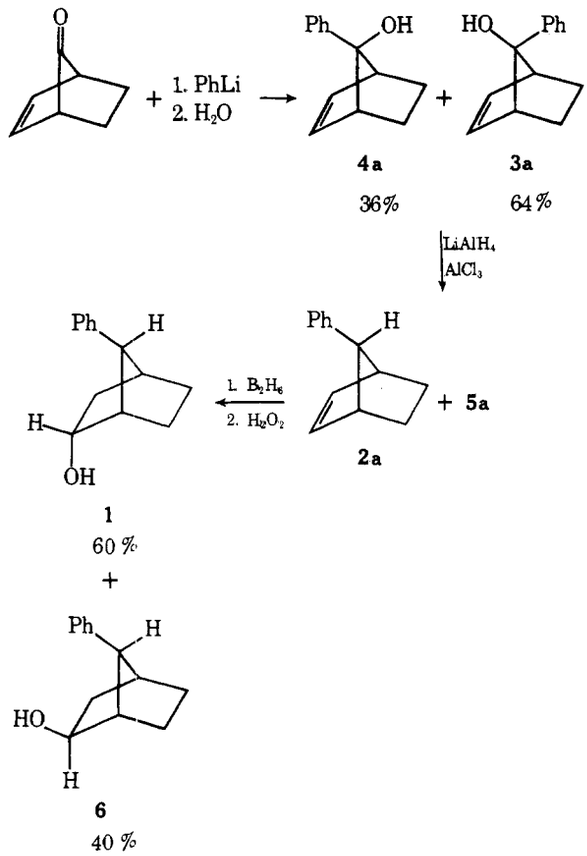
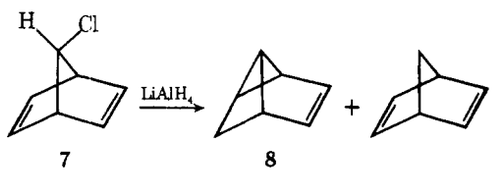
Reduction of a mixture of 7-phenyl-7-norbornenols with $LiAlH_4$–$AlCl_3$ gave 7-*syn*-phenylnorbornene (70%) and 7-phenyltricyclo[4.1.0.$0^{3,7}$]heptane (30%). Tricyclic hydrocarbon with deuterium incorporation exclusively at the endo-2 position was formed when the alcohol mixture reacted with $LiAlD_4$–$AlCl_3$. Reduction of a 7-*p*-anisyl-7-norbornenol mixture afforded 7-*syn*-*p*-anisylnorbornene (62%), 7-*anti*-*p*-anisylnorbornene (32%), and 7-*p*-anisyltricyclo[4.1.0.$0^{3,7}$]heptane (6%). Reduction of 7-*syn*-norbornenol proceeded to 7-norbornanol, whereas 7-*anti*-norbornenol was unaffected by the reduction medium.

In the course of our research on arylnorbornyl derivatives[1] a route to the alcohol 7-*syn*-phenyl-2-*endo*-norbornanol (**1**) was desired. A possible precursor to **1** is the alkene, 7-*syn*-phenylnorbornene (**2a**). Phenyllithium addition to 7-norbornenone gave a 64% *anti*-phenyl:36% *syn*-phenyl ratio of the unsaturated alcohols, **3a** and **4a**, respectively. Treat-

ment of this alcohol mixture with $LiAlH_4$–$AlCl_3$ in ether by the method of Nystrom and Berger[2] afforded the desired alkene (70%) and an isomeric hydrocarbon, **5a**, whose NMR spectrum showed it to be devoid of unsaturation. Hydroboration of this hydrocarbon mixture gave **1**, its epimeric alcohol (**6**), and unreacted **5a**.

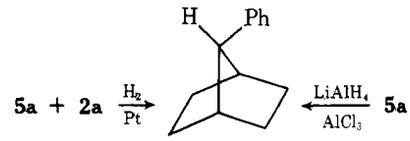


Story[3] found that lithium aluminum hydride reduction of 7-chloronorbornadiene (**7**) produced tricyclo[4.1.0.0^{3,7}]heptene-4 (**8**) as one of the reaction products. He proposed that



this tricyclic hydrocarbon resulted from double bond participation. Aluminum hydride coordination with the chlorine should provide a driving force for ionization, which could in turn be assisted by the proper double bond to give a nonclassical intermediate. Because all prior reactions of 7-substituted norbornadienes involved equilibrium processes, no rearrangement products were observed. However, a hydride reduction is presumably irreversible and attack at any carbon atom other than C-7 will afford a rearrangement product. Subsequent to Story's work other investigators have performed reductions upon 2- and 7-substituted norbornenes and have obtained analogous tricyclic products.[4]

Structural Assignment of 5a. Utilizing the aforementioned precedents, it was presumed that $LiAlH_4$–$AlCl_3$ reduction of **3a** and **4a** led to the tricyclic hydrocarbon 7-phenyltricyclo[4.1.0.0^{3,7}]heptane as the minor product (30%). Hydrogenations of **8** and tricyclo[4.1.0.0^{3,7}]heptane are known to give norbornane as the major product. Similarly, both platinum oxide catalyzed hydrogenation of **5a** and prolonged exposure of **5a** to the $LiAlH_4$–$AlCl_3$ reduction medium gave 7-phenylnorbornane (**9**).



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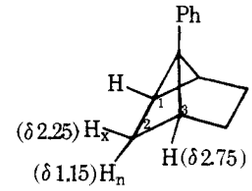
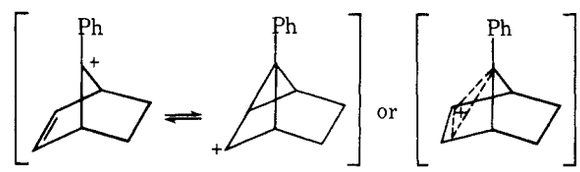
Final confirmation of the structure of **5a** was obtained by detailed analysis of its NMR spectrum. The endo-2 proton of **5a** appears at δ 1.15 as a pair of doublets with $J_{2n,2x}$ = 9.5 and



5a

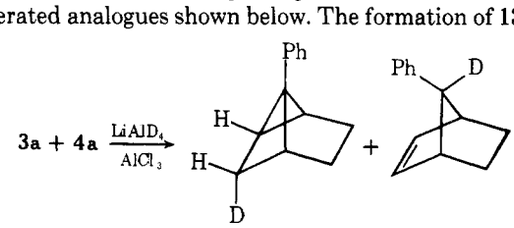
$J_{2n,3}$ = 0.8 Hz, and the exo-2 proton comes at δ 2.75 as a multiplet with $J_{1,2x}$ = 3.5, $J_{2x,3}$ = 7.5 Hz, in addition to the geminal 2x, 2n coupling. A broad doublet at δ 2.75 is assigned to the 3 proton. Spin decoupling experiments were carried out to substantiate these spectral assignments. Irradiation at δ 2.75 removed the small vicinal coupling of 0.8 Hz due to $J_{2n,3}$. In addition, the signal at δ 2.25 collapsed to a doublet pair because the coupling of H-3 with H-2x was removed. Irradiation at δ 1.15 caused the signal at δ 2.25 to collapse to a doublet pair and simplified the broad doublet at δ 2.75 to a pair of triplets, due to $J_{3,4x} = J_{3,4n}$ = 2.3 Hz and $J_{2n,3}$ = 7.5 Hz. Finally, irradiation at δ 2.25 caused a collapse of the endo-2 proton signal at δ 1.15 to a narrow doublet ($J_{2n,3}$ = 0.8 Hz). The coupling constants, $J_{1,2x}$ and $J_{2x,3}$, obtained in this research are similar to those reported by others for analogous tricyclenes.[5]

Mechanistic Considerations. As mentioned earlier in this paper, reduction of both **3a** and **4a** gave the same products. The intermediates presumably formed from these alcohols that could explain how these products were obtained are the equilibrating classical ions, **10** and **11**, and the bridged ion **12**.



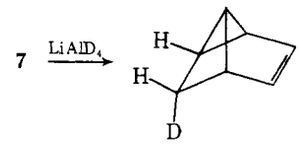
10 **11** **12**

In either case, anti-7 hydride attack and endo-2 hydride attack would give the products **2** and **5a**, respectively. To substantiate further the NMR proton assignments of **5a** and to determine the mode of hydride attack at C-2, a mixture of **3a** and **4a** was reduced with $LiAlD_4$–$AlCl_3$. The reaction afforded the deuterated analogues shown below. The formation of **13** with



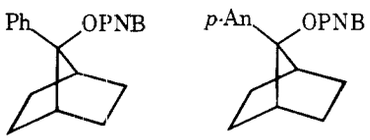
13

deuterium incorporation exclusively at the endo-2 position is analogous to the results of Story[3] shown in the following equation.

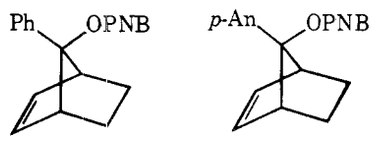


The NMR spectrum of the deuterated tricyclic hydrocarbon (**13**) showed that the absorption at δ 1.15 in **5a** due to the endo-2 proton had vanished.

Driving Force for Double Bond Participation. Relative rate comparisons have served as a means of measuring the amount of double bond participation in solvolysis reactions. Winstein[6] first noted that 7-*anti*-norbornenyl tosylate has a rate which is ca. 10^{11} times faster than that of the saturated analogue, 7-norbornyl tosylate. Using a series of tertiary *p*-nitrobenzoates, Gassman[7] showed that the extent of double bond participation depends on the nature of the nonsolvolyzing 7 substituent. A comparison of the relative solvolysis rates of the 7-aryl-substituted *p*-nitrobenzoates (Ar = Ph vs. Ar = *p*-An) showed a markedly smaller difference, 1 vs. 121, in the unsaturated series as compared with that of the saturated series, 1 vs. 1500.



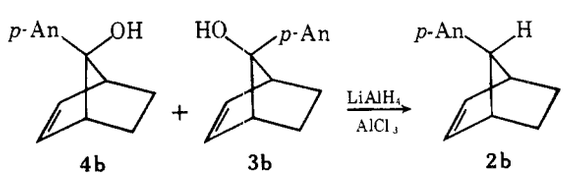
$k_{rel} = 1.0$ $k_{rel} = 1500$



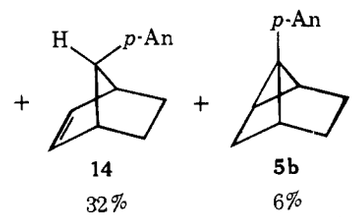
$k_{rel} = 1.0$ $k_{rel} = 121$

The relatively smaller rate increase observed for the unsaturated series suggests that a smaller driving force for double bond participation operates in the *p*-anisyl case; i.e., the *p*-anisyl substituent stabilizes the tertiary cationic intermediate sufficiently so that less assistance from the π bond is required.[8] Gassman[9] further substantiated the difference in degree of double bond participation from his analysis of the products of the solvolysis reactions. The cation formed from the 7-phenylnorbornenyl *p*-nitrobenzoate suffered attack by solvent exclusively from the anti direction to give 100% of the 7-*syn*-phenyl product. However, the cation formed from the 7-*p*-anisylnorbornenyl derivative gave 8% of solvent attack from the syn direction to give 7-*anti*-*p*-anisyl product. This loss of stereospecificity in the solvolysis products was attributed to some classical ion formation in the *p*-anisyl case, indicative of a smaller driving force for double bond participation.

With Gassman's data as a precedent, we decided to reduce the 7-*p*-anisyl-7-norbornenols with $LiAlH_4$–$AlCl_3$ to determine whether the reduction products would indicate less double bond assistance than the phenyl analogues. Reduction was carried out on a 24% *anti*-*p*-anisyl (**3b**): 76% *syn*-*p*-anisyl (**4b**) mixture of the alcohols. The results of this reaction are summarized below.



4b 76% **3b** 24% **2b** 62%



14 32% **5b** 6%

Integration of the δ 5.80 and 6.10 signals ascribed to the *syn*-*p*-anisyl and *anti*-*p*-anisyl substituted alkenes, **2b** and **14**, respectively, in the NMR spectrum of the products gave the indicated percentages. The approximate 6% of 7-*p*-anisyltricyclo[4.1.0.$0^{3,7}$]heptane (**5b**) was determined after hydroboration of **2b** and **14**. The formation of product (32%) of syn hydride attack of the 7-arylnorbornenyl cation demonstrates a decrease in the necessity for π bond stabilization of the cation, which is more dramatic than that displayed by Gassman's *p*-nitrobenzoates. The fivefold reduction (6% vs. 30%) in the amount of tricyclic hydrocarbon formed in the *p*-anisyl system serves as just another measure of this decrease.

Because our work up to this point involved only tertiary systems, it was desired to extend the reduction reaction to secondary systems as well. Consequently, both 7-*syn*-norbornenol and 7-*anti*-norbornenol were treated with $LiAlH_4$–$AlCl_3$. Reduction of 7-*syn*-norbornenol gave neither norbornene nor tricyclo[4.1.0.$0^{3,7}$]heptane but only 7-norbornanol. Evidently, the $LiAlH_4$ complexes with the hydroxyl oxygen, a process that facilitates reduction of the double bond. This result is analogous to that of Franzus,[11] who reported that 7-*syn*-norbornenol is reduced by $LiAlH_4$ in ether solvent to 7-norbornanol. If double bond participation were possible in reduction of the secondary systems, 7-*anti*-norbornenol might be the precursor of choice from which to expect the formation of norbornene and tricyclo[4.1.0.$0^{3,7}$]heptane. However, treatment of 7-*anti*-norbornenol with $LiAlH_4$–$AlCl_3$ resulted in essentially a quantitative recovery of starting alcohol. Evidently the reaction medium is not conducive to the formation of carbonium ions from secondary 7-norbornenols.

Experimental Section

Melting points were determined in soft capillary tubes using a Hoover capillary melting point apparatus (Arthur H. Thomas Co., Philadelphia, Pa.) and are uncorrected. NMR spectra were obtained with a Varian A-60 or a Varian HA-100 spectrometer. Infrared spectra in the 3-μ region were recorded on a Perkin-Elmer Model 257 grating spectrometer calibrated against polystyrene standard. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E recording mass spectrometer. The microanalysis was carried out by F. B. Strauss Microanalytical Laboratory, Oxford, England. All ether and ligroin solutions of products were dried over anhydrous sodium sulfate prior to removal of solvent. Ligroin was distilled over potassium permanganate and had bp 40–55 °C.

7-*anti*-Phenyl-7-norbornenol (3a) and 7-*syn*-Phenyl-7-norbornenol (4a). To an ether solution of phenyllithium, prepared from lithium wire (0.98 g, 0.14 mol) and bromobenzene (10.9 g, 0.0694 mol), was added an ether solution of 7-norbornenone (5.00 g, 0.0463 mol), prepared by the method of Gassman and Pape.[12] Reflux was maintained for 3 h, water was added, and the ether solution was evaporated. Distillation of the residual yellow oil in vacuo gave 6.91 g (80.2%) of a colorless oil, bp 105–110 °C (0.10 mm). The integrated NMR spectrum in the region of the signals at δ 6.10 and 5.80 indicated the mixture to be composed of 64% **3a** and 36% **4a**.

Partial separation of **3a** from the mixture could be obtained by crystallization of **3a** from ligroin and by chromatography over F-20 alumina, **3a** being eluted first with ligroin–ether eluent. Pure **3a** gave mp 60–61 °C. The IR spectrum of **3a** (CCl_4) showed O–H absorption at 3619 (free) and 3563 cm^{-1} (O–H—π bond), whereas the spectrum of **4a**, an oil, showed only the free O–H absorption at 3619 cm^{-1}. (See footnote 13.)

7-*syn*-Phenylnorbornene (2a) and 7-Phenyltricyclo[4.1.0.$0^{3,7}$]heptane (5a). An ether solution of $AlCl_3$ (11.7 g, 0.0877 mol) was added to a stirred solution of the 7-phenyl-7-norbornenols (15.0 g, 0.0805 mol). The reaction solution turned a deep wine red color; this solution was added rapidly to an ether solution of $AlCl_3$ (11.7 g, 0.0877 mol) which had been added dropwise into $LiAlH_4$ (8.1 g, 0.17 mol). After about one-half of the wine-colored solution had been added, salts began to precipitate and the color disappeared. The resulting mixture was refluxed for 12 h and cooled, after which water was added cautiously to hydrolyze the addition compound and to destroy excess $AlCl_3$ and $LiAlH_4$. The ether layer was decanted, and the aqueous layer was extracted with ether. The combined ether layers were flash evaporated, leaving a light yellow oil, 13.1 g (96.5%) of a

70%:30% mixture of **2a** and **5a**. (Distillation in vacuo is accomplished with partial decomposition.) In the NMR spectrum (CCl_4), the absorptions at δ 5.80 (2 olefin H), 3.00 (H-1 and H-4), and 2.82 (H-7a) are assigned to **2a**. The signal at δ 2.75, overlapped by the H-7a signal of **2a**, is assigned to **5a**. Integration of these signals allowed the indicated percentages of **2a** and **5a** to be calculated.

The mixture of **2a** and **5a** was hydroborated by the method of Brown and Zweifel.[14] (The experimental details concerning this reaction and the isolation of 7-*syn*-phenyl-2-*exo*-norbornanol (**6**) and 7-*syn*-phenyl-2-*endo*-norbornanol (**1**) have been reported elsewhere.[15]) Chromatography on F-20 alumina with ligroin as eluent gave pure **5a** before any of the alcohols were eluted with ligroin–ether mixtures. Pertinent NMR assignments of **5a** are discussed in the text. The mass spectrum showed the parent peak at *m/e* 170, rel intensity 11.0 compared to the base peak (100.0) at *m/e* 142. Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.58; H, 8.11.

7-Phenylnorbornane (9). A mixture of **2a** and **5a** (1.0 g, 0.0059 mol) in 15 mL of 95% ethanol and 22 mg of platinum oxide was subjected to a hydrogen pressure of 40 psi in a Parr bomb apparatus for 1 h. Filtration of the catalyst and flash evaporation of the solvent left pure **9**, 0.58 g (57%), as an oil: NMR (CCl_4) δ 7.18 (5 H, Ar H's), 2.80 (1 H, H-7), 2.50 (2 H, H-1 and H-4), 1.05–1.75 (8 H, exo and endo protons); mass spectrum showed the parent peak at *m/e* 172, rel intensity 73.9 compared to the base peak (100.0) at *m/e* 104. Hydrogenation of a sample of pure **5a** by the same procedure gave product with an identical NMR spectrum. These NMR spectra were identical with that taken on the product obtained from catalytic hydrogenation of 7-phenylnorbornadiene (Frinton Laboratories).

A pure sample of **5a** was refluxed with an ether solution of $AlCl_3$ and $LiAlH_4$ for 21 h. Hydrolysis and workup as described under the preparation of **2a** and **5a** gave a mixture of unreacted **5a** and **9** (δ 2.80 signal became evident). Repetition of this experiment caused a further increase in the δ 2.80 signal.

2-*endo*-Deuterio-7-phenyltricyclo[4.1.0.0^{3,7}]heptane (13) and 7-*anti*-Deuterio-7-*syn*-phenylnorbornene. A mixture of **3a** and **4a** (3.01 g, 0.0162 mol) was reduced with 2.34 g of $AlCl_3$ and 1.70 g of $LiAlD_4$ by a procedure similar to that described for the preparation of **2a** and **5a**. Workup gave 2.72 g (97.5%) of an approximate 69:31 mixture of 7-*anti*-deuterio-7-*syn*-phenylnorbornene and **13**, as obtained by NMR analysis. No signal at δ 2.80 was observed, indicative of deuterium incorporation at the 7-anti position.

The mixture of 7-*anti*-deuterio-7-*syn*-phenylnorbornene and **13** was hydroborated as described previously.[15] From the mixture (5.58 g, 0.0324 mol), 1.55 g of $NaBH_4$, and 5.60 g of boron trifluoride etherate there was obtained 5.40 g of a mixture of **13** and the 7-*anti*-deuterio analogues of **1** and **6**. Alumina chromatography yielded a pure sample of **13**. The NMR spectrum showed no signal at δ 1.15, indicative of deuterium incorporation at the endo-2 position.

7-*anti*-*p*-Anisyl-7-norbornenol (3b) and 7-*syn*-*p*-Anisyl-7-norbornenol (4b). To an ether solution of *p*-anisylmagnesium bromide, prepared from magnesium turnings (0.35 g, 0.014 mol) and *p*-bromoanisole (2.6 g, 0.014 mol), was added an ether solution of 7-norbornenone (1.0 g, 0.0092 mol). Reflux was maintained for 2 h, water was added, and the ether solution was flash evaporated, leaving 1.2 g of impure yellow oil. The integrated NMR spectrum in the region of the signals at δ 6.10 and 5.80 indicated the mixture to be composed of 24% **3b** and 76% **4b**.[15] Chromatography on F-20 alumina gave 0.89 g (45%) of a pure mixture of **3b** and **4b**. No complete separation of **3b** or **4b** from the mixture was attained.

7-*syn*-*p*-Anisylnorbornene (2b), 7-*anti*-*p*-Anisylnorbornene (14), and 7-*p*-Anisyltricyclo[4.1.0.0^{3,7}]heptane (5b). The reaction was carried out in a manner similar to that used for the preparation of **2a** and **5a**. From the 7-*p*-anisyl-7-norbornenols (0.89 g, 0.0041 mol), 1.40 g of $AlCl_3$, and 0.48 g of $LiAlH_4$ there was obtained 0.54 g (65%) of a mixture of **2b**, **14**, and **5b**. The ratio of **2b** to **14** was obtained by integration of the signals at δ 5.80 and 6.10 in the NMR spectrum. The amount of **5b** could not be determined accurately at this point because apparently only a very small amount was present.

Hydroboration of this mixture using 0.18 g of $NaBH_4$ and 0.55 mL of boron trifluoride etherate gave an oil which was chromatographed on F-20 alumina. With ligroin as eluent there was obtained 0.028 g of a mixture of 7-*p*-anisylnorbornane and **5b**. Because the 7-*p*-anisylnorbornane is presumably formed from **5b** under the reaction conditions, the total weight was attributed to **5b**. The percentages of **2b**, **14**, and **5b** were then calculated to be ca. 62, 32, and 6%, respectively.

Reduction of 7-*syn*-Norbornenol to 7-Norbornanol. The reaction was carried out in a manner similar to that used for the preparation of **2a** and **5a**. From 7-*syn*-norbornenol (5.0 g, 0.045 mol), mp 79–80 °C, prepared by the method of Gerteisen,[17] 13.4 g of $AlCl_3$, and 4.6 g of $LiAlH_4$ there was obtained 2.8 g (56%) of 7-norbornanol, mp 150–151 °C (lit.[11] mp 149–150 °C). The NMR spectrum was identical with that obtained from the platinum oxide catalyzed hydrogenation of 7-*syn*-norbornenol.

Attempted Reduction of 7-*anti*-Norbornenol. Following the procedure used to reduce 7-*syn*-norbornenol to 7-norbornanol, an ether solution of 7-*anti*-norbornenol (2.00 g, 0.0182 mol), mp 115–116 °C (lit.[18] mp 117–118 °C), 3.20 g of $AlCl_3$, and 1.10 g of $LiAlH_4$ was refluxed for 12 h. After the usual workup, 1.53 g (76.5%) of 7-*anti*-norbornenol was recovered. No other compound was found.

Registry No.—**2a**, 29266-12-4; **3a**, 34098-60-7; **3b**, 13143-81-2; **4a**, 34098-58-3; **4b**, 13118-72-4; **5a**, 61675-24-9; **9**, 24892-78-2; phenyllithium, 591-51-5; 7-norbornenone, 694-98-4; $AlCl_3$, 7446-70-0; $LiAlH_4$, 16853-85-3; *p*-anisyl bromide, 104-92-7.

References and Notes

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(4) For example, see the following: (a) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963); (b) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966); (c) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966); (d) J. J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Commun.*, 1202 (1967).
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(8) Another way of presenting this difference is by comparison of the relative rates of solvolysis of the saturated phenyl compound (rel rate = 1.0) vs. the unsaturated analogue and contrasting said comparison with that obtained from the saturated *p*-anisyl compound (rel rate = 1.0) vs. its unsaturated analogue. The 7-phenylnorbornenyl *p*-nitrobenzoate reacts 41 times faster than the saturated 7-phenylnorbornyl derivative, whereas the *p*-anisyl compounds display only an increase of unsaturated compound relative to saturated derivative of 3.4.
(9) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **92**, 2549 (1970).
(10) A referee has suggested that **3b** and **4b** (as well as **3a** and **4a**) may not yield the same intermediate (or intermediates). If such were to be the case, then **3b** (and **3a**) must be reacting via a backside hydride displacement. Although our results do not exclude such a possibility, we feel that such a displacement at a tertiary center is unlikely, especially in view of the fact that the secondary alcohol, 7-*syn*-norbornenol, underwent no such displacement reaction.
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(15) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, T. E. Dye, and J. H. Long, Jr., *J. Org. Chem.*, **38**, 4127 (1973).
(16) Reaction of phenylmagnesium bromide with 7-norbornenone gave a 24%:76% mixture of **3a** to **4a**.
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