port temperature of 130 °C. The analysis was carried out using a 19 ft × $^1/_8$ in. $AgNO_3$–ethylene glycol on 80/100 Chromosorb P column prepared by a modification of the method of Bednas and Russel.[7] The modifications include (a) a 19 ft instead of an 11 ft column, (b) smaller mesh size for the support, and (c) column packing under 80 psi of nitrogen. The column was operated at 40 °C under a flow of 25 mL/min of N_2 and gave clean separation of all of the isomers.[14] Confirmation of the isomers was done by comparison with authentic samples.[8]

(14) In our hands, the column had a useful lifetime of about 2 weeks under constant use before the quality of separation began to deteriorate.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A generous loan of platinum salts by the Matthey-Bishop Company is also gratefully acknowledged.

Registry No. Methylcyclopropane, 594-11-6; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; *trans*-1,2-dimethylcyclopropane, 2402-06-4; 1-pentene, 109-67-1; *cis*-2-pentene, 627-20-3; 2-methyl-1-butene, 563-46-2; 3-methyl-1-butene, 563-45-1; 1,1-dimethylcyclopropane, 1630-94-0; *cis*-1,2-dimethylcyclopropane, 930-18-7; Zeise's dimer, 12073-36-8.

Competitive Exo Hydroboration of *syn*-7-Arylnorbornenes[1]

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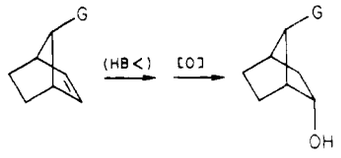
Hydroboration–oxidation of a series of *syn*-7-arylnorbornenes (**2**-Ar) produces an unexpectedly large percentage of exo alcohol (**3x**-Ar, 42–60%, depending upon the aryl group). Substituent effects [*p*-OCH_3, *p*-CH_3, *p*-Cl, *o*-CH_3, 2,4,6-$(CH_3)_3$] are minor. Other addition reactions on *syn*-7-phenylnorbornene itself (**2**-Ph) proceed essentially as expected for a sterically hindered norbornene (oxymercuration, diimide addition, thiophenol addition). The results may be rationalized, when contrasted to those reported for apobornene (7,7-dimethylnorbornene), in terms of a smaller steric size for phenyl relative to methyl, or preferably in terms of π complexation of borane by the aryl group. The latter rationalization appears to be more consonant with the unique behavior of hydroboration compared with the other additions studied.

Considerable documentation supports the contention that addition reactions onto norbornenes are affected both in rate and orientation by the presence of bridge (syn-7) substituents.[2] Groups studied include CH_3,[3] Br,[4] NR_3^+–BH_3^-,[5] and *t*-C_4H_9,[6] and the reactions studied vary from small ring transition state processes (e.g., epoxidation, carbene addition, Ag^+ complexation) to larger ring cases (e.g., 1,3-dipolar cycloaddition, diimide addition) and even noncyclic transition state processes (e.g., CF_3COOH addition, PhSH addition).[2] One of the conclusions reached from these studies was that bulky groups at the syn-7 position force those addends using small ring transition states to add endo to norbornenes or perhaps not to add at all. Larger transition state cycles or stepwise processes were less affected.[7]

Among the processes that added evidence for the mechanistic conclusion above was hydroboration, a process proceeding via a small ring transition state.[8] As shown in eq 1, increased bulk at syn-7 led to more endo hydroboration, as measured by oxidation of the intermediate organoborane(s).



(1)

G = H	0.5% (ref 9)
G = CH_3[3]	~78% (ref 9)
G = *t*-C_4H_9[10]	~100% (ref 6)

During another investigation,[11] a result was obtained

(1) Taken from the M.S. Thesis of V.P.N., 1978.

(2) (a) H. C. Brown, J. H. Kawakami, and K.-T. Liu, *J. Am. Chem. Soc.*, **95**, 2209 (1973); (b) F. Freeman, *Chem. Rev.*, **75**, 439 (1975).

(3) Brown and co-workers[2a] have studied the 7,7-dimethyl grouping extensively, emphasizing the presence of the syn-7 methyl. We know of no study using *syn*-7-methylnorbornene itself. Throughout this paper no distinction is made between the 7,7-dimethyl group's *actual* effect and the *syn*-7 methyl's *putative* effect.

(4) Additions to *anti*-7-bromobenzonorbornadiene (contains a *syn*-7-bromonorbornene moiety) were studied by R. Caple and C. S. Ilenda, *J. Am. Chem. Soc.*, **92**, 3817 (1970).

(5) P. S. Anderson, *Tetrahedron Lett.*, 1141 (1976).

(6) W. C. Baird, Jr., and J. H. Surridge, *J. Org. Chem.*, **37**, 1182 (1972).

(7) For an excellent review of this and other such criteria relating addition processes and their attendant activated complexes, see ref 2b.

(8) Uniform agreement on the transition state for hydroboration is not at hand. A four-membered ring state, using concerted bond formation and cleavage, appears to be favored, although in its usual depiction it would be forbidden by orbital symmetry considerations. Another concerted mode is, however, allowed. Moreover, a π complex preceding this state may occur. For a discussion, see D. J. Pasto, B. Lepeska, and T.-C. Cheng, *J. Am. Chem. Soc.*, **94**, 6083 (1972), and A. Streitwieser, Jr., L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967). Steric effects are clearly observable in hydroboration, but electronic effects are less defined. Correlation with σ^+ (ρ = –0.7) has been claimed in the hydroboration of styrenes by H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, **88**, 5851 (1966), while no correlation with any single Hammett-type parameter has been found for essentially the same process by J. Klein, E. Dunkelblum, and M. A. Wolff, *J. Organomet. Chem.*, **7**, 377 (1967).

(9) H. C. Brown and J. H. Kawakami, *J. Am. Chem., Soc.*, **92**, 1990 (1970).

(10) 9-BBN was used here (20 h, 25 °C). Starting material was recovered (25%) and the yield based on consumed olefin was 54%. The reaction with borane appears to be unreported.

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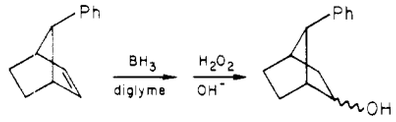
that appeared to be inconsistent with this trend. The alcohols obtained by hydroboration–oxidation of syn-7-phenylnorbornene were predominantly exo (eq 2). Kle-



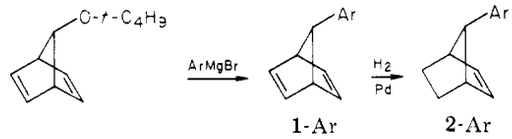
(2)

exo > endo

infelter and co-workers independently and concurrently found the same result and commented briefly upon the unusual product composition.[12] Because intuitively a phenyl group should be "larger" than a methyl group, the preponderance of exo alcohol product deserved investigation. Moreover, a look at processes other than hydroboration also was warranted to establish whether hydroboration was unusual for some reason. The present report details the results of such investigations.

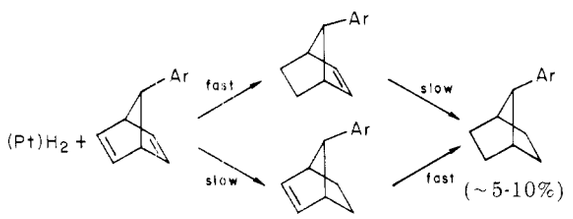
Results

Hydroboration–Oxidation. A series of *syn*-7-arylnorbornenes (**2**-Ar) was prepared as shown in eq 3. Story's



(3)

procedure[13] for the synthesis of 7-phenylnorbornadiene (**1**-Ph) was appropriately modified by choice of the suitable Grignard reagent. The final hydrogenation step[11] led primarily to syn-7-substituted products, an obvious example of the relative steric inaccessibility of the syn double bond toward reduction. Nevertheless, some reduction of the syn double bond did occur. The *anti*-7-arylnorbornene so formed was not detected, however, because it was reduced rapidly to the saturated 7-arylnorbornane (eq 4).



(4)

Routinely, about 10% overreduction to the norbornane was carried out to ensure the absence of starting diene. Such absence was important because purification of the *syn*-7-arylnorbornenes **2**-Ar by distillation was complicated if starting diene was present, due to the isomerization of the latter to arylcycloheptatrienes.[14] Additionally, the saturated contaminant was of course inert to hydroboration, and traces of it present in **2** were tolerable, a situation not true for traces of **1**-Ar or the arylcycloheptatrienes.

The ultraviolet spectra of the series **2**-Ar indicated that a blue shift was observed generally for the series relative to the parent arenes ArH. However, the expected red shift

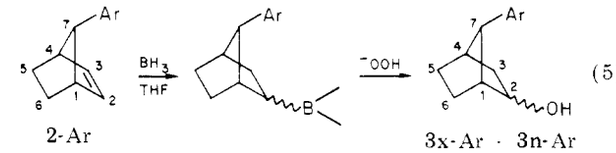
Table I. Hydroboration–Oxidation of *syn*-7-Arylnorbornenes[a]

norbornene 2-Ar		mmol	% exo alcohol
Ar	mmol	of BH_3	3-Ar
p-anisyl (2-*p*-An)	2.3	1.4	60
phenyl (2-Ph)	1.5	0.9	57
	1.6	1.1	56
	0.83	1.8	55
	4.3	3.3	55
	9.92	2.5	52[b]
	~147	~60	60[c]
p-tolyl (2-*p*-Tol)	4.0	2.2	56
	4.5	25	56
p-chlorophenyl (2-*p*-ClPh)	3.5	2.0	54
o-tolyl (2-*o*-Tol)	4.3	2.5	42[d]
	1.9	1.1	52[d]
mesityl (2-Mes)	2.4	1.5	46[e]
	4.8	6.8	48[f]

[a] Reactions were performed in THF overnight (~12 h) under nitrogen at 25 °C unless otherwise noted. The yields of isolated 3-Ar ranged from 60–80%. [b] Reaction time was 4 days. [c] Reference 12 (reaction performed in diglyme). [d] Precision here was unaccountably poorer than in the other cases. [e] Considerable olefin remained after 12 h. [f] Reaction time 7 h.

that attends substitution by alkyl groups, halogen, and ether functions was more pronounced. Thus, λ_{max}(hex) values for **2**-Ph and **2**-Mes were 248 and 267 nm, respectively (compare benzene, λ_{max} 256 nm, and mesitylene, λ_{max} 266 nm). Molar absorptivities were comparable between **2**-Ar and the arenes. There appears to be, therefore, no pronounced electronic interaction between the aryl group and the syn double bond.

The series of *syn*-7-arylnorbornenes so prepared (**2**-Ar) was hydroborated in the standard fashion, using a solution of borane in tetrahydrofuran (THF) at 25 °C under nitrogen overnight. The organoboranes[15] that resulted were then oxidized with alkaline hydrogen peroxide. The alcohols formed (**3**-Ar) were analyzed by ^{1}H NMR spectroscopy, at times aided by the use of lanthanide shift reagent techniques (eq 5). The results of the hydro-



(5)

boration–oxidation studies show a decided absence of any major substituent effect. Even the (presumably) highly hindered mesityl compound **2**-Mes gave considerable exo alcohol, an unexpected result indeed. The data are collected in Table I.

Hydroboration of **2**-Ph, **2**-*p*-Tol, and **2**-Mes was achieved also in short times (~1 h). NMR analysis of the solutions indicated that the olefins were consumed. Reaction of equimolar 7-phenylnorbornadiene (**1**-Ph) and borane/THF *for 15 min* showed 88% dihydroboration, with the balance being monoadduct produced via addition from the anti side

(11) J. W. Wilt, T. P. Malloy, P. K. Mookerjee, and D. R. Sullivan, *J. Org. Chem.*, **39**, 1327 (1974). The hydroboration noted was first performed by T. P. Malloy, Dissertation, 1970, who found a 56% exo and a 44% endo alcohol composition.

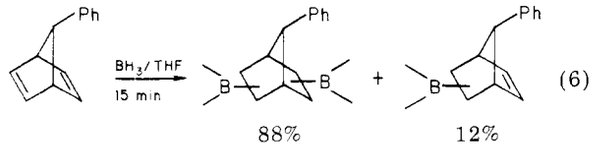
(12) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, T. E. Dye, and J. H. Long, Jr., *J. Org. Chem.*, **38**, 4127 (1973).

(13) P. R. Story and S. R. Fahrenholtz, *J. Org. Chem.*, **28** 716 (1963).

(14) R. K. Lustgarten and H. G. Richey, Jr., *Tetrahedron Lett.*, 4655 (1965).

(15) We have no conclusive data on which organoboranes are present: mono, di, or tri. Hydrogen liberation on workup indicated that all **2**-Ar except **2**-Mes proceeded to the diorganoborane stage. **2**-Mes led to the monoorganoborane. Because there seemed to be no direct relationship between the extent of exo addition and either time or the reactant concentrations (Table I), we did not investigate this point further. Disproportionation among organoboranes and different rates of alkene addition to them complicate the situation tremendously. See a discussion by D. J. Pasto, B. Lepeska, and V. Balasubramaniyan, *J. Am. Chem. Soc.*, **94**, 6090 (1972). The aim of the present paper is to show that *under usual synthetic conditions* considerable exo addition occurs.

(eq 6). Because anti addition should be rapid indeed, the



(6)

result in eq 6 also supports the relatively rapid addition to the syn double bond as well.

No reaction of **2**-Ph with 9-BBN was observed after 5 days, a curious result considering the reported endo addition of 9-BBN to *syn*-7-*tert*-butylnorbornene.[6]

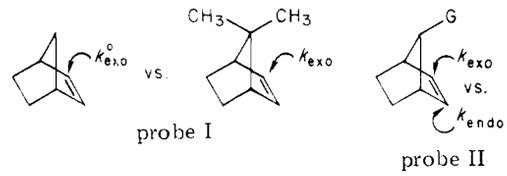
Other Addition Reactions. Other addition reactions of interest were performed on the *syn*-7-phenylnorbornyl system. These are summarized in eq 7–11 (Scheme I). It is noteworthy that the oxymercuration of apobornene is faster[16] (15 min) than that of **2**-Ph (eq 9).

Kleinfelter and co-workers observed the result in eq 9 (total exo addition), but no other details were given.[12]

Assignment of Exo, Endo Configuration. This assignment was made by ^{1}H NMR spectroscopy, using the methine photon (>CHOH) in the alcohols for the characterization. The broad multiplet H-2 resonances in **3**-Ar were in the ranges δ 3.4–3.8 for the endo proton (exo alcohol) and δ 3.9–4.13 for the exo proton (endo alcohol). Use of the Eu(fod)$_3$ shift reagent for **3**-Ph, **3**-*p*-An, **3**-*p*-Tol, and **3**-Mes allowed a better resolution of the broad methine resonances and corroborated the assignments made in the absence of the shift reagent. Gradient studies indicated that the shift order was **H-2n** > **H-2x** in all cases and OCH_3 in **3x**-*p*-An > **3n**-*p*-An. Other than the expected large shift in OH, no other protons in these alcohols were shifted significantly for diagnostic use.

Discussion

Steric Probes. There can be no doubt that syn-7 substituents do indeed influence addition stereochemistry in norbornenes. Several approaches have been used, among them the comparisons of relative rates of addition as illustrated below for probes I and II.[7,17]



Among the factors that affect the rates in these probes are the *size* of the syn-7 substituent, the *transition state* involved in the addition, and the size of the *addend* itself. Some data obtained from probe I are listed in Table II.

Clearly those processes proceeding via cyclic transition states, particularly small ones (three or four membered), are affected more than noncyclic transition state additions. Interestingly, the k^0_{exo}/k_{exo} ratio for norbornene vs. **2**-Ph for diimide reduction at 65 °C has been found to be only 5.5.[18]

Scheme I

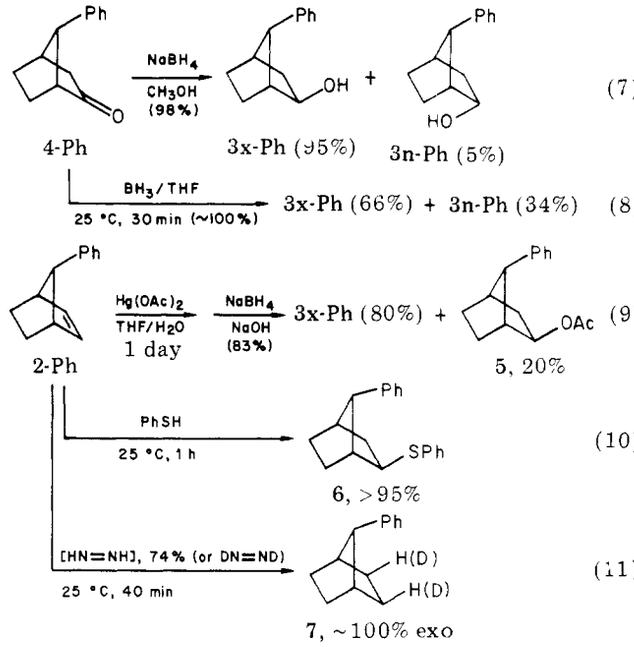


Table II. Rate Effect of the 7,7-Dimethyl Substituent on Norbornene Additions[a] (Probe I)

transition state	addend	$k^0_{exo}/k_{exo(probe\ I)}$
cyclic	PhSCl	1820
	m-$ClC_6H_4CO_3H$	1000
	N_2H_2	950
	9-BBN	480
acyclic	$Hg(OAc)_2$, H_2O[b]	58
	PhSH	30
	HOAc	~3
	HCl	~2

[a] Taken from ref 2b. [b] Some question exists about the transition state here.[2b] As far as probe I is concerned, the reaction resembles an acyclic transition state process.

Table III. Comparisons of "Size" for Methyl and Phenyl

method	term	value: methyl	value: phenyl
acid hydrolysis of ortho substituted benzoates[a]	E_s^0	(0.0)	−0.90[b]
axial/equatorial equilibrium in cyclohexanes[c]	A	1.7	3.0[d]
ring inversion in methylene-dihydroanthracenes[e]		larger or the same	smaller or the same

[a] R. W. Taft in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, p 598. [b] The more negative the value, the larger the group. [c] A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, 1972, p 157. [d] The larger the value, the larger the group. [e] P. T. Leung and D. Y. Curtin, *J. Am. Chem. Soc.*, **97**, 6790 (1975), specifically ref 23 in the paper. No numerical measurement was given.

Other data, though less quantitative, have been obtained using probe II on *syn*-7-*tert*-butylnorbornene.[6] Of the addends studied, diimide, silver ion, mercuric ion, thiophenol, deuterium, and 9-BBN, only the last two added, and in endo fashion at that. Again the strong influence of the syn-7 substituent is manifest.

(16) H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Am. Chem. Soc.*, 89, 1525 (1967). The times given are for decoloration of the yellow reactant solution. The acetate ester accompanying the alcohol product in eq 9 is expected. cf. T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, 85, 2746 (1963).

(17) A third probe involves syn vs. anti addition to 7-substituted norbornadienes. This probe is, however, subject to additional complications such as the formation of nortricyclenes and other manifestations of electronic interaction between the double bonds. As such it is less useful for the present purposes in which steric effects alone are probed. For a discussion and leading references, see W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Org. Chem.*, 34, 2944 (1969).

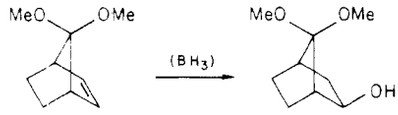
(18) R. J. McCollum, Dissertation, University of Minnesota, 1971. We thank Dr. McCollum for this information.

A comparison of the data now available for additions to norbornene, 7,7-dimethylnorbornene (apobornene), *syn*-7-*tert*-butylnorbornene, and 2-Ph shows that in some reactions phenyl appears to be *larger than methyl* (slower rate of oxymercuration with 2-Ph than with apobornene) and yet in hydroboration it appears to be *smaller than methyl* (more exo addition). Nonetheless, Ph appears to be *smaller than t-Bu* in all cases, allowing exo addition onto 2-Ph with addends that do not react at all with *syn*-7-*tert*-butylnorbornene (thiophenol, mercuric ion).

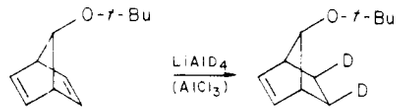
The assignment of "size" to a group is a complex problem, and the values normally assigned to specific atoms or groups are compromised among the many different approaches used to determine them.[19] Specifically, the germane values for the present study would be those for methyl and phenyl. Some comparisons of the two groups are given in Table III. From the available data, one must conclude that their relative sizes are not really well understood. Either their sizes vary from reaction to reaction or no accurate probe yet exists.

Criticisms may be made of all the methods employed in Table III.[19] Indeed, a possible criticism of the "syn-7 substituent technique" in norbornene additions as a probe of "size" may be made as well. Such a criticism is based upon the possibility that complexation by the substituent with the addend may favor exo approach and give thereby anomalous orientation effects when considered against steric effects alone. Such a possibility was, in fact, explicitly mentioned by Brown and co-workers in their development of the syn-7 substituent probe.[2a]

Complexation Effects. Two literature examples exist where substituents at the syn-7 position strongly favored exo addition in norbornene/dienes (eq 12[20] and 13[21]), contrary to steric predictions.[22] In each case, a specific

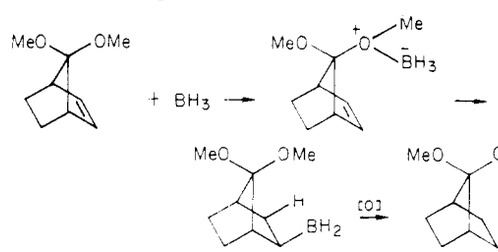


78% (12)



~100% (13)

interaction between the addend and the substituent can explain the result; namely, the ether groups, being n-electron donors, could be expected to form a reasonably strong Lewis complex with the borane or alane (eq 14) and so favor subsequent exo addition. Here, of course, the



(14)

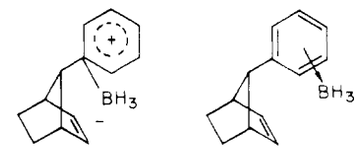
ability of the substituent to complex the borane (alane)

Table IV. A Comparison of Hydroboration Orientation vs. Arene Complexing Ability

2-Ar	exo/endo[a]	relative donor ability of ArH[b] π donor	σ donor
2-Ph	1.2	1	1
2-*p*-Tol	1.1	1.5	790
2-*o*-Tol	0.9	1.5	790
2-*p*-ClPh	1.2	(~1)[c]	(<1)[d]
2-Mes	0.9	2.6	6.3×10^{5}

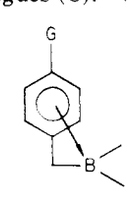
[a] From Table I. [b] Taken from the review by G. Olah, *Acc. Chem. Res.*, 4, 240 (1971). [c] H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, 74, 3570 (1952). [d] Assumed from the lower reactivity of chlorobenzene in typical aromatic substitution reactions.

is comparable to that of the solvent (subject to concentration effects), and the result is a dramatic favorability for exo addition. The ability of aromatic rings to complex in similar fashion is well known, either by σ- or by π-electron sharing. The σ-type complex in the hydroboration of 2-Ar would resemble A below, while the π-type complex would resemble B. The latter type of complex, particu-



A B

larly, would be much less competitive against the donor solvent (THF) complex (n vs. π complexation) and weaken the orientation effect. Because such complexation of borane by arenes would thusly be weaker than that by n-electron donors, complexation could be absent altogether with the bulky 9-BBN, explaining the negative result in this case. Unfortunately, little work has been done on such complexation of borane by aromatic hydrocarbons. In one study, however, Ramsey and Das[23] noted a moderately intensive charge transfer interaction in tribenzylborane and para-substituted analogues (C). With this precedent, the



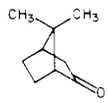
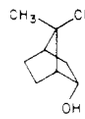
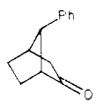
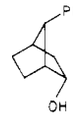
C

possibility of such an interaction between borane and 2-Ar seems likely. To search for such interaction, a comparison of the exo/endo orientation in the hydroboration of 2-Ar against the σ and π complexation ability of the arene moiety was made. The results are given in Table IV. Although the correlations in Table IV are qualitative, they nevertheless clearly favor π complexation over σ complexation as an explanation for the absence of a substituent effect. Admittedly, correlation is not causality, and the relationship between hydroboration and arene π donation may be spurious. The viewpoint also rationalizes, obviously, the unexpectedly competitive exo hydroboration orientation.

Even so, such complexation favors exo hydroboration by only a small amount relative to endo hydroboration

(19) For a comprehensive review of steric interactions, see H. Förster and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, 16, 429 (1977).
(20) P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, 82, 2828 (1960).
(21) B. Franzus and E. I. Snyder, *J. Am. Chem. Soc.*, 87, 3423 (1965).
(22) For other cases, see E. Boerhorst and G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, 95, 50 (1976); D. I. Davies and P. J. Rowley, *J. Chem. Soc. C*, 424 (1969).
(23) B. G. Ramsey and N. K. Das, *J. Am. Chem. Soc.*, 91, 6191 (1969); 94, 4227 (1972).

Table V. Direction of Reduction in Norbornanones

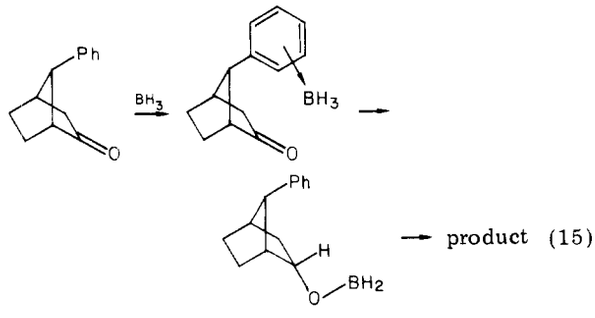
ketone	reagent	product of exo attack (%)
 4-H	$NaBH_4$, *i*-PrOH, 50 °C BH_3/THF, 0 °C	 (80[a]) (98[b])
 4-Me	$NaBH_4$, *i*-PrOH, 50 °C BH_3/THF, 0 °C	 (22[a]) (48[b,c])
 4-Ph	$NaBH_4$, MeOH, 25-60 °C BH_3/THF, 25 °C	 (<5[d]) (34[d])

[a] R. Howe, E. C. Friedrich, and S. Winstein, *J. Am. Chem. Soc.*, 87, 379 (1965). [b] H. C. Brown and V. Varma, *ibid.*, 88, 2871 (1966). [c] For camphor. [d] Present study.

(0.12 kcal mol^{-1} at 25 °C in either ΔG or $\Delta G^{\ddagger}$ depending upon whether thermodynamic or kinetic control exists). Presumably the sum of unfavorable exo steric hindrance and favorable exo complexation caused by the syn-7-aryl group is balanced by the somewhat less unfavorable endo steric hindrance caused by the endo-5,6 hydrogens.

Other Reactions. The results shown in eq 9–11 indicate that exo addition can occur on 2-Ph albeit occasionally at a slower rate than on apobornene. In this regard, phenyl appears to behave "normally" if one assigns it a larger size than methyl. That is, the larger phenyl group simply retards but does not reorient those processes which proceed either stepwise or via larger sized transition states. Reactions in eq 7 and 8 also are informative. Table V lists the attack on related norbornyl ketones by various reagents, including those shown earlier in eq 7 and 8.

The data in Table V illustrate that the hindrance to exo attack on these ketones increases in the order H < Me < Ph, as would be expected on the basis of the steric sizes (as measured by E_s^0 and *A* values), both toward BH_4^- and BH_3/THF. Such a result adds weight to the view that phenyl is indeed "larger" than methyl. Interestingly, however, the ratio of exo attack on 4-Ph by BH_3/THF relative to BH_4^- seems high (~7), especially when compared to the ratios for 4-H (~1.2) and 4-Me (~2.2). As before, for 2-Ph, in the reaction with the Lewis acid borane, the carbonyl group in 4-Ph appears to be disposed more favorably toward exo attack. Potential π complexation as shown in eq 15 is again suggested. However, the (assumed) symmetrical relationship between the double bond and the complexed borane in 2-H is not present in this case. Therefore, the decreased exo addition by borane to 4-Ph (compared with 2-Ph) may be related to the less favorable orientation of the complexed borane vis-à-vis the carbonyl group.



→ product (15)

Summary

The hydroboration of 2-Ar and the reduction of 4-Ph with borane show an increase in exo attack compared to the hydroboration of apobornene or to the reduction of 4-Ph with sodium borohydride. To rationalize the results with borane, one may view the phenyl (and other aryl) groups as smaller than methyl, or one may view the borane exo additions as specifically oriented additions proceeding via π-complexed intermediates. The former view seems specious in that other additions to 2-Ar proceed as expected for a large syn-7 group. The latter view is presently preferred because it correlates the additions with π complexation data and predicts the unusual orientation results for reactions with borane alone. Future work will seek other examples of π (or even σ) complexation in hydroboration reactions.

Experimental Section

General. Melting points were taken on a calibrated Fisher-Johns block. Gas chromatography was performed on a Varian Aerograph Model A-90P, using helium as the carrier gas. Spectra were determined on the following instruments: Perkin-Elmer Model 700 (IR);[24] Cary Model 14 or Perkin-Elmer Model 575 (UV); Varian A-60A or Varian EM-360 (NMR). Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

7-Arylnorbornadienes (1-Ar). The following compounds were prepared from the appropriate arylmagnesium bromide and 7-*tert*-butoxynorbornadiene (Frinton Labs) as described by Story and Fahrenholtz[13] for 1-Ph: 7-phenylnorbornadiene (1-Ph); 69%, bp 72–76 °C (0.7 mm) (lit.[13] bp 80–81 °C [1.7 mm]) (also obtained from Frinton).

7-*p*-Anisylnorbornadiene (1-*p*-An): 32%; bp 88–93 °C (0.8 mm); NMR δ ($CDCl_3$/Me_4Si) 6.76–6.81 (4, ArH, m), 6.84 (2, anti vinyl H's, m), 6.47 (2, syn vinyl H's, m), 3.68 (6, H-1,4 and H-7 under OCH_3, a singlet in a multiplet); IR ν (neat) 1615, 1518, 1310, 1300, 1250, 1180, 1040, 785, 735 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.60; H, 7.25.

7-*p*-Tolylnorbornadiene (1-*p*-Tol): 26%; bp 63–78 °C (0.17 mm) (crude material was purified by GLC on an OV-210 column at 175 °C); NMR δ ($CDCl_3$/Me_4Si) 6.98 (4, ArH, sharp m), 6.90 (2, anti vinyl H's, sharp m), 6.53 (2, syn vinyl H's, broad m), 3.76 (3, H-1,4 and H-7, m), 2.26 (3, $ArCH_3$, s); IR ν (neat) 1520, 1320, 780, 740, 650 cm^{-1}. Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 91.95; H, 7.76.

7-*o*-Tolylnorbornadiene (1-*o*-Tol): 34%; bp 79–84 °C (0.25 mm); NMR δ ($CDCl_3$/Me_4Si) 7.03 (4, ArH, m), 6.93 (2, anti vinyl H's, sharp m), 6.55 (2, syn vinyl H's, m), 3.72 (3, H-1,4 and H-7, m), 2.23 (3, $ArCH_3$, s); IR ν (neat) 1500, 1470, 1320, 740 cm^{-1}. Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.21, H, 7.72.

7-(*p*-Chlorophenyl)norbornadiene (1-*p*-ClPh): 26%; bp 86.87 °C (2.8 mm) (a malodorous compound with remarkable persistence); NMR δ ($CDCl_3$/Me_4Si) 7.05 (4, ArH, AA'BB' q), 6.90 (2, anti vinyl H's, m), 6.52 (2, syn vinyl H's, m), 3.75 (3, H-1,4 and H-7); IR ν (neat) 1490, 1310, 1090, 1015, 870, 780, 730 cm^{-1}. Anal. Calcd for $C_{13}H_{11}Cl$: C, 77.03; H, 5.47. Found: C, 76.30; H, 5.52. This analysis was the best of several obtained. Purification of the compound was complicated by its degradation during GLC.

7-Mesitylnorbornadiene (1-Mes): 35%; bp 87–90 °C (0.1 mm); mp 66–66.5 °C (from ethanol); NMR ($CDCl_3$/Me_4Si) 6.94 (2, anti vinyl H's, m), 6.74 (2, ArH, m), 6.61 (2, syn vinyl H's, m), 3.99 (2, H-1,4, m), 3.82 (1, H-7, m), 2.35 (6, *o*-$ArCH_3$, s), 2.18 (3, *p*-$ArCH_3$, s); IR ν (neat melt) 1610, 1550, 1310, 1020, 880, 850, 740. Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: 91.29; H, 8.71.

(24) Only strong absorptions (to the nearest 5 cm^{-1}) that were of value as characteristics of the compounds are reported. For complete spectra see ref 1.

Unsuccessful attempts were made to prepare other aryl analogues: perfluorophenyl, 9-anthryl, and *p*-trifluoromethyl. The products were easily rearranged (a variety of unassigned NMR signals) upon distillation and/or GLC. Coupling of the Grignard reagent to biaryls was another complication, especially serious in these cases (found to occur in all cases, however).

Samples of 1-Ph, 1-*p*-Tol, and 1-*p*-ClPh were heated at 220 °C for 2.5 h. Analysis by NMR indicated total rearrangement to arylcycloheptatrienes had occurred.[14]

***syn*-7-Arylnorbornenes (2-Ar).** The dienes 1-Ar were selectively hydrogenated in 95% ethanol (THF for 1-Mes) to the syn monoenes by the method earlier described.[11] Hydrogenation was carried out so as to produce 85–90% yields of 1-Ar together with 10–15% 7-arylnorbornanes. No *anti*-7-arylnorbornenes were detected. No difficulty was experienced with the following Matheson catalysts and amounts: 5% Pd/C, 5%; 0.3% Pd/C, 4%; 0.1% Pd/C, 2%; 0.01% Pd/C, 0.2%. The products were separated by preparative GLC on an OV-210 column (10%, 20 ft).

***syn*-7-Phenylnorbornene (2-Ph)** was identical with that reported,[11,25] but the spectra are given here for completeness: NMR δ ($CDCl_3$/Me_4Si) 7.14 (5, ArH, s), 5.85 (2, vinyl H's, t), 3.08 (2, H-1,4, m), 2.90 (1, H-7, m), 1.5–2.0 (2, exo H-5,6, m), 1.0–1.5 (2, *endo* H-5, 6, m); IR ν (neat) 1500, 1340, 740, 720, 700 cm^{-1}; λ_{max}(hex) 243, 248 nm (ϵ 760).

***syn*-7-*p*-Anisylnorbornene (2-*p*-An)**: collected by GLC at 220 °C; NMR δ ($CDCl_3$/Me_4Si) 6.92 (4, ArH, AA'BB' q), 5.88 (2, vinyl H's, t), 3.70 (3, $ArOCH_3$, s), 3.07 (2, H-1,4, m), 2.87 (1, H-7, m), 0.8-2.0 (4, H-5,6, broad m); IR ν (neat) 1620, 1520, 1050, 840, 720 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.80; H, 8.34 (lit.[26] δ 5.80 (vinyl H's)).

***syn*-7-*p*-Tolylnorbornene (2-*p*-Tol)**: collected by GLC at 175 °C; NMR δ ($CDCl_3$/Me_4Si) 7.00 (4, ArH, s), 5.90 (2, vinyl H's, t), 3.05 (2, H-1,4, m), 2.90 (1, H-7, m), 2.30 (3, $ArCH_3$, s), 0.9–2.0 (4, H-5,6, broad m); IR ν (neat) 1520, 1340, 770, 710 cm^{-1}. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.94; H, 9.06.

***syn*-7-*o*-Tolylnorbornene (2-*o*-Tol)**: collected by GLC at 175 °C; NMR ($CDCl_3$/Me_4Si) 7.07 (4, ArH, s), 5.90 (2, vinyl H's, t), 3.13 (2, H-1,4, m), 2.95 (1, H-7, m), 2.30 (3, $ArCH_3$, s), 0.9–2.1 (4, H-5,6, broad m); IR ν (neat) 1500, 1470, 1340, 750, 720 cm^{-1}. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.00; H, 9.00.

***syn*-7-(*p*-Chlorophenyl)norbornene (2-*p*-ClPh)**: collected by GLC at 230 °C; NMR δ ($CDCl_3$/MeSi) 7.06 (4, ArH, AA'BB' q), 5.84 (2, vinyl H's, t), 3.03 (2, H-1,4, m), 2.28 (1, H-7, m), 0.9–2.1 (4, H-5,6, broad m); IR ν (neat) 1500, 1340, 1090, 830, 780, 720 cm^{-1}; λ_{max}(hex) 255, 261 nm (ϵ 907). Anal. Calcd for $C_{13}H_{13}Cl$: C, 76.28; H, 6.40. Found: C, 76.18; H, 6.75.

***syn*-7-Mesitylnorbornene (2-Mes)**: collected by GLC at 225 °C; NMR δ ($CDCl_3$/Me_4Si) 6.72 (2, ArH, s), 5.09 (2, vinyl H's, t), 3.20 (2, H-1,4, m), 2.89 (1, H-7, m), 2.37 (6, *o*-$ArCH_3$, s), 2.17 (3, *p*-$ArCH_3$, s), 0.8-2.0 (4, H-5,6, broad m); IR ν (neat) 1620, 1590, 1560, 860, 790, 770, 720 cm^{-1}; λ_{max}(hex) 267, 269 nm (ϵ 183). Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.21; H, 9.79.

Hydroboration–Oxidation of 2-Ar. The appropriate olefin was weighed into a carefully dried flask, and the system was purged with nitrogen. A solution of preanalyzed borane in tetrahydrofuran (BH_3/THF, Aldrich, ca. 0.3 or 1.1 M) in a known amount (see Table I) was added by syringe through a septum. The mixture was stirred under nitrogen at room temperature, usually overnight (but see Table I). Water (2 mL) was added by syringe, and the hydrogen evolved was measured. Sodium hydroxide solution (6 M, 3 mL) was then added, followed by dropwise addition of hydrogen peroxide (30%, 2 mL) with cooling. The solution was stirred for 30 min, and potassium chloride was added to saturate the aqueous phase. The upper tetrahydrofuran layer was separated and rotary evaporated. The residue was chromatographed on neutral alumina for analytical samples which are mixtures of exo and endo epimers. In other runs the residue was taken up into chlorform (4 mL) and extracted with water (3 × 4 mL). The chloroform layer was evaporated, and the residue was taken up into deuteriochloroform for NMR analysis (see Table I).

***syn*-7-Phenyl-2-norbornanols. 3x-Ph and 3n-Ph**: the NMR spectra agreed with those reported (**3x**-Ph,[27] **3n**-Ph[12]); IR ν (KBr) mix, 3260 (b), 1100, 1050, 1020, 720, 690 cm^{-1}.

***syn*-7-*p*-Anisyl-2-norbornanols. 3x-*p*-An**: NMR δ ($CDCl_3$/Me_4Si) 7.00 (4, ArH, AA'BB' q), 3.5–3.9 (1, H-2, broad m), 3.72 (3, OCH_3, s), 2.92 (1, H-7, m), 2.74 (2, H-1,4, m), 1.0–2.3 (7, (OH, H-3,5,6, broad m). **3n-*p*-An**: NMR δ 6.93 (4, ArH, AA'BB' q), 3.9–4.4 (1, H-2, broad m), 3.72 (3, OCH_3, s), 3.07 (1, H-7, m), 2.57 (2, H-1,4, m), 1.0–2.3 (7, OH, H-3,5,6, broad m). These resonances were determined by shift studies (see below), necessitated by the overlap of the methine and methoxy protons: IR ν (KBr) mix, 3400, 1260, 1050, 1020, 790 cm^{-1}. The chromatographed sample was recrystallized three times from hexane; mp 53–54.5 °C. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.81; H, 8.30.

***syn*-7-*p*-Tolyl-2-norbornanols. 3x-*p*-Tol**: NMR δ ($CDCl_3$/Me_4Si) 6.92 (4, ArH, broad s), 3.5–3.9 (1, H-2, broad m), 2.94 (1, H-7, m), 2.74 (2, H-1,4, m), 2.30 (3, $ArCH_3$, s), 0.9–2.2 (7, OH, H-3,5,6, broad m). **3n-*p*-Tol**: NMR δ 6.92 (4, ArH, broad s), 3.9–4.4 (1, H-2, broad m), 3.07 (1, H-7, m), 2.44 (2, H-1,4, m), 2.30 (3, $ArCH_3$, s), 0.9-2.2 (7, OH, H-3,5,6, broad m). These alcohols could be partially resolved by chromatography to confirm the assignments above: IR ν (KBr) mix, 3310, 1260, 1050, 1020, 790 cm^{-1}. The chromatographed material was sublimed (80 °C (0.1 mm)) and recrystallized from hexane, mp 93.5–94.5 °C. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.86; H, 9.00.

***syn*-7-*o*-Tolyl-2-norbornanols. 3x-*o*-Tol**: NMR δ ($CDCl_3$/Me_4Si) 7.17 (4, ArH, broad s), 3.5–3.9 (1, H-2, broad m), 2.87 (1, H-7, m), 2.70 (2, H-1,4, m), 2.30 (3, $ArCH_3$, s), 0.8–2.2 (7, OH, H-3,5,6, broad m). **3n-*o*-Tol:** NMR δ ($CDCl_3$/Me_4Si) 7.17 (4, ArH, broad s), 3.9–4.4 (1, H-2, broad m), 3.07 (1, H-7, m), 2.50 (2, H-1, 4, m), 2.37 (3, $ArCH_3$, s), 0.8–2.2 (7, OH, H-3,5,6, broad m). These assignments were confirmed by partial separation of the alcohols during chromatography: IR ν (KBr) mix, 3350, 1490, 1450, 1090, 1040, 730 cm^{-1}. The chromatographed sample was recrystallized twice from hexane, mp 78–79.5 °C. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.90; H, 9.03.

***syn*-7-(*p*-Chlorophenyl)-2-norbornanols. 3x-*p*-ClPh**: NMR δ ($CDCl_3$/Me_4Si) 7.27–7.34 (4, ArH, sharp m), 3.6–4.0 (1, H-2, m), 2.80 (1, H-7, m), 2.75 (2, H-1,4, m), 1.0–2.2 (7, OH, H-3,5,6, m). **3n-*p*-ClPh:** NMR δ ($CDCl_3$/Me_4Si) 7.27–7.34 (4, ArH, sharp m), 4.0–4.4 (1, H-2, m), 3.09 (1, H-7, m), 2.55 (2, H-1,4, m), 1.0–2.2 (7, OH, H-3,5,6, m); IR ν (KBr) mix, 3260, 1480, 1090, 820 cm^{-1}. The chromatographed sample was recrystallized twice from 1:1 ether–hexane, mp 87.5–89 °C. Anal. Calcd for $C_{13}H_{15}Cl$: C, 70.11; H, 6.79. Found: C, 69.93; H, 6.42.

***syn*-7-Mesityl-2-norbornanols. 3x-Mes**: NMR δ ($CDCl_3$/Me_4Si) 6.70 (2, ArH, s), 3.3–3.7 (1, H-2, m), 2.90 (1, H-7, m), 2.60 (2, H-1,4, m), 2.28 (6, *o*-$ArCH_3$, s), 2.15 (3, *p*-$ArCH_3$, s), 0.9–1.9 (7, OH, H-3,5,6, broad m). **3n-Mes:** NMR δ 6.70 (2, ArH, s), 3.7–4.2 (1, H-2, m), 3.04 (1, H-7, m), 2.50 (2, H-1,4, m), 2.28 (6, *o*-$ArCH_3$, s), 2.15 (3, *p*-$ArCH_3$, s), 0.9–1.9 (7, OH, H-3,5,6, broad m). These assignments were confirmed by shift studies (see later): IR ν (neat) mix, 3400, 1460, 1380, 1090, 1060, 850 cm^{-1}. The semisolid alcohol mixture was difficult to purify due to its high solubility and poor chromatographic properties. It was therefore oxidized with pyridinium chlorochromate in methylene chloride (30 min, 25 °C) to afford ***syn*-7-mesityl-2-norbornanone** (61% mp 106–108 °C from ethanol). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.74; H, 8.98.

Other Hydrocarbon Studies. (i) Attempted reaction of **2**-Ph with 9-BBN in THF (0.5 M, Aldrich) at 25 °C for periods ranging from 18 h to 5 days led to no detectable alcohols **3**-Ph upon oxidation. Measurement of hydrogen evolution indicated no hydroboration had occurred within 18 h. (ii) Reaction of the following olefins with BH_3/THF solutions at 25 °C in NMR tubes was checked after 1 h by NMR monitoring of the vinyl hydrogen region. The olefins were consumed in the 1 h period [olefin (mmol/mmol of BH_3)]: **2**-Ph (1.09/1.80), **2**-*p*-Tol (0.08/0.22),

(25) *syn*-7-Phenylnorbornene (**2**-Ph) is also available by reduction of the 7-ol.[26] The reducion of 1-Ph is considerably more convenient, however.

(26) D. C. Kleinfelter and G. Sanzero, *J. Org. Chem.*, **42**, 1944 (1977). In this paper the percentages of **3x**-Ph and **3n**-Ph are reversed from those given in ref 12 and are probably misprinted.

(27) D. C. Kleinfelter, *J. Org. Chem.*, **32**, 3526 (1967).

2-Mes (0.49/1.3). (iii) A similar study of 1-Ph (1.4 mmol) with BH_3/THF (1.4 mmol) was performed in an NMR tube. After 15 min, one-eighth of the diene was only monosaturated (syn double bond present by NMR analysis), whereas the balance had been dihydroborated.

Europium Shift Reagent Studies. The $Eu(fod)_3$ shift reagent (Norell Chemical Co.) in deuteriochloroform was added in increments to solutions of 3-Ph, 3-*p*-An, 3-*p*-Tol, and 3-Mes alcohols. NMR gradient graphs ($\Delta\delta$ vs. [shift reagent]) coupled with a plausible model[28] for interaction of the reagent with the alcohols led to the assignments listed above as well as corroboration for the epimeric compositions based upon the expected exo and endo methine (H-2) chemical shifts. For 3-Ph the relative gradient slopes were endo H-2 (exo alcohol) 3.7, exo H-2 (endo alcohol) 3.0, H-7 (exo alcohol) 1.6, H-7 (endo alcohol) 1.0. Similar results were obtained for the other cases. As would be expected, the methoxy protons in **3x**-*p*-An shifted faster than those in **3n**-*p*-An, a fact used to support the epimeric composition based upon the >CHOH resonances. Other proton shifts were noted, but these were less useful. The aryl methyl protons in 3-*p*-Tol and 3-Mes did not shift.

Reduction of syn-7-Phenyl-2-norbornanone (4-Ph). Ketone 4-Ph was prepared[29] by treatment of the mixture of alcohols 3-Ph (1.5 g, 88.2 mmol) with chromium trioxide–pyridine solid complex (Sarett's reagent, 5.3 g) in dry pyridine (60 mL). After the solution was stirred overnight, workup in the usual fashion afforded ***syn*-7-phenyl-2-norbornanone** as a viscous oil (1.26 g, 77%, bp 124–125 °C (1 mm)). The analytical sample was collected by GLC at 210 °C (SE-30 column, 4 ft × 0.25 in.): $n^{28}{}_D$ 1.5454; $d^{26}{}_4$ 1.14; NMR δ ($CDCl_3$/Me_4Si) 7.07 (5, ArH, s), 3.10 (1, H-7, m), 2.73 (2, H-1,4, broad m), 1.3–2.1 (6, H-3,5,6, broad m); IR ν (neat) 1742, 1500, 1450, 1410, 1150, 1090, 1080, 780, 730, 700 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.81; H, 7.48.

To ketone 4-Ph (550 mg, 2.96 mmol) in methanol (3 mL) was added sodium borohydride (190 mg, 5 mmol) with cooling. The solution was then heated under reflux for 30 min. Ice (10 g) was added, and the product was filtered (545 mg, 98%). The alcohol so formed was essentially all **3x**-Ph by NMR analysis (<5% **3n**-Ph). Reaction in ethanol solvent proceeded identically.

To ketone 4-Ph (300 mg, 1.61 mmol) was added BH_3/THF (9.8 mL of 0.3 M material, 3.2 mmol) under nitrogen. The solution was stirred at 25 °C for 30 min. After water and KCl were added, the THF layer was separated and evaporated. The alcohol formed (quantitative yield) was examined by NMR (66% **3x**-Ph, 34% **3n**-Ph).

Oxymercuration–Demercuration of 2-Ph. A solution of mercuric acetate (1.6 g, 5 mmol) in water (5 mL) was added to 2-Ph (0.85 g, 5 mmol) dissolved in THF (10 mL). The decoloration of the solution occurred in 1 day. (Inexplicably, some runs took ~5 days for decoloration. A tandem reaction with norbornene decolorized in 10 min.) Sodium hydroxide (3 M, 5 mL) was then added, followed by sodium borohydride (0.5 M in 3 M sodium hydroxide, 5 mL). Mercury settled out with stirring. The THF layer was separated and washed with brine. Removal of solvent left a mixture of **3x**-Ph (80%) and its acetate ester **5** (20%), as determined by NMR (810 mg, 83%). No evidence for endo product(s) was found.

Reaction of Thiophenol and 2-Ph. A solution of 2-Ph (100 mg, 0.59 mmol) in thiophenol (110 mg, 1 mmol) was allowed to stand 1 h at 25 °C. The material was pipetted into D_2O (3 mL)[30] and extracted with deuteriochloroform. NMR analysis indicated that all of the 2-Ph had reacted. The exo adduct **6** (~100%) was a thick oil: NMR δ ($CDCl_3$/Me_4Si) 7.3 (5, SArH, s), 7.2 (5, CArH, s), 3.0–3.3 (1, H-2, broad m), 3.0 (1, H-7, m), 2.8 (2, H-1,4, m), 1.0–2.1 (6, H-3,5,6, broad m); IR ν (neat) 1580, 1480, 715, 710 cm^{-1}. Trace absorption between δ 3.45 and 4.0 indicated the virtual absence of endo adduct (<5%),[31] as did the "sharpness" of the δ 1.0–2.1 region. Experience with the alcohols 3-Ar showed that multiplets in this region sharpened as one epimer increased significantly over the other.

Reaction of Diimide and 2-Ph. The olefin (0.551 g, 3.24 mmol), freshly made potassium azodicarboxylate (1.8 g 9.3 mmol), and methanol (10 mL) were stirred in a solution of glacial acetic acid (1.22 g, 20.3 mmol) and more methanol (10 mL) was added over a 20-min period as carbon dioxide was evolved. The cloudly, white solution was stirred for another 20 min, after which time water and hexane (20 mL) were added. The organic phase was separated and distilled in a Hickman still to produce 7-phenylnorbornane (**7**, 0.415 g, 74%), identical spectrally with authentic material.[26]

Reaction of Dideuteriodiimide and 2-Ph. Olefin 2-Ph (0.226 g, 1.33 mmol, freshly distilled), potassium azodicarboxylate (prepared immediately beforehand and carefully dried, 0.92 g, 4.74 mmol), and methanol-*O*-*d* (Aldrich, 5 mL) were stirred at room temperature. A solution of acetic acid-*O*-*d* (prepared from acetic anhydride and D_2O, ~10 mmol) and methanol-*O*-*d* (5 mL) was added slowly by syringe through a septum to the stirred reactants. Carbon dioxide was evolved as the yellow color diminished. The pale yellow cloudy solution was stirred overnight. Addition of D_2O (5 mL) caused the solution to turn milky white. Extraction with hexane (10 mL) followed. The hexane layer was separated and evaporated, and the residual oil was distilled in a Hickman apparatus (100 °C bath, ~1 mm) to yield *exo,cis*-2,3-dideuterio-*syn*-7-phenylnorbornane (130 mg, 56%, *m/e* 174, ~100% deuterium uptake, determined on a Varian EM-600 spectrometer at 70 eV).

The exo,cis nature of the deuterium substituents was established by NMR. The deuterium NMR[32] showed only a singlet at δ 1.7 (in $CDCl_3$/Me_4Si). The proton NMR showed a decrease in the exo proton region (δ 1.5–2.0) and a clear singlet for the endo-2,3 hydrogens at δ 1.13 superimposed on the complex multiplet for the remaining 5,6 hydrogens (δ 1.1–1.85). The bridgehead (1,4) and bridge (7) protons were unchanged at δ 2.53 and 2.87 (broad singlets), respectively. The spectral data show conclusively that the deuterium substituents were exo,cis.

Registry No. 1-Ph, 40156-12-5; 1-*p*-An, 71886-41-4; 1-*p*-Tol, 71901-60-5; 1-*o*-Tol, 71901-61-6; 1-*p*-ClPh, 71886-42-5; 1-Mes, 71886-43-6; 2-Ph, 29266-12-4; 2-*p*-An, 71886-44-7; 2-*p*-Tol, 71886-45-8; 2-*o*-Tol, 71886-46-9; 2-*p*-ClPh, 71886-47-0; 2-Mes, 71886-48-1; **3x**-Ph, 14181-14-7; **3n**-Ph, 41770-08-5; **3x**-*p*-An, 71886-49-2; **3n**-*p*-An, 71886-50-5; **3x**-*p*-Tol, 71886-51-6; **3n**-*p*-Tol, 71886-52-7; **3x**-*o*-Tol, 71886-53-8; **3n**-*o*-Tol, 71886-54-9; **3x**-*p*-ClPh, 71886-55-0; **3n**-*p*-ClPh, 71886-56-1; **3x**-Mes, 71886-57-2; **3n**-Mes, 71886-58-3; 4-Ph, 71886-59-4; **5**, 71886-60-7; **6**, 71886-61-8; **7**, 24892-78-2; 7-*tert*-butoxynorbornadiene, 877-06-5; *syn*-7-mesityl-2-norbornanone, 71886-62-9; *exo,cis*-2,3-dideuterio-*syn*-7-phenylnorbornane, 71886-63-0.

(28) The model was constructed from FMO models (Prentice-Hall, Inc.) and string. Expected shifts were deduced from the model and the McConnell-Robertson equation: H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(29) This procedure is taken from T. P. Malloy, Dissertation, Loyola University of Chicago, 1970.

(30) This procedure removed the SH resonance from the unreacted thiophenol and allowed a more accurate inspection of the δ 3–4 region of the NMR spectrum.

(31) *endo*-2-(Phenylthio)norbornene has the exo H-2 resonance at δ 3.45 (m). *endo*-2-(Phenylthio)apobornene has this resonance at δ 3.78 (m). See ref 2a.

(32) We thank Dr. David S. Crumrine of this department for determining this spectrum on a Varian FT-80 spectrometer.