Molecular Rearrangements. XXIII. The Mechanism of Hydride Shift during Hydrolyses of Certain Substituted Norbornyl Tosylates[1,2]

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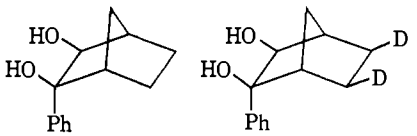
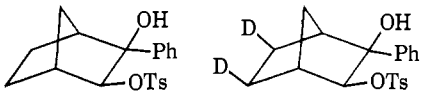
Abstract: The hydrolyses of 2-*exo*-hydroxy-2-phenyl-3-*exo*-tosyloxynorbornane (**2**) and its 5,6-*exo*-dideuterio analog **2a** have been studied. Five products (**3**, **4**, **5**, **6**, and **7**) were identified and shown to be present in combined yields of 88–92%. Hydride shifts accompanying the rearrangements take place by discrete, sequential 1,2 shifts, and not through face-protonated, nortricyclonium-type ions.[8] The products of 6,1-, 1,2-, and 6,2-hydride (or deuteride) shifts have all been identified. The formation of 5-deuterio-3-phenylnortricyclenol-3 (**4a**) takes place with stereospecific loss of the 5-*exo*-deuterium of **2a**. Confirmatory experiments (1) with tosylate **2c** (containing an *endo*-3-deuterium) and (2) with 7-phenyl-7-*syn*-hydroxy-2-norbornyl tosylate (**14**) and its 5,6-*endo*-dideuterio analog **14a** were also performed. Tosylates **2** and **14**, upon hydrolysis, produce **3**, **4**, **5**, and **6** in yields which are identical within experimental error. Tosylates **2** and **2a** give different yields of the products, in a direction which is in accord with the anticipated hydrogen–deuterium isotope effect.

In connection with our investigation of the pinacol rearrangement of 2-phenylnorbornane-2,3-*cis*,*exo*-diol (**1**)[3] and its deuterium-containing isomer **1a**,[4]



1 1a

it seemed evident that a study of the solvolytic behavior of the two tosylates, **2** and **2a**, might answer some of the



2 2a

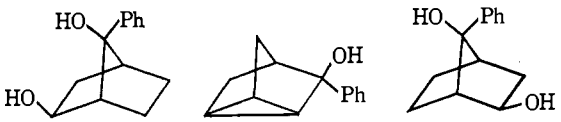
questions concerning the mechanism of hydride migration in norbornyl-type intermediates. The manner in which such hydride shifts occur has been questioned lately,[5-7] Winstein preferring an "edge-protonated" transition state A to the "face-protonated" model B originally proposed by Roberts.[8] Neither the results of Berson and Grubb[6] nor our studies[4] on the pinacol rearrangement of **1a** answered the question definitively, for the introduction[6] of a substituent in the 2 position of a norbornyl derivative destroys the threefold symmetry of the presumed face-protonated intermediate

A B C

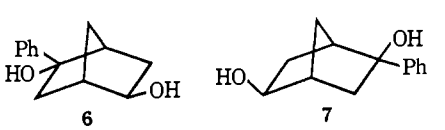
(C, R = phenyl[4] or methyl[6]) formed from it; thus the reactivity of the carbon to which the substituent is attached could be so affected that a discrete shift of hydrogen (or deuterium) to an adjacent carbon might be allowed. In this event, either the edge-protonated or the face-protonated intermediate could produce the same experimental result. Although the phenyl and hydroxyl groups in **2** also destroy the symmetry of the intermediate, here the substituents are remote from the reaction site, and the effect upon the reactivities of the three carbons involved in the charge distribution should be less. It does not appear easy, with present techniques, to use deuterated 2-norbornyl tosylate to study hydride shifts, since solvolyses would lead to inseparable mixtures of isotope position isomers of norborneol or norbornyl esters. The problem, therefore, reduces to one of separation of the various products of deuterium or of hydrogen migration of an appropriately labeled norbornyl derivative, and we hoped that solvolysis of **2a** would provide us with such separable products.

Methods and Results

Hydrolysis of **2** in aqueous acetone at 100° (see Experimental Section) yielded the four diols **3**, **5**, **6**, and **7** plus 3-phenylnortricyclenol-3 (**4**), which were



3 4 5



6 7

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) Paper XXII in this series: C. J. Collins, B. M. Benjamin, and M. H. Lietzke, *Ann.*, **687**, 150 (1965).

(3) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Am. Chem. Soc.*, **86**, 4913 (1964); see also D. C. Kleinfelter and P. von R. Schleyer, *ibid.*, **83**, 2329 (1961).

(4) B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966); preliminary reports of this work appeared: **88**, 1558 (1966); *Tetrahedron Letters*, 5477 (1966)..

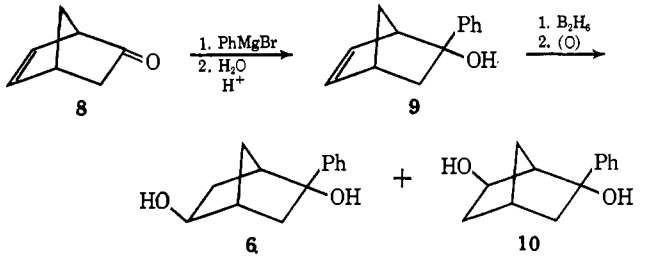
(5) J. A. Berson "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 139-155.

(6) J. A. Berson and P. W. Grubb, *J. Am. Chem. Soc.*, **87**, 4016 (1965).

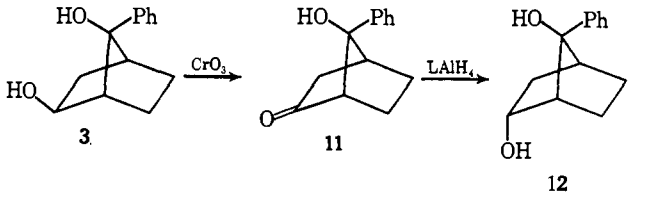
(7) A. Colter, E. C. Friederich, N. J. Holness, and S. Winstein, *ibid.* **87**, 378 (1965).

(8) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

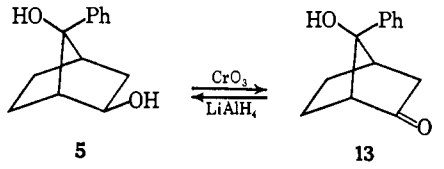
separated by column chromatography (on alumina). The total combined yield of these products was 89%. The yields of **3–6** were determined by isotope-dilution methods using phenyl-labeled (with carbon-14) **2** as the reactant. Compound **7** was not determined in this fashion since it was isolated and characterized long after the completion of the isotope-dilution experiments (Dr. Benjamin S. Benjaminov, unpublished work). The yields are shown in Table I. The structure of **4** was demonstrated by independent synthesis from nortricyclenone and phenylmagnesium bromide. The diol **6** was also synthesized independently from norbornenone (**8**) by the sequence **8** → **9** → **6** (plus **10**). Products **3** and **5** were identified from their nmr and infrared



spectra (see later in this section) and by certain of their chemical reactions. Diol **3** with the two hydroxyls

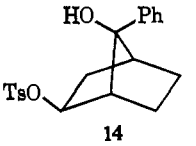


syn to each other was oxidized with chromic acid to the ketone **11** which, when treated with lithium aluminum hydride in ether, was converted predominantly to the diol **12**, in which the 2-hydroxyl group is now



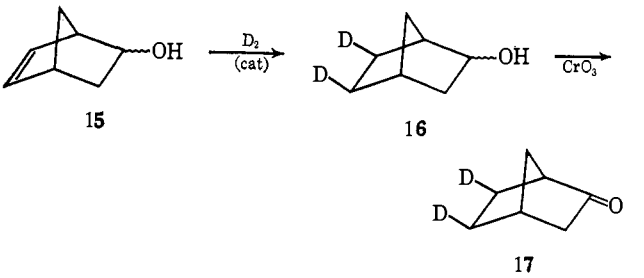
endo. The diol **5** could also be oxidized to a ketone **13** which, when treated with lithium aluminum hydride, was converted to a mixture of diols consisting predominantly of the original diol **5**. These results for the reduction with lithium aluminum hydride of the ketones **11** and **13** are consistent with the structures of their precursors, **3** and **5**, respectively; thus the phenyl group in **13** offers more steric hindrance to attack of the reducing agent upon the carbonyl group than the hydroxyl in structure **11**. Further there is the possibility that the 7-hydroxyl of **11** first reacts with lithium aluminum hydride to give a complex which intramolecularly reduces to yield the diol **12**.

Diol **3** was converted to the tosylate **14** which was in

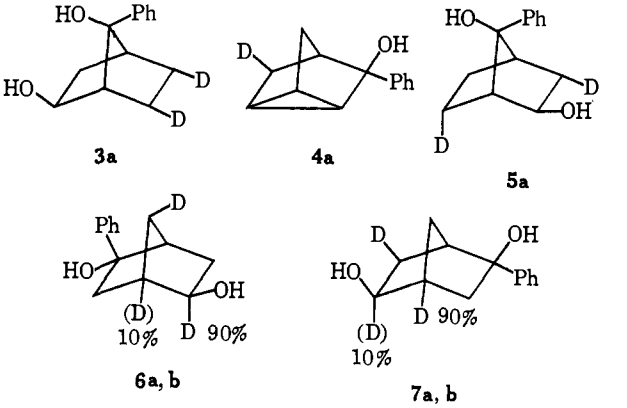


turn submitted to the same conditions of hydrolysis as had been used for tosylate **2**. The same products **3**, **4**, **5**, and **6** were obtained, and their yields as determined by isotope-dilution methods (starting with **14** labeled in the phenyl with carbon-14) were identical, within experimental error, with the yields of these products obtained upon hydrolysis of **2**. The results are also summarized in Table I.

exo-5,6-Dideuterionorbornanone-2 (**17**) was synthesized (by the sequence **15** → **16** → **17**) and then



converted to the diol **1a** and the tosylate **2a** by methods previously recorded.[3] Tosylate **2a** was subjected to hydrolysis under the same conditions used for the hydrolyses of **2** and **14**, and once again the yields of each product were determined by the isotopic dilution method. The yields of the four products are given in the last row of Table I (including **7a** and **b** which was isolated *after* the isotope-dilution experiments). The distribution of deuterium in each product, as determined by analysis of the pertinent nmr spectra, was found to be as follows.



In order to learn more about the mechanism of the loss of a single deuterium atom during formation of **4a**, diol **3a** was converted to the tosylate **14a**, which was

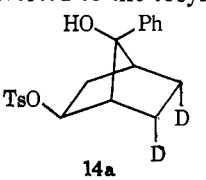


Table I

Starting material	Yield of product, %				
2	43.5 (**3**)	25.9 (**4**)	12.5 (**5**)	3.6 (**6**)	3.6[a] (**7**)
14	45.5 (**3**)	26.5 (**4**)	11.3 (**5**)	4.2 (**6**)	*b* (**7**)
2a	53.5 (**3a**)	17.5 (**4a**)	13.4 (**5a**)	3.8 (**6a**)	*b* (**7**)

[a] By weight. Compound **7** was isolated and identified after all of the isotope-dilution experiments were completed. [b] Diol **7** was isolated, but its yield was not determined.

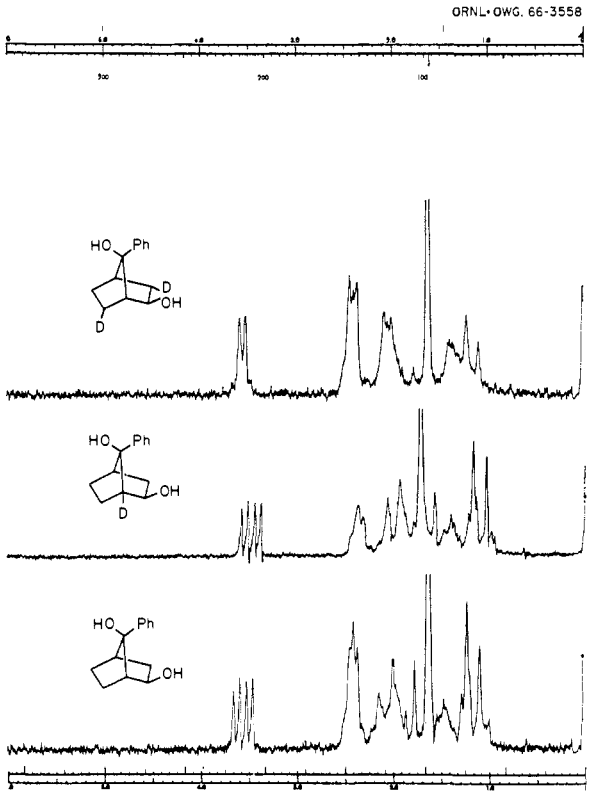
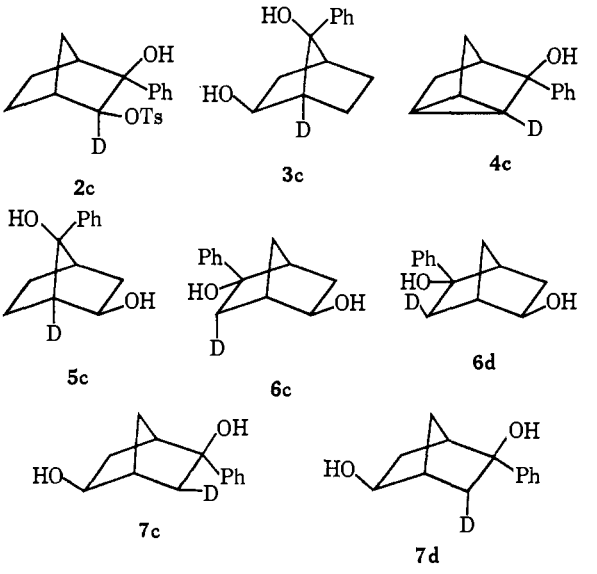


Figure 1. The nmr spectrum of 7-*syn*-phenylnorbornane-7-*anti*,-2-*exo*-diol (**5**) and its 1-deuterio (**5c**) and 3-*endo*,6-*endo*-dideuterio (**5a**) isomers recorded at 60 Mc/sec as approximately 20% solutions in deuteriochloroform. The aromatic region is not shown.

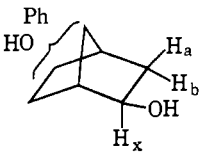
then subjected to the same conditions of hydrolysis as were employed for **2**, **2a**, and **14**. This time the yields of products were not determined, since we were interested primarily in whether the phenylnortricyclenol (**4**) so obtained had lost one of its deuterium atoms, as in **4a**, or still possessed both of the original deuteriums. In fact, **4a** was once again obtained, thus lending credence to the conclusion (see Discussion) that **2** and **14** hydrolyze through the same intermediates. Neither **2** nor **14** underwent internal rearrangement to the other.



Finally the isotope position isomer **2c** was hydrolyzed under the usual conditions and the products **3c**, **4c**, **5c**, **6c** and **d**, and **7c** and **d** were isolated. The positions occupied by the deuterium atoms in **3c**, **4c**, and **5c** were as shown in the appropriate structural formulas. Compounds **6c** and **d** and **7c** and **d** each consisted of the two isotope position isomers in the approximate ratio **6d**:**6c** = **7d**:**7c** = 9:1.

Discussion

Nmr Spectra. We previously reported[4] in part some nmr spectral data for compounds **3**, **4**, **5**, and **6**. Further discussion is given here and the available constants are summarized in Tables II and III. Integration of the nmr spectrum of **5** indicated five aromatic hydrogens at δ = 7.38 ppm (downfield from TMS), a single hydrogen at 3.56 ppm, two exchangeable hydrogens at 1.86 ppm, two hydrogens at 2.4 ppm, and the remaining six hydrogens as a complex series of peaks between 2.2 and 0.9 ppm (Figure 1). The one-proton resonance at 3.56 ppm appeared as a broad multiplet in deuteriochloroform solution. When a trace of acid was added to increase the hydroxyl hydrogen exchange rate, the signal appeared as a sharp quartet indicating the presence in compound **5** of the HCOH grouping. The pattern was simplified to a doublet by double irradiation first of 1.46 ppm and again at 1.78 ppm. That the splittings do not arise from coupling with a bridgehead hydrogen was shown when the appearance of the quartet was not altered by double irradiation in the 2.4-ppm region where the signals for the bridgehead hydrogens appear. The splittings are typical of the couplings of an *endo* proton with adjacent *endo* and *exo* protons.[9] Since it has been demonstrated that *endo*-hydrogens of norbornyl derivatives are not coupled with bridgehead hydrogens,[9c] H_x was assigned the *endo* configuration. The set of four sharp signals at



1.78 ppm is assigned to the *endo*-3 hydrogen (H_b) and the broadened multiplet at 1.48 ppm to the *exo*-3 hydrogen (H_a). Analysis of the foregoing ABX system[10] gives the following constants: $\Delta\nu_{ab}$ = 25.5 cps, J_{ax} = 3.5 cps, J_{bx} = 8.5 cps, and J_{ab} = 13.8 cps. These values are consistent with other observations.[9] The absence of fine structure in the components of the quartets for both the *endo*-2 and *endo*-3 protons suggests that the 7-*anti* position is also substituted.[11] The appearance of the *exo*-3 hydrogen at higher field strength than its *endo*-3 counterpart, though contrary to usual observations,[9d,12] is consistent with combined positive anisotropic effects of the *cis*-2-OH[13] and the 7-*syn*-

(9) (a) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2709 (1963); (b) *ibid.*, **86**, 1171 (1964); (c) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); (d) R. Frazer, *ibid.*, 40, 78 (1962).

(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 132.

(11) A 1-3-cps coupling constant between *endo* protons and 7-*anti* protons is expected: J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(12) (a) J. I. Musher, *J. Mol. Phys.*, **6**, 93 (1963); (b) W. C. Wang and C. C. Lee, *Can. J. Chem.*, **43** (1964).

(13) J. C. Davis, Jr., and U. Van Auken, *J. Am. Chem. Soc.*, **87**, 3900 (1965).

Table II. Chemical Shifts of Phenylnorbornanediols[a]

Compd	1-	*exo*-2-	*endo*-2-	*exo*-3-	*endo*-3-	4-	*exo*-5-	*endo*-5-	*exo*-6-	*endo*-6-	*syn*-7-	*anti*-7-
3[b]	~2.44 (br)	..	3.80 (4)	2.14 (br 2)	1.97 (4)	~2.44 (br)	1.22 (m)	0.83 (m)	1.22 (m)	0.83 (m)	...	...
5[c]	~2.42 (br)	..	3.56 (4)	1.46 (br)	1.78 (4)	~2.42 (br)	2.05 (br)	1.17 (m)	2.05 (br)	1.17 (m)	...	...
6[d]	2.61 (br 2)	..	...	2.34 (4)	1.55 (m)	2.37 (br)	...	4.27 (br 2)	1.55 (m)	3.04 (8)	1.94 (10)	1.55 (m)
7[d]	2.67 (br)	..	...	2.06	2.11	2.51 (br)	...	3.98 (4)	1.57 (m)	1.60 (m)	2.2 or 2.47	2.2 or 2.47

[a] Chemical shifts are reported in ppm downfield from tetramethylsilane standard at 0 ppm; values in parentheses refer to the multiplicity of the signals: br, broad; m, multiplet; 2, doublet; etc. [b] In benzene solution. [c] In deuteriochloroform solution. [d] In pyridine solution. The solutions were about 20% (w/v). All signals are slightly concentration dependent because of the anisotropic effect of the benzene substituent.

Table III. Spin-Spin Coupling Constants of Phenylnorbornanediols[a]

	cps			
J	**3**	**5**	**6**	**7**
exo-3,*endo*-3	−12.82	−13.8	−14.5	
exo-3,*endo*-2	2.5	3.5		
endo-3,*endo*-2	7.4	8.5		
exo-6,1			3.9	
endo-6,*anti*-7			2.3	
endo-6,*endo*-5	5.4		7.0	6.8
endo-6,*exo*-6	−12.2	−11.8	−13.0	−11.5
endo-3,*syn*-7			3.0	
syn-7,*anti*-7			−10.0	−9
syn-7,4			1.5	
syn-7,1			1.5	
exo-5,*endo*-6	3.8	3.7		3.6
exo-3,4	4.1	4.0		

[a] See footnotes *b*, *c*, and *d* of Table II.

phenyl. The configurations of the phenyl and the remaining hydroxyl group of **5** were confirmed as follows: the location of the signal (1.65 ppm) for the two exchanging hydroxyl hydrogens is at extremely high field relative to other norbornanols and diols in comparable concentrations. The expected position of the hydroxyl peak is 3.5–4.5 ppm. In a 20% solution of **5** in chloroform (which does not contain an exchange catalyst) the tertiary hydroxyl signal appears at 2.3 ppm and the secondary hydroxyl signal is at 0.9 ppm. Apparently the large upfield shift is caused by a strong neighboring magnetic anisotropy, which can be ascribed to the presence of the phenyl and can be understood by inspection of molecular models. The plane of the phenyl group when in the 7-*syn* position is disposed directly above the 2 and 3 positions. The 2-*exo*-hydroxyl group will then rotate within the diamagnetic region of the ring current.[14] It is likely that the residence time of the OH hydrogen is longer toward the phenyl group than away from it because of hydrogen bonding to the π electrons. This spatial relationship will contribute to the upfield shift. Inspection of the infrared spectrum of **5** in dilute solutions revealed a strong, free OH band at 3622 cm^{-1} and a bonded OH band as a shoulder at 3605 cm^{-1}. The latter absorption did not change in intensity relative to the CH stretching bands. Hydrogen bonding to phenyl in similar favorable cases has been demonstrated by Schleyer.[15] The latter steric relationship of the phenyl group is also indicated by the course of the reduction of ketone **13** with lithium aluminum hydride. Finally the broad featureless signals at 2 ppm are assigned to the *exo*-5 and *exo*-6 hydrogens, which are deshielded by the 7-OH group, and the sharper signals at 1.10 and 1.24 ppm are due to the *endo*-5 and *endo*-6 hydrogens.

In the spectrum of **5c** the intensity of the signal for the bridgehead hydrogens is reduced to 56% of the value expected for two hydrogens. The intensity of all other signals is unaltered. The only change in line shape because of removal of coupling with the bridgehead hydrogen is observed in the 2-ppm region, where the signals for the *exo*-5 and *exo*-6 hydrogens occur.

It has been pointed out before[4] that in the spectrum of compound **5a** the signal for the *endo*-3 hydrogen at 1.68 ppm is absent and the quartet at 3.56 ppm due to the *endo*-2 hydrogen has collapsed to a doublet. It is also seen by inspection of Figure 1 that the signals due to the *endo*-5 and *endo*-6 hydrogens of compound **5a** are reduced in intensity. Actually, from the integrated intensity of these signals it was shown that there is only one hydrogen at these two positions. There is no criterion for distinguishing between the signals for hydrogens at the *endo*-5 and *endo*-6 positions. However, because one deuterium has already been located at *endo*-3 and because it is not possible from mechanistic considerations to place both deuterium atoms on the same side of the molecule, the *endo*-6 configuration was assigned to the second deuterium.

The structure of **3** was deduced in a similar way. In deuteriochloroform solution two signals are observed for hydroxyl groups: a sharp single peak at 4.72 ppm for the tertiary OH, and a doublet, J = 9.0 cps, at 4.32 ppm for the secondary OH. In the presence of a trace of acid the two hydroxyl resonances merge into a single sharp peak and a signal at 3.78 ppm becomes a quartet with splittings of 5.8 and 3.8 cps. The quartet was observed to collapse to a sharp singlet upon double irradiation of the two-hydrogen multiplet at 1.99 ppm. These signals are assigned to the methylene hydrogens at C-3. The fact that double irradiation of the bridgehead hydrogens at 2.36 and 2.56 ppm and the upfield signals between 1.5 and 0.8 ppm caused neither partial collapse nor sharpening of the quartet pattern is evidence that the hydrogen giving the signal at 3.78 ppm occupies an *endo* configuration and that the 7-*anti* position is substituted. From infrared studies of compound **3** in the hydroxyl absorption region two intense bands were found at 3630 and 3575 cm^{-1}. The

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 125.

(15) P. von R. Schleyer, D. S. Trifan, and R. Dacskai, *J. Am. Chem. Soc.*, 80, 6691 (1958).

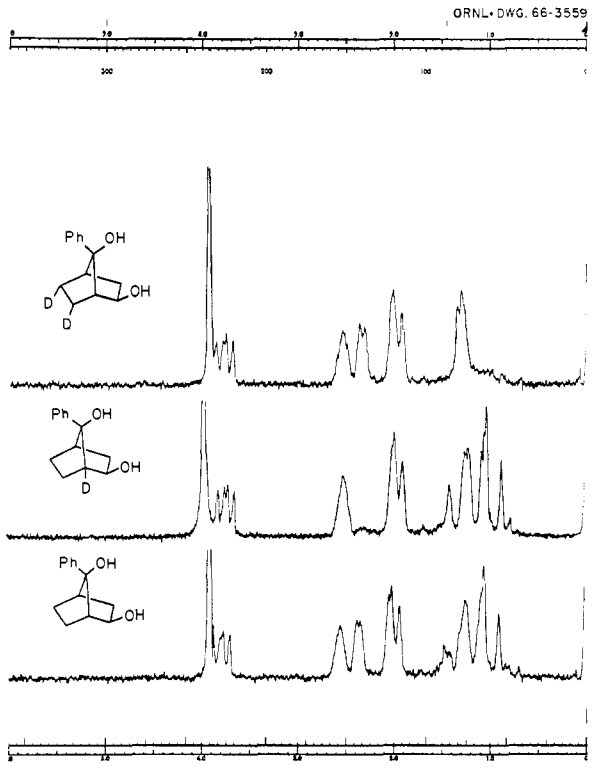


Figure 2. The nmr spectrum of 7-*anti*-phenylnorbornane-7-*syn*,-2-*exo*-diol (**3**) and its 1-deuterio (**3c**) and 5-*endo*,6-*endo*-dideuterio isomers recorded at 60 Mc/sec as approximately 20% solutions in deuteriochloroform. The aromatic region is not shown.

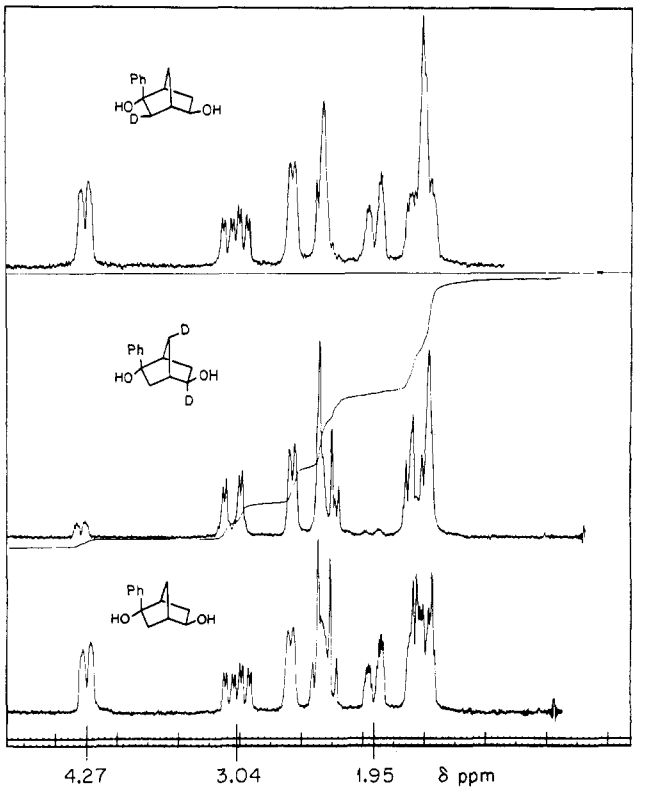


Figure 3. The nmr spectrum of 2-*exo*-phenylnorbornane-2-*endo*,-5-*exo*-diol (**6**) and its 3-*exo*-deuterio (**6d**) and 5-*endo*,7-*anti*-dideuterio (plus 10% 3-*endo*-deuterio) isomers recorded at 100 Mc/sec as approximately 20% solutions in pyridine. The hydroxyl and aromatic regions are not shown.

low-frequency absorption is typical of strong hydrogen bonding and indicates that the two hydroxyl groups are oriented facing each other, a condition which is satisfied by the *exo*-2,*syn*-7 relationship.

In the nmr spectrum of the deuterated diol **3c**, the signal at 2.36 ppm for the 1-bridgehead proton virtually disappears; no more than 12% of its intensity remained (Figure 2). The signals at 0.92 and 1.1 ppm for the *endo*-5 and *endo*-6 hydrogens are absent in the spectrum of **3a**.

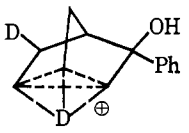
The spectrum of **3** in benzene solution appears somewhat different from that in chloroform. The signals for the two bridgehead hydrogens overlap; the *exo*-3 and *endo*-3 hydrogens give signals which are no longer coincident and, therefore, appear as an AB part of an ABX system while the X portion of the system (*endo*-2 hydrogen) is a nicely resolved quartet and therefore the constants can be calculated.[10] It is interesting to note that in benzene solution each member of the quartet due to *endo*-2 hydrogen is further split by the 1-bridgehead hydrogen giving a coupling constant of 0.6 cps.[16] This splitting is no longer present in the spectrum of **3c** which has deuterium substituted at the 1-bridgehead. A similar coupling between *endo*-3 hydrogen and 4-bridgehead hydrogen is not observed in either compound. The other measurable constants are recorded in Tables II and III. In the higher field region the signals for the hydrogens at the 5 and 6 positions appear nearly the same whether in chloroform or in benzene solution.

Compound **6** is nearly insoluble in chloroform and carbon tetrachloride. Its spectrum in dimethyl sulfoxide-d_6 solution is not amenable to analysis. However, in this solvent the signals for the *endo*-5 hydrogen, 4.27 ppm, and the hydrogen at C-7 and *syn* to the secondary hydroxyl group (*syn*-7 hydrogen), 1.94 ppm, are isolated and clearly identifiable. In this solution the aromatic hydrogens can be used for an internal integration standard. Compound **6a** and **b** dissolved in DMSO-d_6 gives a spectrum showing 0.23 hydrogen at *endo*-5 and 0.12 hydrogen at 7-*syn*. It is clear that a small amount of deuterium should be found at another position in the molecule since the starting material **2a** had about 0.12 hydrogen at the *exo*-5 and *exo*-6 positions. The same results were obtained for spectra of **6a** and **b** in pyridine solution (Figure 3) recorded at 60 and 100 Mc/sec.[17] The relative integrated area for the overlapping *exo*-3 hydrogen and 1-bridgehead hydrogen signals represented 1.93 hydrogens. Integration of the spectra of **6c** and **d** showed 0.26 hydrogen at the *exo*-3 position and 3.90 hydrogens for the total integrated area of *syn*-7, *anti*-7, *exo*-6, and *endo*-3 hydrogens.

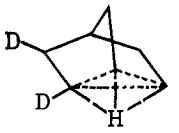
In pyridine solution the spectrum (Figure 3) of **6** can be analyzed. Data are recorded in Tables II and III. Assignments were confirmed by spin decoupling.[17] The hydrogens at *endo*-5, *exo*-6, and *anti*-7 form an AMXY system which can be analyzed by first-order methods. It is interesting to note the combined deshielding effects of the *exo*-5 hydroxyl and *endo*-2 hydroxyl on the *endo*-6 hydrogen which gives the signal at 3.04 ppm. Another feature is the accidental near-

(16) Coupling between *endo* hydrogen and bridgehead hydrogens in norbornyl compounds is usually not observed; see ref 9c.

(17) We are indebted to Dr. H. W. Patton, Dr. V. W. Goodlett, and J. T. Dougherty, Tennessee Eastman Co., Kingsport, Tenn., for obtaining the 100-Mc/sec spectra and for the decoupling experiments.



H–I



H–II

coincidence of the signals for *exo*-3 hydrogen and 4-bridgehead hydrogen. These two hydrogens are strongly coupled in an ABX system involving *endo*-3 hydrogen. Because the signals for *endo*-3 hydrogen appear in the upfield region where they overlap with *anti*-7 hydrogen and *exo*-6 hydrogen, and because the 4-bridgehead hydrogen is further coupled with the C-7 hydrogens, most of the splittings are obscured and the only measurable coupling constant is $J_{exo\text{-}3,endo\text{-}3} = 14.5$ cps. The remaining measurable splitting in this system is 5.4 cps (not a calculated coupling constant).

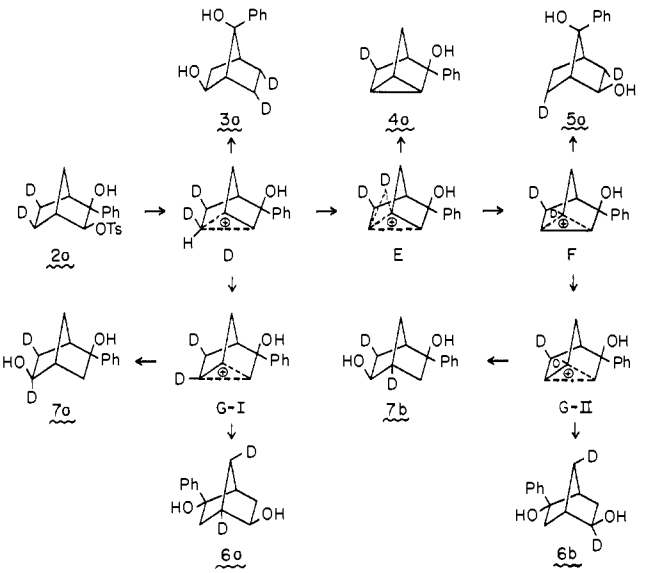
From double irradiation experiments maximum decoupling of *syn*-7, *exo*-3, *endo*-5, and *endo*-6 hydrogens was obtained when ω_2 was at 1.55 ppm. This frequency was thus assigned to *anti*-7, *endo*-3, and *exo*-6 hydrogens.

In our preliminary report the spectrum of **4** was discussed. The two-proton signal at 1.07 ppm was assigned to the C-5 methylene hydrogens and the three-proton signal at 1.23 ppm to the 1, 2, and 6 hydrogens on the three-membered ring. In the spectrum of **4a** the signal at 1.07 ppm had an integrated intensity equivalent to one hydrogen. The deuterium remaining in **4a** was originally at *exo*-5 of **2a**. When **2c** was hydrolyzed the isolated **4c** gave a spectrum in which the signal at 1.23 ppm had a relative intensity equivalent to two hydrogens. Therefore, the deuterium is in the three-membered ring and assignment of it to the 2 position is consistent with the proposed mechanism.

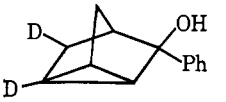
Mechanistic Implications. It is possible to explain the production of compounds **3**–**7** upon hydrolysis of the tosylate **2** by invoking the formation of three nonclassical ionic intermediates (or their classical counterparts) which interconvert through hydride shifts. Product formation alone, however, tells us nothing about the mechanism by which these hydride shifts occur. It is only when we consider the positions occupied by the deuterium atoms in the products **3a**–**7a** and **b** formed on hydrolysis of **2a** that it becomes clear that hydrogen (and deuterium) migration must take place in discrete 1,2 shifts to an adjacent carbon atom. Given in Chart I is the most economical mechanism, we think, which will still explain the results of hydrolysis of **2a**. The ion D formed initially can (1) react with entering hydroxyl to yield the diol **3a**; (2) undergo 5,4 shift of its *exo*-5 deuterium to yield the "edge protonated" intermediate E; or (3) undergo 5,3 shift of its *endo*-5 hydrogen to yield the ion G–I. Intermediate E can eject a deuteron to yield the phenylnortricyclenol **4a**, or proceed to ion F by further migration of deuterium. Ion F can react with solvent to yield **5a**, or it can undergo migration of a hydrogen to produce ion G–II.

It is clear that G–I and G–II, except for the position of one deuterium atom, are identical ions, and these must be the precursors of the diols **6a** and **6b** (and **7a** and **7b**), respectively. It is the formation of **6a** and **b** and **7a** and **b** which makes a "face-protonated" intermediate untenable. Consider, for example, the structures H–I and H–II which depict the only rational "face-deuterated" or "-protonated" species derivable during hydrolysis of **2a**. It is inconceivable to us that H–I could ever yield products (*e.g.*, **6a** and **7b**) containing deuteriums in the *bridgehead positions*. Similarly, H–II does not appear capable of yielding products other than those possessing deuteriums *on adjacent carbons*. It is, of course, possible to depict a complicated series of events by which either H–I or H–II could be transformed to any of the products shown in Chart I. Such schemes, however, have no precedent and seem to us so improbable and prohibited as to be unworthy of serious consideration. It is thus our opinion that only a series of discrete hydride shifts as formulated in the structures D, F, and G through "edge-protonated" intermediates (or transition states) such as E are compatible with the present results.

Chart I



We must now consider the possibility that structure E (Chart I) is a true intermediate, rather than a transition state. Unfortunately, our present data do not allow us to make such a distinction, for there seems to be no very good reason why ions D and F could not each lose a deuteron with almost equal facility to produce the phenylnortricyclenol **4a**. One could ask the question then, why ions D, F, G–I, and G–II could not each lose a *proton* to yield the dideuteriophenylnortricyclenol **4b**. Actually our data do not exclude this possibility. If we make the assumption that D, for example, loses its *endo*-5 proton (*endo*, that is, as D is oriented in Chart I) to the extent of some fraction of the total amount of **6a** formed (less than 0.5% over-all yield), then the

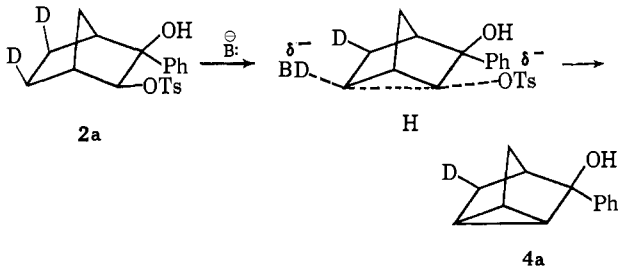


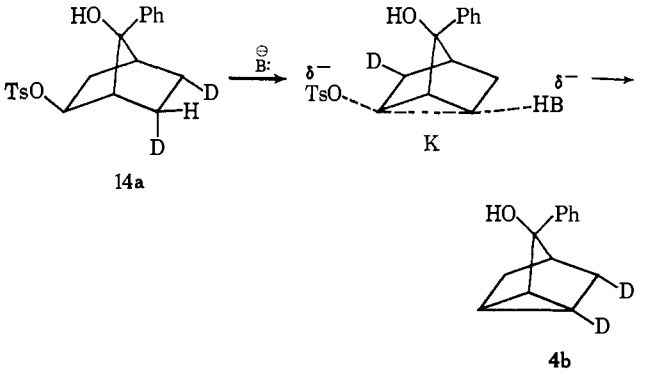
4b

amount of **4b** formed through this route would be undetectable by our nmr methods. The same reasoning holds for any **4b** formed from ions F, G–I, and G–II (probably less than 1–2% **4b** formed from all three ions).

On the basis of the facts so far discussed, the loss of the *exo*-5 deuterium of **2a** as it proceeds to 5-deuterio-3-

phenyl-3-nortricyclenol (**4a**) need not necessarily be a consequence of a carbonium ion mechanism as indicated in Chart I or by the foregoing discussion. An alternate possibility is a "homo-E2" reaction as symbolized in structure H. This possibility is ruled out, however, by the observation that *endo*-5,6-dideuterio-7-phenyl-*syn*-7-hydroxy-2-norbornyl tosylate (**14a**), when hydrolyzed, also yields **4a** containing but one deuterium atom. Were **14a** to proceed to the tricyclenol through a transition state K similar to H, we would expect the base B: to abstract the *exo*-hydrogen rather than the *endo*-deuterium atom, thus leading to **4b** in which both deuteriums remain in the molecule. Further, the fact (Table I) that (without internal rearrangement) **2** and **14** give identical yields of the products **3**–**6** indicates that both of these tosylates hydrolyze through the same intermediates.





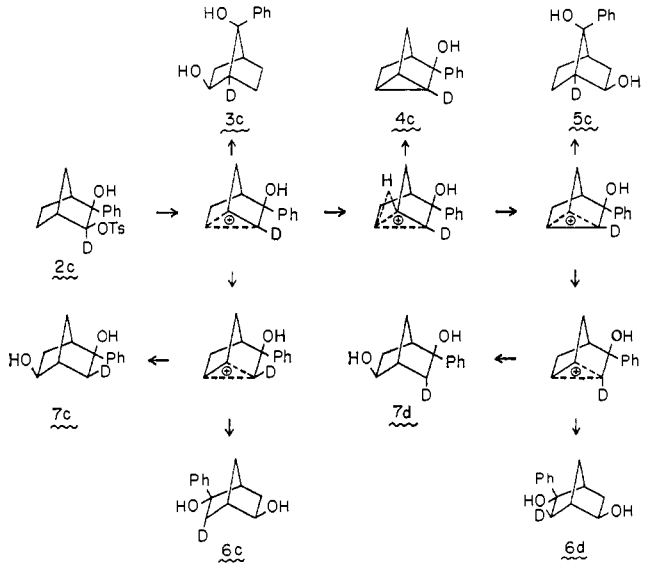
The sequential and reversible nature of hydride shifts in norbornyl systems has been speculated upon many times,[7,18] but we believe our demonstration of the formation of **6b** and **7b** (Chart I) is the first clear evidence for the discrete, consecutive character of these shifts. Their reversibility is not shown by our present data, for as has been pointed out[7] hydride shift does not compete favorably with attack by entering group in the highly nucleophilic solvent water. Because of the low yields of **6a** (*ca.* 0.5%) and **6b** (*ca.* 3.5%) there is a vanishing probability for ion G–II to rearrange to an observable amount of an isotope position isomer of D, or for G–I to rearrange to an isotopic isomer of F. Thus the products of these latter two transformations, if formed, are present in yields so small as to elude our methods of observation. We have already carried out the acetolyses of **2** and **2a**, and plan to perform the formolyses. Acetic and formic acids, being less nucleophilic than water, should allow more complete scrambling of the deuterium atoms during solvolyses of **2a**, thus permitting us to observe the reversible transformations between the several isotope position isomers of ions D, F, and G.

Referring to Table I, we see that the yields of the products **3a**, **4a**, and **5a** from hydrolysis of the deuterated tosylate **2a** are different from the yields of the nondeuterated products **3**, **4**, and **5** obtained from the normal tosylate **2**. These differences are due to intramolecular isotope effects; the combined yield (31%) of the products of deuteron loss (**4a**) and of deuterium migration (**5a**) is less than the combined yield (38%) of the isotope position isomers **4** and **5** formed through proton loss or hydride shift. The relative yields of **3a** (53%) and **3** (43%) are additional evidence for the greater mobility of hydrogen in these reactions. The exact value of the isotope effect is not easy to calculate, for there does not seem to be any common basis by which the two different sets of yield data can be compared. We can only say that the isotope effect is substantial, and in qualitative agreement with the mechanism of Chart I.

Although each of the presumed ions D, F, and G might be expected to yield two products (exclusive of isotope position isomers), we isolated only one each of the anticipated compounds from D and F. One can explain this result by saying that in both the ions D and F the carbonium centers adjacent to the phenyl and hydroxyl groups are rendered less available to nucleophilic attack owing to steric hindrance and to the inductive effects of these two groups. Ion G (G–I and G–II in Chart I) should produce[19] nearly equal amounts of the diols **6** and **7**, and, in fact, each is formed in about 4% yield.

As a final check on the validity of our interpretation of the hydrolysis of **2a**, we repeated one hydrolytic experiment on the tosylate **2c** in which the deuterium is *endo* and in the 3 position of the norbornane skeleton. Given in Chart II is the mechanistic scheme for the hydrolysis of **2c**, showing that the isotope position isomers **3c**–**7c** and **d** actually observed are, in fact, those expected on the basis of the mechanism previously outlined in Chart I.

Chart II



(18) See also J. Berson in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., 1963, p 144.

(19) J. A. Berson, A. W. McRowe, and R. G. Bergman, *J. Am. Chem. Soc.*, **88**, 1067 (1966).

Experimental Section

Proton resonance spectra were recorded using a Varian A-60 nmr spectrometer equipped with a variable-temperature probe. Decoupling experiments were done on a Varian dual-purpose spectrometer at 56.4 Mc using the technique recommended in Varian Associates Technical Information Bulletin, Vol. III, No. 3, 1962. The spectrum of compound **6** was recorded on a Varian A-100 nmr spectrometer.[19] The A-60 spectrometer was calibrated in the usual way with a mixture of TMS (δ = 0) and chloroform (δ = 436 cps). Coupling constants are corrected to within 0.1 cps. Chemical shifts are concentration dependent due to the anisotropy of the phenyl substituent. Infrared spectral data were recorded on Beckman IR-7 and IR-8 spectrometers. Melting points were taken on a Kofler hot bench or in capillary tubes and are uncorrected. Carbon-hydrogen analyses were performed by Huffman Laboratories Inc., Wheatridge, Colo.

2-*endo*-Phenyl-2-*exo*-hydroxy-3-*exo*-norbornyl *p*-Toluenesulfonate (2). To 2 g of 2-phenylnorbornane-2,3-*cis*,*exo*-diol[3] in 7 ml of pyridine was added 2 g of *p*-toluenesulfonyl chloride. The mixture was allowed to stand at ambient temperature overnight after which water was added and the product was extracted with chloroform. The chloroform solution was washed with dilute hydrochloric acid, and the solvent was evaporated. The solid was crystallized from a chloroform–ether mixture, mp 122°. In larger scale preparations 98% yields were obtained.

Anal. Calcd for $C_{20}H_{24}O_4S$: C, 67.01; H, 6.18. Found: C, 66.95; H, 6.04.

2-*endo*-Phenyl-2-*exo*-hydroxy-3-*exo*-norbornane-5,6-*exo*-d_2 *p*-Toluenesulfonate (2a). 5-Norbornen-2-ol (Aldrich) in ethanol solution was deuterated over palladium-on-carbon catalyst using deuterium gas produced as needed by the electrolysis of dilute D_2SO_4. The norbornan-2-ol-5,6-*exo*-d_2 was oxidized[20] to norcamphor-5,6-*exo*-d_2 with chromic acid. The deuterated norcamphor was treated with phenylmagnesium bromide to give 2-*exo*-phenyl-2-*endo*-hydroxynorbornane-5,6-*exo*-d_2. The latter material was treated with the theoretical amount of acetic anhydride in pyridine by boiling the mixture 16 hr under a reflux condenser. The product, 2-phenyl-2-norbornene-5,6-*exo*-d_2, was recovered in the usual way and after purification by vacuum distillation, it was analyzed by nmr spectroscopy as the pure liquid and as a 30% CCl_4 solution; the following data (in ppm) were obtained: aromatic hydrogen, 7.2 (5.0 H); olefinic hydrogen, 6.18 (1.00 H); 1-bridgehead hydrogen, 3.23 (1.00 H); 4-bridgehead hydrogen, 2.91 (1.00 H); 5- and 6-*exo* hydrogens and 7-*syn* hydrogen, 1.50 (1.27 H); and 5- and 6-*endo* hydrogens and 7-*anti* hydrogen, 1.11 (2.97 H). The two *exo* positions, therefore, contained 0.27 atom of hydrogen per mole.

The olefin was treated with performic acid which converted it to the deuterated carbonate ester of 2-*endo*-phenylnorbornane-2,3-*cis*,*exo*-diol-5,6-*exo*-d_2. Nmr analysis (in ppm) of the carbonate ester was as follows: aromatic hydrogens, 7.42 (5.0 H); 3-*endo* hydrogen, 4.88 (0.98 H); bridgehead hydrogens, 2.74 and 2.59 (2.03 H); 7-*syn* hydrogen, 2.05 (1.03 H); 5- and 6-*exo* hydrogens, 5- and 6-*endo* hydrogens, 7-*anti* hydrogen, 0.85–1.8 (3.23 H). The 5- and 6-*exo* positions, therefore, contained 0.23 hydrogen atom per mole.

Hydrolysis of the carbonate ester gave 2-*endo*-phenylnorbornane-2,3-*cis*,*exo*-diol-5,6-*exo*-d_2. Integration of the nmr spectrum gave the following data (in ppm): aromatic hydrogens, 7.26 (5.0 H); hydroxyl hydrogen, 4.23 (2.00 H); 3-*endo* hydrogen, 3.81 (0.99 H); 1-bridgehead hydrogen, 2.30 (1.00 H); 7-*syn* hydrogen, 2.06; 4-bridgehead hydrogen, 1.98 (1.98 H); 7-*anti* hydrogen, 1.1; 5- and 6-*endo* hydrogens and 5- and 6-*exo* hydrogens, 0.8–1.0 (3.25 H). The 5- and 6-*exo* positions were substituted with 0.25 hydrogen and 1.75 deuteriums.

The deuterated tosylate ester **2a** was prepared in the same way as the ester **2**; its melting point was 122°.

2-*endo*-Phenyl-2-hydroxy-3-*exo*-norbornane-3-*endo*-*d* *p*-Toluenesulfonate (2c). Norcamphor was treated with D_2O and NaOD repeatedly to effect exchange of the hydrogens in the 3 position. The norcamphor-3-d_2 was then used to prepare the *p*-toluenesulfonate ester as described above. The ester **2c** was 89% deuterated in the 3-*endo* position as shown by integration of its nmr spectrum

Hydrolysis of 2. In a typical experiment 1.79 g of **2** and 100 ml of acetone were placed in a Pyrex pipe. To this was added a solution of 0.7 g of potassium carbonate in 100 ml of water. The pipe was closed with a clamp and a lead washer. The contents were shaken and then the pipe was heated on the steam bath for 8 hr. It was shaken occasionally during the first 15 min. The contents from four such pipes were mixed and the acetone was removed with the aid of a rotary evaporator. The aqueous portion was extracted four times with 100-ml portions of ether. The ether was evaporated and the organic residue was chromatographed on a column of alumina 2 × 90 cm. The alumina was prepared by adding 10 ml of water to 1 lb of Fisher alumina and heating it on the steam bath 0.5 hr with occasional shaking. The alumina was eluted with 10% ether in benzene until no more material was found in the solvent. This procedure resulted in the recovery of 0.931 g (25%) of almost pure 3-phenyl-3-nortricyclanol (**4**). Pure 7-*syn*-phenylnorbornane-2-*exo*,7-*anti*-diol (**5**), 0.609 g (15%), was recovered from the alumina column by eluting it with ether. Finally the alumina was eluted with 5% methanol in ether. The remaining material, 2.475 g (61.2%), was removed. It consisted mostly of 7-*anti*-phenylnorbornane-2-*exo*,7-*syn*-diol (**3**). Crystallization of the last fraction from ether–hexane mixture gave **3**, mp 98°. After three additional crystallizations the melting point was 101°.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.40; H, 8.02.

7-*syn*-Phenylnorbornane-7-*anti*,2-*exo*-diol (**5**), fraction 2, was crystallized from hexane-ether mixture and sublimed at 0.02 mm, mp 98°.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.34; H, 7.93.

3-Phenyl-3-nortricyclenol (**4**), fraction 1, was crystallized from hexane containing a little ether, mp 61°. The nmr spectrum in carbon tetrachloride solution was as follows (in ppm): 7-*syn* hydrogen, 2.13 (1 H); hydroxyl hydrogen, 2.45 (1 H); 4-bridgehead hydrogen, 1.73 (1 H); 7-*anti* hydrogen, 1.29 (1 H); 1, 2, and 6 hydrogens, 1.23 (3 H); and 5 hydrogens, 1.07 (2 H).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.50; H, 7.49.

The residues from fraction 3 was carefully crystallized from ether. A material, 2-*exo*-phenylnorbornane-2-*endo*,5-*exo*-diol (**6**), melting at 162° was recovered. It was recrystallized from ethanol–ether mixture, mp 163°.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.55; H, 7.97.

In a separate experiment 8 g of **2** was hydrolyzed. By careful chromatography of the product mixture on alumina, 0.162 g (3.8% yield) of **7** was recovered when the alumina column was eluted with 0.5% methanol in ether. The compound was crystallized from chloroform, mp 155°. The melting point was not depressed when mixed with a sample of **7** prepared by another method (Benjamin S. Benjaminov, private communication), and the nmr spectra were identical.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.28; H, 7.71.

Figure 4 shows a comparison of the nmr spectra of **7**, **7a** and **b**, and **7c** and **d**. In the spectrum of **7a** and **b** one of the bridgehead hydrogen signals, 2.52 ppm, is missing and the intensity of the highest field signals, 1.58 ppm, *exo*-6 and *endo*-6, is reduced to approximately half. In addition the relative intensity of the signal at 3.98 ppm, *endo*-5 hydrogen, is about 90% of that expected for one hydrogen. Part of the signal appearing at 2.1 ppm is assigned to the *endo*-3 hydrogen. The intensity of this signal is reduced by approximately one in the spectrum of **7c** and **d**.

2-*exo*-Phenyl-2-*endo*-hydroxy-5-norbornene (9). 5-Norbornen-2-ol, 10 g, in 100 ml of pyridine was slowly added to the complex from 20 g of chromium trioxide in 250 ml of pyridine. The mixture was stirred for 40 min while cooling it with an ice bath. Then it was stirred at ambient temperature for 4 hr. The product was worked up in the usual way and the 5-norbornen-2-one was treated with the Grignard reagent from 30 g of bromobenzene. After the reaction mixture was stirred and heated for 1 hr, water was added to break up the complex, and the ether layer was removed by decantation. The 2-*exo*-phenyl-2-*endo*-hydroxy-5-norbornene was distilled, bp 99° (0.1 mm). The nmr spectrum was as follows (in ppm): aromatic hydrogen, 7.17 (5 H); olefinic protons, 6.12 (2 H); 1-bridgehead hydrogen, 2.98 (1 H); 4-bridgehead hydrogen, 2.80 (1 H); 3-*exo* hydrogen, 2.26 (1 H); hydroxyl hydrogen, 2.12 (1 H); 7 hydrogens, 1.49; and 3-*endo* hydrogen, 1.27 (3 H). The coupling constants (in cps) were: $J_{3\text{-exo},4}$ = 3.87, $J_{3\text{-exo},3\text{-endo}}$ = 12.36, $J_{6,1}$ = 2.83, $J_{4,5}$ = 3.11, $J_{5,6}$ = 5.67, $J_{5,1}$ = 0.82, $J_{6,4}$ = 0.88, and $J_{7,1}$ = 2.1. The signal for the 3-*endo* hydrogen appears as a pair of triplets, the triplet structure having

(20) D. C. Kleinfelter and P. von R. Schleyer, *Org. Syn.*, **42**, 79 (1962).

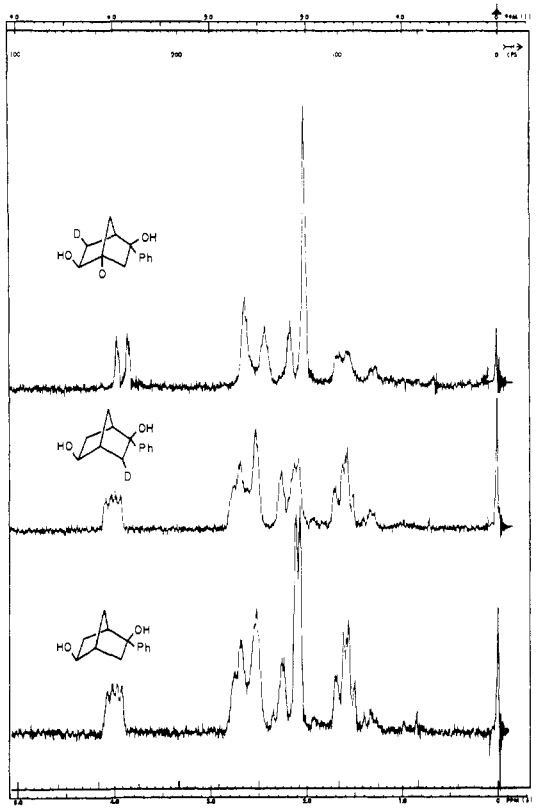


Figure 4. The nmr spectrum of 2-*endo*-phenylnorbornane-2,5-*exo*-diol (**7**) and its 3-*endo*-deuterio (**7d**) and 4,6-*exo*-dideuterio (**7a**) isomers recorded at 60 Mc/sec as approximately 20% solutions in pyridine. The hydroxyl and aromatic hydrogens are not shown.

separation of 1.94 cps probably because of coupling with the 7-*anti* hydrogen and virtual coupling[21] to the 4-bridgehead hydrogen.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.95; H, 7.69.

2-*exo*-Phenylnorbornane-2-*endo*,5-*exo*-diol (6). Diborane, generated externally from 6.8 g of sodium borohydride,[22] was passed into a solution of 20 g of **9** dissolved in 200 ml of tetrahydrofuran and 100 ml of diglyme. The mixture was stirred for 2 hr and then worked up in the usual way.[22] The product crystallized spontaneously in the ether extracts. It was removed by filtration; yield 6.5 g, mp 162°. The nmr spectrum was the same as that from hydrolysis. The solvent fraction was concentrated and another compound, 2-*exo*-phenylnorbornane-2-*endo*,6-*exo*-diol (**10**), crystallized. This material was recrystallized from chloroform; yield 6 g, mp 128°. The nmr spectrum in pyridine solution is as follows (in ppm): hydroxyl hydrogens, 5.81 (2 H); 6-*endo* hydrogen, 2.55 (1 H); 1-bridgehead hydrogen, 2.87 (1 H); remaining 6 hydrogens, 1.3–2.5.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.01; H, 7.98.

3-Phenyl-3-nortricyclanol (4). Norbornadiene, 162 g, was boiled with 450 g of formic acid for 1 hr. Water was added, and the mixture was extracted with ether. The ether layer was treated with sodium carbonate solution, and then the ether was evaporated. The oily material was heated with 20% sodium hydroxide with vigorous stirring for 1 hr. The mixture was cooled and extracted with ether. There remained about 100 g of crude nortricyclanol. A solution of 36 g of nortricyclanol in 50 ml of acetic acid was added to a chromic acid solution composed of 40 g of sodium dichromate, 300 ml of water, 100 ml of acetic acid, and 60 ml of sulfuric acid. Throughout the oxidation the temperature was maintained at 20°. The reaction mixture was diluted with a large volume of water and the product, nortricyclanone, was extracted with ether. Acetic acid was removed from the solution by shaking it with sodium carbonate solution. The ether solution was dried with potassium carbonate. Without further purification, the nortricyclanone was treated with the Grignard reagent from 60 g of bromobenzene. The product was worked up in the usual way and distilled at reduced pressure. The yield was 51 g of 3-phenyl-3-nortricyclanol boiling between 98 and 113°. A fraction was crystallized from hexane containing a little ether. The melting point and nmr spectrum were the same as the material from hydrolysis of **2**.

Isotope-Dilution Experiments. Starting with phenyl-C^{14}-labeled bromobenzene and norcamphor, phenyl-labeled **2** was prepared, 2.522 ± 0.011 mcuries/mole. In a Pyrex pipe was placed 2.3847 g of the tosylate together with 1.85 g of potassium carbonate, 100 ml of acetone, and 100 ml of water. The closed pipe was heated in the steam bath for 8 hr. When it was cooled and opened, the previously prepared and nonradioactive diluents were added as follows: 0.3516 g of the tricyclic alcohol **4**, 0.4302 g of the *syn*-diol **3**, 0.3038 g of the *anti*-diol **5**, and 0.1240 g of the diol **6**. The mixture was made homogeneous, and the diluted, labeled products were reisolated and each was crystallized three times, dried under vacuum, and assayed for carbon-14 content.

Phenyl-C^{14}-labeled **2a**, 2.426 mcuries/mole was prepared in a similar manner. The hydrolysis of **2a**, 2.3144 g, was done as described above. To the reaction products were added the following nonradioactive diluents: 0.3755 g of **4**, 0.3290 g of **1**, 0.3041 g of **5**, and 0.1130 g of **6**. The products were isolated as described above.

A sample of phenyl-C^{14}-labeled **3**, 0.8412 g, prepared by hydrolysis of phenyl-C^{14}-labeled **2**, was treated with 0.86 g of *p*-toluenesulfonyl chloride in 15 ml of pyridine. The ester **14** was isolated after the mixture was left standing a day. The ester **14** was then hydrolyzed as described before, and the product mixture was diluted with the following amounts of nonradioactive materials: 0.3066 g of **4**, 0.4476 g of **3**, 0.3050 g of **5**, and 0.069 g of **6**. The results of the dilution experiments are recorded in Table IV.

Table IV. Yields of Products in Isotope Dilution Experiments

Starting compd, mmoles (mcuries/mole)	Diluent compd	Diluent wt, g	Radioactivity of diluted product, mcuries/mole	Yield, %
2, 6.652 (2.522)	**3**	0.4302	1.459	43.5
	4	0.3516	1.202	25.9
	5	0.3038	0.9065	12.5
	6	0.1244	0.722	3.7
			Total yield	85.5
2a, 6.421 (2.426)	**3**	0.3290	1.675	53.5
	4	0.3755	08925	17.5
	5	0.3041	0.9132	13.4
	6	0.1130	0.744	3.8
			Total yield	88.2
14, 4.115 (2.522)	**3**	0.4476	1.162	45.5
	4	0.3066	1.004	26.5
	5	0.3050	0.600	11.3
	6	0.0690	0.847	4.2
			Total yield	87.5

7-Phenyl-2-norbornanon-1-*syn*-ol (11). A solution of 1.064 g of **3** in 12 ml of pyridine was added to the complex from 2 g of chromium trioxide and 25 ml of pyridine. After 1 hr, water was added, and the mixture was extracted with ether. The ether solution was washed with dilute hydrochloric acid, the ether was evaporated, and the product was crystallized from carbon tetrachloride, mp 155°.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.24; H, 7.00.

The ketone, 10.35 g, was reduced with 0.35 g of lithium aluminum hydride. The product **12** was crystallized from carbon tetrachloride, mp 158°. The nmr spectrum in deuteriochloroform solution showed a multiplet at 4.9 ppm for the 2-*exo* hydrogen.

(21) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).
(22) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 31 (1964).

The shift to low field is consistent with the deshielding effect of the 7-*syn* hydroxyl group and the inductive effect of the 2-*endo* hydroxyl group.

7-Phenyl-2-norbornanon-7-*anti*-ol (13). The pyridine complex from 5 g of chromium trioxide was prepared. To it was added 1 g of **5**. The ketone was isolated in the same way as described for **11**. The product was crystallized twice from hexane–ether mixture, mp 109°.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.14; H, 7.01.

A sample of the ketone **13** weighing 0.47 g was reduced with lithium aluminum hydride. The isolated diol was crystallized from hexane–ether mixture. It was identical in every respect with the starting diol **5**.

Test for Internal Return. Compound **2** was subjected to hydrolysis conditions previously described for a period of 4 hr. Among the products isolated the only tosylate ester found was **2**. The hydrolysis of **14** was complete after the reaction had proceeded for 1 hr. No trace of **2** or **14** could be found in the product mixture.

The Ionic Decomposition of 2-Substituted 2-Propyl *p*-Nitroperbenzoates. Migration to Electron-Deficient Oxygen and Anchimeric Acceleration of Peroxide-Bond Heterolysis[1]

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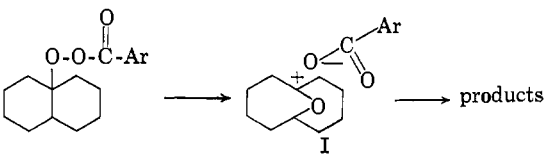
Abstract: A number of 2-substituted 2-propyl *p*-nitroperbenzoates have been prepared and solvolyzed in methanol solvent. The products from the *p*-nitroperbenzoates which were substituted with alkyl groups larger than methyl were those derived from exclusive migration of the alkyl group; these were *p*-nitrobenzoic acid, acetone and its dimethyl ketal, and the alcohol, olefin, and methyl ether derived from the migrating group. The amount of ether or olefin derived from the migrating group was negligible for the ethyl and isopropyl groups, but was substantial for the *t*-butyl or benzyl migrating groups. The relative rates of heterolysis were found to depend markedly on the nature of the migrating group. They were CH_3, 1; $CH_2CH_2C_6H_5$, 14.9; CH_2CH_3, 45.0; $CH(CH_3)_2$, 2.94×10^3; $CH_2C_6H_5$, 1.63×10^3; $CH_2C_6H_4OCH_3$-*m*, 1.54×10^3; $CH_2C_6H_4OCH_3$-*p*, 5.32×10^4; 4-camphyl, 1.42×10^4; C_6H_5, 1.18×10^5; $C(CH_3)_3$, 2.28×10^5. Evidence is presented which shows that steric acceleration of ionization is negligible and that the relative rate order is best interpreted in terms of a nonclassical-type, bridged transition state which collapses to an α-alkoxy carbonium ion intermeditae. In terms of neighboring group theory, these relative rates of heterolysis or migration aptitudes can be considered measures of anchimeric acceleration of ionization. A comparison of neopentyl tosylate and *t*-butyl pertosylate solvolysis leads to an anchimeric acceleration factor for the methyl-substituted perester of about 10^{23} in terms of rate. This enormous anchimeric acceleration coupled with the very large relative rate spectrum observed for the alkyl-substituted *p*-nitroperbenzoates imply that unrearranged *t*-alkoxy cations are very unstable and that there is considerable distribution of positive charge on carbon rather than on oxygen in the transition state for perester solvolysis. The high relative rate for the 4-camphyl-substituted perester furthermore shows that tetrahedral hybridization of the migrating group is retained in the transition state. That there is, nevertheless, considerable positive charge distributed within the migrating group in the transition state was demonstrated by the substantial rate-enhancing effect of *p*-methoxy substitution on the benzyl migrating group. In contrast, *m*-methoxy substitution leads to no rate enhancement compared to benzyl and thus Ar_2-4 type participation for benzyl is ruled out. Furthermore, Ar_1-3, Ar_1-4, and Ar_2-5 styles of participation are probably unimportant on the basis of the solvolysis products and the relatively small, rate-enhancing effect of the 2-phenylethyl substituent. Finally, a comparison of the relative rates of fragmentation of the corresponding *t*-alkoxy radicals with the relative rates of perester solvolysis indicate that the former process is best not rationalized in terms of a bridged transition state as for the latter process.

The ionic decomposition of peresters, involving a 1,2 rearrangement of carbon to electron-deficient oxygen, has been the subject of a number of mechanistic investigations. The general features of the rearrangement were first discovered by Criegee,[3] who studied the decomposition of 9-decalyl peresters. A relatively polar mechanism was indicated by the nature of the products and the enhanced rate of rearrangement in polar solvents and with more acidic leaving groups. Later workers showed that ion-pair exchange with foreign anions[4a,b] did not occur and that the carboxylate oxygens of the leaving group did not equilibrate.[4c] These results were interpreted in terms of a



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(2) U. S. Rubber Company Foundation Fellow in Chemistry, 1960–1961. Presently at the Union Carbide Research Institute.

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