

70 ± 2° for 5 min. Work-up as in II (B) gave a yellow oil from which 8.1 g (85%) of white solid (mp 120–123°) was obtained from ethanol.

The ultraviolet spectrum in 95% ethanol showed λ_{\max} 241 m μ . The nmr spectrum in carbon tetrachloride solution showed the solid to be ca. 50:50 mixture of camphene and tricyclene isomers. Pertinent signals for the nmr spectrum of the camphene compound are recorded in Table III.

2-*o*-Anisyl-3-diphenylmethylenetricyclene.—A solution of 7.0 g (0.017 mole) of the hydrocarbon mixture (*vide supra*) in 160 ml of acetic acid was refluxed for 48 hr. The yellow solution was poured into ice water, and the creamy semisolid material that formed was dissolved in ether. The ether solution was washed with aqueous sodium carbonate, and the ether was removed at reduced pressure leaving a tan oil. From 95% ethanol 5.8 g (70% based on the alcohol) of white solid (mp 122–123°) was obtained.

Anal. Calcd for C₃₀H₃₀O: C, 88.63; H, 7.44. Found: C, 88.45; H, 7.37.

The ultraviolet spectrum in 95% ethanol showed λ_{\max} 253 m μ (log ϵ 4.20). Pertinent signals for the nmr spectrum of the tricyclene compound are recorded in Table III.

Dehydration of 2-Phenylisoborneol.—The dehydration with potassium bisulfate and subsequent work-up were identical with that employed for the preparation of II. A mixture of 19.8 g (0.0859 mole) of 2-phenylisoborneol [bp 159–171° (13–14 mm)] and 15 g of potassium bisulfate was heated at 160–170° for 0.5 hr. After work-up in the usual manner and chromatography over alumina using ligroin solvent, 14.1 g (77.3%) of a mixture of 2-phenylbornene (VII) and 1-phenylcamphene (VIII) as a light yellow oil was obtained.

The infrared spectrum in carbon disulfide showed absorption at 885 cm⁻¹ for the C=CH₂ system of VIII and 826 cm⁻¹ for the alkene C–H-bending vibration of VII.⁶ Pertinent signals for the nmr spectrum of VIII are recorded in Table III. Compound VII showed the following: phenyl hydrogens, 7.18 ppm; 3-olefinic hydrogen, 5.93 ppm, 4-bridgehead hydrogen, 2.33 ppm, nine methyl hydrogen, 0.79, 0.89, and 1.11 ppm.

Integration of the phenyl signals, the 3-hydrogen signal of

VII, and the olefinic methylene signals of VIII gave a ratio of 5.0:0.60:0.80, which calculates for a 60%:40% mixture of VII:VIII. The ultraviolet spectrum in 95% ethanol showed λ_{\max} 251 m μ (log ϵ 3.91) for VII, assuming 60% purity.

Dehydration of 3-Diphenylmethylenisoborneol.—The dehydration with potassium bisulfate and subsequent work-up was identical with that employed for the preparation of II. A mixture of 9.40 g (0.0295 mole) of 3-diphenylmethylenisoborneol²² and 12 g of potassium bisulfate was heated at 150–160° for 0.5 hr. After work-up in the usual manner and chromatography over alumina using ligroin solvent, 7.60 g (85.8%) of a mixture of 7-diphenylmethylenecamphene (X) and 3-diphenylmethylenetricyclene (IX) as a colorless oil was obtained.

The infrared spectrum in carbon disulfide showed absorption at 876 cm⁻¹ for the C=CH₂ system of X.⁶ Pertinent signals for the nmr spectrum of X and IX are recorded in Table III. Integration of the phenyl signals, and the 1- and 4-bridgehead hydrogens' signals gave a ratio of 5.0:0.74:0.74, which calculates for a 74%:26% mixture of X:IX. The ultraviolet spectrum in 95% ethanol showed λ_{\max} 239 m μ (log ϵ 4.14).

Registry No.—I, 14164-35-3; II, 14164-36-4; III, 14164-37-5; IV, 14164-38-6; V, 14164-39-7; VI, 14164-40-0; VII, 7070-09-9; VIII, 7070-29-3; IX, 14164-42-2; X, 14271-25-1; XI, 530-48-3; 3-diphenylmethylenisoborneol, 14164-43-3; 1-phenylbornene, 461-86-9; 2-*o*-anisyl-3-diphenylmethylenisoborneol, 14164-44-4; 1-*o*-anisyl-7-diphenylmethylenecamphene, 14164-45-5; 2-*o*-anisyl-3-diphenylmethylenetricyclene, 14164-46-6.

Acknowledgment.—The infrared hydrogen-bonding measurements of IV and the *o*-anisyl analog by Louis Joris, Department of Chemistry, Princeton University, are sincerely appreciated.

(22) S. Yuan, M.S. Thesis, University of Tennessee, 1967.

Aryl Norbornane Compounds. V. Intramolecular Diamagnetic Shielding in Some Phenylbornyl *p*-Nitrobenzoates and Tosylates^{1,2}

DONALD C. KLEINFELTER

Department of Chemistry, University of Tennessee, Knoxville, Tennessee

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Those *p*-nitrobenzoates which approach a *cis* relationship with their phenyl groups show greater shielding of one *p*-nitrobenzoyl proton pair than another in the nuclear magnetic resonance (nmr) spectrum, while other *p*-nitrobenzoyl protons are magnetically equivalent. Greater anisotropic shielding by phenyl of one proton pair and correlation between degrees of shielding and measured shielding parameters explain the results. Only the *p*-tosyl group of 7-*anti*-phenyl-2-*exo*-norbornyl tosylate shows no diamagnetic shielding by phenyl. Differences between the tosylate and *p*-nitrobenzoate shielding values are attributed to conformational differences.

Recently we reported initial results on the acetolyses of the 3-phenyl-2-norbornyl tosylates³ in which the unexpected rate retardation attributed to a 3-*exo*-phenyl group was demonstrated. In order to understand better the chemistry of the arylbornyl system, we felt that a detailed study of the magnitudes of interaction between the aryl group and an adjacent or other proximately situated substituent was in order. Presumably nuclear magnetic resonance (nmr) spectroscopy could assist in this evaluation since the response of hydrogen nuclei to the orientational depend-

ent diamagnetic anisotropic shielding of a benzene ring is well established.^{4,5} Data in this present paper should assign the preferred phenyl orientations for the *cis*-positioned isomers and further demonstrate a technique introduced previously² for conformational assignments.

Results and Discussion

The norbornyl derivatives involved in this investigation were *exo*- and *endo*-norbornyl *p*-nitrobenzoates

(1) Grateful acknowledgement is made to the National Science Foundation for a research grant (NSF-GP-1574) which supported a large portion of this work.

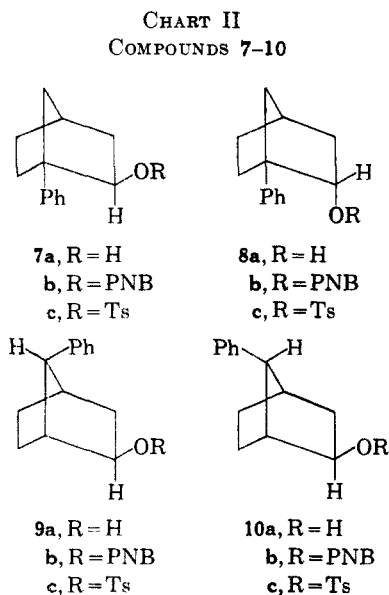
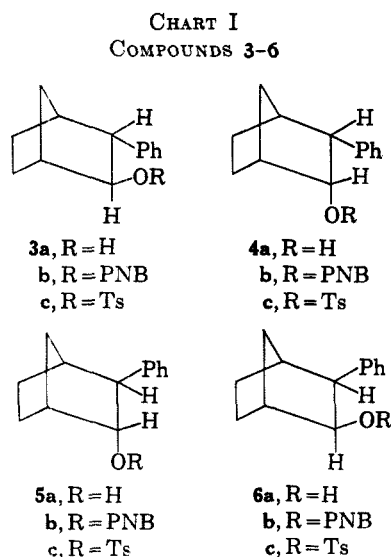
(2) For part IV, see D. C. Kleinfelter, *J. Am. Chem. Soc.*, **89**, 1734 (1967).

(3) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *ibid.*, **88**, 5350 (1966).

(4) L. M. Jackman, "Applications of a Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, (1959), p 126.

(5) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind. (London)*, 1205 (1958); D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961).

(1b and 2b), the 3-phenyl-2-norbornanols (3a-6a) (Chart I), the 1-phenyl-2-norbornanols (7a and 8a),



7-*syn*-phenyl-2-*exo*-norbornanol (9a), 7-*anti*-phenyl-2-*exo*-norbornanol (10a), their *p*-nitrobenzoates (3b-10b), and tosylates (3c-10c). The preparation and characterization of the 3-phenyl-2-norbornyl compounds have been described recently.⁶ The 1-phenyl-2-norbornyl compounds have been prepared previously,^{7,8} but their characterization by nmr spectroscopy has not appeared in the literature. The 7-*syn*- and 7-*anti*-phenyl-2-*exo*-norbornanols (9a and 10a) were prepared by lithium aluminum hydride reduction of the products of kinetically controlled acetolysis of 5c and 3c, respectively, and were isolated by adsorption chromatography. Compounds 7-10 are shown in Chart II.

The nmr spectra of the 1-phenyl-2-norbornyl derivatives and the 7-phenyl-2-*exo*-norbornyl derivatives

were analyzed in the region of the 2-hydrogen signals. In addition, the absorption positions of the 7-hydrogens for the 7-phenyl compounds were determined to ascertain the effects of the 2-*exo* substituents on the 7-*syn*-hydrogen signals. The data are summarized in Table I along with the data for *exo*- and *endo*-norbornanol and their *p*-nitrobenzoates.

TABLE I
NMR SPECTRAL DATA FOR SOME PHENYL
NORBORNYL DERIVATIVES^a

Compd	δ , ppm ^b		Compd	δ , ppm ^b		
	2n	2x		2n	7- <i>anti</i>	7- <i>syn</i>
1a	3.66	...	9a	3.58	2.90	
1b	4.92	...	9b	4.60	2.90	
2a	...	4.15	9c	4.97	3.09	
2b	...	5.27	10a	3.83	...	3.26
7a	3.70	...	10b	4.60	...	3.21
7b	4.54	...	10c	5.02	...	3.35
7c	5.21	...				
8a	...	3.98				
8b	...	4.63				
8c	...	5.26				

^a Chemical shifts (δ) for the alcohols are for very dilute solutions in CCl₄ (see ref 6); those for the tosylates and *p*-nitrobenzoates are for ca. 10 wt % in CDCl₃. ^b δ 's are correct to ± 0.01 ppm.

Assignments of structures to 7-*syn*-phenyl-2-*exo*-norbornanol (9a) and 7-*anti*-phenyl-2-*exo*-norbornanol (10a) can readily be made from analysis of their infrared and nmr spectra. In very dilute carbon tetrachloride (CCl₄) solutions where intermolecular association is absent, 9a shows absorption at 3591 cm⁻¹, corresponding to a $\Delta\nu$ (OH--- π bond) of 28 cm⁻¹ when compared with *exo*-norbornanol.² Under the same conditions 10a shows absorption at 3620 cm⁻¹ ca. identical with that for *exo*-norbornanol. The nmr signals for the 7-hydrogens also assist in assigning structures to these alcohols and their derivatives. When the 7-hydrogen is *syn* to the 2-*exo* substituent the hydrogen is deshielded by an average value of 0.31 ± 0.03 ppm in comparison with the *anti* orientation. Such a downfield shift for hydrogens *syn* to an *exo* substituent has been noted previously by Davis and Van Auken in some *exo*-norbornene derivatives.⁹

All the 2-proton patterns are characteristic of the X part of an ABX system. Since the 3-methylene signals (A and B) were overlapped by peaks from the remaining methylene hydrogens, the coupling constants J_{AX} and J_{BX} could not be determined directly from the spectra as $\Delta\nu_{AB}$ is presumably not large compared to J_{AB} . A similar situation has been discussed in detail in the couplings of the analogous *endo* protons of some substituted bornanes.¹⁰

We were initially surprised to note that certain phenyl norbornyl *p*-nitrobenzoates gave single sharp signals in the nmr for the four *p*-nitrobenzoyl hydrogens while others showed more complex splitting patterns typical of A,A',B,B' systems.¹¹ Upon checking the nmr spectra of 1b and 2b, we found that

(9) J. C. Davis, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **87**, 3900 (1965).

(10) T. J. Flautt and W. F. Erman, *ibid.*, **85**, 3212 (1963).

(11) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press Ltd., London, 1965, p 347.

(6) D. C. Kleinfelter, T. E. Dye, J. E. Mallory, and E. S. Trent, *J. Org. Chem.*, **32**, 1734 (1967).

(7) D. C. Kleinfelter and P. von R. Schleyer, *ibid.*, **26**, 3740 (1961).

(8) D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960.

these, too, showed single sharp peaks for their *p*-nitrobenzoyl protons. The single sharp signals exhibited, apparently due to the magnetic equivalence of the *ortho*-hydrogen pairs, are readily understandable from a consideration of the substituent effects on the proton frequency of benzene. Corio and Dailey¹² have recorded that the *ortho* hydrogens of nitrobenzene and methylbenzoate are deshielded by 0.97 and 0.93 ppm, respectively, relative to benzene. An analysis of those compounds with more complex splitting patterns was then undertaken, and the resulting spectral data along with that observed for the other compounds are listed in Table II.

TABLE II
NMR SPECTRAL DATA FOR SOME NORBORNYL
p-NITROBENZOATES^a

Norbornyl <i>p</i> -nitrobenzoate	δ_A , ppm	δ_B , ppm	$\delta_A - \delta_B$	σ_A^b	σ_B^b
1b 2- <i>exo</i> -	8.25	8.25
2b 2- <i>endo</i> -	8.26	8.26
5b 3- <i>exo</i> -Ph-2- <i>endo</i> -	8.27	8.27
3b 3- <i>endo</i> -Ph-2- <i>exo</i> -	8.19	8.19
10b 7- <i>anti</i> -Ph-2- <i>exo</i> -	8.16	8.16
8b 1-Ph-2- <i>endo</i> -	8.22	8.22
4b 3- <i>endo</i> -Ph-2- <i>endo</i> -	8.15	7.94	0.21	0.11	0.32
7b 1-Ph-2- <i>exo</i> -	8.10	7.81	0.29	0.16	0.45
6b 3- <i>exo</i> -Ph-2- <i>exo</i> -	8.07	7.57	0.50	0.19	0.69
9b 7- <i>syn</i> -Ph-2- <i>exo</i> -	7.99	7.29	0.70	0.27	0.97

^a All recorded spectra data were obtained on ca. 10% by weight solutions in CDCl₃; δ 's are correct to ± 0.01 ppm. ^b σ_A and σ_B are the shielding values for the respective A and B hydrogens relative to 8.26 ppm (an average value for **1b**, **2b**, and **5b**).

The last four compounds in Table II were those showing the splitting patterns typical of A,A',B,B' systems. Using an AX approximation to determine the coupling constants we obtained $J_{AB} = J_{A'B'} = 9.0$ cps, $J_{A,A'} = 1.7$ or 2.3 cps, $J_{B,B'} = 2.3$ or 1.7 cps, and $J_{AB'} = J_{A'B} = 0.3$ cps. These values and the spectral pattern resemble that reported for *p*-chloroanisole.¹³ The calculated signals for the A and B protons in these *p*-nitrobenzoates are all to higher fields than those for the parent compounds. The 8.26-ppm signal was chosen as our standard since **3b**, **10b**, and **8b** (entries 4-6) showed a slight variation with concentration—a downfield shift with dilution. Apparently an intermolecular shielding by phenyl of the *p*-nitrobenzoyl hydrogens is experienced. In line with this reasoning are the phenyl δ 's of 7.30, 7.26, and 7.23 ppm for **10b**, **3b**, and **5b**, respectively, corresponding to an order of decreased intermolecular interaction.¹⁴

In each case where a "cis" relationship exists between the phenyl and *p*-nitrobenzoyl groups, an arrangement of these groups can be achieved where the *p*-nitrobenzoyl hydrogens are held close to the center of the benzene ring where the induced ring currents

are known to cause increased shielding.¹⁵ In this arrangement the hydrogen atoms *ortho* to the carbonyl group are held closer to the benzene ring center than those *ortho* to the nitro group; hence, the respective A and B proton assignments can be made accordingly.

Upon further examination of Table II one notices that the degree of shielding by the benzene ring of the A and B protons increases from entries 7-10 as reflected by the magnitudes of σ_A and σ_B . Moreover, σ_B increases more so than does σ_A as reflected by the magnitude of $\delta_A - \delta_B$. Since Johnson and Bovey¹⁶ have calculated and tabulated shielding values as a function of *Z* along the hexagonal axis of the benzene ring and as a function of *P* in the plane of the carbon atoms, we decided to compare our shielding values with the literature ones. Through the use of Dreiding models in which the *cis* ester conformation is presumably preferred,¹⁷ with the *p*-nitrophenyl ring, carbonyl group, and alkyl oxygen atom all approximately in the same plane, the approximate distance (*r*) and angle (θ) from the center of the benzene ring to the A and B hydrogens were measured. These measurements along with other shielding parameters are included in Table III.

TABLE III
SHIELDING PARAMETERS FOR "cis" PHENYL
NORBORNYL-*p*-NITROBENZOATES

<i>p</i> -Nitrobenzoate	-a (ring radii)-				-a (ring radii)-				Ppm			
	Z _B	P _B	r _B	θ° _B	Z _A	P _A	r _A	θ° _A	σ_B	σ_B^a	σ_A	σ_A^a
4b	2.5	0.1	2.5	5	3.8	1.0	3.9	15	0.32	0.60	0.11	0.15
7b	2.8	0.6	2.9	13	4.4	0.3	4.4	4	0.45	0.39	0.16	0.10
6b	2.5	0.1	2.5	5	3.8	1.0	3.9	15	0.69	0.60	0.19	0.15
9b	2.0	0.5	2.1	14	2.6	2.2	3.5	39	0.97	0.96	0.27	0.10

^a Predicted shielding values from Johnson and Bovey tables.

An examination of the parameters for the last three reveals that the shorter the distance between the shielded hydrogen and the center of the benzene ring, the greater the shielding experienced by that hydrogen. Even though the values for θ are larger in **9b** than the other two, the shielding is greater for the former compound, apparently owing to the smaller *r* value. McConnell¹⁸ has derived a relationship which approximates the shielding of a proton as being proportional to $\cos^2 \theta$ and inversely proportional to r^3 . Hence, the greater dependence on *r* is explicable. Comparison of the recorded shielding values for the B protons with those predicted from the Johnson and Bovey tables reveals a fairly good correlation¹⁹ for the last three compounds. While there appears to be some small disagreement between the predicted and found shielding values for the A protons in **9b**, the over-all agreement is most probably as good as one would have a right to expect.

A priori one might expect that identical parameters for **4b** and **6b** would lead to identical shielding values. However, the shielding values for **4b** are markedly

(15) See, for example, ref 11, p 140.

(16) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958). The tabulated values may be found in Appendix B, ref 12, p 595-604.

(17) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 74.

(18) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(19) The values for σ_B and σ_A in Table III are equal to one-half the values expected for given values of *P* and *Z*. This adjustment is required to compensate for the fact that ca. 50% of the A and B protons can be shielded at one time while the other ca. 50% (180° rotation) are relatively unaffected.

(12) P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956); also see ref 4, p 63.

(13) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 110.

(14) The phenyl hydrogens are apparently intermolecularly deshielded by the *p*-nitrobenzoyl group; at infinite dilution the *p*-nitrobenzoyl hydrogens of **3b** come at 8.26 ppm.

less than those observed for **6b**. This difference is a result of differences in steric factors introduced previously.² In **4b** the phenyl orientation for maximum shielding is one in which an *o*-phenyl hydrogen displays an unfavorable steric interaction with the *endo*-5-hydrogen. To relieve this steric strain the benzene ring rotates somewhat to an energetically more favorable orientation, thus increasing the value of θ and decreasing considerably the extent of the diamagnetic shielding. Finally, while the hydroxyl group of 1-phenyl-2-*endo*-norbornanol showed some interaction with the phenyl group in the infrared (OH free and OH- π bond present),⁸ its *p*-nitrobenzoate (**8b**) exhibited no diamagnetic shielding. Apparently the combined B proton parameters of $r = 3.7a$ and $\theta = 29^\circ$ are too large for any appreciable effect.

The diamagnetic shielding by phenyl of the norbornyl *p*-nitrobenzoates as revealed by this nmr study indicates the relative magnitudes of steric effects associated with the "cis" systems. The relation between the shielding parameters and chemical shifts supports the conformation assignment of the ester framework. Two obvious tests of the utility of our correlations are the following. (1) Can they be used to elucidate structure from nmr spectral data in other compounds? (2) Do structural features so elucidated reflect chemical behavior? The natural extension of this work was to examine the nmr spectra of the phenyl norbornyl tosylates to see if we could obtain the desired answers to these questions. Data for the compounds studied are listed in Table IV.

TABLE IV
NMR SPECTRAL DATA FOR SOME NORBORNYL TOSYLATES^a

Norbornyl tosylate	δ_A	δ_B	$\delta_A - \delta_B$	σ_A^b	σ_B^b	δ_{CH_2}
5c 3- <i>exo</i> -Ph-2- <i>endo</i> -	7.63	7.13	0.50	0.20	0.18	2.30
3c 3- <i>endo</i> -Ph-2- <i>exo</i> -	7.65	7.09	0.56	0.18	0.22	2.29
10c 7- <i>anti</i> -Ph-2- <i>exo</i> -	7.83	7.31	0.53	2.38
8c 1-Ph-2- <i>endo</i> -	7.45	7.04	0.41	0.38	0.27	2.30
4c 3- <i>endo</i> -Ph-2- <i>endo</i> -	7.49	7.13	0.36	0.34	0.18	2.32
7c 1-Ph-2- <i>exo</i> -	7.22	7.06	0.16	0.61	0.25	2.33
6c 3- <i>exo</i> -Ph-2- <i>exo</i> -	7.29	7.12	0.17	0.54	0.19	2.32
9c 7- <i>syn</i> -Ph-2- <i>exo</i> -	7.40	7.17	0.23	0.43	0.14	2.32

^a All recorded spectra were obtained on ca. 10% by weight solutions in CDCl₃; δ 's are correct to ± 0.01 ppm. A downfield shift with dilution of 0.03–0.04 ppm was exhibited by all tosylates. No compensation for this shift was made in the recorded δ 's. ^b σ_A and σ_B are the shielding values for the respective A and B hydrogens relative to those for **10c**.

All the tosylates showed splitting patterns typical of A,A',B,B' systems. As expected, the simplicity of the splitting patterns decreased as the values for $\delta_A - \delta_B$ decreased. For those compounds in which $\delta_A - \delta_B$ was large compared with J_{AB} , an AX approximation gave $J_{AB} = J_{A'B'} = 8.7$ cps, $J_{A,A'} = J_{B,B'} = 1.7$ cps, and $J_{A,B'} = J_{A'B} = 0.3$ cps. In all compounds δ_A and δ_B could be calculated from the observed line positions. The values of δ_A and δ_B for **10c** are to lower fields than the respective signals for the other tosylates. Contrary to the observed spectral properties for the *p*-nitrobenzoates, **5b**, **3b**, and **8b**, which showed no appreciable intramolecular diamagnetic shielding of the *p*-nitrobenzoyl hydrogens by phenyl, the tosylates, **5c**, **3c**, and **8c**, are evidently

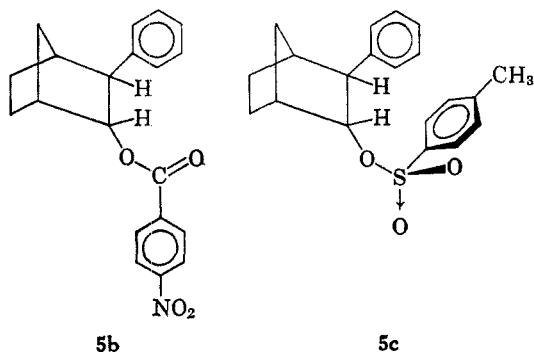
experiencing some shielding. Naturally, no intramolecular interaction would be expected in **10c** since the substituents lie too far apart. A further contrasting situation exists in comparison with the data for the *p*-nitrobenzoate analogs in that for the last five tosylates in Table IV the A protons are shielded by phenyl more so than the B protons, and consequently the values of $\delta_A - \delta_B$ decrease with increased shielding. This behavior is to be expected since the hydrogens *ortho* to the sulfonyl group initially experience a greater deshielding relative to benzene.²⁰ These hydrogens in turn receive the greater diamagnetic shielding by phenyl.

Analysis of the data in Table IV reveals both the positions and relative proximities of the tosylate groups relative to phenyls. The larger the value of σ_A for a given proton pair, presumably the closer that proton pair is to the center of the benzene ring where maximum shielding is experienced. If the values of σ_A and σ_B are approximately the same, as in the first two entries, then either the A and B hydrogens are at approximately an equal distance (r) and equal angle (θ) from the axis normal to the plane of the benzene ring and the shielded hydrogens, or alternatively, one hydrogen lies at a smaller r but larger θ than the other, the values of which lead to nearly identical shielding contributions. Dreiding models reveal that the latter arrangement is preferred, since adoption of the former arrangement would presumably necessitate much larger shielding values than those observed.

As the dihedral angle is reduced from ca. 120° in **3c** and **5c** to ca. 79° in **8c**, the shielding experienced by the A and B protons is increased. As expected, of those "cis" compounds studied, **4c** shows the smallest σ_A value for steric reasons. In the remaining three "cis" compounds there is a reverse order of the degree of shielding in comparison with the corresponding *p*-nitrobenzoates. Now the 1-phenyl-2-*exo* compound exhibits the greatest proximity effect and the 7-*syn*-phenyl-2-*exo* compound the smallest effect. That this change is not due to the greater atomic radius of sulfur (1.06 Å) relative to that of carbon (0.77 Å) which can alter the parameters of r and θ was shown by appropriately modifying the parameters for the A and B hydrogens of the *p*-nitrobenzoates to accommodate this change to sulfur. The increase in the *P* and *Z* distances gave a constant Δr of ca. $+0.4a$ with a corresponding change in θ of only ca. 1° .

The difference in the spectral data for the tosylates relative to the *p*-nitrobenzoates is unquestionably due to the difference between the geometrical requirements and the conformational preferences of the sulfonyl and carbonyl groups. That the *cis* ester conformation was preferred with the phenyl, carbonyl, and alkyl oxygen all approximately in the same plane, was substantiated by agreement of the observed shielding data with the measured shielding parameters. The geometry about the sulfur atom is tetrahedral and free rotation about the O-S bond can lead to a number of possible conformations. Apparently an equilibrium conformation is preferred in which the *p*-tolyl plane is oriented toward

(20) This deshielding is 0.56 ppm relative to benzene (7.27 ppm). Ascribing a shielding value of 0.10 ppm to the hydrogens *ortho* to the methyl group (ref 12), one obtains a deshielding value for the sulfonyl group on the *meta* protons of 0.14 ppm.



the phenyl π cloud. An illustration of the difference between the *p*-nitrobenzoate **5b** and its tosylate analog **5c** is depicted above.

The extent of resonance interaction of an aromatic ring with a sulfonyl group²¹ is not known, and consequently the orientation of the tolyl group relative to the sulfonyl group is open to question. Evidently the coordinately bound oxygens are oriented away from the phenyl group. The extent of interaction between the phenyl group and tosylate hydrogens then depends on the degree of rotation of the O-S bond and *p*-tolyl group away from (or toward) the phenyl ring.

Possible Theoretical Implications

With the data from Table IV and the shielding parameters from the *p*-nitrobenzoates (Table III), approximate values of r and θ and a preferred position for the tosylate groups relative to phenyls can be obtained. An important feature of this nmr study is that it allows one to determine the approximate interaction of the phenyl with the tosylate group in the ground state of the bicyclic system. The second test of the utility of the correlations is as to whether this ground state interaction can be found to reflect chemical reactivity. Two possibilities naturally suggest themselves. If the magnitude of the observed interaction increases in the transition state for the solvolysis reaction, then the rate should be slower than expected in comparison with the unsubstituted parent compound; *i.e.*, the effect will be steric hindrance to ionization.²² If, however, the magnitude of this interaction decreases in the transition state for the solvolysis, then the rate should be faster than what one might expect; *i.e.*, the effect will be steric acceleration for ionization. To see which effect may predominate in a solvolysis of a compound with the leaving group and phenyl group in a *cis* relationship, one can merely look to the relative reaction rates.

Unfortunately, possible variations in the contributing factors of inductive effects and steric inhibition to solvation of the leaving group and of the developing positive charge in the transition state³ may complicate the analysis. However, some measure of the unexpected slow acetolysis rate for 3-*exo*-phenyl-2-*exo*-norbornyl tosylate (**6c**) may be attributable to steric hindrance to ionization in light of the nmr data. If the ionization of **6c** proceeds with the tosylate group departing somewhat into the face of the benzene ring with an accompanying increase in activation energy,

then rate retardation can result. A similar proposal could assist in explaining the initially unexpected slow acetolysis rate for 1-phenyl-2-*exo*-norbornyl tosylate (**7c**)²³ which exhibited the greatest degree of interaction between the phenyl and tosylate groups in the nmr. As the positive charge is generated at C-2, and then subsequently at C-1 in the procession to the transition state, one can visualize the tosylate group passing more severely into the face of the benzene ring. Consequently, the energy of the transition state may be increased, and the position of the transition state along the reaction coordinate can lie closer to that for the starting material than normally expected. Therefore, the extent of participation by the 1-6 bonding electrons and the degree of positive charge at C-1 in the transition state may not be large enough to cause any great rate enhancement.

Experimental Section

Melting points were determined in soft capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are corrected. Infrared spectra for the 3- μ region were recorded on a Perkin-Elmer Model 421 grating spectrometer. A Varian A-60 nmr spectrometer, calibrated with tetramethylsilane ($\delta = 0$) and chloroform ($\delta = 436.5$ cps), was used for the nmr determinations. Chemical shifts should be correct to ± 0.01 ppm. Differences in chemical shifts between the values recorded herein and those found in Table I are due to differences in concentration. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Unless otherwise specified, all ether and ligroin solutions of products were dried over anhydrous sodium sulfate prior to removal of solvent. Ligroin was distilled over potassium permanganate and had bp 40-55°.

exo-Norbornyl and endo-Norbornyl *p*-Nitrobenzoates.—The *p*-nitrobenzoates were prepared by the method of Shriner, Fuson, and Curtin.²⁴ Recrystallization from ethanol gave light yellow crystals. *exo*-Norbornyl *p*-nitrobenzoate gave mp 86-87°. *Anal.* Calcd for C₁₄H₁₅NO₄: C, 64.36; H, 5.791. Found: C, 64.57; H, 5.86. *endo*-Norbornyl *p*-nitrobenzoate gave mp 80-81°. *Anal.* Calcd for C₁₄H₁₅NO₄: C, 64.36; H, 5.79. Found: C, 64.51; H, 5.80.

7-*syn*-Phenyl-2-*exo*-norbornanol (9a).—A solution of 18.3 g (0.0535 mole) of 3-*exo*-phenyl-2-*endo*-norbornyl tosylate (**5c**) and 10.6 g (0.100 mole) of sodium carbonate in 500 ml of glacial acetic acid was refluxed for 112 hr, cooled, and poured into 1 l. of water. The oily product mixture was extracted with three 200-ml portions of ligroin. The combined extracts were washed with aqueous sodium carbonate, and the ligroin was removed at reduced pressure to give 12.2 g of acetolysis product.

The acetolysis product was dissolved in 300 ml of ether and reduced with 4.0 g (0.10 mole) of lithium aluminum hydride in the standard manner.²⁵ A saturated sodium sulfate solution was used to destroy the excess hydride and to decompose the lithium salts. Removal of the ether at reduced pressure left 8.65 g of colorless oil.

Chromatography of this oil was carried out on Alcoa F-20 alumina with ligroin solvent. After initial elution of 1.65 g of 3-phenylnortricyclicene with ligroin, there was obtained with 40% ether-60% ligroin 1.2 g (14%) of **9a**, mp 89-90° after recrystallization from ligroin.²⁶ *Anal.* Calcd for C₁₃H₁₆O: C, 82.93; H, 8.57. Found: C, 82.84; H, 8.62.

(23) D. C. Kleinfelter, *Dissert. Abstr.*, **22**, 428 (1961); D. C. Kleinfelter and P. von R. Schleyer, Third Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1960, p 33; 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 43P; quoted by J. A. Berson in "Molecular Rearrangements," Part I, de Mayo, P., Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 182; also quoted in numerous publications by H. C. Brown and co-workers.

(24) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 246.

(25) W. G. Brown, *Org. Reactions*, **6**, 469 (1951).

(26) The complete details of this product analysis will be reported in a future publication.

(21) For example, see H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., 1962, pp 483-490.

(22) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp 140-158, 174-178; H. C. Brown, *Chem. Brit.*, 199 (1966).

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

The *p*-nitrobenzoate (**9b**) was prepared in the usual manner. Recrystallization from ethanol gave mp 139–140°. *Anal.* Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_4$: C, 71.20; H, 5.68. Found: C, 70.99; H, 5.66.

The tosylate (**9c**) was prepared in the usual manner⁸ and gave mp 106–107°. *Anal.* Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{S}$: C, 70.16; H, 6.48. Found: C, 70.37; H, 6.62.

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

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

In very dilute carbon tetrachloride solution **10a** showed absorption at 3620 cm^{-1} in the infrared region. The nmr spec-

trum in carbon tetrachloride solution (*ca.* 10 mole %) showed the following: five aromatic hydrogens, 7.13 ppm; 2-*endo*-hydrogen, 3.78 ppm; hydroxyl hydrogen, 3.67 ppm; 7-*syn*-hydrogen, 3.26 ppm; 1- and 4-bridgehead hydrogens, 2.48 ppm; and remaining alkane hydrogens, 0.8–1.8 ppm.

The *p*-nitrobenzoate (**10b**) gave mp 89–90°. *Anal.* Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_4$: C, 71.20; H, 5.68. Found: C, 70.92; H, 5.77.

The tosylate (**10c**) gave mp 98–99°. *Anal.* Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{S}$: C, 70.16; H, 6.48. Found: C, 70.19; H, 6.43.

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

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Stereochemistry and Mechanism of Carbon–Carbon Double-Bond Reduction in Methyl Cinnamate by Lithium Aluminum Hydride¹

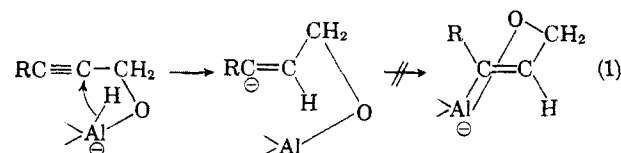
EUGENE I. SNYDER

Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268

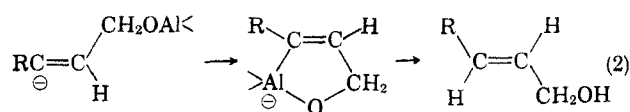
Received March 8, 1967

The reduction of the double bond in methyl cinnamate by lithium aluminum deuteride is shown to lead, after deuterolysis, to an approximately equimolar mixture of *erythro*- and *threo*- $\text{C}_6\text{H}_5\text{CHDCHDCH}_2\text{OH}$. Olefin reduction can be completely avoided by using hydrocarbons as the reaction medium. A self-consistent hypothesis is advanced to account for the observed lack of stereospecificity in reduction and for effects of various solvents on the course of hydride reductions.

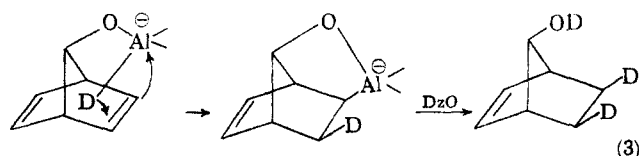
Although reduction of olefinic bonds by lithium aluminum hydride has been known for some time, especially in the case of α,β -unsaturated carbonyl systems, there seem to be only two contradictory studies of its stereochemistry. Reduction of some acetylenic alcohols and glycols are reported² to yield only the *trans* olefins, which implies a stereospecific *trans* reduction. On the other hand, reduction³ of 7-substituted norbornadienes by LiAlD_4 followed by deuterolysis by D_2O results in *anti*-7-substituted norbornenes in which both deuteriums at carbons 5 and 6 are *exo*, which implies a stereospecific *cis* reduction. Although these results appear contradictory both are reasonable if one considers that in each case it is the constraints of the unsaturated system which determine the over-all stereochemistry. In the case of the acetylenic systems *cis* reduction would require the formation of a structure analogous to a *trans*-cyclopentene (eq 1).⁴ Since



such geometry is forbidden by the constraints of the test substance an alternative path is followed and the over-all addition occurs *trans* (eq 2). In the case of



7-substituted norbornadienes the intramolecular nature³ of the reaction requires *exo* hydride transfer, ultimately leading to *cis* reduction (eq 3).⁴ Note that *trans* reduction would require an intermediate of type I



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

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

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

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