

Time, (hr.)	$\log \frac{[\text{norbornadiene } 0 \text{ hr.}]}{[\text{norbornadiene } X \text{ hr.}]}$	$\log \frac{[\text{norbornene } 0 \text{ hr.}]}{[\text{norbornene } X \text{ hr.}]}$
0.5	0.097	0.080
1.0	.246	.155
1.5	.406	.230
2.0	.563	.310
2.5	.823	.436

0.0–0.25 hr. The ratio of the respective slopes was used to determine the relative rates of addition.

$$\frac{k_{\text{diene}}}{k_{\text{monoene}}} = \frac{0.316}{0.153} = 2.06$$

The possibility of hydrogen abstraction by a radical species rather than addition was tested in an independent experiment in which carbon tetrachloride was used as the source of trichloromethyl radicals. In this instance, any hydrogen-abstraction from bridgehead or ring methylene position of norbornene or norbornadiene would result in the formation of chloroform, which would in turn be detected by v.p.c. analysis. Moreover, H-abstraction by a phenyl radical (derived from benzoyl peroxide) would give rise to benzene, also detectable by v.p.c. A 10-ft. column of Carbowax 6000 on Chromosorb W, operated at 70°, was shown to be capable of separating carbon tetrachloride, benzene, and chloroform (eluted in that order). In no

instance, even after considerable reaction time, was any chloroform or benzene detected.

3-Chloronorbornene.—3-Norbornene¹¹ (56 g., 0.509 mole) and thionyl chloride (121 g., 1.11 moles) were stirred together for 15 min. at room temperature, then heated to 95°, with continued stirring, for 3 hr. Distillation yielded unreacted thionyl chloride and 3-chloronorbornene (b.p. 55–57° at 12 mm., n_D^{20} 1.4979, infrared spectrum consistent with structure), which was shown to be homogeneous by v.p.c.

Anal. Calcd. for C₇H₉Cl: C, 65.37; H, 7.00. Found: C, 65.69; H, 6.99.

Dipole Moment Determinations.—The method of Guggenheim¹⁰ was employed in obtaining dipole moments of compounds VII, IX, and XII. Solutions of 2–13% in benzene were prepared for each of these compounds. Refractive indices were measured on an Abbe refractometer, Model G (Carl Zeiss) at 25°. Dielectric constants were determined with a General Radio 716 C capacitance bridge, employing a frequency of 1 Kc. at 25°.¹⁴

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(64) We are indebted to Mr. A. F. Rogers for the dielectric constant determinations.

[CONTRIBUTION FROM THE PROCTER AND GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO]

The Nuclear Magnetic Resonance Spectra and Stereochemistry of Substituted Bornanes¹

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Correlations between n.m.r. spectra and *exo/endo* isomerism in substituted bornanes are presented. Some of the features of the n.m.r. spectra which are sensitive to stereoconfiguration are the chemical shift of the methyne proton on the same carbon as the substituent and the multiplet structure of this α -methyne proton peak. Calculations have been made to arrive at reasonable mechanisms for the change of the multiplet structure with stereoconfiguration.

Nuclear magnetic resonance has been shown to be useful in the determination of stereoconfiguration in several rigid ring systems—sugars,² steroids,³ nucleotides,⁴ and bicyclo[2.1.1]hexane derivatives.⁵ We wish to present here the unique stereochemical correlations in the n.m.r. spectra of substituted bornanes. N.m.r. spectra have been reported for some bicyclo[2.2.1]heptane compounds closely related to the substituted bornanes: by Kumler, *et al.*,⁶ and by Anet.⁷ In all of the work published, there are differences in the spectra of the stereoisomers for 2- and 3-substituted bicyclo[2.2.1]heptanes. Kumler, *et al.*, found that the position of the n.m.r. peak of the proton on the same carbon as the chlorine in *exo*-2-chlorocamphor is higher by 0.48 p.p.m. than the resonance for the corresponding *endo*-2-chlorocamphor. Anet has found that the spin coupling constants in α -methyne protons⁸ of the four 2,3-bornane diol stereoisomers are consistent with Karplus' theory⁹ relating the spin coupling constant of protons on adjacent singly bound carbons to the dihedral angle of the two C–C–H bonds. He also found that long range spin coupling constants of ~ 1 c.p.s. may appear when the α -methyne proton is *exo*—they did not appear for the corresponding *endo*- α -methyne

proton. In our work the n.m.r. spectra of some twenty-one well characterized substituted bornanes are reported.¹⁰ It is felt that enough compounds have now been examined so that the spectra/structure correlations will have general significance.

Chemical Shifts in Substituted Bornanes

Assignment of N.m.r. Peaks.—With the exception of the proton on the same carbon as the substituent R (and, of course, any protons which may be in R), all of the proton resonance peaks for the substituted bornanes are found at 7.0–9.5 τ . The methylene and angular protons appear as a complicated band with considerable structure throughout this region; the methyl groups appear as sharp peaks. The resonances of the protons in the substituent R may be easily assigned from previous work on the resonance positions of such groups.^{11,12}

Chemical Shifts of the Methyl Groups.—Kumler, Shoolery, and Brucher⁶ have proposed that the position of the methyl peaks might be a test of configuration for the group substituted at the 2-position on the [2.2.1]-bicycloheptane ring of the chlorocamphors. Striking differences of the methyl positions in the substituted bornanes have been observed in this study between *exo* and *endo* substitution at the 2-position. For example, in Fig. 1 it is seen that the methyl peaks of borneol (I) are superimposed. The methyl peaks of isoborneol (II) are separate. However in a perusal of the other spectra, no clear pattern which may be

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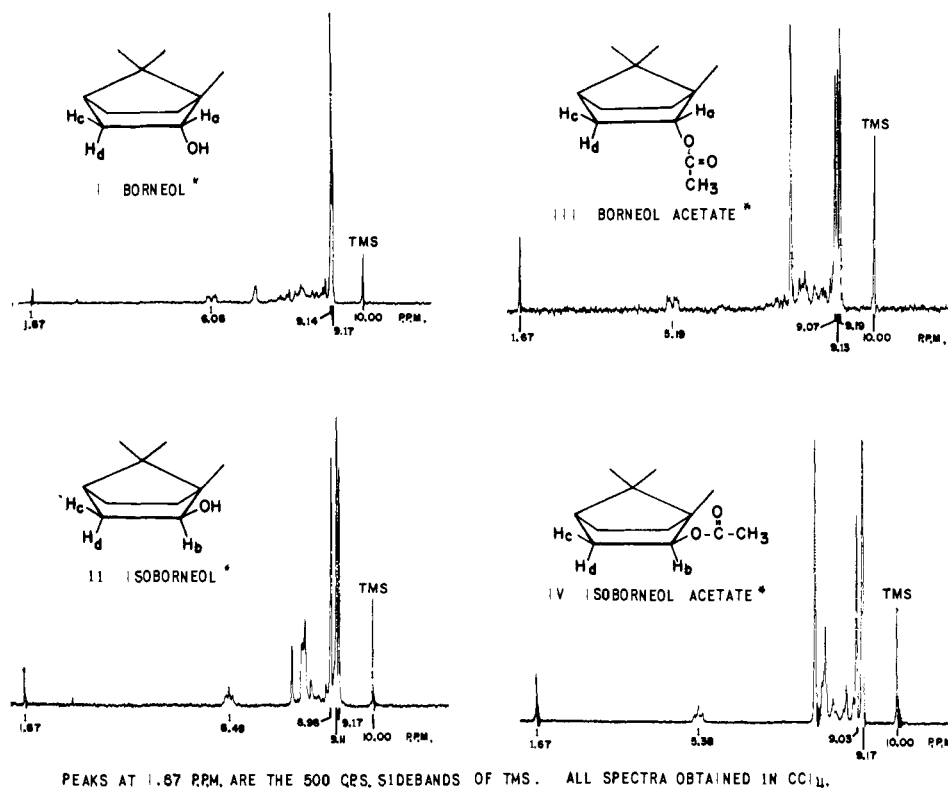
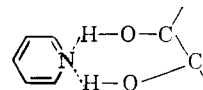


Fig. 1.—Shifts of the methyl peaks with stereoconfiguration.

attributed to *exo/endo* isomerism has been recognized in the chemical shifts of the methyl groups. For example, the methyl peaks of bornyl acetate (III) are not superimposed and two of the methyl peaks of isobornyl acetate (IV) are superimposed.

Chemical Shifts of the α -Methyne Proton.—The α -methyne proton peak is found in the region downfield from the 7–9 τ region owing to the electron-withdrawing power of the substituent, and is therefore easily identified in the spectra of the substituted bornanes. In all of the compounds in this study it has been found that the α -methyne peak of the *exo* substituted isomer (proton *endo*) is located at higher field than the peak of the corresponding *endo* isomer (proton *exo*). This observation is in agreement with the spectra of the 2-chlorocamphors observed by Kumler, *et al.*⁶ The regularity of the difference in chemical shift is analogous to the regularities seen in the substituted sugars, since the *endo*-protons are located essentially perpendicular to the base of the bornane molecule—hence may be thought of as “pseudo-axial” while the *exo*-protons are located essentially in the basal plane of the bornane molecule (“pseudo-equatorial”). According to Jackman,¹¹ $\Delta\tau_{\text{axial-equatorial}} = 0.13\text{--}0.51$. This corresponds well to $\Delta\tau_{\text{endo-exo}} = 0.08\text{--}0.48$. The origin of the axial-equatorial shift is thought to arise from the magnetic anisotropy of the carbon-carbon single bond.^{6,13} In Table I are presented the chemical shifts of the α -methyne proton for the series of compounds studied in this Laboratory when the compound was dissolved in CCl_4 . For reasons discussed below, some of these compounds were also dissolved in pyridine and their n.m.r. spectra obtained. The values of the chemical shift of the α -methyne proton for pyridine solvent are included when they were taken. Finally, the data of Kumler, *et al.*,⁶ and Anet⁷ have been included so that a comparison may be made of the chemical shifts. It is seen that, for all the cases of monosubstituted bornanes whose chemical shifts

have been measured in pyridine, the same correlation obtains for the chemical shifts of the α -methyne protons; that is, the relative chemical shift is in the same direction although the absolute value is not. For the diols studied by Anet,⁷ there does not appear to be a clear correlation. It is felt that the presence of the adjacent hydroxyl groups may stabilize hydrogen bonded complexes of the form



The variation of strength and orientation of these complexes with *exo/endo* isomerism could affect the chemical shift of the nearby α -methyne protons because of the large magnetic anisotropy of the pyridine ring.¹⁴

Chemical Shift in Phenyl Substituted Bornanes.—The four pairs of *exo/endo* isomers in which the substituent is a *p*-substituted phenyl group show an interesting correlation: the difference δ_{ϕ} in chemical shift of the A and B protons of the A_2B_2 multiplet¹⁵ of the benzene ring is larger when the substituent is *exo*. The most striking case observed is that of the 2-*p*-anisylepicamphors: in the *endo* isomer, the phenyl resonance is a singlet; in the *exo* isomer, it appears as a quartet. This is illustrated in Fig. 2. Approximate values of δ_{ϕ} (obtained by treating the A_2B_2 multiplet as an AB quartet) are listed in Table I. Interestingly there appears to be no correlation between the chemical shift (τ_{ϕ}) of the A_2B_2 multiplet and *exo/endo* isomerism.

Spin Coupling Pattern of the α -Methyne Proton in Monosubstituted Bornanes

A perusal of the multiplet structure of the α -methyne proton in monosubstituted bornane spectra will indicate two regularities which correlate with *exo/endo* isomerism of the substituent. For the compounds in

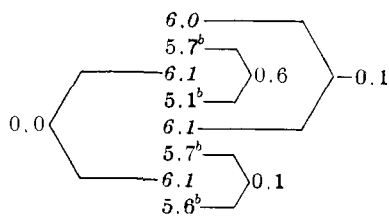
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TABLE I
 CHEMICAL SHIFTS FOR PEAKS IN SUBSTITUTED BORNANES AND CLOSELY RELATED COMPOUNDS

		α-Methyne proton ^a				τ _φ	δ _φ	Methyl protons in CCl ₄		
		τ _{CCl₄}	Δτ ^c	τ _{pyr}	Δτ ^c					
I	Borneol	6.09	0.40	5.80	0.46			9.14	9.14	9.17
II	Isoborneol	6.49		6.26		8.98	9.11	9.17		
III	Borneol acetate	5.19	.19	4.95	.28			9.07	9.13	9.19
IV	Isoborneol acetate	5.38		5.23		9.03	9.17	9.17		
V	<i>p</i> -Bornylphenol ^g	7.13	.08	6.94	.16	3.23	0.26	8.98	9.07	9.30
VI	<i>p</i> -Isobornylphenol ^g	7.21		7.10		3.33	.64	9.19	9.19	9.28
VII	2- <i>endo-p</i> -Anisylepicamphor ^g	6.71	.21			3.29	.00	8.94	8.98	9.06
VIII	2- <i>exo-p</i> -Anisylepicamphor ^g	6.92		6.54	3.19	.29	9.03	9.06	9.06	
IX	2- <i>endo-p</i> -Anisylepiborneol									
X	<i>p</i> -toluenesulfonate ^g	7.17	.21	6.82	0.24	2.94	.25	8.97	9.04	9.45
	2- <i>exo-p</i> -Anisylepiborneol									
	<i>p</i> -toluenesulfonate ^g	7.38		7.08		2.77	.47	9.13	9.13	9.37
XI	Bornylcarboxylic acid	7.30						8.96	9.08	9.08
XII	Bornyl chloride	5.93	.23					9.06	9.10	9.11
XIII	Isobornyl chloride	6.16							8.89	8.98
XIV	Bornyl phenyl ether	5.74	.28					9.08	9.08	9.08
XV	Isobornyl phenyl ether	6.02							8.95	9.02
XVI	<i>p</i> -Bornylanisole ^g	7.02	.15			3.20	0.25	9.02	9.11	9.33
XVII	<i>p</i> -Isobornylanisole ^g	7.17					3.18	0.35	9.18	9.18
XVIII	<i>o</i> -Bornylphenol	6.43	.46					8.93	9.07	9.25
XIX	<i>o</i> -Isobornylphenol	6.89							9.12	9.16
XX	<i>o</i> -Bornylanisole	6.2 ^f	.5					8.83	9.08	9.32
XXI	<i>o</i> -Isobornylanisole	6.74							9.14	9.19
	3- <i>endo</i> -Chlorocamphor ^d	5.68 ^b	.48				
	3- <i>exo</i> -Chlorocamphor ^d	6.16 ^b						
	2- <i>exo-3-exo</i> -Bornane diol ^e						
	2- <i>exo-3-endo</i> -Bornane diol ^e						
	2- <i>endo-3-exo</i> -Bornane diol ^e						
	2- <i>endo-3-endo</i> -Bornane diol ^e						



^a All α-methyne protons are at the 2-position unless otherwise indicated. ^b 3-Position. ^c Δτ refers to τ of α-methyne proton in *exo*-substituted compound — τ of α-methyne proton in *endo*-substituted compound. ^d Kumler, Shoolery, and Brucher.⁶ ^e Data taken from Anet's spectra.⁷ ^f Exact position obscured by OCH₃ peak. ^g Some of the data for these compounds have been previously reported by Erman and Flautt.¹⁰

 TABLE II
 MULTIPLET SPACINGS FOR SUBSTITUTED BORNANES AND CLOSELY RELATED COMPOUNDS IN CCl₄

		<i>J</i> _{AX'} , c.p.s.	<i>J</i> _{BX'} , c.p.s.	<i>j</i> , c.p.s.
Borneol	I	9.6	3.5	1.6
Isoborneol	II	5.2	5.2	0
Borneol acetate	III	9.8	3	1.9
Isoborneol acetate	IV	5.1	5.1	0
<i>p</i> -Bornylphenol ^c	V	11.4	5.5	1.7
<i>p</i> -Isobornylphenol ^c	VI	8.3	8.3	0
2- <i>endo-p</i> -Anisylepicamphor ^c	VII	0	0	0
2- <i>exo-p</i> -Anisylepicamphor ^c	VIII	0	0	0
2- <i>endo-p</i> -Anisylepiborneol ^c				
<i>p</i> -toluenesulfonate ^c	IX	10.4	..	~2
2- <i>exo-p</i> -Anisylepiborneol ^c				
<i>p</i> -toluenesulfonate	X	..	6.4	0
Bornylcarboxylic acid	XI	8.0	8.0	3 ^b
Bornyl chloride	XII	9.9	4.2	1.9
Isobornyl chloride	XIII	8.0	5.4	0
Bornyl phenyl ether	XIV	9.3	2.8	~2
Isobornyl phenyl ether	XV	5.2	5.2	0
<i>p</i> -Bornylanisole ^c	XVI	11.4	5.8	1.5
<i>p</i> -Isobornylanisole ^c	XVII	8.7	8.7	0
<i>o</i> -Bornylphenol	XVIII	11.5	6.0	2.0
<i>o</i> -Isobornylphenol	XIX	8.7	8.7	0
<i>o</i> -Bornylanisole	XX	^a	6.0	2.0
<i>o</i> -Isobornylanisole	XXI	8.8	8.9	0

^a Obscured by OCH₃ peak. ^b Widths of triplet peaks. ^c The spacings for these compounds have been previously reported by Erman and Flautt¹⁰ as "spin coupling constants."

which the substituent is *endo* (proton *exo*), the pattern usually appears as a quartet of two characteristic spacings *J*_{AX'} and *J*_{BX'} split by a much smaller spacing *j*. The single exception to this regularity is bornylcarboxylic acid which gives a triplet multiplet with broadened peaks. For the compounds in which the substituent is *exo* (proton *endo*), the pattern appears as a triplet, or a near triplet (*J*_{AX'} is almost equal to *J*_{BX'}) and there is no additional splitting (*j* = 0). Figure 3 gives some examples of the patterns obtained. Table II lists the spacings obtained on the substituted bornanes in this study.

ABX Pattern.—The multiplet structure, exclusive of the small coupling constant *j*, is that characteristic of the X proton of an ABX multiplet.¹⁶ It is tempting to identify the spacings of this multiplet *J*_{AX'} and *J*_{BX'} with the spin coupling constants *J*_{AX} and *J*_{BX}; however, a study of the complete analysis of the ABX

(16) Reference 15, pp. 132-138. It is not intended to imply that the ABX approximation applies rigorously for the interpretation of the α-proton peaks in these compounds. However, it is felt that this represents the simplest analysis which will satisfactorily explain the main features of the multiplet structure, particularly the observed changes in an interacting solvent. A more complete analysis would be needed if there were major features in the multiplet which could not be explained by the ABX approximation. Furthermore, it is expected that the spin coupling constants of the X proton at position 1 with the other protons at positions 4, 5, and 6 will be weak (with the exception of the long range coupling *j* which has already been mentioned). There is probably a coupling of 4 c.p.s. of the *exo*-proton at position 3 with the angular proton: this will affect the X proton peak only if the chemical shift of the two protons are comparable to or smaller than 4 c.p.s. In such a case the X multiplet will become much more complicated than a triplet or pair of doublets.

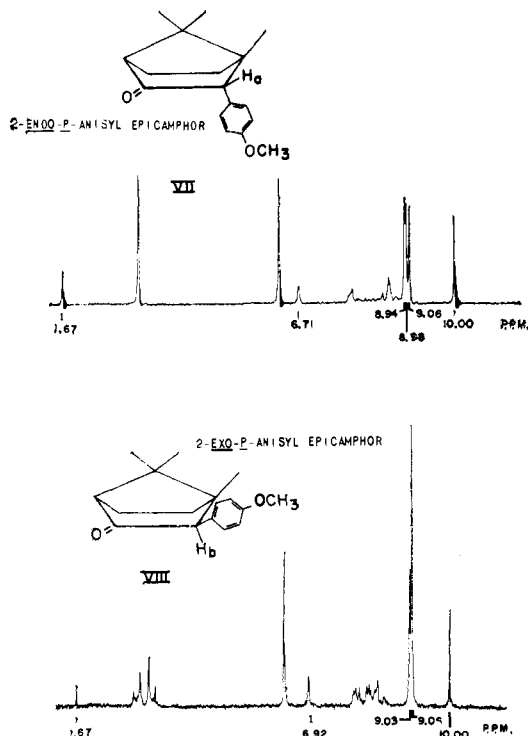


Fig. 2.—Change of the aromatic proton pattern with stereo-configuration.

multiplet shows that these spacings may be identified with the appropriate spin coupling constants only when the chemical shift difference in cycles/second, $\Delta\nu_{AB}$, between the A and B protons is large compared to their mutual coupling constant J_{AB} . Otherwise, $J_{AX'} < J_{AX}$ and $J_{BX'} > J_{BX}$. In the limiting case, when $\Delta\nu_{AB} = 0$, $J_{AX'} = J_{BX'}$ and the activated proton multiplet has the appearance of a triplet.¹⁷ Thus the correlation of quartet structure with an *endo* substituent and a triplet structure with an *exo* substituent may reflect either a change in spin coupling constants, J_{AX} and J_{BX} , or a change in $|\Delta\nu_{AB}|$, so that for *endo*-substituted bornanes, $J_{AX} \neq J_{BX}$ or $\Delta\nu_{AB} \neq 0$ and for *exo*-substituted bornanes $J_{AX} = J_{BX}$ or $\Delta\nu_{AB} = 0$. Since the peaks of the AB protons cannot be examined (they are overlapped by peaks from the remaining methylene protons) it is impossible to decide from the spectrum if the correlation arises from differences in the coupling constants or chemical shifts. However, it is possible to take advantage of specific solvent interactions upon the chemical shift which are known to change the relative chemical shift of different protons on a rigid molecule without affecting their spin coupling constants¹⁶ to make, in some cases, $|\Delta\nu_{AB}| > 0$. Figure 4 shows the results of dissolving several compounds with triplet patterns in such solvents. In two of the cases, the triplet seen in CCl_4 was resolved into two doublets; in the other two cases, the triplet remained. The resolution of the triplet seen in CCl_4 into four peaks in an interacting solvent is a positive indication that $\Delta\nu_{AB} = 0$ in CCl_4 and $J_{AX} \neq J_{BX}$. The failure to resolve the triplet implies that $J_{AX} = J_{BX}$, since if $\Delta\nu_{AB}$ is different in the two solvents, the triplet can be explained only by equality of the coupling constants; however, it is conceivable that $\Delta\nu_{AB} = 0$ in both solvents—hence the test is negative evidence that $J_{AX} = J_{BX}$ when the triplet fails to resolve.

Long Range Coupling Constant.—The small spacing j , of magnitude 1–2 c.p.s., is similar to that observed

(17) When $\Delta\nu_{AB} = 0$, the ABX spectrum becomes one of the cases of "deceptively simple spectra" discussed by R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

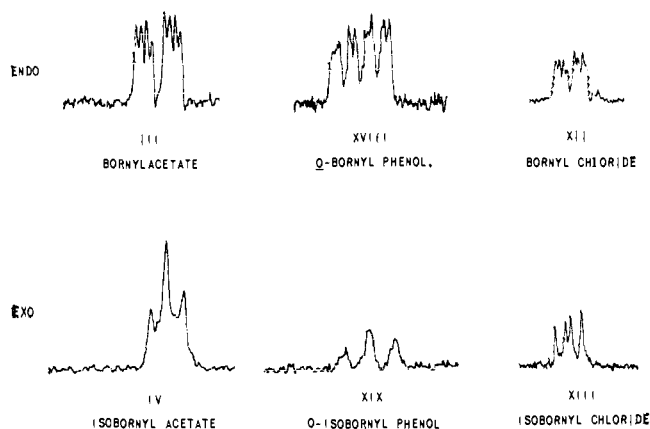


Fig. 3.— α -Proton multiplet structure of representative mono-substituted bornanes.

by Anet⁷ in the bornane diols and assigned to coupling with a proton on the opposite side of the bornane ring. It always appears in the peak of the *endo*-substituted bornanes (with the exception of bornylcarboxylic acid) as evidenced by the data in Table II. Hence its presence seems to be a good test of the *endo*-substituted configuration. This correlation does not seem to carry over to the substituted camphors—the spectra reported by Kumler, Shoolery, and Brucher⁸ of the chlorocamphors and the spectra of the *p*-anisylepicamphors (VII and VIII) show no evidence for this long range spin coupling constant.

Discussion of the α -Proton Multiplet Pattern

The multiplet patterns of the monosubstituted bornanes imply regularity in the chemical shifts of the methylene protons on position 3 and in the spin coupling constants of these methylene protons with the α -proton on position 2. The regularity in chemical shift may be thought due to the influence of the substituent at the 2-position. If this group were absent (for example, in bornane) the *exo*-proton at position 3 would be expected to absorb at lower field than the *endo*-proton, according to the correlation of the α -proton peak at position 2 with stereochemistry already discussed. Hence, in the isomers where the substituent at position 2 is *exo*, the *exo*-proton on the adjacent methylene at position 3 must be shifted upfield relative to the resonance of this proton in bornane to cause the *exo*- and *endo*-proton at position 3 to have the same chemical shift. The same effect in the isomer where the substituent is *endo* would move the chemical shifts of the *exo*- and *endo*-protons at position 3 farther apart, since the *endo*-proton would be expected to be upfield from the *exo*-proton if the influence of the substituent were absent.

Magnetic Anisotropy of C-R and C-H Bonds.—These observations may be explained by a consideration of the magnetic anisotropy of the C-H and C-R bonds using the equation developed by McConnell¹⁸

$$\sigma = \frac{\Delta\chi}{3\rho^3N} < 1 - 3\cos^2\gamma >$$

σ represents the contribution of the axially symmetric magnetically anisotropic bond to the chemical shift of the proton on the adjacent carbon; $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$, the difference of magnetic susceptibility along the symmetry axis from the magnetic susceptibility perpendicular to the symmetry axis; ρ is the distance from the center of the bond to the proton affected; γ is the angle between the symmetry axis of the bond and the vector connecting the substituent with the proton affected; N is Avogadro's number. The replace-

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

ment of the *exo*-proton at the 2-position by an *exo* substituent involves removing the effect of the C-H bond and introducing the effect of the C-R bond. The net effect may be expressed by a term $\Delta\chi_{\text{sub}} = \Delta\chi_{\text{R}} - \Delta\chi_{\text{H}}$ (the diamagnetic anisotropy of the carbon-substituent bond - the diamagnetic anisotropy of the carbon-hydrogen bond). Zürcher¹⁹ has recently evaluated $\Delta\chi_{\text{H}}$ using an equation proposed by Gans and Mrowka²⁰ which relates the magnetic susceptibility tensor to the electrical polarizability tensor. This equation with the constants evaluated for an axially symmetric bond gives the expression

$$\Delta\chi = 1.5 \times 10^6 \left[\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2} - \frac{(\alpha_{\parallel}^{1/2} - \alpha_{\perp}^{1/2})^2}{\alpha_{\parallel}^{1/2} + \alpha_{\perp}^{1/2}} \right] n^{1/2}$$

α_{\parallel} and α_{\perp} represent the respective polarizabilities parallel and perpendicular to the axis of symmetry in units of cubic centimeters; n is the number of electrons participating in the bond. Zürcher uses this expression together with several other relationships to arrive at a "best value" for $\Delta\chi_{\text{H}} = -0.74 \times 10^{-6}$. This expression may be evaluated for the C-Cl bond for which the polarizability tensor has been measured unambiguously from Raman intensity measurements.²¹ Assuming that $n = 2$, it is found that $\Delta\chi_{\text{Cl}} = +0.91 \times 10^{-6}$. It is important to note that the sign of the magnetic anisotropy is *positive*, implying that the bond is more polarizable perpendicular to the C-Cl bond than parallel to the C-Cl bond. For values of bond polarizabilities α_{\perp} and α_{\parallel} which have been reported,^{22,23} it is seen that $\Delta\chi_{\text{R}}$ will be positive for most C-R bonds. Hence for isobornyl chloride $\Delta\chi_{\text{sub}} = \Delta\chi_{\text{Cl}} - \Delta\chi_{\text{H}} = +1.65 \times 10^{-6}$. From a molecular model of bornyl chloride it is seen that $\rho \sim 2.2 \text{ \AA.}$ and $\gamma \sim 80^{\circ}$ for the *exo*-proton. This leads to a contribution of $+0.09$ p.p.m. for the *exo*-proton. The *endo*-proton has $\rho \sim 2.6 \text{ \AA.}$ and $\gamma \sim 135^{\circ}$, leading to a contribution of -0.02 p.p.m. Thus the relative chemical shift of the *exo*- and *endo*-protons at the 3-position would tend to be decreased by ~ 0.11 p.p.m. according to this mechanism. This decrease is not as much as the difference found for some of the *exo*- and *endo*-protons of the α -methylene protons in this study (0.08-0.50 p.p.m.): hence the influence of the C-R bond anisotropy is probably greater than indicated by this calculation. It is not surprising that quantitative agreement is not found, since the dipole model is not accurate at small distances.¹⁸ The most important agreement is that the sign of the shift is correct.²⁴ Because the angular relationships for other C-R bonds will be approximately similar and because $\Delta\chi$ will generally be positive,^{22,23} the same mechanism will explain the coincidence of the chemical shifts of the protons at the 3-position.

Correspondence of J_{AX} and $J_{\text{AX}'}$, J_{BX} and $J_{\text{BX}'}$.—In the *endo* isomers the effect of the C-R bond will be exactly opposite: to separate the chemical shifts of the protons at the 3-position. Therefore the pattern seen for the X proton reflects the difference in J_{AX} and J_{BX} —a multiplet of two characteristic spacings $J_{\text{AX}'}$ and $J_{\text{BX}'}$. In a previous paper¹⁰ reporting the synthesis of some of the compounds in this study, multiplet spacings $J_{\text{AX}'}$ and $J_{\text{BX}'}$ were reported as spin coupling constants J_{AX} and J_{BX} . In view of the analysis in this paper, it is believed that this assumption is close to correct (at least within 1 c.p.s.) for *endo*-substituted

bornanes, since $\Delta\nu_{\text{AB}}$ for the protons at the 3-position should be approximately double the difference between the *exo*- and *endo*-protons at the 2-position due to the influence of the *endo* substituent at the 2-position. This is about 0.16-1.0 p.p.m. or 10-60 c.p.s. at 60 Mc./sec. The critical parameter which determines the correspondence of J_{AX} and J_{BX} with the multiplet spacings is the ratio of J_{AB} to $\Delta\nu_{\text{AB}}$; J_{AB} has been found to be from 9-15 c.p.s. for saturated aliphatic carbons of the usual bond angles.²⁵ Taking J_{AX} and J_{BX} to be the values found by Anet⁷ in the bornane diols—8.9 and 2.3 c.p.s., and assuming that J_{AB} is 13 c.p.s. and $\Delta\nu_{\text{AB}} = 20$ c.p.s., it is found that $J_{\text{AX}'}$ and $J_{\text{BX}'}$ are 8.4 and 2.8 c.p.s., in close agreement with J_{AX} and J_{BX} .

For the *exo* compounds reported in the previous paper¹⁰ there is some doubt concerning the correspondence of the multiplet spacings and coupling constants because of the observation of the near equivalence of the chemical shift for the protons at the 3-position in other bornanes. However, it is felt that this triplet probably reflects equality of the spin coupling constants J_{AX} and J_{BX} because the triplet of *p*-isobornylphenol failed to split when the compound was dissolved in pyridine.

Steric Interference in *exo*-Substituted Bornanes.—Because there is evidence for the near equality of J_{AX} and J_{BX} in some of the *exo* isomers to explain the triplet structure, it is worthwhile to seek a possible explanation for this effect. Since both *exo* compounds which show a triplet in pyridine have a bulky substituent, steric interference between this substituent and the C-8 methyl group may distort bond angles so as to change the spin coupling constants J_{AX} and J_{BX} according to the theory of Karplus.⁹

This theory relates the spin coupling constant between protons on adjacent saturated carbons to the dihedral angle between the two planes defined by the C-C-H bonds. It has been found to be reliable in predicting the relative magnitude of coupling constants between protons on adjacent carbons of various dihedral angles, but the absolute magnitudes predicted by this theory (which uses simple wave functions) have been found to be too low in some cases.²⁶ For unsubstituted bornanes, the dihedral angles between an *exo*-proton at the 2-position and the *exo*- and *endo*-protons at the 3-position are 0 and 122° , respectively, according to a model proposed by Wilcox for calculation of dipole moments of substituted bicyclo[2.2.1]-heptanes.²⁷ According to Karplus' theory, the corresponding coupling constants for these dihedral angles would be 8.2 c.p.s. (J_{AX}) and 2.4 c.p.s. (J_{BX}). In the *endo*-substituted bornanes the spacings J' (which are approximately equal to the coupling constant J) are 9-11 c.p.s. and 3.6 c.p.s., higher than that predicted by Karplus' theory but with one considerably larger (2-3 times) than the other in qualitative agreement with the theory. In the *exo*-substituted bornanes, the spacings J' are approximately equal, and, in some cases at least, J_{AX} and J_{BX} are probably equal. Calculations of distance of approach (based on Wilcox's model²⁷) between the *exo* substituent and the 8-methyl group indicate that it is less than the sum of the van der Waals radii for the two groups—for example, in isoborneol, the distance between the C-8 methyl group and the oxygen is 2.77 Å.; the distance between the C-10 methyl group and the oxygen is 2.88 Å.; the sum

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of the van der Waals radii for CH_3 and O is 3.40 Å.²⁸ In the case of the more bulky substituents such as a phenyl or an acetyl group it is expected that steric interference would be even larger. It is reasonable, therefore, to expect that the dihedral angles in *exo*-substituted bornanes will be distorted from those normally encountered in bicyclo[2.2.1]heptane. The distortion should make both dihedral angles larger so that they would be somewhat greater than 0 and 122°. In such a case the near equality of the two coupling constants J_{AX} and J_{BX} follows as a result of Karplus' theory since increasing the one angle to something greater than 0° would decrease the coupling constant J_{AX} (which is larger in *endo*-substituted bornanes) and increasing the other angle to something greater than 122° would increase J_{BX} (which is smaller in *endo*-substituted bornanes).

Exception.—The exception to correlation of multiplet spacings with *exo/endo* isomerism is bornylcarboxylic acid (XI). The triplet appearance in CCl_4 is caused by the near equality of chemical shifts in the protons at the 3-position, since in benzene this triplet splits into two doublets (Fig. 4). It is felt that the large magnetic anisotropy of the carbonyl group²⁹ substituted at the 2-position in this compound may be contributing to equalize the relative chemical shift of the protons at the 3-position. Also absent in this compound is the splitting normally seen in *endo*-substituted bornanes associated with a long range coupling constant j . The absence of this splitting does not necessarily mean that j is zero—if there happens to be a coincidence of chemical shift of another proton which is spin coupled to the proton that gives rise to the long range splitting. In such a case the second proton would "virtually couple" with the α -methylene proton.³⁰ The observed broadening of the activated proton multiplet is consistent with "virtual coupling."

Conclusion

The chemical shift difference of the α -methylene proton appears to be the best test for *exo/endo* isomerism. The appearance of a small additional splitting j in a multiplet of characteristic spacing J_{AX} and J_{BX} appears to be equally reliable evidence for an *endo*-substituted isomer. However, the nonappearance of this splitting is only negative evidence for the presence of the *exo* isomer. "Virtual spin coupling" may cause the multiplet pattern to broaden rather than split. Quartet and triplet patterns of the α -methylene proton are indicative but not definitive evidence for *endo* and *exo* isomers, respectively. In phenyl-substituted bornanes, the relative chemical shift of the aromatic protons appears to be a good indicator of *exo/endo* configuration.

Experimental

N.m.r. Spectra.—All spectra were obtained with a Varian DP-60 or A-60 nuclear magnetic resonance spectrometer at an operating frequency of 60 Mc./sec. The peaks of interest for stereochemical information about chemical shifts were calibrated by nearby sidebands to an accuracy of ± 0.01 p.p.m. on the DP-60. The A-60 has an inherent reproducibility of ± 0.01 p.p.m. The samples were dissolved in carbon tetrachloride to approximately 10% by volume (or if the material was less soluble, to a saturation concentration). A small amount (approximately 1% by volume) of tetramethylsilane was added as an internal reference. The τ convention was adopted for reporting chemical shifts, *i.e.*, the position of the tetramethylsilane reference was called 10.00 p.p.m. and resonances at lower field have lower values.³¹

Preparation of Bornane Derivatives.—All compounds were optically inactive *dl*-forms unless otherwise stated. The purity

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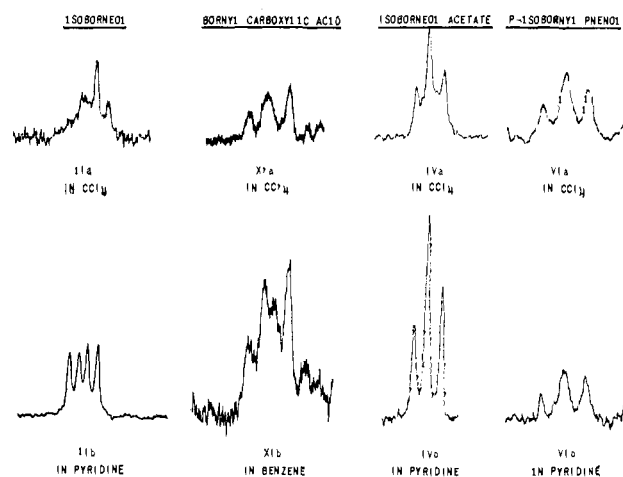


Fig. 4.—Comparison of α -proton multiplet in CCl_4 and a magnetically anisotropic solvent.

of liquids was confirmed by gas chromatographic analysis on a 10-ft. column packed with 30% succinic acid-triethylene glycol polymer on 60/80 mesh Chromosorb or on a 5-ft. column packed with 20% GE-silicone on firebrick.

p-Bornylphenol (V, m.p. 151-152°), *p*-isobornylphenol (VI, m.p. 135-136°), 2-*endo-p*-anisylepicamphor (VII, m.p. 91.5-93°), 2-*exo-p*-anisylepicamphor (VIII, m.p. 121.2-122.4°), 2-*endo-p*-anisylepiborneol *p*-toluenesulfonate (IX, m.p. 137.0-138.5°), 2-*exo-p*-anisylepiborneol *p*-toluenesulfonate (X, m.p. 102.6-103.6°), *p*-bornylanisole (XVI, b.p. 114°, n_D^{25} 1.5410), and *p*-isobornylanisole (XVII, m.p. 41.0-42.4°) were the compounds previously described by Erman and Flautt.¹⁰

The syntheses of *o*-bornylphenol (XVIII, m.p. 63.0-64.6°), *o*-isobornylphenol (XIX, m.p. 85.5-86.0°), *o*-bornylanisole (XX, b.p. 107° (2.4 mm.), n_D^{25} 1.5410), and *o*-isobornylanisole (XXI, m.p. 75.8-78.5°) will be described elsewhere.³² The authors are indebted to Mr. C. L. Benford for samples of borneol (I, m.p. 204-205°, sealed tube) and isoborneol (II, m.p. 211-212°, sealed tube), and to Dr. R. Welir for samples of bornyl phenyl ether (XIV, b.p. 156-158° (10 mm.), n_D^{25} 1.5312) and isobornyl phenyl ether (XV, b.p. 147° (8 mm.), n_D^{25} 1.5265), prepared essentially by the method of Kursanov³³ for the preparation of menthyl phenyl ethers. Isobornylphenyl ether (XV, b.p. 99-101° (0.3 mm.), n_D^{25} 1.5260) also was prepared as described by Kitchen.³⁴ Bornyl chloride (XII, m.p. 133-134° was prepared according to the method of Frankforter and Frary.³⁵ Isobornyl chloride (XIII, m.p. 155-156°) was prepared by the procedure of Nevell, de Salas, and Wilson.³⁶ *l*-Bornyl acetate (III, b.p. 86° (6 mm.), n_D^{25} 1.4620) was obtained from the Aldrich Chemical Co., Milwaukee, Wis., and was purified by distillation. Isobornyl acetate (IV, b.p. 91° (8 mm.), n_D^{25} 1.4633) was obtained from K and K Laboratories, Inc., N. Y., and was purified by repeated fractional distillation.

Bornylcarboxylic Acid (XI).—Essentially the method of Bartlett, Webster, Dills, and Richey³⁷ for preparation of 2-*exo*-methyl-norbornane-2-*endo*-carboxylic acid was employed for preparation of bornylcarboxylic acid from *p*-bornylanisole. Into a solution of 7.8 g. (0.0325 mole) of *p*-bornylanisole in 400 ml. of anhydrous methylene chloride maintained below 0° was passed 9.3 g. (0.194 mole) of ozone at the rate of 4.5×10^{-4} mole per hour. A solution of 24.4 g. (0.61 mole) of sodium hydroxide in 245 ml. of water was then added dropwise to the solution of ozonide followed by 69 ml. (20.7 g., 0.61 mole) of 30% hydrogen peroxide. The mixture was heated at reflux for 1 hr., and the methylene chloride removed by distillation. Another 15 ml. of 30% hydrogen peroxide was added and the mixture heated at reflux 1 hr. longer. The mixture was cooled, unreacted starting material removed by washing with ether, the water layer acidified with concentrated hydrochloric acid, and extracted with ether. The solvent was dried over magnesium sulfate and evaporated to afford 4.6 g. (80%) of bornylcarboxylic acid as colorless needles, m.p. 80-90°. Three recrystallizations from 88% formic acid gave a constant m.p. 90.8-92.6°.

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Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0. Found: C, 72.4; H, 9.6.

A mixture melting point of the acid, m.p. 90.8–92.6°, above with a sample of bornylcarboxylic acid, m.p. 79.6–83.0°, prepared from bornylmagnesium chloride and carbon dioxide according to the method of Rupe and Hirschman,³⁸ showed a m.p. 85.0–90.0°.

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Nuclear Magnetic Resonance Spectroscopy. Cyclopropane Derivatives¹

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Chemical shifts and coupling constants have been determined from the analysis of proton nuclear magnetic resonance spectra for a series of cyclopropane derivatives. The geminal and vicinal cyclopropyl couplings have opposite signs. Additional ¹³C–H coupling constants have been obtained for cyclopropanes which support the conclusion that the hybridization of the carbon–hydrogen bonding orbitals in cyclopropanes is close to sp². The chemical shifts for several cyclopropane hydrocarbons seem consistent with a ring-current effect.

Proton n.m.r.³ and fluorine n.m.r.⁴ spectroscopy have been utilized for structure determinations of substituted cyclopropanes. Coupling constants and chemical shifts of cyclopropane derivatives^{5,6} have recently been reported and interpreted in terms of substituent effects and molecular geometries.⁶

In the present research, the spin–spin splittings in the proton n.m.r. spectra of several substituted cyclopropanes have been analyzed using standard methods^{7,8} with results shown in Table I.

The Wiberg,⁹ the Bothner-By, and the Swalen¹⁰ computer programs were used to obtain the best agreement between the observed and the calculated spectra. The AB cyclopropyl proton patterns in the n.m.r. spectra of tetrasubstituted cyclopropanes yielded the cyclopropyl couplings directly. The *trans*-cyclopropyl couplings in the ABX type spectra of *trans*-3-(*trans*-2'-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid and its dimethyl ester were determined directly from the AB portion of the spectrum, the downfield part of which was split by the adjacent vinyl hydrogen. The n.m.r. spectra of neat samples of 1,1-dimethylcyclopropanecarboxylic acid, dimethyl 1-methylcyclopropane-*cis*-1,2-dicarboxylate, and dimethyl 1-methylcyclopropane-*trans*-1,2-dicarboxylate were analyzed as ABC systems. Identification in the observed spectrum of the three quartets and repeated spacings between lines gave approximate values of the chemical shifts and coupling constants, respectively. Best calculated frequency fits for the four possible combinations of relative signs of couplings were then obtained using the Swalen program.¹⁰ The best fit between observed and calculated intensities was found for the assignments with geminal coupling having an opposite sign to the vicinal couplings in the three ABC

systems studied. The analysis of the n.m.r. spectrum of dimethyl 1-methylcyclopropane-*trans*-1,2-dicarboxylate in benzene gave magnitudes and signs of couplings in agreement with the neat compound.

The ¹³C satellite n.m.r. spectra of 1,1-dichlorocyclopropane, 1,1-dimethylcyclopropane, spiropentane, and spirohexane were analyzed as AA'XX' systems. The center of each multiplet of the ¹³C satellites was determined by the moment method.¹¹ Similar calculated spectra in agreement with the observed spectrum were found with two geminal couplings having different magnitudes and opposite signs in each AA'XX' system studied. However, the best fit to the intensities was found for 1,1-dichlorocyclopropane with the geminal and vicinal couplings having opposite signs and this sign assignment was assumed for the other three AA'XX' systems. The *cis* and *trans* couplings which have the same sign are interchangeable without affecting the spectrum and have been assigned assuming the *cis* coupling has the greater magnitude. The errors involved in the determination of coupling constants are large owing to a low signal-to-noise ratio in the ¹³C satellite spectra, and also because small changes in the geminal coupling do not have much effect on the calculated spectra.

The AA'BB' type proton n.m.r. spectrum of neat 1-phenyl-1-bromocyclopropane was solved with the aid of the Swalen program. The only satisfactory fit was obtained with the geminal coupling taken to have the opposite sign to the vicinal couplings. Interchange of the two *cis* couplings and interchange of the geminal and *trans* couplings does not affect the calculated spectrum. The assignment of geminal and *trans* couplings with opposite signs appears to be definite and is supported by analysis of the spectrum of 1-phenyl-1-bromocyclopropane in chloroform (where the chemical shifts are different).

Gutowsky and co-workers¹² on the basis of valence-bond calculations have predicted a positive geminal coupling for H–C–H angles less than 120°. However, a recent publication¹³ on the proton n.m.r. spectra of small-ring compounds indicates that the geminal coupling has an opposite sign to the vicinal couplings in cyclobutane derivatives. With the aid of spin decoupling, Anet¹⁴ has shown that the geminal proton–

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