

reached in the study of the hydration of styrene^{19,20} and stilbene.²¹

The linearity of the plots of $\log k$ vs. H_0 is not significant of itself, as H_0 is approximately proportional to the acid concentration over these ranges of acidity,^{16,17} and so $\log k$ is also approximately proportional to the log of the acid concentration. Thus

(19) Y. Pocker and A. E. Miller, unpublished results; A. E. Miller, Ph.D. Thesis, University of Washington, 1968.

(20) W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964); W. M. Schubert and B. Lamm, *ibid.*, **88**, 120 (1966).

(21) D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, **90**, 4633 (1968).

the presence or absence of a water molecule in the transition state is a moot point. However, the observed slopes of 1.22 in water and 1.49 in 40% dioxane agree nicely with the suggestion that higher slopes correspond to transition states more weakly solvated by water,¹⁸⁻²¹ since there is clearly less water available for solvation in the mixed solvent.

It is proposed to further this research by undertaking a parallel study on the rearrangement of 1-phenyl-3-(trideuteriomethyl)allyl alcohol and the dehydration of 3-phenyl-1-(trideuteriomethyl)allyl alcohol and the hydration of 1-phenyl-4,4-dideuterio-1,3-butadiene.

Hydroxyl Proton Magnetic Resonance Study of Aliphatic Alcohols^{1a}

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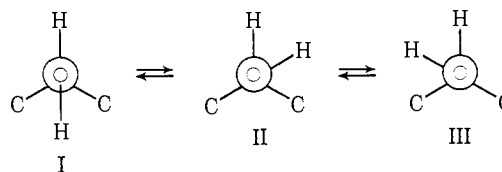
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Abstract: The constancy of the hydroxyl-carbinol proton coupling constant (J_{HCOH}) for rotamerically homogeneous methanol in hydrogen-bonding media indicates that J_{HCOH} variations for different alcohols in these media may be attributed to conformational changes. J_{HCOH} measurements for sterically unhindered primary alcohols suggest that the three C-O bond rotamers are approximately equally populated. Similar measurements for unhindered secondary alcohols suggest the rotamer with the OH staggered between the two C-C bonds to be significantly less populated than the other two. For both primary and secondary alcohols substitution of alkyl groups on a carbon β to the OH consistently increases J_{HCOH} . This is attributed to a slight but significant decrease in the equilibrium H-C-O-H dihedral angle of some of the C-O bond rotamers in which the OH is staggered between a C-H and a C-C bond. For secondary cyclic alcohols in which the hydroxyl hydrogen is constrained to be only *gauche* or *anti* to the carbinol hydrogen, J_{HCOH} values reveal the simplified Karplus relation ($J_{\text{HCOH}} = A \cos^2 \phi$) to be followed to a good approximation. In dimethyl sulfoxide the hydroxyl proton chemical shift, relative to that of the neat alcohol, can be correlated with the degree of steric crowding around the OH group.

Methods for the facile observation of spin-spin coupling between the hydroxyl and other protons of alcohols are now well known.² As a result, the recent literature reports a number of studies involving vicinal³ and long-range⁴ coupling of the hydroxyl proton. The preponderance of these studies have been carried out in polar solvents which can donate an electron pair to form a hydrogen bond with the O-H proton and thus decrease its rate of exchange. The observation of this coupling in nonpolar solvents requires that greater attention be given to both solvent and solute purity.

Much experimental evidence may now be found for the existence, at least in a qualitative sense, of a Karplus type relation⁵ between the H-C-O-H coupling constant

(J_{HCOH}) and the corresponding dihedral angle. A previous study in these laboratories⁶ and a similar one by Uebel and Goodwin⁷ have shown that for a pair of epimeric cyclohexanols J_{HCOH} is greater for the equatorial epimer due to the existence of a significant population of the *anti* rotamer (I) of this epimer,



whereas, for the axial epimer steric considerations require that this conformer have a population much less than that of II or III. Other researchers have reported⁸⁻¹⁰ cases where J_{HCOH} is unusually large due to the OH existing primarily, if not entirely, in the *anti* conformation (I) as a result of intramolecular hydrogen bonding. These and other studies indicate that hy-

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(2) (a) P. L. Corio, R. L. Rutledge, and J. R. Zimmerman, *J. Am. Chem. Soc.*, **80**, 3163 (1963); (b) O. L. Chapman and R. W. King, *ibid.*, **86**, 1256 (1964); (c) J. M. Bruce and P. Knowles, *J. Chem. Soc.*, 5900 (1964); (d) E. Krakower and L. W. Reeves, *Trans. Faraday Soc.*, **59**, 2528 (1963).

(3) (a) W. B. Moniz, C. F. Poranski, Jr., and T. N. Hall, *J. Am. Chem. Soc.*, **88**, 190 (1966); (b) J. G. Traynham and G. A. Knesel, *ibid.*, **87**, 4220 (1965); (c) B. Casu, M. Reggiani, G. G. Gallo, and A. Vigevani, *Tetrahedron Letters*, 2253 (1965).

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(5) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

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(7) J. J. Uebel and H. W. Goodwin, *J. Org. Chem.*, **31**, 2040 (1966);

(8) N. L. Bauld and Y. S. Rim, *ibid.*, **33**, 1303 (1968).

(9) A. L. Ternay, Jr., and D. W. Chasar, *ibid.*, **33**, 2237 (1968).

(10) R. D. Stolow and A. A. Gallo, *Tetrahedron Letters*, 3331 (1968).

hydroxyl-carbinol coupling in alcohols offers many potential applications in structure determination, conformational analysis, and the theoretical study of spin-spin coupling.

This paper reports a study of the variation of hydroxyl-carbinol coupling as a function of solvent and structure for an extensive series of aliphatic alcohols. A proper understanding of the factors governing H-C-O-H coupling requires that the variation of this coupling be examined for the simple aliphatic alcohols. The variations found in these alcohols should be reflected in the J_{HCOH} values of more complex acyclic and cyclic alcohols. The coupling constants should reflect the prevailing conformation(s) of the carbon chain and, by comparison to appropriate model compounds, permit an estimation of the relative populations of the three C-O bond rotamers.

Results and Discussion

Solvent Effects on J_{HCOH} . The variation of proton coupling constants with solvent is well established but poorly understood.¹¹ In general, the solvent variation is greater for one-bond (1J) and geminal (2J) coupling constants than for vicinal (3J) coupling constants involving the H-C-C-H fragment, with the 3J variation being insignificant in many cases.¹² It is logical to classify solvent effects on 3J as either *direct* (i.e., those involving no significant rotation about the two central atoms of the fragment involved) or *conformational* (i.e., those involving significant rotation about the two central atoms).

Due to the marked tendency of the OH group to form hydrogen bonds and the greater polarity of the H-C-O-H fragment over that of the H-C-C-H one, one would expect the susceptibility of H-C-O-H to solvation effects to be greater than that of H-C-C-H. Thus, carbinol-hydroxyl coupling constants should likely be susceptible to significant direct solvent effects (i.e., those not involving any rotation about the C-O bond). The rigorous application of J_{HCOH} values to conformational studies requires a knowledge of the magnitude of these direct solvent effects.

To delineate the magnitude of the direct solvent effects upon H-C-O-H J values, we have measured J_{HCOH} for methanol in a variety of solvents over a broad concentration range. Methanol should serve as a valid model compound for delineating the direct solvent effects on hydroxyl-carbinol coupling. All of its three rotational conformers are equivalent by virtue of symmetry, and any change in J_{HCOH} resulting from solvent effects cannot be ascribed to a change in the relative populations of the three rotational conformers.

The vicinal coupling constant of methanol (Table I) varies slightly but significantly as a function of solvent and concentration. In neat methanol, dimethyl sulfoxide (DMSO), and tetramethylurea (TMU) J_{HCOH} remains essentially constant. This constancy of J_{HCOH} compares to an upfield chemical shift variation of 0.79 ppm when neat methanol is diluted to very low concentration with DMSO.¹³ In TMU and DMSO the

hydroxyl hydrogen is hydrogen bonded to a solvent molecule, whereas, in the neat alcohol both the O and H participate in hydrogen bond formation. Our J_{HCOH} values in DMSO agree excellently with a previous nmr study¹⁴ of methanol in DMSO.

Table I. Carbinol-Hydroxyl Proton Coupling Constants of Methanol as a Function of Solvent and Concentration

Solvent	Concn, M	$J_{\text{H-C-O-H}}$, Hz ^a
Neat		5.18 ^b
Dimethyl sulfoxide	3.00	5.16
	0.50	5.14
	0.100	5.21
	0.030	5.23
Tetramethylurea	3.00	5.17
	0.50	5.22
	0.100	5.20
	0.030	5.22
Carbon tetrachloride	0.50	5.31
	0.100	5.34
	0.030	5.37
Benzene	0.50	5.41
	0.100	5.46
	0.030	5.53
Cyclohexane	0.150	5.41
	0.100	5.48
	0.030	5.58

^a J_{HCOH} values accurate to ± 0.05 Hz. ^b Obtained by extrapolation of data of Powles and Strange [J. G. Powles and J. H. Strange, *Mol. Phys.*, **8**, 169 (1964)] to 39°.

In the nonpolar solvents, J_{HCOH} experiences a slight but significant increase which parallels a diminishment of the degree of hydrogen bonding of the OH group. The data of Liddell and Becker¹⁵ have been used to calculate that in 0.03 M carbon tetrachloride solution at 40° more than 90% of the OH groups of methanol are not hydrogen bonded. Thus, breaking more than 95%¹⁶ of the hydrogen bonds in neat methanol, by diluting the neat liquid to 0.03 M in carbon tetrachloride, is accompanied by an increase in J_{HCOH} from 5.18 to 5.37 Hz. This slight shift in the coupling constant contrasts with the dramatic change in the chemical shift of the hydroxyl proton during the same dilution.¹⁷

Upon dilution of neat methanol in cyclohexane, the hydrogen bonding behavior parallels approximately that in carbon tetrachloride, with an increase in J_{HCOH} which is roughly twice that resulting in the latter solvent. Even in benzene, which forms a weak hydrogen bond with the solute hydroxyl hydrogen, the J_{HCOH} value is slightly greater than in carbon tetrachloride. A comparison of the data in the three nonpolar solvents indicates that factors other than hydrogen bonding influence J_{HCOH} . Attempted correlation of the data in Table I with solvent dielectric constant (ϵ) is only partially successful, since ϵ (at 20°) decreases¹⁸ in the order DMSO (48.9) > MeOH (33.6) > TMU (23.1) > benzene (2.28) > carbon tetrachloride (2.24) > cyclohexane (2.02).

(13) W. Drinkard and D. Kivelson, *J. Phys. Chem.*, **62**, 1494 (1958).

(14) D. Kivelson and M. G. Kivelson, *J. Mol. Spectry.*, **2**, 518 (1958).

(15) U. Liddell and E. D. Becker, *Spectrochim. Acta*, **10**, 76 (1957).

(16) This value assumes that in neat methanol each molecule participates in an average of two hydrogen bonds and in 0.03 M CCl_4 solution only monomeric and linear dimeric species exist.

(17) (a) M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958); (b) J. C. Davis, Jr., K. S. Pitzer, and C. N. R. Rao, *J. Phys. Chem.*, **64**, 1744 (1960).

(18) A. Luttringhaus and H. W. Dirksen, *Angew. Chem.*, **75**, 1059 (1963); (b) H. L. Schlafer and W. Schaffernicht, *ibid.*, **72**, 618 (1960).

(11) P. Laszlo, *Progr. Nucl. Magnetic Resonance Spectry.*, **3**, 335 (1967).

(12) (a) L. S. Rattet, A. D. Williamson, and J. H. Goldstein, *J. Mol. Spectry.*, **26**, 281 (1968); (b) S. L. Smith and R. H. Cox, *J. Chem. Phys.*, **45**, 2848 (1966); (c) S. L. Smith and A. M. Ihrig, *ibid.*, **46**, 1181 (1967); (d) an exception to this general rule has been reported by: S. L. Smith and R. H. Cox, *J. Mol. Spectry.*, **25**, 232 (1967).

The sign of J has been shown to be positive for the H-C-O-H¹⁹ as well as the HCSH²⁰ fragment. Thus, the direct solvent effect appears to shift J_{HCOH} for alcohols in the negative direction upon formation of a strong hydrogen bond. In contrast, $^1J_{\text{CH}}$, which is known to have a positive sign, has been observed in numerous instances¹¹ to be shifted to larger positive values upon transfer from a nonpolar solvent such as cyclohexane to a polar solvent. $^2J_{\text{HCH}}$ values, the preponderance of which is negative in sign, are known¹¹ to be shifted in the negative direction upon going from nonpolar to polar solvents. It has been proposed^{12c,21} that the effects of solvent upon a coupling constant be used as a means of deducing the sign of the constant. Comparison of our results with those from the literature indicates that this practice should be followed with much caution.

The direct solvent effect upon J_{HCOH} for methanol should be at least as great as the effect upon the conformer J values for primary (IV, V, or VI) and secondary (I, II, or III) alcohols. It is therefore reasonable to conclude that in different solvents with which the O-H hydrogen can form a moderately strong hydrogen bond direct solvent effects upon J_{HCOH} will be insignificant. The J_{HCOH} variations thus observed should be due to conformational solvent effects.

J_{HCOH} , **Primary Alcohols.** Beginning with ethanol, the hydroxyl-carbinol proton coupling constant was measured for a series of primary alcohols with increasing chain length and substitution. Since direct solvent effects on J_{HCOH} are insignificant in media in which the OH is hydrogen bonded, these measurements were carried out in (1) the neat alcohol and (2) dilute DMSO, in which the J_{HCOH} values were constant (± 0.02 Hz) between concentrations of 3.00 and 0.10 M .

In dilute DMSO (Table II) the J_{HCOH} values for all of the primary alcohols, except those with substitution at the β carbon, are slightly less than J_{HCOH} for methanol. They are essentially constant at 5.10 ± 0.05 Hz. Substitution at the β carbon increases J by 0.08–0.17 Hz for each substituent methyl group. The coupling constants in the neat alcohols are consistently lower than those in DMSO, except where β substitution is present, in which cases J_{HCOH} is greater in the neat alcohol.

The parameters which can cause a variation in vicinal coupling constants have recently been summarized by Bothner-By.²² For the H-C-O-H fragment the most important parameters include (1) the dihedral angle (ϕ), (2) the orbital hybridization of carbon and oxygen, (3) the H-C-O and C-O-H bond angles, θ and θ' , respectively, and (4) the C-O bond length. In interpreting our coupling-constant data, it will be assumed that parameters 2, 3, and 4 remain essentially constant throughout the series of alcohols studied, at least in the hydrogen-bonding solvents employed here, and that the measured variations in J_{HCOH} result from changes in the dihedral angle. This practice has been followed

(19) F. Hruska, T. Schaefer, and C. A. Reilly, *Can. J. Chem.*, **42**, 697 (1964).

(20) V. F. Bystrov and O. P. Yablonsky, *J. Mol. Spectry.*, **26**, 213 (1968).

(21) C. L. Bell and S. S. Danylyuk, *J. Am. Chem. Soc.*, **88**, 2344 (1966).

(22) A. A. Bothner-By, *Advan. Nucl. Magnetic Resonance*, **1**, 201 (1966).

Table II. Hydroxyl-Carbinol Proton Coupling Constants and Dilution Shift of OH Resonance for Primary Alcohols

Alcohol	J_{HCOH} , ^a Hz		$\Delta\delta$, ^b ppm
	Neat Alcohol	Dilute DMSO	
Ethanol	4.94	5.07	<i>c</i>
1-Propanol	5.04	5.15	0.89
1-Butanol	5.03	5.10	0.82
1-Pentanol	5.05	5.10	0.81
1-Hexanol	4.97	5.11	0.79
1-Heptanol	5.00	5.10	0.73
2-Methyl-1-propanol	5.28	5.24	0.87
3-Methyl-1-butanol	4.95	5.09	0.81
2,2-Dimethyl-1-propanol	5.59 ^d	5.41	0.43

^a J_{HCOH} values accurate to ± 0.05 Hz. ^b Upfield shift, relative to methyl protons, of OH proton resonance upon going from neat alcohol to dilute (0.50 M) DMSO. ^c $\Delta\delta$ not evaluated for ethanol. ^d Measured at 52°, the melting point.

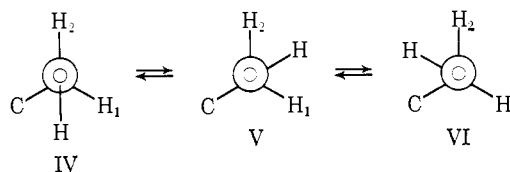
numerous times for the H-C-C-H fragment in series of compounds of quite similar structure.

Our J_{HCOH} values thus should reflect directly conformational changes resulting from rotation about the C-O bond. The relative populations of C-O bond conformers for a given alcohol should be ancillary to the conformation adopted by the carbon skeleton of the molecule. The nonbonded interactions which arise between the O-H hydrogen and other hydrogens in the molecule can, to a large extent, be relieved by rotation about the C-O bond to a position in which the hydroxyl hydrogen is less sterically hindered, with the unshared pairs of electrons staggered in the more sterically hindered conformer positions.²³ This means of relieving steric strain is not available for rotational conformers about the C-C bond. It is thus reasonable to consider our H-C-O-H coupling constants within the context of the conformers which prevail in the hydrocarbon from which the alcohol is derived.

IV, V, and VI depict the three C-O bond conformers for a primary alcohol. J_{HCOH} for a primary alcohol is related to the conformer J values by the expression

$$J_{\text{HCOH}} = J_{\text{IV}}N_{\text{IV}} + J_{\text{V}}N_{\text{V}} + J_{\text{VI}}N_{\text{VI}} \quad (1)$$

where the N 's denote the mole fractions of the respective



conformers. N_{IV} and N_{VI} are equivalent by virtue of symmetry.²⁵ For the coupling between the hydroxyl and a given carbinol proton, it appears reasonable to assume that the two conformers in which the OH is *gauche* to the proton concerned will have the same J

(23) This implicitly assumes that the space requirement or "size" of the unshared oxygen electrons is less than that of the hydroxyl proton. We have previously published nmr⁵ and infrared²⁴ evidence that such is the case. The literature contains abundant evidence that the "size" of the unshared pairs of electrons on oxygen is less than that of hydrogen directly bonded to carbon. See, for example: E. L. Eliel and M. C. Knoeber, *J. Am. Chem. Soc.*, **90**, 3444 (1968); K. Pihlaja, *Acta Chem. Scand.*, **22**, 716 (1968).

(24) (a) H. S. Aaron and C. P. Rader, *J. Am. Chem. Soc.*, **85**, 3046 (1963); (b) H. S. Aaron, C. P. Ferguson, and C. P. Rader, *ibid.*, **89**, 1431 (1967).

(25) This equivalency is not valid for cases where the molecule has a center of asymmetry reasonably close to the OH group.

value. Thus, for H-O-C-H₁ coupling J_{IV} and J_V are assumed equivalent, whereas, J_V and J_{VI} are assumed equivalent for H-O-C-H₂ coupling. This assumption assumes implicitly that for a given H-C-O-H the dihedral angles are equal for the two conformers where the hydroxyl and carbinol protons are *gauche* to each other.²⁶ Due to the equivalence of N_{IV} and N_{VI} , J_{HCOH} for each of the two carbinol protons is equal to J_{HCOH} for the other and to the J_{HCOH} measured experimentally.

A knowledge of J_{gauche} and J_{anti} for a sterically unhindered primary alcohol would permit the estimation of the mole fractions of C-O bond conformers by means of eq 1. In dilute DMSO the J_{HCOH} value for methanol may be used to approximate J_{gauche} and J_{anti} , since

$$J_{HCOH} = \frac{1}{3}J_{anti} + \frac{2}{3}J_{gauche} \quad (2)$$

The familiar Karplus relation⁵ is commonly employed in the form

$$J = A \cos^2 \phi + B \quad (3)$$

where ϕ is the dihedral angle, and A and B are constants. For the H-C-C-H fragment, A is much greater (by a factor of approximately 30) than B and has values for the 0-90° and 90-180° ϕ ranges which differ by approximately 10%. In computing J_{gauche} and J_{anti} we shall take (1) B to be negligible and (2) A to be constant over the entire dihedral range. These assumptions have previously been made²⁷ in applying H-C-C-H coupling constant data to conformational analysis. Employing dihedral angles of 60 and 180° for J_{gauche} and J_{anti} , respectively, our experimental J_{HCOH} of 5.19 Hz for methanol gives J_{gauche} a value of 2.60 Hz and J_{anti} a value of 10.40 Hz.

All of the primary alcohols (Table II) with no β substitution give a J_{HCOH} value extremely close to 5.10 Hz. Employing eq 1 and the above values for J_{gauche} and J_{anti} , one obtains an N_V value of 0.36 and a value of 0.32 for N_{IV} and N_{VI} . Due to the assumptions made to permit their computation, these mole fractions must be regarded as only approximate. They do seem to indicate, however, that the three conformers of primary alcohols with no β substitution are comparably populated in DMSO.

Whereas substitution on carbons more remote than the β position appears to have no significant effect on J_{HCOH} and, presumably, on the C-O bond conformational equilibria, substitution on the β -carbon produces a consistent increase in J_{HCOH} , as evidenced by the series ethanol, 1-propanol, 2-methyl-1-propanol, 2,2-dimethyl-1-propanol. At least in part, this increase in J_{HCOH} results from the steric effect of the methyl groups attached to the β -carbon. One cannot attribute

(26) For the conformers with the OH proton staggered between a C-H and the C-C bond, the dihedral angle between this C-H and the O-H could in principle be less than 60° due to the larger size of the alkyl group. Dreiding stereomodels show a 60° dihedral angle for this conformer to produce very little steric interaction with the alkyl group so long as there is no β substituent on the same side of the C $_{\alpha}$ -C $_{\beta}$ bond as the OH proton.

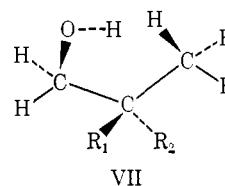
(27) E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1165 (1966). This paper points out and discusses the approximate nature of eq 3 and the two simplifying assumptions made to arrive at the $J = A \cos^2 \phi$ expression. This approximate nature must be kept in mind in regarding numerical answers obtained by this expression. It is most likely, however, that these numerical answers will have qualitative or semiquantitative significance.

it to an increase in the population of conformer V at the expense of the other two conformers, since a decrease in J_{HCOH} should result if this were the case. It is suggested that this increase is primarily due to a slight but significant decrease in the equilibrium dihedral angle of conformers IV and VI as the OH hydrogen is rotated away from the C $_{\alpha}$ -C $_{\beta}$ bond. For a given C-O bond conformer eq 3 indicates that the decrease in ϕ will produce an increase in OH proton coupling with the *gauche* carbinol hydrogen and a decrease in coupling with the *anti* hydrogen. If eq 3 is differentiated

$$dJ/d\phi = -2A \sin \phi \cos \phi \quad (4)$$

According to eq 4, the effect of decreasing ϕ for both *gauche* and *anti* coupling, for a given conformer, will be much greater for the former since its dihedral angle is near 60°, as opposed to 180° for the latter. Thus, the net effect of this decrease in ϕ should be an increase in the observed coupling constant.

Stereomodels reveal (VII) that quite significant non-bonded interactions can arise between the OH hydrogen in IV and VI and a hydrogen on the γ -carbon atom



when the C $_{\alpha}$ -C $_{\beta}$ bond conformation has the OH and γ -carbon *gauche* to each other. This interaction can be relieved significantly by the equilibrium H-C-O-H dihedral angle being decreased by a few degrees. The probability of this interaction arising in IV or VI increases with the degree of substitution on the β -carbon, in agreement with our data. Approximating increments by means of eq 4 and assuming (1) A to be 10.40 Hz, (2) the effect of γ -hydrogen interaction on *anti* coupling (*ca.* 180° dihedral angle) to be negligible compared to that on *gauche* coupling (*ca.* 60° dihedral angle) and (3) ΔJ to be 1.02 Hz, three times the difference in DMSO between J_{HCOH} for ethanol and 2,2-dimethyl-1-propanol (in which rotamers IV and VI must experience γ -hydrogen interaction), the decrease in ϕ from 60° for *gauche* HCOH coupling can be calculated to be of the order of 6-8°. For rotation about the C-O bond the potential energy (V) function may be approximated by²⁸

$$V = 0.5V_0(1 + \cos 3\phi) \quad (5)$$

where V_0 is the barrier height to rotation (approximately 1.0 kcal/mol).²⁹ The existence of γ -hydrogen interactions should perturb this function quite significantly. For *gauche* HCOH coupling at a dihedral angle near 60° the nonbonded interaction between the OH hydrogen and the γ -hydrogen should be sufficient to shift the equilibrium dihedral angle to a value approximately 6-8° less.³⁰

(28) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 7.

(29) E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 370 (1959).

(30) The very small decrease in J_{HCOH} upon proceeding from methanol to ethanol and its higher homologs with no β substitution could be explained by assuming a decrease in the dihedral angle of conformers IV and VI which almost offsets a decrease in J_{HCOH} resulting from a V population greater than that calculated. We consider this to be an

In the neat alcohols with no β substitution, the J_{HCOH} values (Table II) are slightly but significantly less than in DMSO. This conformational solvent effect most likely results from the participation of the hydroxyl group oxygen, as well as the hydrogen, in hydrogen-bond formation. This participation requires that the unshared electron pairs on the oxygen be sterically available to the hydroxyl hydrogen of another molecule and makes the OH group more susceptible to steric effects. In agreement with this, we have previously reported⁶ that epimeric axial and equatorial cyclohexanols form hydrogen-bonded alcohol-DMSO complexes with equal facility; whereas, the more sterically accessible equatorial alcohol autoassociates more readily than its axial epimer.³¹ In the neat alcohols the effect of β -carbon substitution on J_{HCOH} is even greater than in DMSO. This may logically be attributed to a greater decrease in the H-C-O-H dihedral angle of the neat alcohols, as a result of the greater steric requirements of the OH group.

Moniz, Poranski, and Hall^{3a} have published J_{HCOH} values in dilute DMSO for a series of primary alcohols possessing a variety of functional groups. Their J_{HCOH} values for three of the alcohols covered by this study agree excellently with ours. With other functional groups in the molecule, they found J_{HCOH} to increase quite significantly (by as much as 1.5 Hz). These increases are likely due to the presence of electronegative substituents on the β -carbon (*e.g.*, halogen, nitro) and the opportunity for the OH group to form intramolecular hydrogen bonds with some of the β substituents. Since the alcohols covered by our study all possess a single OH group attached to an acyclic hydrocarbon radical, the interactions producing the observed variations in J_{HCOH} may be attributed primarily to steric effects.

J_{HCOH} , Secondary Alcohols. For a secondary alcohol J_{HCOH} is related to the conformer J values by the expression

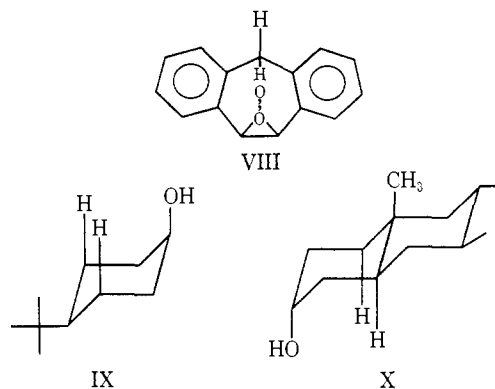
$$J = J_{\text{I}}N_{\text{I}} + J_{\text{II}}N_{\text{II}} + J_{\text{III}}N_{\text{III}} \quad (6)$$

If the two alkyl groups attached to the carbinol carbon are identical, the two *gauche* conformers (II and III) will be equivalent by virtue of symmetry. J_{II} will thus be equivalent to J_{III} and N_{II} equivalent to N_{III} . To a good approximation, this identity is valid for secondary alcohols unsymmetrically substituted on the carbinol carbon (*e.g.*, cyclohexanols) with no β -carbon substituents capable of sterically interacting with the hydroxyl hydrogen.

To obtain J_{I} and J_{II} values for a secondary alcohol with insignificant steric hindrance about the OH group, we have measured J_{HCOH} for model secondary alcohols in which the OH group is constrained to reside in either the *gauche* or *anti* conformation the great preponderance of the time, if not exclusively. Bauld and Rim⁸ have shown that in nonpolar solvents dibenzo[*b,f*]-2,4,6-cycloheptatriene-1-ol 4-oxide (VIII) exists exclusively

unlikely possibility. Stereomodels show the γ -hydrogen-hydroxyl-hydrogen nonbonded interaction for IV and VI to be much greater than the interactions existing in C_{α} - C_{β} conformers where the former is not possible. Thus the decrease in H-O-C-H dihedral angle for IV and VI in the latter C_{α} - C_{β} conformers should be relatively insignificant.

(31) (a) G. Chiurdoglu, A. Cardon, and W. Masschelein, *Bull. Soc. Chim. Belges*, **68**, 388 (1959); (b) E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **23**, 2041 (1958).



in the *anti* conformation (I) with the hydroxyl group intramolecularly hydrogen bonded to the epoxy oxygen. The infrared OH stretching band of VIII gives a ν_{max} of 3440 cm^{-1} (CHCl_3) in comparison to a ν_{max} of $3420\text{--}3430 \text{ cm}^{-1}$ (CCl_4) for sterically unhindered secondary alcohols hydrogen bonded to DMSO.^{6,32} The intramolecular hydrogen bond in VIII is thus of comparable strength to that in a secondary alcohol-DMSO bond. Direct solvent effects are therefore of no consequence here. The presence of the two phenyl groups should have very little, if any, effect on J_{HCOH} , since benzyl alcohol in acetone gives³³ a J_{HCOH} value (5.6 Hz) which is very close to that we have found for 2,2-dimethyl-1-pentanol. VIII thus appears to be a suitable model compound for the determination of J_{anti} for sterically unhindered secondary alcohols. We have measured J_{HCOH} for VIII and obtained the values given in Table III.

Table III. J_{HCOH} for Secondary Alcohols Constrained to Exist in Primarily a *gauche* or the *anti* C-O Bond Conformation

Alcohol	Solvent ^a	J_{HCOH} , Hz ^b
<i>cis</i> -4- <i>t</i> -Butylcyclohexanol	DMSO	3.05
Androsterone	DMSO	3.07
Dibenzo[<i>b,f</i>]-2,4,6-cycloheptatriene-1-ol 4-oxide	CCl_4	12.11
	CDCl_3	11.97

^a Concentrations, 0.50–2.00 M. ^b J_{HCOH} values accurate to $\pm 1\%$.

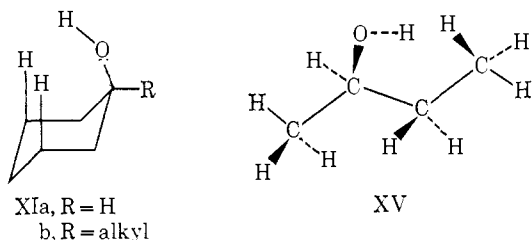
The model compounds chosen for the estimation of J_{gauche} were two conformationally biased axial cyclohexanols—*cis*-4-*t*-butylcyclohexanol (IX) and androsterone (X). In both of these alcohols, severe nonbonded interactions result in conformer I between the OH hydrogen and the two *syn* axial hydrogens (XIa). This interaction may be relieved to a large extent by rotation about the C-O bond to II or III where an unshared electron pair interacts with the two *syn*-axial hydrogens. As a result, one would expect the population of I for axial alcohols to be quite small, likely negligible, in comparison to that of II and III. Infrared²⁴ and nmr^{6,7} studies support this conclusion. This conclusion has recently been questioned by Joris, Schleyer, and Osawa,³⁴ who have offered an alternative interpretation for the infrared evidence²⁴ supporting it.

(32) C. P. Rader, unpublished research.

(33) (a) D. E. McGreer and M. M. Mocek, *J. Chem. Educ.*, **40**, 358 (1963); (b) P. L. Corio, R. L. Rutledge, and J. R. Zimmerman, *J. Mol. Spectry.*, **3**, 592 (1959).

(34) L. Joris, P. von R. Schleyer, and E. Osawa, *Tetrahedron*, **24**, 4759 (1968).

These authors have compared ν_{\max} values of symmetrical components of free OH stretching bands (dilute CCl_4 solution) for tertiary axial cyclohexanols with the ν_{\max} values for model tertiary cyclic alcohols and have arrived at the conclusion that tertiary axial cyclohexanols possess a significant population of conformer XIb. By inference they then conclude that conformer



XIa is significantly populated in the case of secondary axial cyclohexanols. For a given cyclohexanol system, the population of XIa for the secondary alcohol should be less than that of XIb for the corresponding tertiary alcohol.

Joris, Schleyer, and Osawa³⁴ do not mention the nmr evidence^{6,7} supporting the presumed low population of conformer XIa. The fact that J_{HCOH} is 1.0–1.5 Hz greater for equatorial cyclohexanols than for their axial epimers is quite difficult to explain if the population of conformer XIa cannot be assumed to be much less than that of the other two conformers. In at least a qualitative sense, vicinal coupling constants are known to follow a Karplus type relation for the H–C–C–H,²² H–C–C–F,³⁵ F–C–C–F,³⁵ ¹⁴N–C–C–H,³⁶ ¹³C–C–C–H,³⁷ ³¹P–C–C–H,³⁸ and ¹⁹⁹Hg–C–C–H³⁹ fragments. It is extremely likely that a similar type of relation governs the coupling constant variation of the H–C–O–H fragment with dihedral angle.

Another factor which must be kept in mind here is that the infrared data were obtained in dilute CCl_4 solution; whereas, the nmr data were gotten in DMSO solution, in which the OH proton is strongly hydrogen bonded to a solvent molecule. Since an O–H...O hydrogen bond of the strength involved here cannot deviate greatly from linearity, the presence of the two *syn* axial hydrogens in XIa should greatly destabilize the OH–solvent hydrogen bond, a destabilization which does not exist in the other two C–O bond conformers. This leads to the clear conclusion that in DMSO or any other hydrogen-bonding medium, conformer XIa should exist in a smaller population than in carbon tetrachloride.

Based on the considerations given here we feel that conformationally biased axial alcohols such as *cis*-4-*t*-butylcyclohexanol (IX) and androsterone (X) are reasonable models for estimating J_{gauche} for a sterically unhindered secondary alcohol. Accordingly, we have determined J_{HCOH} for IX and X in DMSO and obtained

(35) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, New York, N. Y., 1966, p 889.

(36) Y. Terui, K. Aono, and K. Tori, *J. Am. Chem. Soc.*, **90**, 1069 (1968).

(37) G. J. Karabatsos, C. E. Orzech, Jr., and N. Hsi, *ibid.*, **88**, 1817 (1966).

(38) C. Benezra and G. Ourisson, *Bull. Soc. Chim. France*, 1825, (1966).

(39) M. Kreevoy and J. Schaefer, *J. Organometal. Chem.* (Amsterdam), **6**, 589 (1966).

values (Table III) which are experimentally indistinguishable.

If one can assume that J_{HCOH} for VIII and J_{HCOH} for IX and X serve as valid values for J_{anti} and J_{gauche} , respectively, the data in Table IV yield a most interesting result. Taking the averages of the measurements of J_{anti} and J_{gauche} , the $J_{\text{anti}}/J_{\text{gauche}}$ ratio is found to be 3.94. Assuming dihedral angles of 60 and 180° for the *gauche* and *anti* conformers, respectively, and the validity of a simplified Karplus relation (eq 4 with $B = 0$ and A constant for all values of ϕ) as previously employed for primary alcohols, the $J_{\text{anti}}/J_{\text{gauche}}$ ratio should be 4.00. Considering the approximations involved here, the excellent agreement between the two $J_{\text{anti}}/J_{\text{gauche}}$ values is likely to be somewhat fortuitous. This agreement does seem to indicate that the model compounds selected give reasonable approximations of J_{gauche} and J_{anti} for a sterically unhindered secondary alcohol. In addition, the $J = A \cos^2 \phi$ relation appears to have at least qualitative or semiquantitative significance for the H–C–O–H fragment. These results provide additional evidence that in DMSO conformer XIa for an axial secondary alcohol has a very low, if not negligible, population.

Table IV. Hydroxyl–Carbinol Proton Coupling Constants and Dilution Shift of OH Resonance for Secondary Alcohols

Alcohol	$J_{\text{HCOH}},^a$ Hz		$\Delta\delta,^b$ ppm
	Neat alcohol	Dilute DMSO	
2-Propanol	4.28	4.20	<i>c</i>
2-Butanol	4.81	4.54	0.60
2-Pentanol	4.93	4.63	0.59
2-Hexanol	4.86	4.57	0.62
3-Pentanol	5.51	5.20	0.43
4-Heptanol	5.61	5.32	0.31
3-Methyl-2-butanol	4.99	4.61	0.29
2-Methyl-3-pentanol	5.93	5.49	–0.05
2,4-Dimethyl-3-pentanol	6.52	6.09	–0.51
2,2,4-Trimethyl-3-pentanol	6.56	5.97	–1.30
2,2,4,4-Tetramethyl-3-pentanol	6.06 ^d	6.55	–1.76

^a J_{HCOH} values accurate to $\pm 1\%$. ^b Upfield shift, relative to methyl protons at highest field, of OH proton resonance upon going from neat alcohol to dilute (0.50 M or less) DMSO. Negative sign indicates downfield shift. ^c $\Delta\delta$ not evaluated for 2-propanol. ^d Measured for the supercooled alcohol at 39°.

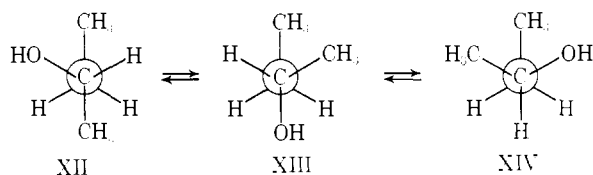
The J_{gauche} (3.06 Hz) and J_{anti} (12.04 Hz) values obtained from the model compounds may be employed in conjunction with eq 6 to calculate N_I , N_{II} , and N_{III} for a sterically unhindered secondary alcohol. For 2-propanol J_{HCOH} in DMSO (Table IV) gives an *anti* conformer population (N_I) of 0.13. We have measured in DMSO a J_{HCOH} value of 4.37 Hz for *trans*-4-*t*-butylcyclohexanol, which in the vicinity of the OH group has a steric situation very similar to that of 2-propanol. This J_{HCOH} value gives an *anti* conformer population (I) of 0.15. These conformer populations, though obtained without any resort to the Karplus relation, must be regarded as only approximate. They do strongly suggest that for sterically unhindered secondary alcohols the *anti* conformer population is in the 10–20% range.

In principle, it is possible to measure C–O bond conformer populations by resolving asymmetrical free-OH stretch infrared bands of simple alcohols (CCl_4

solvent) into symmetrical components, each of which may be assigned to a specific conformer, and comparing the relative areas of the component bands.⁴⁰ This procedure gives relative populations which contain as much error (and likely more) as the one employed by us here. For example, with ethanol^{34,41} the component band areas suggest that the V population is roughly twice as great as that for IV and VI combined, a result in gross variance with our conclusions. With 2-propanol,^{34,41} on the other hand, the relative band areas suggest the I population to be approximately equal to that of II or III. It appears that a higher degree of experimental and computational sophistication is needed, if this method is to be reliably applied to the evaluation of C–O bond rotamer populations.

We have measured J_{HCOH} for a series of acyclic secondary alcohols with an increasing degree of substitution about the carbinol carbon (Table IV). In dilute DMSO (<3.00 M) J_{HCOH} was found to be invariant (± 0.02 Hz) with concentration. For 2-propanol J_{HCOH} is much below the value for primary alcohols with no β substitution. Substitution of an alkyl group for hydrogen on a β carbon produces a much greater effect on J_{HCOH} than does substitution on a more remote carbon, in agreement with the data for primary alcohols. This increase in J_{HCOH} with β substitution can best be interpreted within the context of the prevailing carbon-chain conformers of the various alcohols. Thus, in 2-butanol the *anti* C–C–C–C conformation (XII) will prevail over the *gauche* (XIII and XIV), and in 2- and 3-pentanol the C–C–C–C chain will exist primarily in approximately equivalent amounts of (1) a single *anti-anti* conformer and (2) four different *anti-gauche* conformers.⁴² In the prevailing carbon-chain conformers for the various alcohols, the number of 1–4 *gauche* interactions will be minimized as far as possible.

Consideration of 2-butanol in the prevailing (60–65%)⁴³ *anti* C–C–C–C conformer (XII) reveals for one of the two *gauche* C–O bond conformers steric interaction between the hydroxyl hydrogen and a γ hydrogen (XV), as in the case of the β -substituted primary alcohols. This should logically decrease the



H–O–C–H angle and, as discussed for primary alcohols, increase J_{HCOH} . Another consideration is that any destabilization of C–O bond conformer XV, due to the γ -hydrogen interaction, should increase the relative population of the *anti* conformer (I) and thus J_{HCOH} . This destabilization by a γ -hydrogen interaction is most

(40) M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 950 (1959). This paper and ref 34 give a thorough discussion of the procedure with numerous literature references.

(41) L. Joris, P. von R. Schleyer, and R. Gleiter, *J. Am. Chem. Soc.*, **90**, 333 (1968).

(42) (a) K. L. Pitzer and E. Catalano, *ibid.*, **78**, 4844 (1956); (b) K. Ito, *ibid.*, **75**, 2430 (1953); (c) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *ibid.*, **81**, 4765 (1959); (d) N. Sheppard and G. J. Szasz, *J. Chem. Phys.*, **17**, 86 (1949); (e) G. J. Szasz and N. Sheppard, *ibid.*, **17**, 93 (1949).

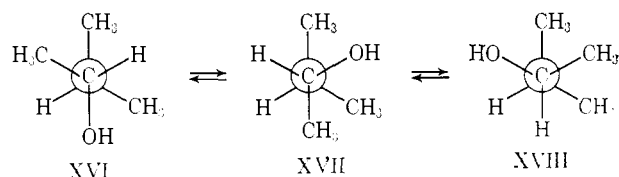
(43) Calculated by assuming a ΔH of 0.7–0.8 kcal/mol⁴² between the one *anti* and two equivalent *gauche* conformers of *n*-butane.

likely of minor consequence, since with primary alcohols it would produce a decrease in J_{HCOH} upon β substitution, the opposite of our observations (Table II).

The increase in J_{HCOH} upon β substitution is much greater for secondary alcohols than for primary alcohols. This appears to be determined at least in part by interaction with the γ hydrogen requiring a *gauche* O–C $_{\alpha}$ –C $_{\beta}$ –C $_{\gamma}$ conformation. Primary alcohols should prefer an *anti* O–C $_{\alpha}$ –C $_{\beta}$ –C $_{\gamma}$ conformation wherever possible, in order to minimize the unfavorable *gauche* interactions between the OH group and the groups attached to the γ -carbon. With secondary alcohols the probability of *gauche* interaction between the OH group and a β -alkyl group is greater, due to the predominance of carbon-chain conformational equilibria over those involving C–O bond rotation. Another possible determining factor here is that for primary alcohols rotation away from the β -alkyl group, for a given C–O bond conformer, produces a decrease in the coupling with the *anti*-carbinol hydrogen and an increase in the coupling with the *gauche* hydrogen, with the latter effect prevailing. Since secondary alcohols have but a single carbinol hydrogen, this rotation can *only* reduce the single H–C–O–H dihedral angle (of approximately 60°) to a significantly smaller angle.

An interesting and consistent trend in the J_{HCOH} data in DMSO (Table IV) is that as one proceeds from 2-propanol to the higher homologs, by successive replacement of β -hydrogens with methyl groups, J_{HCOH} increases by greater steps when the addition of the methyl group gives more symmetrical substitution about the H–C–O–H fragment. Thus, J_{HCOH} increases less upon proceeding from 2-propanol to 2-butanol than from the latter to 3-pentanol. In a more marked example, J_{HCOH} actually decreases slightly on going from 2,4-dimethyl-3-pentanol to 2,2,4-trimethyl-3-pentanol and then increases greatly to the value of 2,2,4,4-tetramethyl-3-pentanol.

Another demonstration of the effect of symmetrical substitution on J_{HCOH} in DMSO is seen in the 0.07-Hz increase upon proceeding from 2-butanol to 3-methyl-2-butanol and the 0.66-Hz increase upon proceeding from the former to 3-pentanol. In 2-butanol the γ -hydrogen–hydroxyl hydrogen interaction can arise in only one of the two *gauche* C–O bond conformers, a consideration which is also valid for 3-methyl-2-butanol. This γ -hydrogen interaction in 2-butanol can arise only when the C–C–C–C chain is in the *anti* conformer (XII), which exists 60–65%⁴³ of the time; it cannot arise in the two C–C–C–C *gauche* conformers (XIII and XIV). In 3-methyl-2-butanol the 2-methyl-butane skeleton should exist in conformers XVI and XVII more than 90%⁴⁴ of the time. Stereomodels



show that the γ -hydrogen interaction can arise with one, but not both, of the *gauche* C–O bond rotamers

(44) Calculated by assuming conformer XVIII to have a 1.2 kcal/mol higher enthalpy^{42b} than XVI or XVII which are assumed to have approximately equal enthalpy.

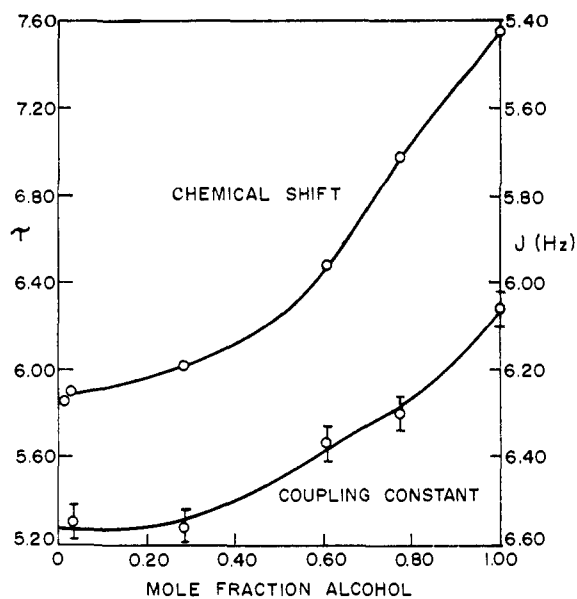


Figure 1. Variation of hydroxyl proton chemical shift and J_{HCOH} with 2,2,4,4-tetramethyl-3-pentanol concentration in DMSO.

in XVI and XVII, but not at all in XVIII. For 3-pentanol γ -hydrogen interaction can arise for both of the *gauche* C-O bond rotamers. For a given *gauche* C-O bond rotamer for this alcohol, γ hydrogen interaction can arise when the C-C-C-C chain is in the *anti-anti* (approximately 43% population)^{42c} or two of the four *gauche-anti* (approximately 12.5% population each)^{42c} conformations but not in the other two *gauche-anti* or the two *gauche-gauche* conformations. Thus, the likelihood of a γ -hydrogen interaction with the hydroxyl hydrogen increases much more as one proceeds from 2-butanol to 3-pentanol than from the former to 3-methyl-2-butanol.

For the neat secondary alcohols, J_{HCOH} is consistently greater than in DMSO, with the salient exception of 2,2,4,4-tetramethyl-3-pentanol, the most sterically hindered member of the group. The anomalous behavior of this alcohol is likely derived from the space requirements of the unshared pairs of O electrons as they participate in intermolecular hydrogen bonding in the neat alcohol. In agreement with this, J_{HCOH} for this alcohol under conditions of negligible hydrogen bonding (dilute CCl_4) has been found to be 5.4 Hz.⁴⁵ We have measured J_{HCOH} for 2,2,4,4-tetramethyl-3-pentanol as a function of concentration in DMSO and compared it to the hydroxyl proton chemical shift (Figure 1). The variation of J_{HCOH} with concentration in DMSO parallels that of the OH proton chemical shift. The factors governing the variation of these two hydroxyl proton parameters thus appear to be the same.

Hydroxyl Proton Chemical Shift Variation in DMSO.

For methanol¹³ and cyclohexanol⁶ it has previously been reported that the hydroxyl proton resonance is shifted to progressively higher field upon dilution in DMSO, with the chemical shift being essentially constant in dilute solution. For each of the acyclic alcohols used in this study, we have measured the chemical-shift variation of the OH proton as the neat alcohol

(45) L. K. Patterson and R. M. Hammaker, *J. Org. Chem.*, **70**, 3745 (1966).

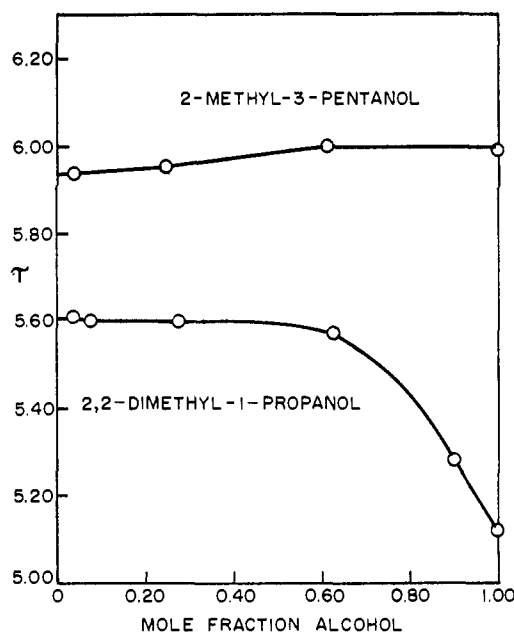


Figure 2. Variation of hydroxyl proton chemical shift with alcohol concentration in DMSO.

is diluted with DMSO. This variation is expressed (Tables II and IV) as the shift in OH proton resonance between the neat alcohol and dilute (0.50 *M* or less) DMSO solution, measured relative to the methyl protons at highest field. These reference protons were located on a γ or an even more remote carbon from the OH, and they should be relatively inert to solvent effects upon chemical shifts.⁴⁶

The shift of the OH resonance upon DMSO dilution is observed to reflect quite markedly the degree of steric crowding around the hydroxyl proton. For primary alcohols the upfield dilution shift of 2,2-dimethyl-1-propanol, the most sterically hindered primary alcohol studied, is approximately half that of the other primary alcohols. With the secondary alcohols the upfield dilution shift decreases greatly with substitution on the β carbons. Figure 2 depicts the τ_{OH} variation for 2,2-dimethyl-1-propanol, which gives the general shape of the dilution curves for the less sterically hindered alcohols (*i.e.*, those with $\Delta\delta$ values no less than that for this alcohol). For 2-methyl-3-pentanol, the degree of steric crowding around the OH is sufficient to give a slight downfield shift in the OH proton resonance upon DMSO dilution (Figure 2). This downfield shift progressively increases with substitution on the β -carbons. Figure 1 gives the concentration variation of τ_{OH} for the highly sterically hindered 2,2,4,4-tetramethyl-3-pentanol.

It is now well established that for O-H...O hydrogen bonds the OH proton resonance is shifted to progressively lower fields as the strength of the bond is increased. Our chemical shift data thus indicate that primary alcohols and secondary alcohols with little or no steric crowding about the OH autoassociate to form stronger hydrogen bonds than they form with DMSO. Sterically hindered secondary alcohols, on the other hand, form stronger hydrogen bonds with DMSO.

(46) The effect of solvent upon the chemical shift of "inert" acyclic or cyclic protons has been shown to be perceptible (ref 11, p 241) but much, much smaller than the effect upon hydroxyl protons, especially in non-aromatic solvents.

This result is derived primarily from the DMSO-HO hydrogen bond formation requiring access only to the hydroxyl hydrogen; whereas, the formation of an autoassociated chain of OH groups requires access to an unshared pair of oxygen electrons as well as the OH hydrogen. Alcohol autoassociation is thus more susceptible to steric crowding about the OH group than is association with DMSO, as our chemical-shift data clearly indicate.

Experimental Section

Materials. Except where stated otherwise, all alcohol samples were procured from commercial sources, with reagent grade alcohols being obtained wherever possible. Each alcohol sample was analyzed for purity by glpc on either a Carbowax 20M or Carbowax 1540 column. Where necessary, the alcohol samples were redistilled through either a 24-in. column packed with glass helices or a 1-m column packed with iron mesh, with literature boiling points being obtained in all cases. Glpc analysis revealed all alcohol samples employed for spectral work to be of >99% purity except for 1-hexanol, where the purity was >98%, and 1-pentanol, where the purity was >95%. No irregularities were found in the pmr spectra of either of these two alcohols.

2,2,4,4-Tetramethyl-3-pentanol was prepared by reduction of hexamethylacetone with sodium borohydride. To hexamethylacetone (5.0 g) in 95% ethanol was added a 20% *M* excess of sodium borohydride in 0.039 *N* aqueous sodium hydroxide and the mixture refluxed 30 min. After stripping off the EtOH from the reaction mixture, distilled water (30 ml) was added and the mixture extracted with three 30-ml aliquots of ether which were combined and dried overnight over Drierite. Following solvent removal, the residue was distilled to give 3.0 g of product (bp 163°). Upon cooling the product gave mp 46–48° (lit.⁴⁷ 50°).

Androsterone and *cis*- and *trans*-4-*t*-butylcyclohexanols were obtained from a previous study in these laboratories.⁶ Dibenzob[*b,f*]2,4,6-cycloheptatriene-1-ol 4-oxide (VIII) was prepared by the procedure previously reported.⁴⁸ Upon recrystallization from

(47) "Dictionary of Organic Compounds," Vol. 5, 4th ed, Oxford University Press, New York, N. Y., 1965, p 3025.

(48) N. L. Bauld and Y. S. Rim, *J. Am. Chem. Soc.*, **89**, 179 (1967). The author is extremely grateful to Professor Bauld for unpublished information concerning this preparation.

hexane-acetone (2:1) the product gave mp 136–137°. Its infrared and pmr spectra were in agreement with the structure VIII, the pmr spectrum being identical with that previously reported.^{8,48}

Reagent grade dimethyl sulfoxide solvent was redistilled and stored over activated Linde Type 4A Molecular Sieve. Tetramethylurea solvent was redistilled through a 1-m column packed with iron mesh, giving a constant boiling distillate (bp 178°). Spectroquality carbon tetrachloride solvent was dried with P₂O₅, shaken with anhydrous Na₂CO₃, passed through an alumina column and then stored over silica gel. Reagent grade benzene solvent was shaken with anhydrous Na₂CO₃ and then stored over a mixture of alumina and silica gel. Spectroquality cyclohexane solvent was shaken with a mixture of Na₂CO₃, silica gel, and activated alumina and then stored over this mixture. Reagent grade chloroform solvent was used without further purification.

Proton Magnetic Resonance Spectra. All pmr spectra were taken with a Varian A-60 spectrometer at a probe temperature of 39° unless noted otherwise. Probe temperature was monitored by the peak separation of the two peaks of neat ethylene glycol. Pmr measurements were taken only after the sample had been in the probe for a minimum of 10 min and was at thermal equilibrium.

J_{HCOH} values were measured with a 50-Hz sweep width, the average of a minimum of five sweeps in different directions being taken. To correct for minor day-to-day variations in the sweep width, the vicinal coupling constant of a standard sample of acetaldehyde was measured either immediately before or after the J_{HCOH} scans were made on the alcohol sample. The measured J_{HCOH} for the alcohol was then corrected to a standard value in direct proportion to an acetaldehyde coupling constant of 2.83 Hz.⁴⁹ Our J_{HCOH} values may thus be considered accurate within 1%.

In dimethyl sulfoxide, hydroxyl-carbinol coupling was readily observed for the various alcohols. In some of the neat alcohols the peaks of the hydroxyl proton multiplet were either only partially resolved, or a broadened singlet was obtained. The addition of a small amount of adsorption alumina to the sample tube or the passage of the alcohol through a small chromatographic column of alumina directly into the sample tube gave a well resolved OH proton multiplet from which J_{HCOH} could be accurately measured. Only in the case of neat methanol were we unable to obtain sufficient splitting of the OH proton multiplet to permit the measurement of J_{HCOH} at probe temperature (39°), in spite of numerous attempts with various techniques.

(49) (a) J. G. Powles and J. H. Strange, *Mol. Phys.*, **5**, 329 (1961); (b) see Powles and Strange, Table I, footnote b.

Proton Nuclear Magnetic Resonance Analysis of the Stable, Classical 2-Phenyl-2-norbornyl and Related Cations

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Abstract: The 100-Mc nmr spectrum of the 2-phenyl-2-norbornyl cation has been analyzed with the aid of deuterium labeling, spin decoupling, and computer simulation. From a comparison with several related norbornyl and bicyclo[2.2.2]octyl systems it is concluded that the title cation is classical. Some dramatic examples of the low-field chemical shifts of bridgehead norbornyl hydrogens are described.

It has been suggested by some workers that tertiary 2-norbornyl cations (1), are classical, especially where R = Ph.¹ Because of our interest in the structural analysis of stable carbonium ions,² we undertook a

(1) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2693 (1968), and earlier papers; P. von R. Schleyer, *ibid.*, **89**, 699, 701 (1967).

(2) (a) D. G. Farnum, *ibid.*, **89**, 2970 (1967); (b) D. G. Farnum and C. F. Wilcox, *ibid.*, **89**, 5379 (1967).

reanalysis of the nmr spectra of the 2-phenyl-2-norbornyl cation³ (1, R = Ph) and several model compounds. It was our expectation that the results

(3) This cation has already been observed and its nmr spectrum determined by Schleyer.⁴

(4) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963); N. C. Deno, P. von R. Schleyer, and D. C. Kleinfelter, *Tetrahedron Letters*, No. 12, 414 (1961).