(c 2.38, methylene chloride) after four recrystallizations; after seven recrystallizations, $[\alpha]^{25}_{578}$ $-87.8°$, $[\alpha]^{25}_{546}$ $-101.5°$, $[\alpha]^{25}_D$ $-83.5°$ (c 1.35, methylene chloride); and after ten recrystallizations the rotation was $[\alpha]^{25}_{578}$ $-89.0°$, $[\alpha]^{25}_{546}$ $-103.4°$, $[\alpha]^{25}_D$ $-84.6°$ (c 1.32, methylene chloride). The solution infrared spectra (chloroform) of complexes 1a and 2a were identical.

Anal. Calcd for C$_{17}$H$_{23}$Cl$_2$NOPtS: C, 36.75; H, 4.17; Cl, 12.76; N, 2.52; Pt, 35.14; S, 5.77. Found: C, 36.83; H, 4.13; Cl, 12.59; N, 2.63; Pt, 34.75; S, 5.72.

(−)-**Ethyl p-Tolyl Sulfoxide.** A solution of 6.0 g (0.011 mole) of (+)-*trans*-dichloro(ethyl p-tolyl sulfoxide)(α-methylbenzylamine)platinum(II) (1a) in 120 ml of methylene chloride was treated with 120 ml of a 10% aqueous sodium cyanide solution as described previously.[2] The reaction mixture was worked up as described and the solvent was removed at reduced pressure. Distillation of the resulting yellow oil gave 1.27 g (70%) of (−)-ethyl p-tolyl sulfoxide, bp 76–77° (0.01 mm), $[\alpha]^{25}_{578}$ $-214.5°$,

$[\alpha]^{25}_{546}$ $-250.5°$, and $[\alpha]^{25}_D$ $-203.6°$ (c 0.93, acetone). The nmr spectrum of this material was identical with that previously described[5] for (+)-ethyl p-tolyl sulfoxide.

Anal. Calcd for C$_9$H$_{12}$OS: C, 64.24; H, 7.19; S, 19.06. Found: C, 63.91; H, 7.44; S, 18.87.

(+)-**Ethyl p-Tolyl Sulfoxide.** (−)-*trans*-Dichloro(ethyl p-tolyl sulfoxide)(α-methylbenzylamine)platinum(II) (2a) (1.0 g, 0.0018 mole) in 20 ml of methylene chloride was treated with 20 ml of a 10% aqueous sodium cyanide solution as described above. The solvent was removed under reduced pressure to give a yellow oil, which upon distillation gave 0.063 g (21%) of (+)-ethyl p-tolyl sulfoxide, $[\alpha]^{25}_{578}$ $+214.2°$, $[\alpha]^{25}_{546}$ $+250.0°$, and $[\alpha]^{25}_D$ $+203.2°$ (c 0.60, acetone). The infrared spectrum of the (+)-sulfoxide was identical with that of the (−)-sulfoxide; both were identical to that of dl-ethyl p-tolyl sulfoxide.

Anal. Calcd for C$_9$H$_{12}$OS: C, 64.24; H, 7.19; S, 19.06. Found: C, 64.14; H, 7.27; S, 19.36.

Conformational Study of Cyclohexanols in Dimethyl Sulfoxide

Charles P. Rader

Contribution from the Research Department, Organic Chemicals Division, Monsanto Company, St. Louis, Missouri 63166. Received November 3, 1965

Abstract: Proton magnetic resonance spectra of epimeric cyclohexanols in dimethyl sulfoxide reveal that in all cases the hydroxyl proton of the axial alcohol resonates at higher field than the equatorial one. The spin–spin coupling between the hydroxyl and carbinol protons is found to be greater for the equatorial epimer. This difference in coupling is readily related to the effect of dihedral angle upon the coupling constant and the different populations of rotational isomers about the C–O bond. Factors other than the relative strength of the axial and equatorial O–H---DMSO hydrogen bonds appear to influence the chemical-shift difference, since infrared data show cyclohexanol and each of the 4-*t*-butylcyclohexanols to form with DMSO hydrogen bonds of comparable strength. Further structural applications of the magnitude of the hydroxyl–carbinol proton coupling are discussed.

Proton magnetic resonance (pmr) spectra of alcohols are known to show spin–spin coupling between hydroxyl and carbinol protons, provided there is an extremely low concentration ($<10^{-5}$ M) of acids or bases which catalyze O–H proton exchange. It is generally more difficult to observe this coupling in nonpolar solvents[1] than in polar ones which can donate an electron pair to the hydroxyl group.[2] It is reasonable to presume[3] that hydrogen bond formation increases the O–H proton lifetime on a single molecule sufficiently to permit splitting of its resonance signal to be observed.

Dimethyl sulfoxide (DMSO) has been found to be an excellent solvent for the facile observation of H–C–O–H splitting. In DMSO Chapman and King[4] have shown that pmr spectra of alcohols may be used for classification purposes according to the multiplicity of the O–H resonance. More recently the use of DMSO

as solvent for pmr studies of OH groups of sugars has been reported.[5]

This paper reports a study of hydroxyl proton chemical shifts and coupling constants for a series of epimeric cyclohexanols in DMSO and the structural correlation of these parameters. The relationship between vicinal coupling constants and dihedral angle for H–C–C–H systems is well established[6] and has been extremely useful in conformational studies. It is reasonable to expect H–C–O–H coupling constants to vary with dihedral angle in a manner similar to that for H–C–C–H systems. Thus, one should be able to correlate the magnitude of carbinol–hydroxyl proton splitting with the rotational conformations of the OH group. These nmr results should complement previous infrared studies[7] of conformational equilibria resulting from rotation about the C–O bond of alcohols.

Results

For reasons previously mentioned,[4] DMSO was found to be a superior solvent for the study of hydroxyl pmr spectra of alcohols. In dilute DMSO the OH proton resonance occurs in the τ 5.5–6.3 region, a

(1) (a) J. M. Bruce and P. Knowles, *Proc. Chem. Soc.*, 294 (1964); (b) J. M. Bruce and P. Knowles, *J. Chem. Soc.*, 5900 (1965); (c) C. P. Rader, unpublished observations.

(2) (a) W. G. Schneider and L. W. Reeves, *Ann. N. Y. Acad. Sci.*, 70, 858 (1958); (b) D. E. McGreer and M. M. Mocek, *J. Chem. Educ.*, 40, 358 (1963); (c) P. L. Corio, R. L. Rutledge, and J. R. Zimmerman, *J. Mol. Spectry.*, 3, 592 (1959); (d) F. Hruska, T. Schaefer, and C. A. Reilly, *Can. J. Chem.*, 42, 697 (1964); (c) B. Cernicki, *Ber. Bunsenges. Physik. Chem.*, 69, 57 (1965).

(3) P. L. Corio, R. L. Rutledge, and J. R. Zimmerman, *J. Am. Chem. Soc.*, 80, 3163 (1958).

(4) O. L. Chapman and R. W. King, *ibid.*, 86, 1256 (1964). It has recently been reported (J. G. Traynham and G. A. Knesel, *ibid.*, 87, 4220 (1965)) that electronegative substituents near the OH group prevent the observation of carbinol–hydroxyl proton coupling.
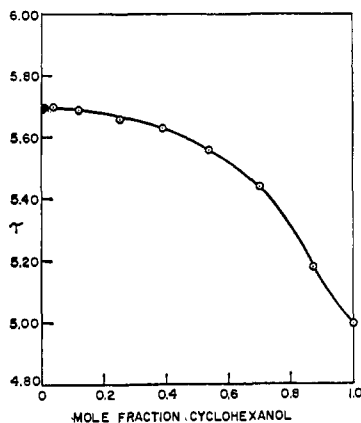
(5) B. Casu, M. Reggiani, G. G. Gallo, and A. Vigevani, *Tetrahedron Letters*, 2839 (1964); (b) B. Casu, M. Reggiani, G. G. Gallo, and A. Vigevani, *ibid.*, 2253 (1965).

(6) For a recent summary see, N. L. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 49.

(7) H. S. Aaron and C. P. Rader, *J. Am. Chem. Soc.*, 85, 3046 (1963); H. S. Aaron, C. P. Ferguson, and C. P. Rader, to be published.

Figure 1. Variation of hydroxyl proton chemical shift with cyclohexanol concentration in DMSO at 40°.

Figure 2. Variation of cyclohexanol hydroxyl proton chemical shift with temperature (0.121 mole fraction of alcohol in DMSO).

portion of the spectrum relatively free from peaks due to other protons. A variety of established techniques was used to assign the OH proton peaks readily and unambiguously.

Hydroxyl proton chemical shifts are known to be very sensitive to both temperature and concentration, due to the critical effect of hydrogen bond formation upon chemical shift. Figure 1 shows the variation of OH proton chemical shift with cyclohexanol concentration in DMSO. The OH proton doublet was clearly observed at all cyclohexanol mole fractions less than 0.70, with no significant change in doublet separation. Above this concentration only a broadened singlet (5.0–5.5-cps peak width at half-height) could be obtained.

As illustrated in Figure 1, the chemical shift of a number of alcohols was found to be independent of concentration below 0.12 mole fraction solute. This indicates that in dilute solution the relative populations of the O–H---(DMSO)$_n$ species present do not change.[8] The shift to higher field upon dilution of pure cyclohexanol with DMSO indicates the OH proton to be more strongly hydrogen bonded in the neat liquid than in DMSO. It therefore appears that ----O–H----
O–H---- hydrogen bonds are somewhat stronger than the OH---DMSO one, a conclusion previously reached[9] from chemical-shift studies of water and methanol in DMSO. It should be pointed out that the chemical-shift difference between the neat alcohol and its dilute solution in DMSO is much less than the chemical-shift differences previously observed[10] between neat alcohols and their dilute solutions in carbon tetrachloride, a solvent which does not hydrogen bond with the OH group.

The temperature variation of the OH proton chemical shift is given in Figure 2 for cyclohexanol. This variation is clearly linear with $\Delta\tau/\Delta t = 0.0069$ ppm/deg. The shift to higher field with temperature results from the decrease in solvent–solute association. At all temperatures the OH proton doublet was clearly dis-
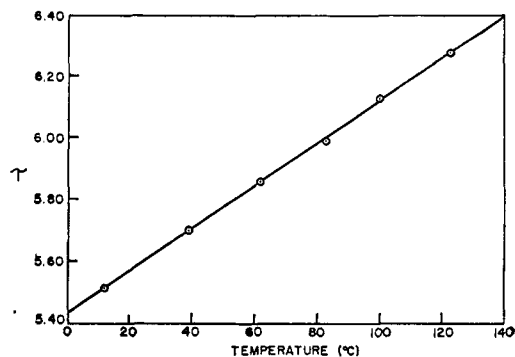
cernible. The curves in Figures 1 and 2 provide clear evidence why chemical-shift data for hydroxyl protons have real significance only at a stated concentration and temperature.

For a series of sets of epimeric cyclohexanols of known prevailing conformation, pmr spectra of the OH proton were obtained in the dilute concentration region in which the chemical shift had been established as invariant. Table I summarizes these data. With one exception the expected doublet was always obtained, since the hydroxyl and carbinol proton resonances were sufficiently separated ($\Delta\tau/J > 3$) that simple first-order coupling rules could be applied to obtain both chemical shift (τ) and coupling constant (J).[11] The broadened carbinol proton resonances were found at τ values slightly higher (approximately 0.1 ppm) than those previously observed[12] in carbon tetrachloride. In the case of neomenthol the chemical shifts of the carbinol and hydroxyl protons very nearly coincided, so that only a broadened singlet was observed for the latter. This was established by a combination of sample deuteration, peak integration, and repeated experiments with ultrapure neomenthol.

Table I gives the clear correlation that in every epimeric set the axial OH proton is found at significantly higher field (0.21–0.27 ppm) than its equatorial counterpart, as previously noted for the 4-t-butylcyclohexanols.[4] For both axial and equatorial alcohols vicinal substitution shifts this proton resonance to higher field, the magnitude of the shift increasing with the bulk of the substituent. Thus, cis-2-t-butylcyclohexanol provided the only instance where the OH doublet occurs at higher field than the corresponding broad carbinol proton peak (τ 5.95).

The coupling constant data in Table I also lend themselves to ready correlation with conformation. In each set of epimers the equatorial alcohol coupling constant is 1.0–1.5 cps greater than that of its axial epimer. Further, for both axial and equatorial alcohols vicinal substitution increases the coupling, with the magnitude of this increase growing with the bulk of the vicinal substituent.

(8) From infrared spectral data (C. D. Ritchie, R. Uschold, and A. L. Pratt, to be published) it has been calculated that pure DMSO is >90% dimerized. The author wishes to thank Professor Ritchie for a draft copy of this manuscript.

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

(10) E. D. Becker, U. Liddell, and J. N. Schoolery, J. Mol. Spectry., 2, 1 (1958); M. Saunders and J. B. Hyne, J. Chem. Phys., 29, 1319 (1958).

(11) All alcohols except cis-2-t-butylcyclohexanol ($\Delta\tau/J = 3.3$) and cis-2-ethylcyclohexanol ($\Delta\tau/J = 4.0$) gave $\Delta\tau/J$ values greater than 5. The chemical shift error introduced by first-order treatment of these two alcohols was 0.32 and 0.26 cps, respectively, both of which are approximately one-half the uncertainty in the OH τ values.

(12) E. L. Eliel, N. H. Gianni, T. H. Williams, and J. B. Stothers, Tetrahedron Letters, 741 (1962).

Table I. Hydroxyl Proton Chemical Shifts and Coupling Constants of Epimeric Cyclohexanols in DMSO[a]

	Equatorial alcohol			Axial alcohol	
	Chemical shift, τ	Coupling constant, J (cps)		Chemical shift, τ	Coupling constant, J (cps)
Cyclohexanol[b]	5.70	4.2			
trans-2-Methylcyclohexanol	5.75	5.3	cis-2-Methylcyclohexanol	5.96	4.0
trans-2-Ethylcyclohexanol	5.78	5.3	cis-2-Ethylcyclohexanol	6.03	4.2
Menthol	5.84	5.6	Neomenthol	6.09	c
trans-2-t-Butylcyclohexanol	5.98	5.7	cis-2-t-Butylcyclohexanol	6.20	4.4
cis-3-Methylcyclohexanol	5.67	4.5	trans-3-Methylcyclohexanol	5.89	3.5
trans-4-Methylcyclohexanol	5.68	4.5	cis-4-Methylcyclohexanol	5.89	3.5
trans-4-t-Butylcyclohexanol	5.65	4.5	cis-4-t-Butylcyclohexanol	5.92	3.0
Epiandrosterone	5.67	4.5	Androsterone	5.92	3.0

[a] At ≤ 0.12 mole fraction and 40°. [b] Prevailing conformation. [c] No splitting observed due to near identical chemical shifts of hydroxyl and carbinol protons.

Discussion

The difference between the hydroxyl–carbinol coupling constants for epimeric cyclohexanols may be readily understood from a consideration of the isomers resulting from rotation about the C–O bond. The O–H group may be staggered either between the two C–C bonds (I) or between the C–H bond and a C–C one (II and III). Since the rate of rotation about the

I	II	III
anti	gauche	gauche
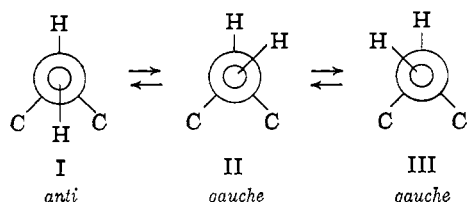
C–O bond[13] and the rate of formation of solute–solvent hydrogen bonds[14] are several orders of magnitude greater than $\Delta\tau$ between the OH protons of I, II, and III, the experimental coupling constant (J) will vary with the mole fractions (N) of conformers I–III according to the relation

$$J = N_I J_I + N_{II} J_{II} + N_{III} J_{III} \quad (1)$$

As previously shown by infrared data,[7] N_I is negligible for an axial alcohol due to the steric repulsion between the hydroxyl hydrogen and those syn-axial to it in the 3 and 5 positions. For an equatorial alcohol N_I is significantly different from zero.

Karplus[15] has shown that for H–C–C–H systems the vicinal proton coupling constant varies with dihedral angle (θ) according to the expression

$$J_{\text{vic}} = A \cos^2 \theta + B \quad (2)$$

where A and B are constants for a given system. It is now known that A and B are functions of HCC bond angles, C–C bond length, and the electronegativity of the substituents attached to the two carbons.[16,17] If the hydroxyl–carbinol proton coupling constant may be assumed to follow eq 2, at least in a qualitative manner, then

$$J_I > J_{II} = J_{III} \quad (3)$$

One is therefore led to the conclusion that an equatorial alcohol should have a larger J than its axial epimer, due to the contribution of the anti conformer (I) to the former.[18]

In the conformationally homogeneous 4-t-butylcyclohexanol and androsterone–epiandrosterone systems, the coupling constant data (Table I) are identical. The 3.0-cps J value for the two axial epimers is thus equal to J_{gauche} for these alcohols, if the mole fraction of anti conformer can be neglected. J_{anti} could in principle be estimated from J_{gauche} if a valid quantitative relationship between coupling constant and dihedral angle existed for the H–C–O–H fragment. A knowledge of J_{anti} should permit N_{anti} for the two equatorial epimers to be obtained from eq 1.

The reason for the increase in coupling upon vicinal substitution is not clear. In these cases conformers II and III are no longer the same, even to an approximation. The increase in J may result from (1) a change in conformer mole fractions, (2) a change in the minimum energy dihedral angles of I, II, and III, or (3) a change in one of the factors affecting constants A and B of eq 2. Published infrared data[19] show that 2-alkyl substitution does not significantly alter the polarity of the cyclohexanol O–H bond, suggesting the electron-releasing effect (+I) of the alkyl group to have little influence upon the increased coupling constant.

The chemical-shift difference between the epimeric alcohols should certainly be related to solute–solvent hydrogen bonding. Solute–solute hydrogen bonds may be neglected due to the invariance of chemical shift with concentration in the region of interest. Hydrogen bonding is known to influence profoundly the chemical shift of a participating proton. Qualitatively at least, the proton resonance is shifted to lower field as the strength of the bond increases.[20] This shift parallels infrared criteria based on the frequency decrease ($\Delta\nu$), half-band width ($\nu_{1/2}$) increase, and integrated intensity increase of the O–H vibration upon hydrogen bond formation.[21]

(13) M. Oki and H. Iwamura, Bull. Chem. Soc. Japan, 32, 950 (1959).
(14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 417.
(15) M. Karplus, J. Chem. Phys., 30, 11 (1959).
(16) M. Karplus, J. Am. Chem. Soc., 85, 2870 (1963).
(17) K. L. Williamson, ibid., 85, 516 (1963).

(18) In a paper which appeared during the latter stages of this work (R. G. Ouelette, ibid., 86, 4379 (1964)) essentially the same explanation given here was advanced for the single case of the J difference between the 4-t-butylcyclohexanols.
(19) G. Chiurdoglu and W. Masschelein, Bull. Soc. Chim. Belges, 68, 484 (1959).
(20) (a) S. Forsen, Svensk Kem. Tidsk., 74, 439 (1962); (b) G. J. Korinek and W. G. Schneider, Can. J. Chem., 35, 1157 (1957); (c) A. L. McClellan and S. W. Nicksic, J. Phys. Chem., 69, 446 (1965). One exception to this general rule is in cases involving the π-electron system of an aromatic ring as electron donor (e.g., C. J. Creswell and A. L. Allred, ibid., 66, 1469 (1962).
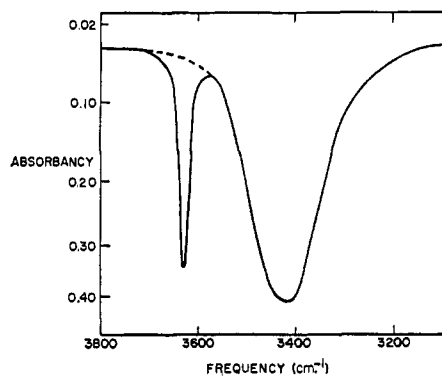
Figure 3. Infrared spectrum of CCl_4 solution containing 8.80 × 10^{-3} M cyclohexanol and 0.1031 M DMSO.

It is logical to presume that the relative strength of the axial and equatorial O–H---solvent hydrogen bonds will be determined primarily by steric effects, since polar contributions to the bond strengths should be nearly the same.[19] Therefore, one could be led to predict that with a given electron donor an equatorial alcohol forms a stronger hydrogen bond than its epimer, due to its greater steric accessibility. Relative glpc retention data of epimeric six-membered ring alcohols on polar substrates with which the hydroxyl hydrogen can bond support this conclusion.[22] Infrared and boiling point studies[23] of methylcyclohexanols reveal the alcohols of prevailing equatorial conformation to autoassociate more readily than their epimers. These considerations might lead one to the conclusion that a hydrogen bonded equatorial hydroxyl proton should resonate at significantly lower field than its axial counterpart. All of the chemical shift data in Table I clearly agree with this conclusion.

For the 4-t-butylcyclohexanols, Ouelette[18] has recently shown that at infinite dilution in (1) DMSO, (2) pyridine, and (3) carbon tetrachloride the OH proton chemical-shift differences between the two epimers are identical. Since carbon tetrachloride is widely conceded not to donate an electron pair to the OH of alcohols, these chemical-shift data clearly do not agree with the rationalization in the preceding paragraph.

In an attempt to resolve this discordance, we have studied by infrared spectra in dilute carbon tetrachloride the formation of hydrogen bonded complexes of DMSO with cyclohexanol and each of the conformationally homogeneous 4-t-butylcyclohexanols. Figure 3 gives a typical spectrum obtained with cyclohexanol and DMSO in the alcohol concentration region where only ROH monomer is present. For the dilute alcohol the sharp free OH stretching band (ν_{max} 3624 cm^{-1}) is the only band in this region. Addition of DMSO gives rise to the broad symmetrical band at 3418 cm^{-1} which is obviously due to the hydrogen-bonded O–H

stretch of the alcohol–DMSO complex. Addition of further amounts of DMSO produces an increase in the intensity of the hydrogen-bonded OH stretch band and a decrease in that of the free OH stretch.

For each of the three alcohols studied the free OH band absorbancy change upon DMSO addition was used to quantitatively assess the degree of hydrogen bonding taking place. The equilibrium constant (K_{eq}) for the formation of a 1:1 alcohol–DMSO complex was evaluated and found to be constant within experimental error over a fivefold concentration variation of both donor and acceptor.[24] Table II summarizes these K_{eq} data along with the frequency shifts ($\Delta\nu$) and half-band widths ($\nu_{1/2}$) of the bonded OH stretching bands.

Table II. Infrared Results for Alcohol–DMSO Complexes[a]

Cyclohexanol	K_{eq}	$\Delta\nu$, cm^{-1}	$\nu_{1/2}$, cm^{-1}
Unsubstituted	6.35 ± 0.67[b]	206	150
cis-4-t-Butyl-	6.50 ± 0.79	207	155
trans-4-t-Butyl-	6.39 ± 0.71	208	154

[a] Dilute CCl_4 solvent at 27°. [b] Error is twice the standard deviation.

Within experimental error the equilibrium constants are the same for cyclohexanol, cis-4-t-butylcyclohexanol, and trans-4-t-butylcyclohexanol, the latter two known to be >99% axial and equatorial, respectively. Further, the frequency shifts and half band widths are identical within experimental error. For hydrogen bonds involving structurally similar compounds, which is the case for the alcohols studied here, both $\Delta\nu$ and $\nu_{1/2}$ are a semiquantitative measure of the hydrogen bond strength. All three of the independent criteria listed in Table II show no significant difference between the strengths of the ROH---DMSO hydrogen bonds of the three alcohols studied. One may therefore conclude that at least in carbon tetrachloride solution axial and equatorial epimers form with DMSO hydrogen bonds of comparable strength. It must therefore be stated that factors other than hydrogen bonding appear to influence the chemical shift difference of axial and equatorial OH protons in DMSO. One of these factors is likely the differences in OH proton shielding experienced by the various rotational conformers (two axial and three equatorial), as a result of the magnetic anisotropy of the C–C bonds. Such shielding differences certainly affect the relative chemical shifts of axial and equatorial carbinol protons bonded directly to the ring.[12]

Comparison of our hydrogen bonding data with autoassociation studies of epimeric cyclohexanols[23] suggests that with equal facility axial and equatorial

(21) (a) J. R. Merrill, J. Phys. Chem., 65, 2023 (1961); (b) P. Jouve, Compt. Rend., 260, 3371 (1965); T. M. Connor and C. Reid, J. Mol. Spectry., 7, 32 (1961); (c) D. N. Shigorin, N. N. Shapetko, A. P. Skoldinov, and G. S. Ryagchikova, Dokl. Akad. Nauk SSSR, 148, 1141 (1963); (d) A. I. Cohen, B. T. Keeler, E. D. Becker, and P. A. Diassi, J. Org. Chem., 30, 2175 (1965).

(22) H. S. Aaron, G. E. Wicks, Jr., and C. P. Rader, ibid., 29, 2248, (1964); W. Hückel, D. Maucher, O. Fechtig, J. Kurz, M. Heinzel, and A. Hubele, Ann., 645, 115 (1961); W. J. A. Vandenheuvel and E. C. Horning, Biochim. Biophys. Acta, 64, 416 (1962).

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

(24) There is evidence[8] that in dilute carbon tetrachloride, DMSO dimerizes with a dimerization constant of the order of 3–7 (stated value, 4.8 M^{-1}). This value means 25–55% dimerization in the DMSO concentration region (0.05–0.25 M) employed in our work. Our observation of a single symmetrical bonded OH stretch band requires that either the alcohol bonds with a single species or that both DMSO monomer and dimer cause virtually the same $\Delta\nu$. The constancy of our K_{eq} values suggests that the DMSO dimerization constant is less than 4.8 M^{-1}. If the alcohol bonds to both monomer and dimer in 1:1 complexes of comparable strength, this dimerization constant value should cause our K_{eq} values to vary by ±12% from the mean. This is approximately the error involved in their measurement. However, no systematic variation of K_{eq} with DMSO concentration was found.

epimers can donate a proton to form a hydrogen bond, whereas, the equatorial alcohol can accept a hydrogen-bonding proton more readily than its epimer. This conclusion agrees with the OH oxygen being more susceptible than the hydrogen to steric effects of the cyclohexane ring, as is readily shown by stereomodels.

The A value for the OH group may be obtained from both the chemical-shift and coupling-constant data in Table I by employing the familiar equations[25]

$$K_{a,e} = \frac{N_e}{N_a} = \frac{\tau_a - \tau}{\tau - \tau_e} = \frac{J_a - J}{J - J_e} \qquad (4)$$

$$A = -\Delta G_{a,e} = RT \ln K_{a,e} \qquad (5)$$

where the subscripts a and e denote axial and equatorial, respectively. Taking cis-4-t-butylcyclohexanol as a 100% axial alcohol and its epimer as a 100% equatorial one, one obtains from the chemical shift of cyclohexanol an A value in DMSO of 0.92 kcal/mole. Similarly, from the coupling constant data an A value of 0.86 kcal/mole is obtained. These two values agree excellently with each other and are in good accord with literature values.[26] This excellent agreement may in part be fortuitous.

For the 3- and 4-methylcyclohexanols the equatorial alcohols give J values identical with that of an exclusively ($>99\%$) equatorial alcohol, whereas their epimers give values intermediate to those of axial and equatorial hydroxyls, indicating conformational nonhomogeneity. Applying eq 4 and 5, assuming no interaction between the hydroxyl and methyl groups, and using our hydroxyl A value of 0.86 kcal/mole, the J values for trans-3-methyl- and cis-4-methylcyclohexanol yield for the methyl group an A value of 1.3 kcal/mole, a value slightly below the accepted one of 1.7 kcal/mole[26] but in reasonable agreement with it when the accuracy of our measurement is considered.

There now exists an abundance of spectral correlations which may be used to readily distinguish between an axial alcohol and its equatorial epimer. In the infrared the free OH stretching band of the axial alcohol will occur at slightly higher frequency[27] and have greater symmetry.[7] The pmr multiplet of the carbinol proton of the axial hydroxyl epimer will occur at lower field[12] and be significantly narrower.[28] As shown in this study, in DMSO the axial hydroxyl proton will resonate at higher field and, if the alcohol is secondary, its doublet will be less separated.

This pmr study supports the concept that the symmetry or asymmetry of the free OH stretching band of alcohols is determined by the rotational isomers about the C–O bond,[7,13,29] rather than by some other phenomenon such as an overtone, combination band, Fermi resonance, or intramolecular hydrogen bond with a nonactivated paraffinic C–H bond.[30] The support

provided by this study gains importance when one considers that it comes from a different spectral method.

Experimental Section

Materials. All alcohol samples were checked for purity by gas–liquid chromatography and, where applicable, gave correct melting points. Reagent grade cyclohexanol was redistilled through a Vigreux column with a center fraction (bp 159.5°) being taken. Epimeric mixtures of the 2-methyl- and 2-ethylcyclohexanols were preparatively separated on a glpc column of 15% glycerol (1 m × $^3/_8$ in.) on Anachrom ABC (60–80). The 3- and 4-methylcyclohexanols were preparatively separated on a column (2 m × $^3/_8$ in.) of Carbowax 20 M (20%) on Gas Chrom P (60–80). Neomenthol was purified by recrystallization from petroleum ether (bp 30–60°) and by passage through a Carbowax 20 M glpc column. The 2-t-butylcyclohexanols were prepared by hydrogenation of redistilled 2-t-butylphenol on platinum dioxide in glacial acetic acid at room temperature and 20–70 psi hydrogen pressure. The resulting mixture of 2-t-butylcyclohexanols (86:14, cis:trans) was redistilled and the epimers separated on a glpc column of Carbowax 20 M. A mixture of cis- and trans-4-t-butylcyclohexanol was separated by the procedure of Winstein and Holness.[31] The individual epimers were then further purified by sublimation.

Spectroquality carbon tetrachloride was redistilled and stored over P_2O_5 to ensure absolute dryness. Reagent grade dimethyl sulfoxide was distilled through a Vigreux column and stored over Linde type 4A molecular sieves.

Proton Magnetic Resonance Spectra. All pmr spectra were taken with either a Varian A-60 or A-56/60 spectrometer at a probe temperature of 40° unless noted otherwise. Spectra were obtained on at least two different alcohol samples of independent origin with three to five scans being made per sample. Tetramethylsilane was used as internal standard. Probe temperature was monitored by the peak separation of either the two ethylene glycol (neat) peaks or those of methanol (neat); sweep-width calibration was monitored by the peak separation of a 5% solution of TMS in chloroform. Chemical shift values of OH proton doublets were found to be reproducible within ±0.01 ppm (0.6 cps). In a few instances where the OH splitting was marginal or poorly defined, a few milligrams of adsorption alumina was added, which settled to the bottom of the sample tube, greatly improving the O–H proton splitting.[32] Hydroxyl–carbinol proton coupling constants were measured on an expanded abscissa with the value found to be reproducible to the nearest 0.1 cps.

Infrared Spectra. All infrared spectral data were taken with a Perkin-Elmer Model 221 spectrophotometer employing a grating in the OH stretching region and 927 × 1 slit program. A pair of matched quartz cells, transparent at frequencies >2500 cm^{-1}, with 1.00-cm path length was employed. All calculations were performed from the maximum absorbancy of the free OH stretching band of dilute carbon tetrachloride solutions in the absence and presence of a given amount of DMSO. In the absence of DMSO the cell in the reference beam contained only solvent; in the presence of DMSO this cell contained a DMSO solution of the same concentration as that in the sample beam. At least three absorbancy readings were made of each sample, with the free OH stretch band being scanned manually. Absorbancy readings were taken within 3 min after the sample was inserted into the spectrophotomer in order to avoid a significant temperature increase. As indicated in Figure 3, the free OH stretch absorbancy was corrected for the slight absorption of the bonded O–H stretch at this frequency, this correction being taken as proportional to the absorbancy maximum of the bonded OH band.

In the alcohol concentration range studied (0.0018–0.012 M) Beer's law was followed in all cases, indicating negligible alcohol autassociation. The DMSO concentration range was 0.05–0.25 M. The equilibrium constant (K_{eq}) for alcohol–DMSO association was calculated by essentially the same method employed by previous workers[33] for similar alcohol–base systems. From eq 6 K_{eq} was calculated, where A denotes the absorbancy maximum of the free OH band, the superscript denotes the alcohol solution prior to

$$K_{eq} = \frac{C_A^0 - C_A}{C_A(C_D - C_A^0 + C_A)} = \frac{A^0 - A}{A(C_D - C_A^0 + C_A)} \qquad (6)$$

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the addition of DMSO, and the subscripts A and D denote alcohol and DMSO, respectively. The quantity $(C_A{}^0 - C_A)$ was obtained from $(A^0 - A)$ by using the Beer's law plot.

The Photoisomerization of Heteroatomic Eight π Electron Systems. Long-Range Coupling in Some Bicyclo[3.2.0]hepta-3,6-dienes[1]

Leo A. Paquette[2a] and James H. Barrett[2b]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio. Received November 27, 1965

Abstract: The heteroatomic eight π electron systems N-carbethoxyazepine and 2,7-dimethyloxepin undergo light-induced valence tautomerism to bicyclo[3.2.0]hepta-3,6-dienes, a reaction paralleling that of cycloheptatrienes. Structure proof of the products has been achieved by spectroscopic methods. Application of double-resonance techniques to the nmr spectra of the photoisomers has permitted the complete derivation of chemical shift and coupling constant assignments. The variations in the magnitude of long-range coupling caused by the introduction of electronegative substituents are discussed.

The early unsuccessful attempts to prepare hetero-tropylidenes have usually been ascribed to the fact that they are isoelectronic with the cycloheptatri-enide anion,[3] and as such were expected, on the basis of MO theory, to be endowed with unfavorable properties.[4,5] More recently, however, the synthesis of various derivatives of oxepin (1)[6] and 1H-azepine (2)[5,7] has been achieved, and such compounds are now readily available.[8] Although the ground-state properties of these interesting heterocycles have as yet not been completely defined, we have been led to a study of their excited-state behavior.
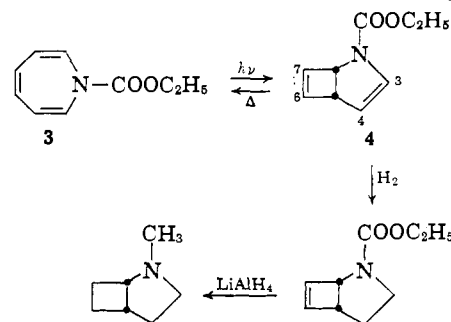
Specifically, the present investigation of the photochemical transformations of N-carbethoxyazepine (3) and 2,7-dimethyloxepin (7) was conducted as part of our continuing interest in the photochemistry of unsaturated heterocyclic molecules.[9] In particular, it appeared of importance to determine if these eight π elec-tron systems would undergo transformations from their electronically excited states paralleling, or differing, from those observed with cycloheptatrienes.[10] Because of the known ability of oxepin, for example, to undergo valence tautomerism to benzene epoxide with relative ease,[6] it was not clear how such molecules would behave under conditions of ultraviolet irradiation.

Results

When a 2% tetrahydrofuran solution of N-carbethoxyazepine (3) was irradiated under a nitrogen atmosphere with an unfiltered 450-w mercury arc for 2–3 days, there resulted the total disappearance of 3 and the concomitant formation of a single photoproduct. The progress of the reaction was followed by vapor phase chromatographic (vpc) analysis of aliquots removed periodically during the irradiation.[11] The resulting photoisomer was obtained as a very pale yellow oil (N-carbethoxyazepine is bright orange in color) in 43% yield by careful vacuum distillation. The isomeric nature of this photoproduct was delineated easily because of its facile thermal reversal to 3 when the distillation was effected at a bath temperature

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