1,3-dioxolane is approximately 5 eu more positive than those for the phenyl-substituted compounds but is still 9 eu more negative than that for acetone diethyl ketal.

Acknowledgment.—This work was supported by grants from the National Institutes of Health and the American Cancer Society.

The Structure of Paraldol

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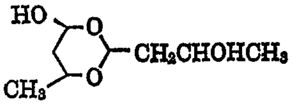
Received December 31, 1965

The structure and stereochemistry of paraldol are deduced by means of infrared and nmr spectroscopy. Equilibria which exist in solutions of paraldol are observed and discussed. Paraldol diacetate is shown to be a mixture of epimers.

It is only recently that the complexity of the relatively simple system acetaldehyde–water–base has begun to be understood. Experimental study of the mechanism of the aldol reaction has been hindered by the existence of several complicating conditions. For example, acetaldehyde exists in aqueous solution equilibrium with its hydrate,[2] the kinetic order of the aldol reaction is a function of the concentration of acetaldehyde,[3] and there is consumption of base during the reaction, perhaps because of a Cannizzaro reaction of acetaldehyde.[4] The facile conversion of the aldol product to crotonaldehyde and other compounds also interferes with easy study of the reaction;[4] if careful control of reaction conditions is not maintained, formation of brown resins occurs. Indeed, the discrete existence of aldol in aqueous solution has been questioned by Gruen and McTigue[4] who postulate the initial product formed in their study of the aldol reaction to be the cyclic hemiacetal from aldol and acetaldehyde. Various spectral examinations of commercial "aldol," a viscous liquid, have shown it to contain no carbonyl function.

It has long been known that commercial "aldol" may be carefully distilled under vacuum to give a mobile liquid which is the true aldol (3-hydroxybutanal); under normal conditions, the distillate rapidly and exothermically converts itself to a viscous, water-soluble fluid. Upon standing for several days, the viscous liquid begins to deposit white crystals of paraldol. These transformations were studied by Späth who deduced their nature and the gross structures of the products.[5] Paraldol was shown to be the cyclic hemiacetal I, a dimer of aldol. Crystalline paraldol was shown to be in equilibrium with a liquid isomer and it was suggested that the isomers differed in their stereochemistry at the hemiacetal carbon atom, analogous to the α and β forms of the pyranoses.



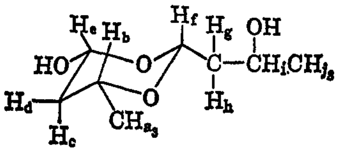
I

In connection with other work on the chemistry of acetaldehyde, we have investigated the structure of paraldol by infrared and nmr spectroscopy, determined its stereochemistry, and made observations of equilibria which exist in solutions of paraldol.

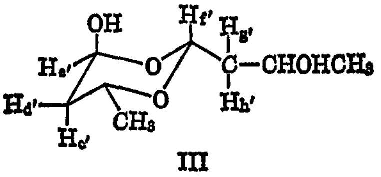
Results and Discussion

The infrared spectrum of crystalline paraldol in a potassium bromide pellet (Figure 1) is notable for the complete absence of any carbonyl absorption and the presence of strong hydroxyl absorption at 3.0 μ, in agreement with the Späth structure (I). The proton nmr spectrum of paraldol was investigated next, and not only was structure I confirmed but also the stereochemistry of the dioxane ring could be deduced readily.

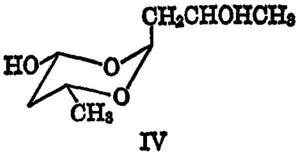
The Späth formula for paraldol (I) contains four asymmetric carbon atoms and, consequently, there are eight possible racemic pairs of diastereomers. Ignoring the asymmetric center in the side chain, there are four possible pairs of isomers involving geometrical isomerism of the dioxane ring, II–V (only one mirror image is depicted in each case). The conformations illustrated



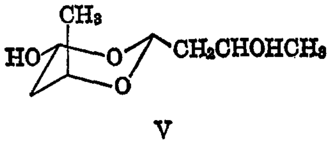
II



III



IV



V

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[1] (a) Rutgers, The State University. (b) To whom inquiries should be sent at Air Reduction Co.

[2] L. C. Gruen and P. T. McTigue, *J. Chem. Soc.*, 5217 (1963).

[3] A. Broche and R. Gilbert, *Bull. Soc. Chim. France*, **131** (1955); R. P. Bell and M. J. Smith, *J. Chem. Soc.*, 2983 (1960).

[4] L. C. Gruen and P. T. McTigue, *Australian J. Chem.*, **17**, 953 (1964).

[5] (a) E. Späth and H. Schmid, *Ber.*, **74**, 859 (1941); (b) E. Späth, R. Lorenz, and E. Fruend, *ibid.*, **75**, 1029 (1942); (c) E. Späth, R. Lorenz, and E. Fruend, *ibid.*, **76**, 62, 1196 (1943); (d) E. Späth and J. Meinhard, *ibid.*, **76**, 504 (1943).

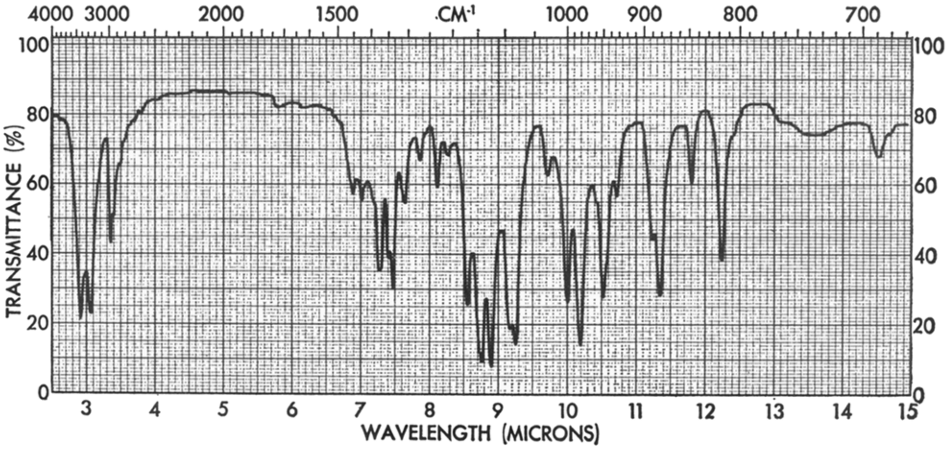

Figure 1.—Infrared spectrum of paraldol in a potassium bromide pellet.

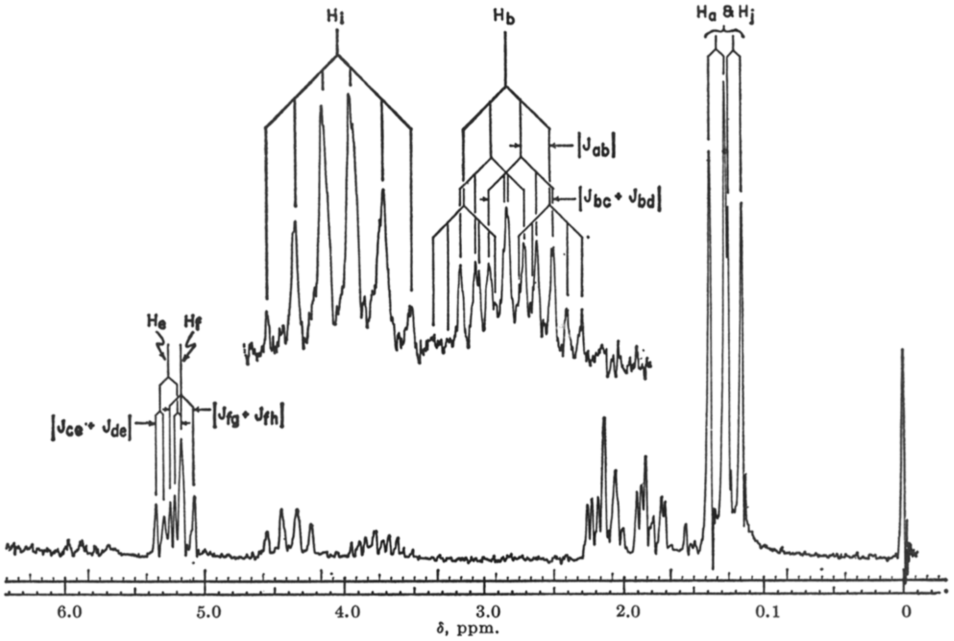

Figure 2.—Proton nmr spectrum of paraldol in pyridine solution (15% by weight) 10 min after mixing. Solvent and hydroxyl absorptions are not shown.

for II–V may not be the only important ones but we will consider this complication later.

Nmr spectra of deuterium oxide or pyridine[6] solutions of paraldol change with time owing to chemical reaction. This behavior frustrated our initial attempts to interpret the spectra but eventually not only proved to be highly interesting but also vital to the structure determination of paraldol itself. The spectra of fresh solutions in either deuterium oxide or pyridine (Figure 2) indicate the presence of only a single isomer to which we have assigned structure II.

There are 10 chemically distinct aliphatic protons, labeled a–j in formula II; Hg and Hh are not chemically equivalent because of the asymmetry of the molecule.[8]

The splitting patterns are easily recognized except in the one region where Hc, Hd, Hh, and Hg all absorb; we were not able to decipher this complex pattern which contains as many as 32 first-order lines. For the remaining splitting patterns, first-order methods were used wherever possible. The Hh and Hi regions were each analyzed as the M part of an $ABMX_3$ system;[9] the $ABMX_3$ case can be broken down into four ABM (usually designated ABX) problems for which explicit solutions are available.[10] However, in both the $ABMX_3$ systems of paraldol, the AB part is obscured and under these circumstances only the parameters $|J_{AM} + J_{BM}|$, $|J_{MX}|$, ν_M, and ν_X can be specified. These correspond to $|J_{cb} + J_{db}|$, $|J_{ab}|$, ν_a, and ν_b, respectively, for one of the $ABMX_3$ systems and $|J_{gi} + J_{hi}|$, $|J_{ij}|$, ν_i, and ν_j, respectively, for the other.

The He and Hf patterns were each analyzed as the X part of an ABX system; in both ABX groupings the AB portion is obscured and only $|J_{AX} + J_{BX}|$ and ν_X can be determined, corresponding to $|J_{de} + J_{ce}|$ and ν_e for one ABX system and $|J_{gf} + J_{hf}|$ and ν_f for the other.

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[6] Pyridine proved to be the better of the two solvents in that chemical shifts were more spread out; splitting patterns, overlapping less, were more readily analyzed. The use of pyridine as solvent was suggested to us by the work of Finegold and Kwart.[7]

[7] H. Finegold and H. Kwart, *J. Org. Chem.*, **27**, 2361 (1962).

[8] E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963), and references cited therein.

[9] The terminology is that of J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., p 98.

[10] Reference 9, p 134.

In order to determine $|J_{AX} + J_{BX}|$ from the X part of an ABX spectrum, it is necessary to know the relative signs of J_{AX} and J_{BX}; these couplings are all of the vicinal type in the four ABX situations in paraldol mentioned above. Theory and experiment indicate that all vicinal proton–proton couplings should be of the same sign, namely, positive (except vicinal protons with dihedral angles near 90° and strongly electron-withdrawing substituents).[11] Direct experimental comparisons of vicinal couplings invariably show them to be of the same sign.[12] Therefore, we may take these vicinal couplings in paraldol to be of the same sign.

The X part of an ABX system usually mimics the X part of an AMX spectrum in that it contains four strong lines (Figure 3). However, the spacings 9–11 and 10–12 become equal to $|J_{AX}|$ and the spacings 9–10 and 11–12 become equal to $|J_{BX}|$ only in the classical limit (AMX case). One can readily show,[13] using the explicit expressions for the positions of lines 10 and 11,[10] that lines 10 and 11 always move together, never apart, as $\nu_A - \nu_B$ is made progressively smaller; *i.e.*, with J_{AX} and J_{BX} of the same sign (as in paraldol), $|J_{BX}| \geq$ 9–10 or 11–12 (and $|J_{AX}| \leq$ 9–11 or 10–12). Minimum values for $|J_{bc}|$ and $|J_{ce}|$ of paraldol can be specified in this way and are given in Table I together with all other determinable coupling constants and chemical shifts.

Table I

Chemical Shifts and Coupling Constants of Paraldol (II)[a]

	16% w/w in D_2O	15% w/w in pyridine
δ_a	1.18 or 1.23	1.22 or 1.34
δ_b	4.0	3.77
δ_c	1.4–2.0	1.6–2.2
δ_d	1.4–2.0	1.6–2.2
δ_e	5.03	5.22
δ_f	4.87	5.16
δ_g	1.4–2.0	1.6–2.2
δ_h	1.4–2.0	1.6–2.2
δ_i	3.98	4.38
δ_j	1.18 or 1.23	1.22 or 1.34
$\lvert J_{ab}\rvert$	6.3	6.5
$\lvert J_{bc} + J_{bd}\rvert$	...	13.8 $\lvert J_{bc}\rvert \geq 10.4$
$\lvert J_{ce} + J_{de}\rvert$	12.5 $\lvert J_{ce}\rvert \geq 9.5$	13.0 $\lvert J_{ce}\rvert \geq 9.0$
$\lvert J_{fg} + J_{fh}\rvert$	10.5	10.6
$\lvert J_{gi} + J_{hi}\rvert$	12.6	13.0
$\lvert J_{ij}\rvert$	6.3	6.5

[a] Chemical shifts (δ) are parts per million downfield from internal tetramethylsilane for pyridine solution and parts per million from internal 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt for aqueous solution. Coupling constants are reported in cycles per second.

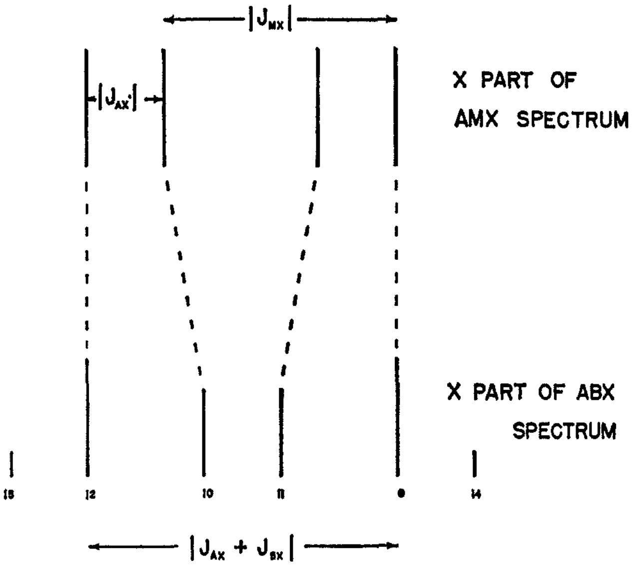

Figure 3.—The relationship between the X part of an ABX spectrum and the X part of an AMX spectrum with J_{AX} and J_{BX} of the same sign. The numbering of lines is that of ref 10. J_{AX} is held constant and J_{BX} is taken to be equal to J_{MX}.

The spectra of paraldol and the derived data in Table I are completely consistent with structure II. In particular, the hydroxyl and methyl substituents on the chair-like[14] dioxane ring must occupy equatorial positions. This assertion is based on the well-known dependence of the coupling constant of vicinal protons on the dihedral angle between them: axial–equatorial and equatorial–equatorial pairs of vicinal protons (dihedral angle, 60°) in chair-like six-membered rings have coupling constants in the range of 1–7 cps while axial–axial pairs (dihedral angle, 180°) are coupled by 8–14 cps.[11] This generality appears to hold for substituted 1,3-dioxanes quite well.[16] The large minimum values of $|J_{ce}|$ in Table I, then, are consistent with an axial–axial relationship between Hc and He which places the hydroxyl group equatorial; also, the large minimum value for $|J_{bc}|$ suggests the diaxial arrangement of Hb and Hc and the methyl substituent would then be equatorial.

The major new material which forms when paraldol is dissolved in water or pyridine can be assigned structure III. The spectral evidence (Figure 4) consists of two triplets with equal areas which grow with time at the expense of the absorptions due to He and Hf in II; the triplets are ascribed to He′ and Hf′ in III. The determinable chemical shifts and coupling constants are given in Table II. The remainder of the spectrum of III is obscured by the spectrum of paraldol. After several days, the ratio of II/III reaches a steady value of 1.2 in pyridine solution and 2.4 in aqueous solvent as measured by the relative areas of He and Hf to He′ and Hf′. At room temperature, the formation of half the

Table II

Chemical Shifts and Coupling Constants of III[a]

	16% w/w D_2O soln	15% w/w pyridine soln
$\delta_{e'}$	5.37	5.67
$\delta_{f'}$	5.34	5.96
$\lvert J_{c'e'} + J_{d'e'}\rvert$	4.7	4.7
$\lvert J_{f'g'} + J_{f'h'}\rvert$	11.7	11.0

[a] The units are the same as those of Table I.

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[11] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif. 1964, pp 49–52.

[12] *E.g.*, B. D. N. Rao, J. D. Baldeschwieler, and J. I. Musher, *J. Chem. Phys.*, **37**, 2480 (1962); R. R. Fraser, *Can. J. Chem.*, **40**, 1483 (1962); H. Feingold, *Proc. Chem. Soc.*, 213 (1962); R. Freeman, K. A. McLauchlan, J. I. Musher, and K. G. R. Pachler, *Mol. Phys.*, **5**, 321 (1962).

[13] M. Vogel, unpublished results.

[14] Although II undoubtedly is most stable in the chair form, one cannot be equally confident about III–V. Substitution of oxygen atoms for two of the methylene groups of cyclohexane might remove an appreciable portion of the unfavorable interactions[15] which make the boat form of cyclohexane unstable. Since III–V in their chair forms are destabilized by at least one axial substituent, they may prefer the boat form.

[15] E. I. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 205 ff.

[16] C. Barbier, J. Delman, and J. Ranft, *Tetrahedron Letters*, 3339 (1964), and references cited therein; Y. Fujiwara and S. Fujiwara, *Bull. Chem. Soc. Japan*, **37**, 1010 (1964).

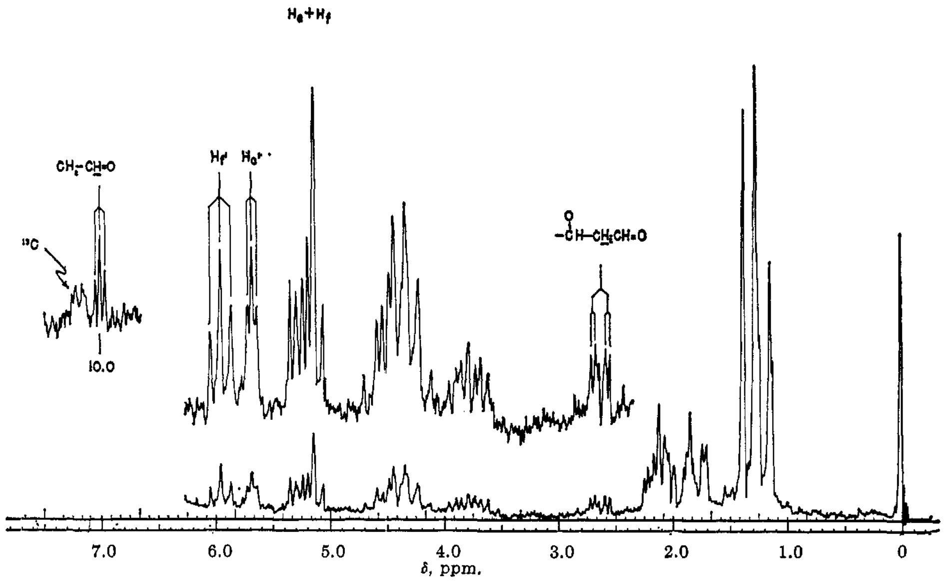
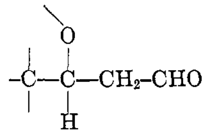


Figure 4.—Proton nmr spectrum of paraldol in pyridine solution (15% by weight) after 26 days. Solvent and hydroxyl absorptions are not shown except for a ^{13}C side band of pyridine.

steady-state amount of III from II requires about 10 min in water but several hours in pyridine. The small values of $|J_{c'e'} + J_{d'e'}|$ in Table II rule out the possibility that He′ is axial to a chair-like ring, consistent with the assigned structure.

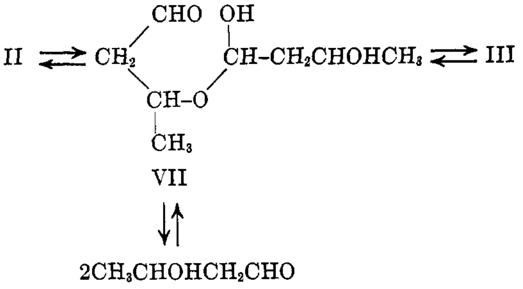
In addition to the absorptions ascribed to III, a triplet (J = 2 cps) gradually develops at 9.7 ppm in water and 10.0 ppm in pyridine (see Figure 4). The absorption is readily assigned to the aldehyde proton in the group $-CH_2CHO$. The methylene protons can be seen at 2.6 ppm in both solvents split into doublets (J = 2 cps) by the aldehyde proton but split again into doublets (J = 6 cps) by the β protons in structure VI. This partial structure is found both in aldol and its open-chain dimer VII. The methylene protons in VI are chemically unequivalent[8] but they do not have detectably different chemical shifts in our spectra. The aldehyde develops as rapidly as does III in aqueous solutions of paraldol; assuming that the aldehyde absorption is due to the dimer VII, the concentration reaches about 20% of the initial concentration of paraldol, judging from the integrals. The behavior of pyridine solutions of paraldol is quite different. After 24 hr, when the ratio of II/III has reached a steady 1.2, the aldehyde is barely detectable (about 5% based on VII). However, the concentration of aldehyde keeps on increasing, reaching a steady value of about 15% (based on VII) after several weeks. This gradual increase in concentration of aldehyde is not due to the slow absorption of atmospheric moisture by the pyridine solution since solutions sealed under glass, loosely capped, or deliberately contaminated with water[17] all behave essentially the same in this respect.



$$-\overset{|}{\underset{|}{C}}-\overset{\diagdown O}{\underset{H}{C}}-CH_2-CHO$$

VI

CHART I



The changes in the nmr spectra of solutions of paraldol in water and in pyridine indicate the establishment of the equilibrium in Chart I. Since the formation of III from II presumably occurs through VII as an intermediate, the concentration of VII should approach its equilibrium value at least as fast as III. The tardy appearance of aldehyde absorption in pyridine solutions may be due to the slow generation of some other aldehyde with structure VI such as aldol.

The equilibrium concentrations of II and III correspond to free energy differences of 0.1 and 0.5 kcal/mole in pyridine and aqueous solutions, respectively. This destabilization of III compared to II can be attributed to the axial hydroxyl group of III. Cyclohexanols with axial hydroxyl groups are destabilized by 0.4–0.9 kcal/mole compared to their equatorial counterparts.[18] Eliel[18] has pointed out that axial hydroxyl groups should be less destabilizing in pyridine solution than in water, consistent with observations in the literature; the stabilities of II and III follow this generalization.

The deshielding of Hf′ in III compared to Hf in II (0.47 ppm in water and 0.80 ppm in pyridine) suggests at first glance that Hf has moved from an axial position in II to an equatorial position in III,[19] contrary to our

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[17] Pyridine solutions of paraldol containing a few per cent of water slowly develop a doublet at 9.5 ppm (J = 8 cps) indicative of the group C=CH—CH=O. No such absorption is detectable in anhydrous pyridine solutions or, for that matter, aqueous solutions.

[18] E. L. Eliel, *J. Chem. Educ.*, **37**, 126 (1960).

[19] Not only are axial protons more shielded than their equatorial counterparts in general,[20] but also the same order has been inferred for protons at the 2-position of substituted 1,3-dioxanes.[21]

[20] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., London, 1959, pp 115–119.

[21] C. Barbier, M. Davidson, and J. Delman, *Bull. Soc. Chim. France*, 1046 (1964).

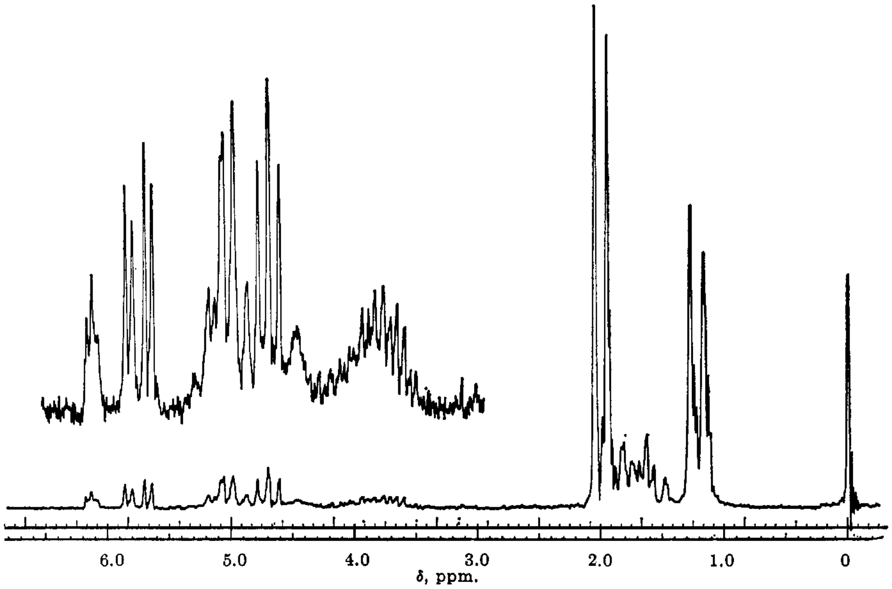

Figure 5.—Proton nmr spectrum of paraldol diacetate in carbon tetrachloride solution (20% by weight).

assigned structure. However, this deshielding is to be expected on the basis of structure III in that the close proximity of Hf′ to the axial hydroxyl group in III should cause a considerable deshielding effect. Similar proximity effects quite generally cause deshielding of the affected protons;[22] a close analogy to our situation is provided by the work of Tori and Komeno[23] who observed that axial 3α protons of steroids were deshielded by 0.45 ± 0.05 ppm upon introduction of an axial 5α-hydroxyl group.

From the data in Tables I and II it can be seen that, in both water and pyridine solvent, the axial He of II is more shielded than the equatorial He′ of III as expected.[20]

The spectrum of paraldol was observed, also, in dimethyl sulfoxide solution; the hemiacetal linkage was completely stable analogous to the stability of the hemiacetal linkage of pyranoses in the same solvent.[24] The spectrum was similar to those of fresh aqueous and pyridine solutions with the notable addition of a doublet at 6.57 ppm (J = 7.0 cps) and a doublet at 4.30 ppm (J = 5.0 cps). Both doublets disappeared when deuterium oxide was added to the dimethyl sulfoxide solution. The less shielded doublet we ascribe to the hemiacetal hydroxyl proton of II split by the single α proton; the other doublet is due to the side-chain hydroxyl proton. The slowing down of the otherwise rapid exchange of hydroxylic protons in dilute dimethyl sulfoxide solution so that individual hydroxyl protons and their splitting may be observed is quite general.[25]

Casu, *et al.*,[24] found that the α and β forms of pyranoses could be distinguished by means of the chemical shifts and coupling constants of the hemiacetal hydroxylic protons in dimethyl sulfoxide solution: the protons of equatorial anomeric hydroxyl groups absorbed at 6.42–6.60 ppm and were split by 6.0–7.0 cps while their axial counterparts absorbed at 6.04–6.30 ppm split by 4.0–4.5 cps. Both the chemical shift (6.57 ppm) and the coupling constant (7.0 cps) of the hemiacetal hydroxyl proton of paraldol, then, suggest an equatorial placement as in II.

All our evidence is completely consistent with the assignment of structure II to paraldol and III to its less stable isomer. We cannot exclude, rigorously, isomers IV and V as possible structures for either paraldol or the new isomer because of the possibility that IV and V would exist preponderantly in the mobile boat form[14] for which virtually nothing is known regarding conformational preferences and/or nmr parameters. However, it seems very unlikely to us that IV and V would have all the characteristics that we observe that can be readily rationalized in terms of isomers II and III. The strongest single argument we can muster against IV and V is as follows: in aqueous or pyridine solutions, where paraldol readily equilibrates with the open-chain form VII and presumably with aldol, too, all four geometrical isomers II–V should come to equilibrium with one another. Under these conditions, paraldol is the most stable geometrical isomer; there is one other isomer almost as stable and no signs of a third or fourth. Since III is expected to be only slightly less stable than II,[18] either the two detectable isomers are II and III or IV and V. It seems extremely unlikely that IV and V are so much more stable than II and III that the latter two isomers are undetectable although the converse is reasonable.

The configuration of the asymmetric carbon atom in the side chain of paraldol with respect to those in the ring cannot be specified with our present data. Paraldol might even be a mixture of the two isomers of II epimeric at the side-chain asymmetric carbon atom. The corresponding protons of the two epimers might have slightly different chemical shifts but we did not see any such indication in our nmr spectra. This and the relatively narrow melting point range of paraldol suggest that it is not a mixture of epimers but neither piece of evidence is conclusive.

We have also examined the nmr spectrum of paraldol diacetate (Figure 5) prepared after the method of Späth;[5a] the spectrum clearly indicates a mixture of geometrical isomers, namely VIII and IX. The epimeric ring proton of VIII gives rise to the four lines centered at 5.75 ppm while in IX it appears as a triplet

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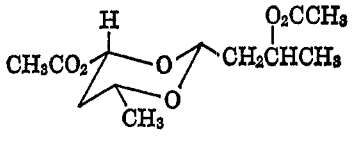
[22] Ref 11, pp 188–190.

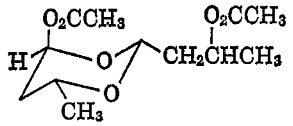
[23] K. Tori and T. Komeno, *Tetrahedron*, **21**, 309 (1965).

[24] B. Casu, M. Reggiani, G. G. Gallo, and A. Vigevani, *Tetrahedron Letters*, 2839 (1964).

[25] O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).



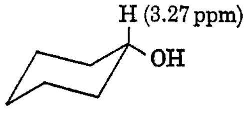
VIII



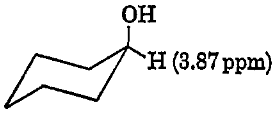
IX

at 6.15 ppm. The ratio VIII/IX was about 2.3 in our sample of diacetate, judging from the areas of the two multiplets.

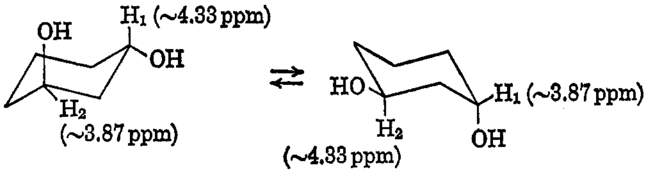
At the time this work was done, the data of Tori and Komeno[23] on the deshielding of an axial proton by an axial γ-hydroxyl group was not available. We attempted to measure the same effect by comparing the chemical shifts of the α protons of cyclohexanol (X) with those of *trans*-1,3-cyclohexanediol (XI). Neikam and Dailey[26] reported chemical shifts of 3.27 and 3.87 ppm for the α protons of cyclohexanol in conformers Xa and Xb, respectively, in carbon disulfide solution at low temperatures where the rapid conformational equilibrium between Xa and Xb is "frozen out." We have taken 3.87 ppm as an approximate value for the shift of H_2 in conformation XIa and H_1 in XIb, assuming that the equatorial hydroxyl groups γ to these protons do not exert a significant effect. Because of the rapid conformational equilibrium XIa ⇄ XIb (whose equilibrium constant must be unity), H_1 and H_2 have the same observed chemical shift which we determined to be 4.10 ppm in chloroform solution (2% w/w) and 4.05 ppm in deuterium oxide (2% w/w). If we use 4.10 ppm as the averaged chemical shift and 3.87 ppm as the shift of H_2 in XIa (and H_1 in XIb), then the shift of H_1 in XIa (and H_2 in XIb) is calculated to be 4.33 ppm. Therefore, the axial α protons of XI, in proximity to the axial γ-hydroxyl groups, are deshielded by *ca.* 1.06 ppm compared to the axial proton in Xa; this rather crude estimate[27] is in qualitative agreement with the deshielding of 0.45 ± 0.05 ppm found by Tori and Komeno[23] in the steroid series.



Xa



Xb



XIa XIb

Experimental Section[30]

Paraldol was obtained by allowing the distillate from "aldol" (Matheson Coleman and Bell, technical grade), bp 40–50° (2 mm), to crystallize over a period of several days. The white crystals were slurried with ether, filtered, washed with ether several times, and dried. The ether was stripped from the mother liquor and the residue was allowed to crystallize further. The new crystals were collected as above. Several crops were obtained in this manner with mp 95–98°, lit.[5a] mp 95–97°. A Fisher-Johns melting point apparatus was used.

Paraldol diacetate was prepared by the acetylation of paraldol following Späth.[5a] The product showed no hydroxyl absorption in its infrared spectrum and had bp 108–110° (0.2 mm), lit.[5d] bp 118–120° (1 mm).

***trans*-1,3-Cyclohexanediol** was a gift from Professor H. Kwart and had mp 115–116°, lit.[7] mp 116.0–116.5°.

The nmr spectra were obtained with a Varian A-60 spectrometer. The field sweep was calibrated repeatedly *vs.* a sample of tetramethylsilane in chloroform (δ = 436 cps) and peak positions were read from the graphs. Tetramethylsilane was added to all samples as an internal reference except for aqueous solutions where 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt[31] was used instead. Chemical shifts are believed accurate to ±0.02 ppm and coupling constants are accurate to ±0.3 cps. Samples were either deoxygenated with a nitrogen stream or sealed under vacuum before observing their spectra. The sample temperature was 35–40°.

The solvents for the nmr spectra were obtained commercially and were used without further purification. Pyridine (ACS grade, Analyzed Reagent) was obtained from Matheson Coleman and Bell as was the dimethyl sulfoxide (mp 18–19°) and the carbon tetrachloride (Spectroquality Reagent). Deuterium oxide (99.5%) was obtained from Isomet Corporation and deuteriochloroform from Varian Associates.

Acknowledgment.—We wish to thank Professor Harold Kwart for a generous sample of *trans*-1,3-cyclohexanediol and the National Science Foundation for a grant toward the purchase of the Varian A-60 spectrometer.

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[26] W. C. Neikam and B. P. Dailey, *J. Chem. Phys.*, **38**, 445 (1963).

[27] Both the diamagnetic anisotropy of the C–O bond[28] and the C–O dipole[29] of the equatorial hydroxyl groups in XI should act to deshield the γ-equatorial protons by an amount that we calculate[28,29] to be 0.1–0.2 ppm. Our estimate of the deshielding caused by proximity to the axial hydroxyl group should be reduced by the same amount.

[28] L. D. Hall, *Tetrahedron Letters*, 1457 (1964).

[29] A. D. Buckingham, *Can. J. Chem.* **38**, 300 (1960).

[30] All melting points and boiling points are corrected.

[31] G. V. D. Tiers and R. I. Cook, *J. Org. Chem.*, **26**, 2097 (1961).