30 ± 3°. The reaction mixture was stirred for 2 hr. and neutralized with a solution of 5.5 g. of sulfuric acid in 40 ml. of water.

In another flask, pentaerythritol (0.075 mole) was prepared by adding a mixture of acetaldehyde (3.30 g., 0.075 mole) and formalin (30.3 g. of 37%, 1% methanol, 0.375 mole) to a slurry of calcium hydroxide (3.90 g., 0.052 mole) in 45 ml. of water. The mixture was heated at 50° for 1 hr. and allowed to cool slowly to room temperature. Additional calcium hydroxide (4.40 g., 0.06 mole) and 4.2 ml. of 30% hydrogen peroxide were added, and the mixture was stirred for 1 hr. at room temperature to remove unreacted formaldehyde. After neutralization with solid oxalic acid, the mixture was filtered and evaporated to about 40 ml. and added to the neutralized aldehyde solution. After the pH was adjusted to 3 with *p*-toluenesulfonic acid, the mixture was heated at 70–75° for 4.5 hr. The solid material was removed by filtration, washed, and dried. The yield of product was 8.72 g. (37.8%), m.p. 185–194°.

A Re-examination of the Conformational Analysis of the Tropine–Pseudotropine System[1]

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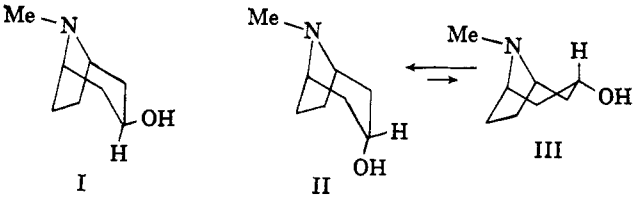
Although the configurations of pseudotropine (I) and tropine (II) have been unequivocally proven, the conformational equilibrium for the ground state of the piperidinol ring in these two compounds has not been rigorously established. The first interpretations according to the then emerging principles of conformational analysis led to divided opinions as to whether the chair (II) or the boat (III) form predominates in this ring system.[2]



Evidence for the boat conformation rests mainly on infrared spectral data which have been interpreted[3] (and continue to be cited[4]) to indicate that intramolecular hydrogen bonding exists between the nitrogen and the hydroxyl group of the pseudotropine system. The data, however, do not meet established criteria[5] for intramolecular hydrogen bonding, because the intensity of the bonded hydroxyl stretching band is concentration dependent, a characteristic typical of intermolecularly hydrogen-bonded systems. However, the fact that residual bonded hydroxyl absorption was observed[3] at 0.023 *M* in carbon disulfide solution prompted us to re-examine this system at greater dilution.

Infrared spectra of tropine and pseudotropine were recorded in carbon disulfide, carbon tetrachloride, and tetrachloroethylene solutions at 2×10^{-3} *M*, using a high-resolution grating spectrophotometer. Under these conditions, it was observed that (1) the bonded O–H stretching absorption is completely eliminated in both alcohols, and (2) the free O–H stretching band of tropine occurs at a slightly higher frequency (5 cm.$^{-1}$ in carbon tetrachloride) than that of pseudotropine (see Table I). Furthermore, when examined on an expanded abscissa (5 cm.$^{-1}$/cm.), the tropine absorption appears as a single, highly symmetrical band, while that of pseudotropine appears as an unsymmetrical band, apparently an unresolved doublet. Comparable results were obtained for the first overtone of the hydroxyl stretching absorptions.

TABLE I

FREE OH STRETCHING MAXIMA, pK_a, AND G.L.C. DATA FOR TROPINE AND PSEUDOTROPINE

Compd.	$\tilde{\nu}_{max}$ cm.$^{-1}$ CS_2	CCl_4	C_2Cl_4	pK_a[a]	G.l.c. retention time, min.[b]
Tropine	3613	3626	3627	10.44	6.5
Pseudotropine	3609	3621	3623	9.98	8.0

[a] Ionic strength 0.005 at 30°. [b] Column (10 ft. × 0.25 in.) of Carbowax 20 M (15%) on Gas-Chrom P (60–80) at 205° and 120 ml./min. (He). The value for 3-tropinone (Aldrich Chemical Co.) was 4.9 min. under these conditions.

The absence of any detectable intramolecular hydrogen bonding[6] indicates that the piperidinol ring of the pseudotropine system must exist in a chair conformation, and the per cent of molecules in a boat conformation must be smaller (undoubtedly less than 2%; see Experimental) than can be detected by infrared methods.

Tropine, of course, cannot bond intramolecularly in either a chair or a boat conformation. Here, however, the position and shape of the free O–H stretching band may be used as criteria for conformational assignment. Thus, it has been shown that in dilute carbon tetrachloride solution, the axial hydroxyl group will have a symmetrical stretching band[7] which occurs[5,8] about 5–10 cm.$^{-1}$ higher then that of its equatorial epimer, which has an unsymmetrical band. These distinctions are apparently due to the relative populations of isomers which correspond to rotational conformations of the hydroxyl group about the C–O bond. In this respect, the band of tropine in a boat conformation (III) should resemble that of an equatorial alcohol. The lack of any significant population of tropine molecules in a boat conformation, therefore, is suggested by the highly symmetrical shape of its hydroxyl stretching band.

(1) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, Abstracts of Papers, p. 42Q.

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(5) A. R. H. Cole, "Technique of Organic Chemistry," Vol. XI (part 1), A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(6) (a) The erroneous report[3] of intramolecular hydrogen bonding in pseudotropine was corrected by House, *et al.*,[6b] in a paper which appeared simultaneously with our earlier presentation[1] of these results. (b) H. O. House, H. C. Müller, C. G. Pitt, and P. P. Wickham, *J. Org. Chem.*, **28**, 2407 (1963).

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

(8) I. L. Allsop, A. R. H. Cole, D. E. White, and R. L. S. Willix, *J. Chem. Soc.*, 4868 (1956).

Relative pK_a data[9] and gas–liquid chromatographic (g.l.c.) retention data[10] (see Table I) agree with the above assignments (I and II)[12] when compared with the data obtained for the conformationally related epimers of 2-hydroxyquinolizidine,[11] 7-hydroxyindolizidine,[13] and 3-granatanol.[13]

Experimental

Samples of tropine (m.p. 63.0–64.5°, cor.) and pseudotropine (m.p. 106.0–107.5°, cor.) were obtained from Regis Chemical Co. and shown to be epimerically pure and free of any detectable contaminants by gas–liquid chromatography[14] (see Table I). The carbon disulfide and carbon tetrachloride solvents were Baker and Adamson reagent grade chemicals which were used without further purification. Eastman White label tetrachloroethylene was fractionally distilled through a Vigreux column to remove the ethanol stabilizer. All spectra were obtained immediately after the solutions were prepared. In carbon tetrachloride solutions, a fine white precipitate slowly formed upon standing.[15]

The data for the fundamental O–H stretching bands were obtained on a Perkin-Elmer Model 421 grating spectrophotometer, using 1-cm. matched quartz high infrared transmission cells (The Ultracell Co.). The maxima of the free O–H stretching bands were read directly from the frequency dial as summarized in Table I. The 12- to 14-cm.$^{-1}$ shift in the absorption maxima upon going from carbon disulfide to carbon tetrachloride or tetrachloroethylene is in agreement with recent studies.[16]

The first overtone of the hydroxyl stretching band was scanned on a Cary Model 14 spectrophotometer, using 0.020 M carbon tetrachloride solutions in 10-cm. matched quartz cells. The observed maxima (mμ) were as follows: tropine, 1413 (symmetrical band); pseudotropine, 1415 (unsymmetrical band). pK_a values (see Table I) were measured electrometrically[12] and found to agree with those previously reported.[17]

The per cent of boat conformers present in the pseudotropine system was determined to be less than 2% by measuring the concentration of intramolecularly bonded lupinine (Mann Research Laboratories) which was detectable in a pseudotropine solution.[18] Thus, a 1.0×10^{-4} M concentration of lupinine could be detected as a slight bonded absorption ($\tilde{\nu}_{max}$ 3290 cm.$^{-1}$) in a 4.7×10^{-3} M solution of pseudotropine in carbon tetrachloride in a 2-cm. quartz cell. A 4.6×10^{-3} M solution of pseudotropine showed no detectable bonded hydroxyl absorption in the 2-cm. cell.

(9) For substituted N-alkyl 4-piperidinols in the chair conformation, that epimer which has an *anti* diaxial hydroxyl/N-electron pair relationship has been found to be a slightly stronger base (0.4 ± 0.1 pK_a unit at 0.005 μ) than its corresponding *syn* (OH equatorial) epimer. Although not measured under the same conditions, three such pairs of epimeric azabicycloalkanols which were recently reported[6b] apparently also show this pK_a correlation. It is our intention to discuss the pK_a data for an extended series of epimeric amino alcohols more fully at a later date.

(10) Strongly intramolecularly bonded amino alcohols show g.l.c. retention times on a Carbowax column which are significantly shorter than that of their corresponding ketones.[11] Nonintramolecularly bonded amino alcohols have longer retention times than their corresponding ketones. Generally speaking, the equatorial hydroxyl isomer has a longer retention time than its axial epimer.

(11) H. S. Aaron, G. E. Wicks, Jr., and C. P. Rader, *J. Org. Chem.*, **29**, 2248 (1964).

(12) These assignments have also been made on the basis of a recent high resolution n.m.r. study by J. Parello, P. Longevialle, W. Vetter, and J. A. McCloskey, *Bull. soc. chim. France*, 2787 (1963).

(13) H. S. Aaron and C. P. Rader, to be published.

(14) G.l.c. data for this system on an Apiezon L column has recently been reported: C. Van der Vlies and B. C. Caron, *J. Chromatog.*, **12**, 533 (1963).

(15) Presumably the hydrochloride; *cf.* J. Sicher, M. Horak, and M. Svoboda, *Collection Czech. Chem. Commun.*, **24**, 950 (1959); R. F. Collins, *Chem. Ind.* (London), 704 (1957). This phenomenon resulted in an experimental problem only in obtaining spectra of the overtone region on the Cary Model 14 spectrophotometer. Here, the high-intensity light source accelerates the reaction; hence, the available scanning time was limited to a few minutes.

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(17) T. A. Geissman, B. D. Wilson, and R. B. Medz, *ibid.*, **76**, 4182 (1954).

(18) These measurements were kindly performed for us by Mr. C. Parker Ferguson of these laboratories.

A Study of the Rhodium Catalyzed Hydrogenation of 1-Naphthol. An Improved Preparation of 1- and 2-Decalols[1]

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Due to the interest in recent years in total steroid synthesis wherein the 1-decalones have been employed as a starting material, it seemed advisable to investigate improved methods of obtaining these substances, particularly *via* the 1-decalols. Previous methods involved the hydrogenation of 1-naphthol using platinum catalysts[3] which required several days and relatively large amounts of this costly element. High pressure reduction of 1-naphthol using Raney nickel[4] or Raney copper[5] resulted in low yields and a high degree of hydrogenolysis. Similar results have been obtained with 2-naphthol although in several instances[6] selective ring reduction has been accomplished in high yields. Upon reexamination of several of the methods for the reduction of the naphthols in an attempt to achieve more efficient and complete reaction, the yields could not be improved upon. On many occasions little or no reduction was observed unless considerable care was taken to clean the apparatus to remove catalyst poisons.

The recent interest in rhodium catalysts[7] for aromatic ring hydrogenations at ambient temperatures and moderate pressures (3 atm.) suggested that this element might afford a convenient route for obtaining improved yields of the decalols. The fact that the degree of hydrogenolysis was reportedly[7c,d] small was also attractive.

The hydrogenation of 1-naphthol in ethanol and methanol gave good yields (Table I, entries 1 and 2) of the isomeric decalols in the ratio of 13.3:3.2:1 (integrated areas under gas chromatographic peaks) and a small amount of the isomeric decalones. The major decalol product was isolated and shown to be the *cis,cis* isomer by comparison with an authentic sample.[3b] The two minor components in the decalol mixture were not isolated in sufficiently pure form to afford positive identifications. The degree of hydrogenolysis in these experiments was extremely low as evidenced by a 3% yield of the decalins. The hydrogenation was complete within 12 hr. at room temperature using a starting pressure of 60 p.s.i. When dioxane and ethyl acetate (en-

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(2) Research Associate on leave from the Institute of Chemistry, "Alonso Barba," Madrid, Spain.

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