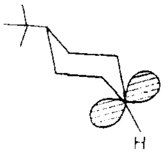
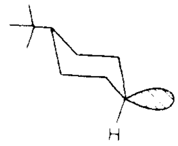
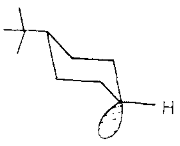
The preferential formation of *cis*-4-*t*-butylcyclohexyl chloride[7] implies that the radical is better represented by non-planar forms such as (2) and (3) rather than the planar form (1) since considerations of product control or of accessibility to the radical would both favor attack from the equatorial direction on (1).



1



2



3

The chain decomposition of alkyl hypochlorites should prove of value in the investigation of many questions of stereochemistry and selectivity of carbon radicals.

[7] Reactions leading to the preferential formation of *trans*-bromide over *cis*-bromide are reported for the reaction of the silver salts of *cis*- and *trans*-4-*t*-butylcyclohexanecarboxylic acid with bromine in carbon tetrachloride (E. L. Eliel and R. V. Acharya, *J. Org. Chem.*, **24**, 151 (1959)) and for the decomposition of the diacyl peroxides of *cis*- and *trans*-4-*t*-butylcyclohexanecarboxylic acid in tetrabromoethane (H. H. Lau and H. Hart, *J. Am. Chem. Soc.*, **81**, 4897 (1959)). These cases, among others, will be discussed in the full account of this work.

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RECEIVED APRIL 28, 1962

N.M.R. SPECTRA AND CONFORMATIONAL ANALYSIS OF 4-ALKYLCYCLOHEXANOLS[1]

Sir:

For conformational analysis of *cis*-4-alkyl-substituted cyclohexanols one of the methods we had been employing depends on proton magnetic resonance spectroscopy, since it is well known that *axial* and *equatorial* protons show different chemical shifts.[2,3] Assuming that a 4-*t*-butyl group guarantees conformational homogeneity[4] but has no effect on the chemical shift of the 1-proton,[2] we were using the *trans*- and *cis*-4-*t*-butylcyclohexanols to determine the chemical shifts for purely *axial* and *equatorial* 1-protons, δ_e and δ_a, respectively (corresponding to purely *equatorial* and *axial* hydroxyl groups). Then these values were employed along with measured values in conformational analysis of conformationally heterogeneous *cis*-4-alkyl-substituted cyclohexanols with the aid of equation[3-5] (1), where N_e and N_a are mole fractions of conformations with *equatorial* and *axial* hydroxyl groups, respectively, and K_{ae} is a conformational equilibrium constant. However, a discouraging note was introduced recently by Musher,[6a] who reported that the 4-*t*-butyl group exerts considerable effect on the 1-hydrogen resonance, invalidating the present method. Also, his listed chemical shifts for three *trans*-4-alkylcyclohexanols[6b] show considerable variation as the alkyl group is varied from *t*-Bu through *i*-Pr to Me. Our own findings differ substantially from those of Musher and serve to clarify this situation.

$$K_{ae} = (N_e/N_a) = (\delta_a - \delta)/(\delta - \delta_e) \qquad (1)$$

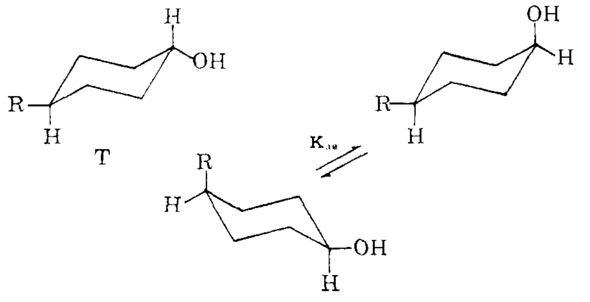
Our spectra of the 4-alkylcyclohexanols (Table I) were measured on a Varian A-60 Analytical NMR Spectrometer with tetramethylsilane as internal standard. The solutions in CCl_4 were 15% by weight of the appropriate cyclohexanol. For the *trans*-4-alkylcyclohexanols the change in the chemical shift of the 1-proton with change of the 4-alkyl group shows a trend in the opposite direction to the one reported by Musher. This disagreement in results is not surprising in view of the broadness of the signals of the 1-proton, which are unresolved spin–spin multiplets. Musher[6b] claimed that the peaks are virtually symmetrical and that the geometrical center and the position of maximum peak height give the same value for the chemical shift. However, the signals are only superficially symmetrical and measurement of the maximum peak height in these cases may be somewhat unreliable for determination of the chemical shift value. We have also carried out measurements in 2-D-2-propanol as solvent on solutions containing 40% by weight of the appropriate cyclohexanols; while these spectra are better resolved, the resolu-

TABLE I

N.M.R. DATA FOR 4-ALKYLCYCLOHEXANOLS (CPS.[a] FROM TMS)

	Carbon Tetrachloride			2-D-2-Propanol	
4-R	Musher[b]	H[c]	D	H[c]	D
			Trans		
t-Bu	211.0	201.5[d]	202.0	207.5	207.0
i-Pr	209.5	204.5	202.5	207.5	208.0
Et	...	...	203.0	208.0	207.0
Me	206.5	207.0	203.0	209.0	206.0
H	211.0	...	209.5	212.5	213.0
			Cis		
t-Bu	243.0	233.5[e]	234.5[e]	238.0	239.0
i-Pr	240.0	233.5	232.0	236.0	236.0
Et	...	...	229.0	232.0[f] 235.5[f]	233.0
Me	235.0	...	229.0	231.5[f] 235.0[f]	231.5

[a] Values to ±0.5 cps. [b] The reported values in ppm.[6b] were changed to cps.; 3.5 cps. was then added to each value in order to convert from HMDS to TMS as standard. [c] Peaks were mostly not resolved; center visually estimated. [d,e] Eliel and Gianni[5] report: [d] 202. [e] 236. [f] Two sharp maxima observed in these cases.



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[1] Research sponsored by the U. S. Army Research Office (Durham).

[2] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

[3] E. L. Eliel, *Chemistry and Industry*, 568, (1959).

[4] S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

[5] E. L. Eliel and M. H. Gianni, *Tetrahedron Letters*, No. 3, 97 (1962).

[6] (a) J. I. Musher, *J. Am. Chem. Soc.*, **83**, 1146 (1961), footnote 16; (b) J. I. Musher, *J. Chem. Phys.*, **35**, 1159 (1961), Table II.

tion is not sufficient to permit a complete analysis of the system.

To alleviate the spin–spin coupling problem we had also measured the spectra of the corresponding 2,2,6,6-tetradeuterio-4-alkylcyclohexanols. Deuteration in the β,β'-positions does indeed eliminate the spin–spin coupling problems, and the signals for the 1-protons now appear as sharp singlets.[7] With the deuterated alcohols in both solvents, our results show remarkable constancy of the chemical shift of the 1-proton in the four *trans*-4-alkylcyclohexanols which are expected[4] to exist nearly exclusively in the *ee*-conformation T. Also, the *cis*-alcohols exhibit a trend of decreasing chemical shift with decrease in the size of the alkyl group.

TABLE II

A VALUES (KCAL./MOLE) FROM N.M.R. AT 30°

Group	CCl_4	2-D-2-Propanol
i-Pr	2.28 ± 0.08	2.25 ± 0.08
Et	1.74 ± 0.06	1.77 ± 0.07
Me	1.74 ± 0.06	1.60 ± 0.06
OH	0.78 ± 0.02	0.88 ± 0.02

Using the chemical shifts for conformational analysis of cyclohexanol, K_{ae} is obtained with the aid of equation (1) and this leads to a value for A_{OH}, the free energy of preference of the hydroxyl group for an *equatorial vs.* an *axial* position.[4] Similar treatment of the *cis*-4-alkylcyclohexanols leads to A values which are differences between A_R and A_{OH}. As is clear from Table II, essentially identical values of A_R are obtained in both solvents, in spite of differences in the nature of the solvent and the cyclohexanol concentration. Even the A_{OH} values agree quite well. Also, A_R and A_{OH} concur with those obtained by other methods.[7,8] The figure for $A_{i\text{-Pr}}$ is much more reasonable than the previous rough estimate[4] (>3.3) based on old saponification rate constants[9] which we have remeasured[10] and found to be erroneous.

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[7] As this manuscript was being submitted a Communication by F. A. L. Anet appeared [*J. Am. Chem. Soc.*, **84**, 1053 (1962)] reporting simplification of the spin–spin coupling pattern by remote deuteration at carbon atoms 3, 4 and 5 and the conformational analysis of cyclohexanol based on coupling constants.

[8] (a) E. L. Eliel, *J. Chem. Ed.*, **37**, 126 (1960); (b) H. Van Bekkum, P. E. Verkade, B. M. Wepster, *Koninkl. Ned. Akad. Wetenschap, Proc. Ser. B*, **64**, No. 1, 161 (1961).

[9] G. Vavon, *Bull. Soc. Chim. France*, [4] **49**, 1002 (1931).

[10] A. H. Lewin, unpublished work.

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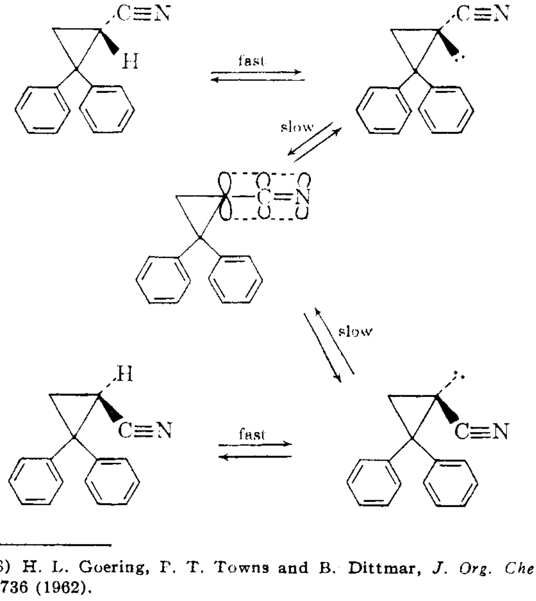
CYCLOPROPANES. XII. THE CYCLOPROPYL CARBANION

Sir:

A comparison of the rate of deuterium exchange with the rate of racemization in the phenyl 2-octyl sulfone system has revealed that the exchange rate is faster than the rate of racemization.[1-3] This has been interpreted in terms of "asymmetric solvation"[1] or by postulating that the intermediate carbanion has retained its asymmetry.[1,2] In the case of sulfones the asymmetry can be maintained by having the electron pair in a 2p or sp^3 orbital conjugating with the 3d orbital of sulfur in a Case II type[4] of structure.[2] In contrast to the work on sulfones the rates of deuterium exchange and rates of racemization of several optically active nitriles were found to be equal.[5] Apparently, "asymmetric solvation" is unimportant in these cases, presumably due to the ambident nature of the intermediate anion.[5]

We wish at this time to report our findings on the base-catalyzed deuterium exchange of 2,2-diphenylcyclopropylnitrile (I). In connection with our studies on the cyclopropyl carbanion[6] we had occasion to determine the pseudo first-order rate constants k_1 for the sodium methoxide catalyzed racemization of I. At 75.7° and at 92.6° the k_1's in methanol (0.09 M in I and 0.99 M in methoxide) are $0.363 \pm 0.007 \times 10^{-6}$ sec.$^{-1}$ and $3.25 \pm 0.05 \times 10^{-6}$ sec.$^{-1}$, respectively. The extrapolated k_1 at 50° is $6.78 \pm 0.13 \times 10^{-9}$ sec.$^{-1}$. Under comparable conditions (0.096 M in I and 0.88 M in methoxide) the rate of deuterium–hydrogen exchange at 50.0° using methanol-*d* as the solvent was found[7] to be $5.48 \pm 0.13 \times 10^{-5}$ sec.$^{-1}$. The ratio of $k_1$exc./$k_1$rac. is 8,080 with the half-life for racemization being 3.5 years and the half-life for exchange being 3.51 hours. The k_{1H}/k_{1D} ratio for the exchange reaction was found to be 1.69 ± 0.04.

Since "asymmetric solvation" is not important when methanol is used as a solvent[8] and since



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[1] D. J. Cram, C. A. Kingsbury and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961).

[2] E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961).

[3] H. L. Goering, F. T. Towns and B. Dittmar, *J. Org. Chem.* **27**, 736 (1962).

[4] H. P. Koch and W. E. Moffitt, *Trans. Far. Soc.*, **47**, 7 (1951).

[5] D. J. Cram, B. Rickborn, C. A. Kingsbury and P. Haberfield, *J. Am. Chem. Soc.*, **83**, 3678 (1961); D. J. Cram and P. Haberfield, *ibid.*, **83**, 2354 (1961).

[6] (a) H. M. Walborsky and F. M. Hornyak, *ibid.*, **77**, 6026 (1955); (b) H. M. Walborsky and F. M. Hornyak, *ibid.*, **78**, 872 (1956).

[7] The rate was measured by infrared intensity analysis (at 1189 for I-D and at 1137 for I-H) and a number of points checked by the combustion method.

[8] D. J. Cram, D. A. Scott and W. D. Nielsen, *J. Am. Chem. Soc.*, **83**, 3696 (1961).