Attempts to dehydrate tricyclopropylcarbinol by distillation *in vacuo* from small amounts of sulfuric acid or phosphorus pentoxide lead to rearranged alcohol IV, 2,2-dicyclopropyltetrahydrofuran V, identified by analysis, n.m.r. and independent synthesis from γ-butyrolactone and cyclopropyllithium, and the bis-ether VI, in varying proportions depending on reaction conditions.[11] No methylenecyclopropane type product was observed, but polymer, possibly arising from 1,1-dicyclopropylbutadiene, was obtained in varying amounts.[12]

II must be stored in a refrigerator or it rearranges to the allylcarbinyl benzoate III. The rearrangement is slow at 50° but complete in 30 minutes at 100°. In contrast, I_2 (X-benzoate) shows only slight rearrangement after 70 minutes at 100°. These rearrangements are being investigated with O^{18}.[13]

Tricyclopropylcarbinol is hydrogenolyzed readily (*cf.* arylcarbinols[14]) to tricyclopropylmethane (VII) by hydrogen over copper chromite at 175°, the structure of the product being clear from its analysis, n.m.r. and integrated near infrared spectrum. Overhydrogenation results in some hydrogenolysis of one cyclopropane ring.

Extensions to solvolyses of related aryl and vinyl (for example, dicyclopropylvinylcarbinol) derivatives are in progress.

(10) τ_m is the τ-value using the methyl protons of methanesulfonic acid as an internal reference. The value 6.76 τ is assigned to the methyl group, the latter having been measured by Dr. C-Y. Wu directly against tetramethylsilane in trifluoroacetic acid, a mutual solvent. We have found this internal reference particularly useful in n.m.r. studies of stable mono- and dicarbonium ions in sulfuric acid.

(11) *Cf.* N. Zelinsky, *Ber.*, **34**, 3887 (1901); N. V. Keersbilck, *Bull. Soc. Chim. Belg.*, **38**, 205 (1929); T. A. Favorskaya, N. V. Scherbinskaya and E. S. Golovacheva, *Zhur. Obshcheĭ Khim.*, **23**, 1878 (1953).

(12) *Cf.* M. Hanack and H. Eggensperger, *Angew. Chem.*, **74**, 116 (1962).

(13) For an O^{18} study of cyclopropylcarbinyl benzenesulfonate, see D. B. Denney and E. J. Kupchik, *J. Am. Chem. Soc.*, **82**, 859 (1960).

(14) H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper–Chromium Oxide and Nickel Catalyst," The University of Wisconsin Press, Madison, 1937, p. 69.

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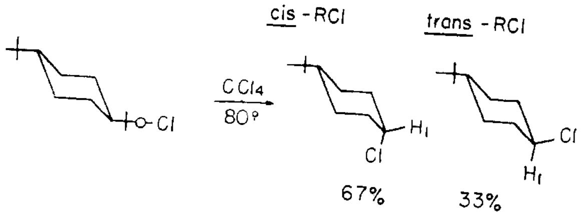
RECEIVED APRIL 25, 1962

ON THE NATURE OF THE CYCLOHEXYL RADICAL[1]

Sir:

We wish to report results of interest in the general problem of the geometry of carbon radicals, and to call attention to the suitability of the decomposition of hypochlorites[2] for the study of radicals.

Decomposition of dimethyl-(*trans*-4-*t*-butylcyclohexyl)-carbinyl hypochlorite[3] in carbon tetrachloride (*cis*-initial concn., 0.3–0.5 *M*) afforded acetone and and *trans*-4-*t*-butylcyclohexyl chloride (79–94% yields). *The ratio of* **cis**-*chloride to* **trans**-*chloride is two to one.*



These chlorides were identical in all respects with samples prepared by the action of thionyl chloride on a *cis–trans* mixture of 4-*t*-butylcyclohexanol in ether containing tri-*n*-butylamine. The chlorides were separated by vapor phase chromatography on a nitrile silicone column at 97° (*cis*-chloride, Calcd.: C, 68.74; H, 10.96; Cl, 20.30. Found: C, 68.91; H, 10.97; Cl, 20.40. *trans*-chloride, found: C, 68.62; H, 10.88; Cl, 20.28). Assignment of *cis*-stereochemistry to the chloride of shorter retention time is based on: (1) its enhanced ease (in comparison with the *trans*-isomer) of conversion by base to 4-*t*-butylcyclohexene[4]; (2) location of the C-1 hydrogen at 5.63 τ (*vs.* 6.36 τ for the *trans*-isomer[5]; (3) the marked similarity in infrared spectra with the corresponding *cis*- and *trans*-bromides of known configuration.[6]

Decomposition of dimethyl-(*cis*-4-*t*-butylcyclohexyl)-carbinyl hypochlorite[3] in carbon tetrachloride affords exactly the same product composition as that obtained from the *trans*-isomer described above. Both hypochlorites are stable in the dark, are readily decomposed by weak irradiation or heating, and in agreement with other tertiary alkyl hypochlorites,[2] decompose by a free radical chain reaction of long chain length.

$$R—C(CH_3)_2—O—Cl + R\cdot \longrightarrow R—C(CH_3)_2—O\cdot + Cl—R$$

$$R—C(CH_3)_2—O\cdot \longrightarrow R\cdot + (CH_3)_2C{=}O$$

That the observed two-to-one ratio of *cis*-chloride to *trans*-chloride is the result of kinetic control is established by: (1) the stability of the products to the reaction conditions (in separate control experiments) and (2) the thermodynamic preference of *trans* (equatorial) over *cis* (axial) chloride.[5]

Decomposition of the hypochlorites in carbon tetrachloride shows a small *decrease* in the ratio of *cis* to *trans* chloride with decreasing temperature (67/33 at +80°; 65/35 at 0°, 62/38 at −30°). The *cis*-hypochlorite affords exactly the same product ratio as the *trans* at all temperatures measured (+80°, 0°, −30°). This exact correspondence is strong evidence for the intermediacy of the 4-*t*-butylcyclohexyl radical in the two decompositions.

(1) This work was supported by the National Science Foundation and by the Atomic Energy Commission.

(2) (a) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **82**, 2207 (1961); (b) F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz and W. N. Smith, *ibid.*, **83**, 2196 (1961).

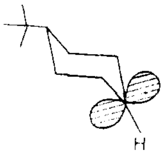
(3) The hypochlorite was prepared from the corresponding alcohol by the action of hypochlorous acid [see F. D. Greene, *J. Am. Chem. Soc.*, **81**, 2688 (1959), and references cited therein]. The dimethyl-(*trans*- and *cis*-4-*t*-butylcyclohexyl)-carbinols employed in this study were prepared by the procedures of R. D. Stolow and C. B. Boyce, *J. Org. Chem.*, **26**, 4726 (1961).

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

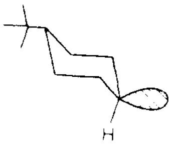
(5) A. J. Berlin and F. R. Jensen, *Chem. and Ind.*, 998 (1960); L. W. Reeves and K. O. Strømme, *Can. J. Chem.*, **38**, 1241 (1960).

(6) E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959). We wish to thank Professor Eliel for infrared spectra of the *cis* and *trans*-bromides.

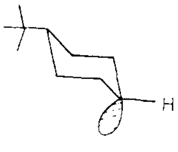
The preferential formation of *cis*-4-*t*-butylcyclohexyl chloride[7] implies that the radical is better represented by non-planar forms such as (2) and (3) rather than the planar form (1) since considerations of product control or of accessibility to the radical would both favor attack from the equatorial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

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[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.

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

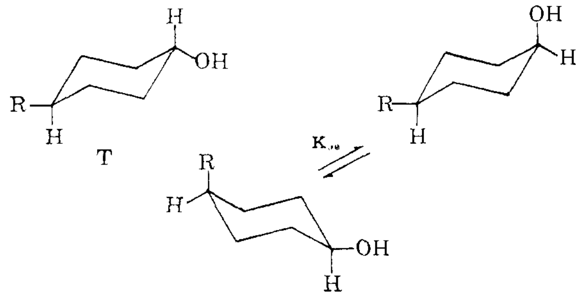
Our spectra of the 4-alkylcyclohexanols (Table I) were measured on a Varian A-60 Analytical NMR Spectrometer with tetramethylsilane as internal standard. The solutions in CCl_4 were 15% by weight of the appropriate cyclohexanol. For the *trans*-4-alkylcyclohexanols the change in the chemical shift of 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. 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.