Differentiation of *cis*- and *trans*-4-Substituted-1-methylcyclohexanes by Their NMR Signal Envelopes

STANLEY I. GOLDBERG, FUK-LUEN LAM, and MUHAMMAD S. SAHLI
Department of Chemistry, University of South Carolina, Columbia, S.C. 29208

Nuclear magnetic resonance spectra of a number of isomeric 4-substituted-1-methylcyclohexanes are reported. These spectra substantiate the useful stereochemical generalization that the signals due to the ring protons of a diequatorial isomer appear as a significantly broader envelope than do those which arise from the ring protons of the corresponding nondiequatorial form.

BROWNSTEIN and Miller (2) pointed out in 1959 that in the nuclear magnetic resonance (NMR) spectra they determined from a number of disubstituted cyclohexanes, the ring protons of those isomers existing in the essentially rigid diequatorial conformations gave significantly wider signal envelopes that did the ring protons of the corresponding diastereomers. Thus, the NMR signal envelopes due to the ring protons of the *trans*-1,2, *cis*-1,3, and *trans*-1,4 isomers were all wider than those due to the ring protons of the corresponding *cis*-1,2, *trans*-1,3, and *cis*-1,4 isomers,

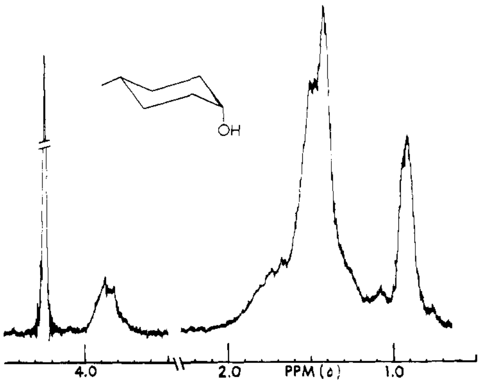


Figure 1. *cis*-4-Hydroxy-1-methylcyclohexane (4)

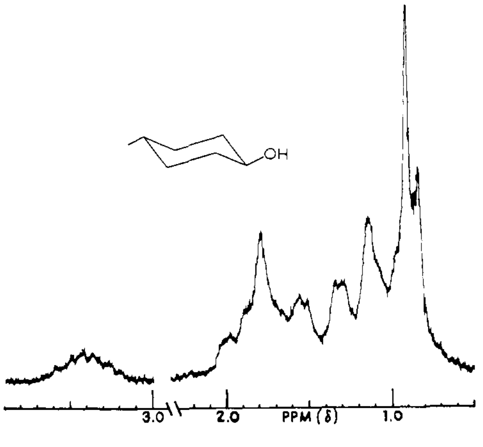


Figure 2. *trans*-4-Hydroxy-1-methylcyclohexane (4)

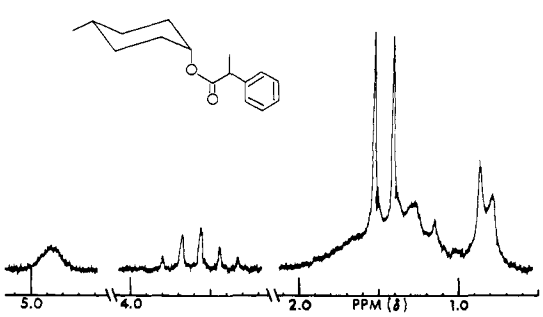


Figure 3. *cis*-1-Methylcyclohex-4-yl hydratropate (4)

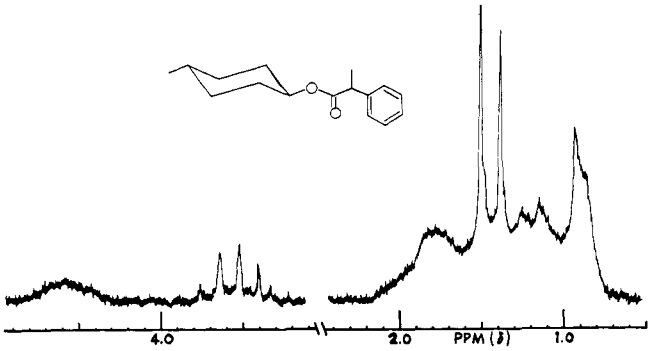


Figure 4. *trans*-1-Methylcyclohex-4-yl hydratropate (4)

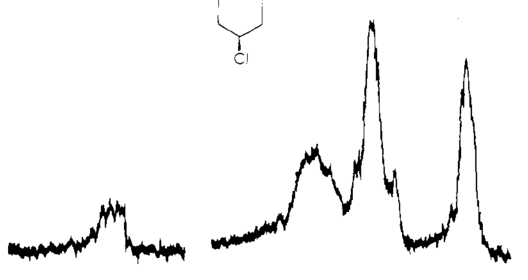


Figure 5. *cis*-4-Chloro-1-methylcyclohexane (6)

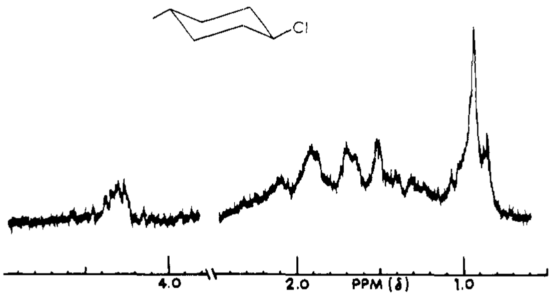


Figure 6. *trans*-4-Chloro-1-methylcyclohexane (*6*)

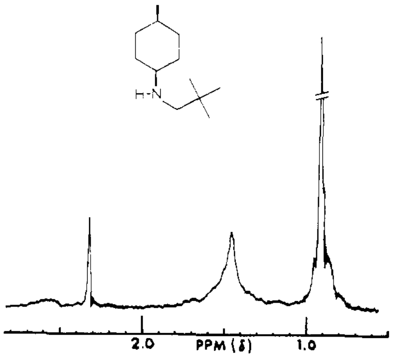


Figure 7.
cis-4-Neopentylamino-1-methylcyclohexane (*5*)

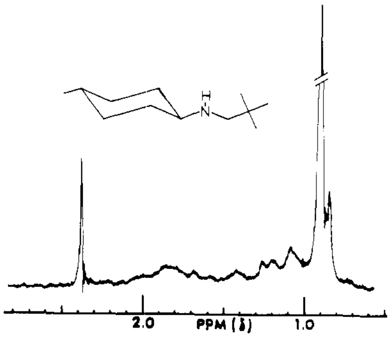


Figure 8.
trans-4-Neopentylamino-1-methylcyclohexane (*5*)

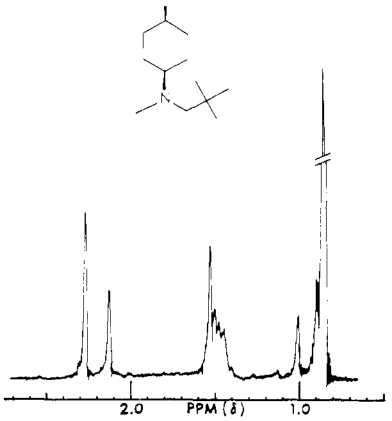


Figure 9.
cis-4-(*N*-Methyl-*N*-neopentylamino)-1-methylcyclohexane (*5*)

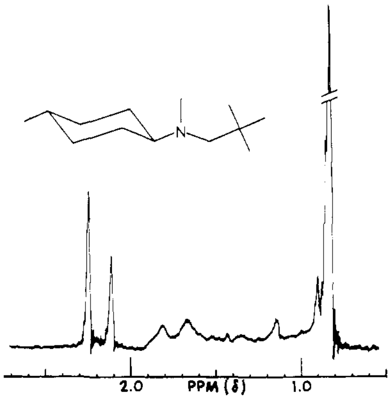


Figure 10.
trans-4-(*N*-Methyl-*N*-neopentylamino)-1-methylcyclohexane (*5*)

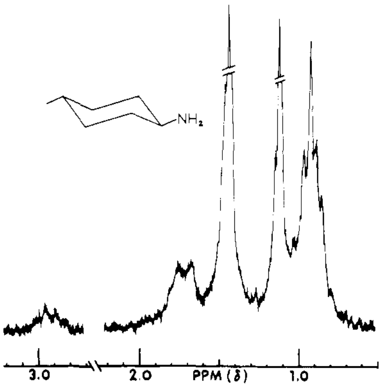


Figure 11. *trans*-4-Amino-1-methylcyclohexane (*10*)

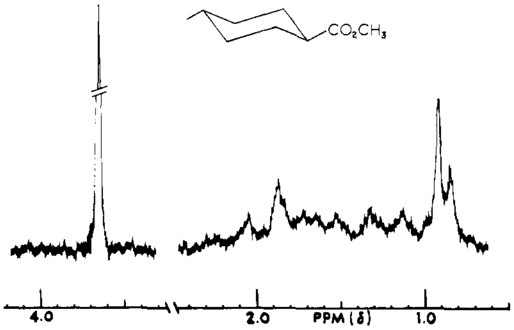


Figure 12.
trans-4-Carbomethoxy-1-methylcyclohexane (*6*)

respectively. Formally related to the isomeric 1,2-disubstituted cyclohexanes are the *cis*- and *trans*-decalins, and similar correlations regarding their NMR signal envelopes (*3, 7, 8*), as well as their derivatives and their aza-analogs (*1*), have been made.

The effect may be attributed (*2, 3, 8*) to the difference in conformation of a pair of *cis*- and *trans*-disubstituted cyclohexanes. The broader signal envelope of the rigid diequatorial isomer is due to the distinguishable axial and equatorial protons and their complex spin-spin interactions. The sharper signal envelope displayed by the non-diequatorial isomer is probably due to rapid interconversion or conformers, and/or to fortuitous near-equivalence of chemical shifts of protons of different but significantly populated conformation (*3, 9*).

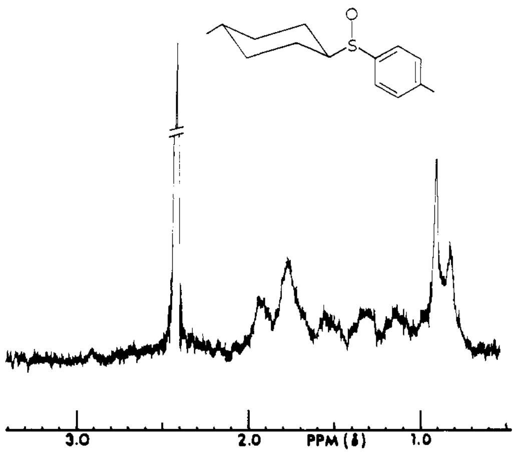


Figure 13.
trans-4-(*p*-Tolysulfonyl)-1-methylcyclohexane (*6*)

Studies have been made (*4, 5, 6*) which required preparation of a number of stereoisomeric 4-substituted-1-methylcyclohexanes. The NMR spectra of these compounds were determined routinely with a Varian A-60 spectrometer at ambient temperatures in chloroform-*d* containing tetramethylsilane internal standard. These spectra (Figures 1-13) provide additional corroboration of the general applicability of the useful stereochemical correlation originally suggested by the observations of Brownstein and Miller (*2*). Larger copies of the figures are available from ASIS.

LITERATURE CITED

(1) Armarego, W.L.F., *J. Chem. Soc.* **1967**, 337.
(2) Brownstein, S., Miller, R., *J. Org. Chem.* **24**, 1886 (1959).
(3) Gerig, J.T., Roberts, J.D., *J. Am. Chem. Soc.* **88**, 2791 (1966).
(4) Goldberg, S.I., Lam, F-L., *J. Org. Chem.* **31**, 2336 (1966).
(5) Goldberg, S.I., Lam, F-L., "Abstracts of Papers," p. P-31, 155th Meeting, ACS, San Francisco, Calif., April 1968.
(6) Goldberg, S.I., Sahli, M.S., *J. Org. Chem.* **32**, 2059 (1967).
(7) Jensen, F.A., Beck, B.H., *Tetrahedron Letters* **1966**, 4523.
(8) Musher, J., Richards, R.E., *Proc. Chem. Soc.* **1958**, 230.
(9) Riddell, F.G., Robinson, M.J.R., *Chem. Commun.* **1965**, 227.
(10) Smith, D.R., Maienthal, M., Lipton, J., *J. Org. Chem.* **17**, 294 (1952).

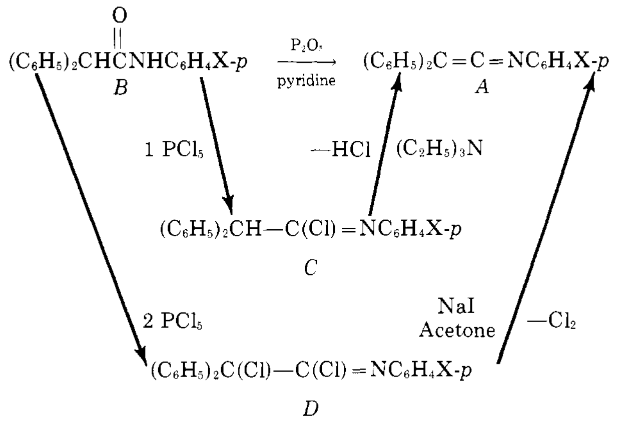
RECEIVED for review October 7, 1968. Accepted April 11, 1969. The authors acknowledge the Petroleum Research Fund of the American Chemical Society for the grant under which this work was carried out. For larger copies of the figures in this article, order NAPS Document NAPS-00474 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, New York 10001; remit $1.00 for microfiche or $3.00 for photocopies.

A Novel Method for the Preparation of Ketenes and Ketenimines

GOPAL H. SINGHAL and HERBERT Q. SMITH
Pennsalt Chemicals Corp. Technological Center, King of Prussia, Pa. 19406

A novel method of preparation of ketenes and ketenimines by the dechlorination of the corresponding α-chloroacid chlorides and α-chloroimino chlorides with copper powder is described.

IN RECENT years, three general methods for the synthesis of ketenimines have been introduced by Stevens and coworkers. These are the dechlorination of α-chloroimino chlorides with sodium iodide in acetone (*10*), the dehydrochlorination of imino chlorides with a tertiary amine (*11*), and the dehydration of amides with phosphorus pentoxide in combination with a tertiary amine (*12*). Basically, these methods involve the removal of a molecule of water from the amide (*B*) either directly or by converting the amide to an imino chloride (*C*) or an α-chloroimino chloride (*D*), followed by removal of a molecule of hydrogen chloride or chlorine, as illustrated.



These methods work very well when X is an electron-donating group—e.g., CH_3—, CH_3O—, etc. However, when X is a strong electron-withdrawing group, such as NO_2, these methods do not work well. Thus, the nitroketenimine (*A*, X = NO_2) could not be prepared by the dehydration of the corresponding amide (*12*). The amide (*B*, X = NO_2), on treatment with even 1 mole of phosphorus pentachloride, gives mainly the α-chloroimino chloride (*1*) (*D*, X = NO_2) and unreacted starting material, rendering the dehydrochlorination method via the imino chloride inapplicable. On the other hand, sodium iodide in acetone under the conditions described in the literature (*10*) for the preparation of *A* (X = CH_3), failed to dehalogenate *D* (X = NO_2). *D* (X = NO_2) could be obtained in excellent yield (*6, 9*) with these reagents in a sealed tube at 100° C., under strictly anhydrous conditions, or (*1*) in a moderate yield of 31% from sodium iodide in a higher-boiling ketone, 3-pentanone. However, the isolation procedure by this method is involved, tedious, and unsuitable for large scale preparations.

The authors were interested in the nitroketenimine, and the dechlorination route seemed to be the logical method of choice. Staudinger and Meyer (*8*) have reported that zinc failed to dechlorinate an α-chloroimino chloride to a ketenimine, even though this is a common method for the preparation of ketenes from α-haloacid halides (*3*).

Staudinger and Klever (*7*) also reported the preparation of ketene by debromination of bromoacetyl bromide with zinc in ether. This claim was later disputed by Hurd and