Conformational Analysis. XIX.[1] Optical Rotatory Dispersion Studies. L.[2] The Conformers of *trans*-2-Chloro-5-methylcyclohexanone

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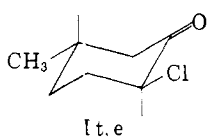
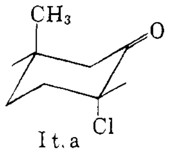
Earlier papers described studies of the conformational equilibria of 2-bromocyclohexanone,[3] 2-bromo-5-methylcyclohexanone,[4] and 2-chlorocyclohexanone.[5] This paper completes the studies in this series and is aimed at covering a number of specific points. First, it was intended to obtain another example of a system in which the chlorine atom could be shown to prefer the equatorial position to a greater extent than with the bromine analog, which there is reason to believe is generally true.[5,6] A number of explanations have been offered for this situation,[7] many of which have considerable merit, but none of them have been shown to be of deciding importance. Second, as this compound was the first example found in which the sign of the Cotton effect curve changed upon changing solvent,[8] it was of particular interest to learn the conformational composition of the compound as a function of solvent polarity. Third, with the recent demonstration of the nonexistence of a 2-alkyl ketone effect,[9] it seemed worthwhile to look more critically at the 3-alkyl ketone effect in simple systems. Fourth, as all of the energies involved in the molecule, with the possible exception of the 3-alkyl ketone effect, are known, and a number of methods have been developed for experimentally determining the composition of conformational mixtures,[5] the system at hand becomes a good test of the agreement between the predictions of theory and the results of experiment.

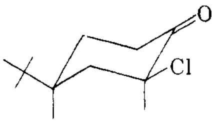
From the dipole moment data obtained in the study of the conformationally pure *cis*-2-chloro-4-*t*-butylcyclohexanone (equatorial chlorine, IIc,e) and the *trans* isomer (axial chlorine, IIt,a)[5] the energy of the axial chlorine (relative to the equatorial) was found to be −0.74 kcal./mole in heptane, +0.02 kcal./mole in benzene, and +0.33 kcal./mole in dioxane. The dipole moment of *trans*-2-chloro-5-methylcyclohexanone (It) in benzene was 4.14 D, and this value corresponds to a conformational composition which is 85% It,e and 15% It,a. The latter has the greater energy by 1.06 kcal./mole, and from the data on 2-chlorocyclohexanone, the energy of the axial methyl is found to be +1.04 kcal./mole. This value is identical with that found with the bromo analogs,[4] and is close to that predicted by Klyne.[10] Using this energy for the 3-methyl group in It together with the energies of the chlorine atom found in the various solvents with 2-chlorocyclohexanone,[5] the conformer composition of It in various solvents was calculated, and these values are given in Table I.



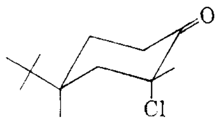
It,e



It,a



IIc,e



IIt,a

TABLE I

Summary of Conformer Compositions Found for It

	Per Cent It,e by Various Methods				
Solvent	Calcd.	μ	I.R.	U.V.	R.D.
n-Heptane	58		66	82[a]	82[a]
CCl$_4$	60		68		
CHCl$_3$			70		
Benzene	85	85	76		
Dioxane	92		78	88	100
Methanol				100	99
Dimethyl sulfoxide			90		

[a] Isooctane used as solvent.

Three spectral methods have been employed in the past for the determination of conformational composition, ultraviolet, infrared, and optical rotatory dispersion. These methods generally have given analytical results good to perhaps ±10%. The complete rotatory dispersion curves of It (both peak and trough) were obtained[8] in the solvents methanol, dioxane, and isooctane and a partial curve was realized for carbon tetrachloride. The date were analyzed in the general manner described for the bromo analog.[4] A more accurate experimental value has been obtained for the molecular am-

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[1] Paper XVIII, N. L. Allinger, M. A. DaRooge, and R. B. Hermann, *J. Org. Chem.*, in press.

[2] Paper XLIX, C. Djerassi and A. Luttringhaus, *Ber.*, in press.

[3] (a) J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958); (b) N. L. Allinger, J. Allinger, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 2926 (1960).

[4] N. L. Allinger, J. Allinger, L. E. Geller, and C. Djerassi, *J. Org. Chem.*, **25**, 6 (1960).

[5] N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 5876 (1960).

[6] E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **77**, 5418 (1955).

[7] A summary of these explanations and references are to be found in ref. 5. See also the important paper of E. M. Kosower, G. Wu, and T. S. Sorensen, *J. Am. Chem. Soc.*, in press.

[8] (a) C. Djerassi, L. E. Geller, and E. J. Eisenbraun, *J. Org. Chem.*, **25**, 1 (1960); (b) C. Djerassi and L. E. Geller, *Tetrahedron*, **3**, 319 (1958).

[9] N. L. Allinger and H. M. Blatter, *J. Am. Chem. Soc.*, **83**, 994 (1961).

[10] W. Klyne, *Experientia*, **12**, 119 (1956).

TABLE II

CARBONYL ABSORPTION INFRARED DATA OF *trans*-2-CHLORO-5-METHYLCYCLOHEXANONE

Solvent	Frequency of Absorption Maxima, Cm.$^{-1}$ It,a	It,e	Extra Band	Parent	Optical Densities It,a	It,e	Extra Band
n-Heptane	1729	1739	1747	1725	0.280	0.420	0.288
Carbon tetrachloride	1724	1734	1745	1720	0.378	0.700	0.349
Chloroform	1721	1731	1739	1708	0.199	0.413	0.247
Benzene	1723	1733	1745	1716	0.240	0.659	0.238
Dioxane	1721	1734	1745	1718	0.170	0.525	0.195
Dimethyl Sulfoxide	1717	1730	1747	1713	0.117	1.00	0.156

plitude of (+)-3-methylcyclohexanone than was used previously[4] and this value (+2492°) was assigned to the molecular amplitude of the conformer It,e (axial haloketone rule[11]). The revised analysis of the dipole moment data of *trans*-2-bromo-5-methylcyclohexanone using newer data from model compounds afforded a value of −29,670° for the diaxial conformer of the related bromo compound. As in a number of cases no significant difference between the molecular amplitudes of an axial α-chloro and the corresponding α-bromo keto compound have been found,[12] this same value was employed for the molecular amplitude of conformer It,a. The percentage compositions calculated from the optical rotatory dispersion measurements of It were 99%, 100% and 81% It,e in the solvents methanol, dioxane, and isoöctane, respectively. The conformational composition in each solvent was found to be in reasonable agreement with the predictions.

The infrared carbonyl absorption bands of It at high resolution were composed of three maxima which were poorly resolved from one another, but in all solvents the most intense of these maxima occurred at a wave length relative to the parent 3-methylcyclohexanone which was consistent with its assignment[3–5,13] to It,e absorption. The shoulder on the low frequency side, by similar rational was assigned to the It,a conformer. The third maximum was a shoulder which occurred at 22–29 cm.$^{-1}$ higher frequency than that of the parent compound and was of nearly the same intensity as the It,a maximum. Such anomolous bands in the carbonyl region have been observed with the related bromo compound and with 2-chlorocyclohexanone, and have been discussed.[4,14] The results of the analyses of these carbonyl absorption curves (see Experimental for details) are summarized in Table I and are in agreement with those obtained by the other methods.

The ultraviolet spectrum of It in polar solvents showed a smooth rather symmetrical curve with a single maximum. Some fine structure was displayed in octane. It is known that the axial chlorine causes both the wave length and the extinction coefficient to increase, while equatorial chlorine has only a very small effect, and there is not much change in the values with change in solvent if the conformational composition does not change.[5,15] Table IV gives pertinent ultraviolet data which lead to the conclusions summarized in Table I, namely that It contains about 82% equatorial conformer in octane and 100% in methanol, in agreement with the results of other methods.

EXPERIMENTAL

The synthesis and physical properties of optically active *trans*-2-chloro-5-methylcyclohexanone and (+)-3-methylcyclohexanone have been described.[8]

Optical rotatory dispersion studies. These measurements were made according to the published procedure[12] and have been reported.[8] More accurate measurements for both It and the parent compound were since obtained and the newer data were used for the present work. *trans*-2-chloro-5-methylcyclohexanone, R. D. in methanol, 20°, (*c*, 0.100): $[\alpha]_{700}$ +8°. $[\alpha]_{589}$ +32°, $[\alpha]_{305}$ +764°, $[\alpha]_{267}$ −756°, $[\alpha]_{255}$ −572°. R. D. in dioxane, 25°, (*c*, 0.100): $[\alpha]_{700}$ +4°, $[\alpha]_{589}$ +12°, $[\alpha]_{312}$ +948°, $[\alpha]_{275}$ −848°, $[\alpha]_{262}$ −736°. R. D. in isoöctane *c*, 0.105): $[\alpha]_{700}$ −49.5°, $[\alpha]_{589}$ −61°, $[\alpha]_{332}$ −1270°, $[\alpha]_{295}$ +988°, $[\alpha]_{255}$ + 246°. R. D. in carbon tetrachloride (*c*, 0.051): $[\alpha]_{700}$ −23°, $[\alpha]_{589}$ −20°, $[\alpha]_{332}$ −1002°, $[\alpha]_{300}$ + 795°. (+)-3-Methylcyclohexanone, R. D. in methanol (*c*, 0.165): $[\alpha]_{700}$ +3°, $[\alpha]_{389}$ +105°, $[\alpha]_{310}$ +950°, $[\alpha]_{265}$ −1275°, $[\alpha]_{256}$ −1140°.

The calculated molecular amplitudes of It were +2209°, +2622°, −3267° for methanol, dioxane and isoöctane, respectively, and that of (+)-3-methylcyclohexanone was +2492° in methanol. A minimum molecular amplitude of −2623° for It in carbon tetrachloride was calculated.

Infrared studies. The infrared carbonyl absorption spectra were obtained as described earlier.[5] The solvents employed for the study were either spectral-grade materials or else were reagent-grade solvents purified by methods described earlier.[4,5] The carbonyl absorptions of It and (+)-3-methylcyclohexanone in each solvent were recorded consecutively and all of the data were obtained in uninterrupted sequence. The experimentally recorded optical densities and wave lengths of the It,a, It,e, and "extra" bands are given in Table II. To determine the conformational composition in each medium, the observed optical density of the It,e band was multiplied by the factor 1.25 to account for the antici-

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(11) (a) C. Djerassi and W. Klyne, *J. Am. Chem. Soc.*, **79**, 1506 (1957) (b) C. Djerassi, *Optical Rotatory Dispersion*, McGraw-Hill, New York, 1960, p. 120.

(12) C. Djerassi, J. Osiecki, R. Riniker, and B. Riniker, *J. Am. Chem. Soc.*, **80**, 1216 (1958).

(13) (a) R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952); (b) E. J. Corey, *J. Am. Chem. Soc.*, **75**, 2301 (1953).

(14) P. Yates and L. L. Williams, *J. Am. Chem. Soc.*, **80**, 5896 (1958).

(15) R. C. Cookson, *J. Chem. Soc.*, 282 (1954).

pated lower absorption intensity of this conformer relative to that of It,a[3], and the mole fraction (N) of It,e was found from the optical densities (d) with the relationship:

$$1.25\ d_{It,e}/d_{It,a} = N_{It,e}/1 - N_{It,e}$$

The results are summarized in Table I. Because of the poor resolution (similar to that found with the bromo analog)[4] these values are only good to perhaps ±20%, although the relative values are much better.

Dipole moment. The apparatus used for the measurement of the dielectric constants has been described.[16] The dielectric constant and density were measured with solutions of various mole fractions of solute and these values are presented in Table III. The calculations were made following essentially the procedure of Halverstadt and Kumler[17] employing an IBM 650 Computer.[18] The molar refractivity was calculated from standard values of atomic refractivities[19] and had the value 37.20 cc. The mole fraction of each conformation was calculated using Equation 1 and the values 4.29 D and 3.17 D for μ_e and μ_a, respectively.

$$\mu^2 = N_e\mu^2_e + N_a\mu^2_a \qquad (1)$$

TABLE III

DIPOLE MOMENT DATA FOR *trans*-2-CHLOROMETHYLCYCLOHEXANONE

	Benzene Solvent, 25°	
N_2	d_{12}	ϵ_{12}
0.000000000	0.872413	2.2672
0.00152136	0.872953	2.3024
0.00198221	0.873113	2.3138
0.00273943	0.873372	2.3317
0.00323172	0.873546	2.3433
0.00403953	0.873817	2.3622
$\alpha = 23.572$	$\epsilon_1 = 2.2670$	$d_1 = 0.87242$
$\beta = 0.348$	$P_{2\infty} = 387.0$ cc.	$\mu = 4.14 \pm 0.02$D

Ultraviolet studies. The data available from the earlier work (Table IV) with the isomers of II were insufficient to make possible a real quantitative analysis of the present data. If the approximation is made that ϵ for a conformational mixture is linearly related to the composition and independent of solvent, assigning $\epsilon = 15$ to It,e and $\epsilon = 49$ to It,a, the conformational compositions in various solvents are found and are given in Table I.

TABLE IV

ULTRAVIOLET SPECTRAL DATA

Compound	Octane		Dioxane		Methanol	
	λ	ε	λ	ε	λ	ε
IIt,a	306	49	306	49	—	—
IIc,e	286	17	283	15	—	—
It	295	21	289	19	283	15

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[16] M. T. Rogers, *J. Am. Chem. Soc.*, **77**, 3681 (1955).

[17] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[18] N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

[19] J. A. Leermakers and A. Weissberger, in H. Gilman's *Organic Chemistry*, Vol. II, second ed., Wiley, New York, p. 1750.

On the Rearrangement of *t*-Cycloalkyl Hypochlorites[1]

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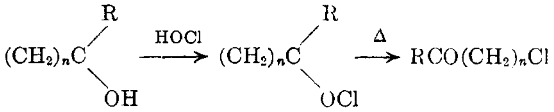
Recently the long known decomposition of *t*-alkyl hypochlorites has received renewed attention from several workers.[2] In particular, the rearrangement of *t*-cycloalkyl hypochlorites to chloro ketones[2a,b,3] interested us, as claims of generality for this reaction have been made but no report on its scope, together with experimental details, has appeared. We here report the results of an investigation on the scope of this process. 1-Methyl- and 1-phenylcycloalkanols of ring sizes five through seven were prepared and rearranged to ω-chloro ketones as shown.



$$(CH_2)_nC(R)(OH) \xrightarrow{HOCl} (CH_2)_nC(R)(OCl) \xrightarrow{\Delta} RCO(CH_2)_nCl$$

$n = 4, 5, 6$; $R = -CH_3, -C_6H_5$

Data on the products of these rearrangements are found in Tables I and II.

Yields in Table I do not necessarily represent optimum yields, but rather those yields obtained using reported techniques.[2d,e] The low yields of III and VI reflect the considerable difficulty experienced in their isolation, as well as the apparently less favorable overall reaction with this ring size. It appears, however, that ω-chloro ketones of the types given can be prepared in this relatively simple fashion from readily obtained starting compounds.

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[1] Taken from the M.Sc. thesis of Jimmy W. Hill, Loyola University, January, 1961. Some early work was done by Messrs. G. Gapski and A. Danielzadeh.

[2] (a) T. L. Cairns and B. E. Englund, *J. Org. Chem.*, **21**, 140 (1956); (b) B. E. Englund, U. S. Pat. **2,675,402**, Apr. 13, 1954, and U. S. Pat. **2,691,682**, Oct. 12, 1954; (c) A. D. Yoffe, *Chem. & Ind.*, 963 (1954); (d) D. B. Denney and W. F. Beach, *J. Org. Chem.*, **24**, 108 (1959); (e) F. D. Greene, *J. Am. Chem. Soc.*, **81**, 2688 (1959).

[3] F. D. Greene, paper presented at the 135th Meeting of the American Chemical Society, Boston, Mass., 1959, p. 44-0 of the Abstracts.