[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY]

Conformational Analysis. VIII.[1,2] The Dipole Moments of *cis*- and *trans*-2-Bromo-4-*t*-butylcyclohexanone

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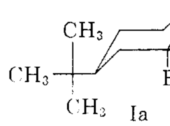
The dipole moments of *cis*- and *trans*-2-bromo-4-*t*-butylcyclohexanone were found to be 4.27 and 3.20 D., respectively, in benzene. These values prove that the stereochemistry assigned to these compounds earlier was correct. The moment of 2-bromocyclohexanone in benzene was 3.49 D., which indicates that under the experimental conditions 76% of the molecules have the bromine in the axial conformation.

Introduction

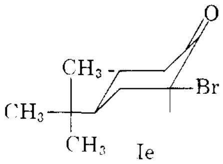
The conformational isomers of 2-bromocyclohexanone and the related 2-chlorocyclohexanone have been the subject of a substantial number of papers in the past few years.[3-10] The early conclusion of Corey[10] that the halogen of each of these compounds was mainly in the axial position was questioned by Kumler and Huitric[9] on the basis of dipole moment measurements. Subsequently it was shown that all of the available data for 2-bromocyclohexanone could be rationalized in terms of an equilibrium mixture of conformational isomers in which the axial form predominated by an amount which varied with solvent.[6] Josien and co-workers[7] and, more recently, Kozima and Yamanouchi[4] have drawn rather different conclusions concerning the position of the 2-chlorocyclohexanone conformational equilibrium. Although the conclusions of Josien rested on spectral assignments,[11] which Bellamy and Williams[12] have subsequently shown were incorrect, the question as to whether a parallelism of the spectral properties of steroidal equatorial and axial α-haloketones and their monocyclic analogs existed seemed to be deserving of an answer based on a clear-cut and unambiguous experiment. Such an experiment is described in the present work.

Results

The *cis*- and *trans*-2-bromo-4-*t*-butylcyclohexanones (I) are a pair of conformationally pure epimers which are ideally suited to solution of this problem. These compounds exist in the chair form[3] and, consequently, the *cis* isomer Ie has the bromine in the equatorial conformation. While the *trans* isomer Ia has the bromine in the axial conformation. The spectral properties of these compounds, together with the corresponding properties of the parent 4-*t*-butylcyclohexanone, were reported earlier.[5] The exact relationship of the spectral properties of monocyclic α-bromoketones to the conformational environment of the halogen atom can thus be established if an unambiguous structural assignment can be made to each of these epimers. In the present work these compounds were prepared according to the literature procedures[5] and their dipole moments were determined in benzene solvent. The experimental values obtained were 4.27 and 3.20 D.



Ia



Ie

The geometry of each compound is rather accurately known (within the limits defined by the assumption of no distortion from ideal geometry) and the dipole moment of each conformational isomer has been calculated.[6,9] The equatorial conformer Ie has the bond moments in nearly the same plane, and the moment calculated for it was much larger than for the axial epimer Ia. The observed dipole moments are in reasonable agreement with those calculated and the data are summarized in Table I.

TABLE I

DIPOLE MOMENTS OF Ia AND Ie IN BENZENE AT 25°

Compound	Dipole moments, D. Exptl.	Dipole moments, D. Calcd.[6]
Ia	3.20	2.82
Ie	4.27	4.34

The difference between the experimental and calculated moments in the case of Ia is probably due in part to the carbon–bromine bond being bent outward from the repulsion of the axial hydrogens. A bending which reduced the angle between the dipoles by 12° would be sufficient to account for the difference. It is also clear that the effect of mutual induction, if properly taken into account in Ie, has been over-estimated in Ia, and this would tend to give too small a calculated moment in the latter case by an amount which is not easy to estimate, but may be 0.1 D. or so. It can be seen, however, that the agreement between the calculated and found values for the moments is reasonable. No evidence for the existence of the flexible form[9] is apparent from these experimental data.

Most important, the configurations of Ia and Ie are now unequivocally established as being those assigned earlier[5] on the basis of spectral properties. Therefore, the suggestion of Josien,[7] that the spectral shifts characteristic of the different conformations of a halogen adjacent to a carbonyl may be reversed in steroidal compounds relative to the simple

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[1] Sponsored by the Office of Ordnance Research, U. S. Army.

[2] Paper VII, *J. Org. Chem.*, **25**, 262 (1960).

[3] N. L. Allinger, THIS JOURNAL, **81**, 5727 (1959).

[4] K. Kozima and Y. Yamanouchi, *ibid.*, **81**, 4159 (1959).

[5] N. L. Allinger and J. Allinger, *ibid.*, **80**, 5476 (1958).

[6] J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958).

[7] (a) M. L. Josien, C. Castinel, G. Chiurdoglu and E. Vanlanduyt, *Compt. rend.*, **244**, 2383 (1957); (b) M. L. Josien and C. Castinel, *Bull. soc. chim. France*, 801 (1958).

[8] A. Julg, *J. chim. phys.*, 453 (1956).

[9] W. D. Kumler and A. C. Huitric, THIS JOURNAL, **78**, 3369 (1956).

[10] (a) E. J. Corey, *ibid.*, **75**, 2301 (1953); (b) E. J. Corey and H. J. Burke, *ibid.*, **77**, 5418 (1955).

[11] S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953).

[12] L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4294 (1957).

monocyclic analogs, need not be considered further. At least in the case where the halogen is bromine,[13] the spectral properties that hold for each conformation in the α-bromo steroidal ketones carry over exactly to the related α-bromocyclohexanones.

Turning to the equilibrium between the conformational isomers of 2-bromocyclohexanone, it appeared desirable to measure the moment of this compound at the same time with the same equipment so that there would be no question as to the comparison of the data of Kumler and Huitric[9] with those of compounds Ie and Ia. The moment was measured in benzene solution and the agreement with the previous value is excellent (Table II).

TABLE II

CONFORMATIONAL ANALYSIS OF 2-BROMOCYCLOHEXANONE FROM DIPOLE MOMENT DATA AT 25°

2-Bromocyclohexanone		*axial*-2-Bromocyclohexanone, %	
Solvent	μ obsd., D.	Dipole moment measurements[a]	Infrared measurements[6]
n-Heptane	3.37[9]	85	..
Carbon tetrachloride	...	..	74
Benzene	3.49[b]		
	3.50[9]	76	60
Dioxane	3.64[9]	62	57

[a] Calculated with the equation $\mu_{obsd}^2 = N_a\mu_a^2 + N_e\mu_e^2$ where μ_a and μ_e are the experimentally obtained dipole moments for Ia (3.20 D.) and Ie (4.27 D.), respectively. Solvent independence of these constants is assumed. [b] This study.

Consequently, it seems safe to accept the values determined by Kumler and Huitric in dioxane and heptane as being directly comparable with those determined in the present work. If this is done it is possible to calculate the percentages of axial- and equatorial-2-bromocyclohexanone in various solvents more accurately than previously,[6] and the results are summarized in Table II. These values differ by about 15% from the earlier values[6] which were obtained from the calculated moments. A few of the corresponding values obtained by infrared measurements[6] are also listed for comparison, and the agreement is good.

Acknowledgment.—The authors are indebted to Dr. M. T. Rogers of Michigan State University for the use of his apparatus for the dielectric constant measurements.

Experimental

Materials.—The pure *cis*-(Ie) and *trans*-2-bromo-4-*t*-butylcyclohexanone[5] (Ia) and 2-bromocyclohexanone[6] were prepared as previously described. Compound Ia was stored in Dry Ice from when prepared until the moment was obtained. The others were stored at 0.° The purity of Ia and Ie, before and after the dipole moment measurements, was clearly established upon examination of the infrared spectrum of each in carbon disulfide solution. The *cis* isomer Ie showed a strong band at 692 cm.$^{-1}$ (equatorial C–Br stretch[14]) and this absorption was totally absent in the spectrum of the *trans* isomer Ia obtained at twice the concentration and in the parent 4-*t*-butylcyclohexanone. A definitive band for pure Ia occurred at 820 cm.$^{-1}$.

The benzene solvent employed for the dipole moment measurements was C.P. thiophene-free reagent which was dried by refluxing with (12 hours) and distillation from sodium metal.

Dipole Moment Measurements.— The apparatus used for the dielectric constant measurements has been described[15] and the measurements were made at 25° in benzene solution. The experimental data were treated according to the method of Halverstadt and Kumler[16] and the calculations were performed employing an IBM 650 computer as described.[17] The molar refractivity, identical for Ia and Ie, was calculated from standard values of atomic refractivities[18] and had the value 44.720 cc. Atomic polarization was neglected. The data are summarized in Table III.

TABLE III

DIPOLE MOMENT DATA, BENZENE SOLUTION, 25°

N_2	d_{12}	ϵ_{12}
2-Bromocyclohexanone		
0.00481544	0.876543	2.3488
.00351020	.875435	2.3268
.00266465	.874703	2.3126
.00178446	.873981	2.2972
.00109944	.873477	2.2852
.00000000	.872453	2.2678
α = 16.9305	β = 0.841754	ϵ_1 = 2.26724
d_1 = 0.8724853	$P_{2\infty}$ = 284.322	μ = 3.489 D.
cis-2-Bromo-4-*t*-butylcyclohexanone (Ie)		
0.00321371	0.875217	2.3483
.00248632	.874596	2.3313
.00172836	.873930	2.3119
.00101454	.873369	2.2931
.00042239	.872816	2.2778
.00000000	.872453	2.2678
α = 25.3443	β = 0.857930	ϵ_1 = 2.26758
d_1 = 0.8724624	$P_{2\infty}$ = 426.985	μ = 4.272 D.
trans-2-Bromo-4-*t*-butylcyclohexanone (Ia)		
0.00338668	0.875210	2.3156
.00238950	.874477	2.3020
.00160562	.873761	2.2908
.00081193	.873141	2.2795
.00054254	.872929	2.2758
.00000000	.872453	2.2678
α = 14.1259	β = 0.817925	ϵ_1 = 2.26799
d_1 = 0.8724707	$P_{2\infty}$ = 262.735	μ = 3.196 D.

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[13] The other halogens will be discussed in subsequent papers.

[14] E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959), assign absorptions at 692 and 670 cm.$^{-1}$ to the C–Br stretching frequency for the compounds *trans*- and *cis*-4-*t*-butylcyclohexyl bromide, respectively. The infrared spectra were not obtained below 670 cm.$^{-1}$ in the present work.

[15] M. T. Rogers, THIS JOURNAL, **77**, 3681 (1955).

[16] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

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

[18] J. A. Leermakers and A. Weissberger, "Organic Chemistry," Vol. II, H. Gilman, ed., J. Wiley and Sons, Inc., New York, N. Y., 1947, p. 1751.