2-Phenyl-6-hydroxy-7-methyl-(1H)2-boradihydropurine (I); (a) From 4-Amino-1-methyl-5-imidazolecarboxamide (VIII) and Dibutyl Phenylboronate.—Using method b for preparing III, the boraropurine I was obtained from the imidazolecarboxamide VIII[17] in 63% yield. It dissolved in a large volume of ethanol on prolonged boiling, but no solid separated on cooling. Crystals of I began to form only when the solution had been concentrated to a very small volume; Compound I had no m.p., subliming slowly above 300° (copper block).

Anal. Calcd. for $C_{11}H_{11}ON_4B$: C, 58.41; H, 4.87; N, 24.78; B, 4.9. Found: C, 58.40; H, 4.78; N, 24.66; B, 4.9.

(b) From VIII and Phenylboronic Anhydride.—Using method c for III, Compound I was obtained in 97% yield.

2,8-Diphenyl-6-hydroxy-(1H)2-bora-8-azidihydropurine (X).—A mixture of 3-amino-2-phenyl-1,2,5-triazole-4-carboxamide (XI)[25] (3.0 g.) and dibutyl phenylboronate (3.4 g.) was heated to 160° until the initial vigorous reaction had subsided. The temperature was then raised to 190°. After 3 hours the mixture was cooled and the solid which had separated filtered and washed with hot dry benzene to give the borazadihydropurine X as pale brown crystals (1.0 g., 23%). Crystallization from ethanol gave only XI; X

(25) E. Richter and E. C. Taylor, *J. Am. Chem. Soc.*, **78**, 5850 (1956).

was insoluble in all other solvents. Sublimation at 240° (2 mm.) gave colorless needles, m.p. 300°, which gave a poor carbon analysis.

Anal. Calcd. for $C_{15}H_{12}ON_5B$: C, 62.28; H, 4.15; N, 24.22; Found: C, 60.75; H, 4.24; N, 24.36.

2-Phenyl-2-boradihydroperimidine (VII).—Recrystallized "pure" grade 1,8-diaminonaphthalene (1.9 g.) and phenylboronic anhydride (1.3 g.) were mixed intimately and fused under high vacuum for 1 hour at 100°; the liquid bubbled and turned brown. The temperature was raised briefly to 140° and then the liquid was allowed to cool to a glass. This was crystallized from ether–petroleum ether (b.p. 40–60°) to give 2-phenyl-2-boradihydroperimidine (2.1 g., 71%), m.p. 92–95°. Sublimation at 180° (1 mm.) gave the material pure in very pale yellow needles (which turned deep red on standing in air for 4 days), m.p. 95–96°.

Anal. Calcd. for $C_{16}H_{13}N_2B$: C, 78.69; H, 5.33; N, 11.47; mol. wt., 244. Found: C, 78.55; H, 5.15; N, 11.22; mol. wt. (Rast), 225.

The Dipole Moment and Structure of Some α-Halocamphors, α-Haloindanones and 2-Bromo-4-phenylcyclohexanone

BY W. D. KUMLER, N. PEARSON AND F. V. BRUTCHER, JR.

The dipole moments of α-chlorocamphor, α'-chlorocamphor, α-bromocamphor, α,α'-dibromocamphor, 1-chloro-2-indanone, 1-bromo-2-indanone and 2-bromo-4-phenylcyclohexanone have been measured in different solvents. α-Chlorocamphor and α'-chlorocamphor have identical moments indicating that the chlorine atoms occupy an intermediate bisectional position between axial and equational in these compounds. The α-haloindanones have smaller moments than the α-halocamphors by an amount expected to result from the presence of the phenyl ring. The moments are in keeping with the geometry, about the halogen and carbonyl groups, being essentially the same in the two cases. The lack of variation of the dipole moment with change of solvent in the case of the halocamphors, indicates a rigid five-member ring structure, and the variation of the moment in case of the indanones suggests some flexibility in this five-membered ring structure. The moment of 2-bromo-4-phenylcyclohexanone indicates the bromine is in the axial position.

Introduction

Dipole moments have been of use in the elucidation of the structure of α-halocyclohexanones and α-halocyclopentanones.[1–4] Infrared spectra[4] have been used to study the conformation of substituted cyclopentanes including the important α-halocamphors and α-haloindanones. It is of interest to measure the dipole moments to see if the two methods are in agreement with regard to the conformation of these compounds.

Experimental

The dipole moments were measured using an apparatus described previously,[5] and the solvents were purified as before.[5] The dipole moments were calculated using the equation and method of Halverstadt and Kumler.[6]

(1) W. D. Kumler and A. C. Huitric, *J. Am. Chem. Soc.*, **78**, 3369 (1956).

(2) N. L. Allinger, J. Allinger and N. A. Le Bel, *ibid.*, **82**, 2926 (1960).

(3) N. L. Allinger, J. Allinger, L. A. Frieberg, R. F. Czaja and N. A. Le Bel, *ibid.*, **82**, 5876 (1960).

(4) F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, *ibid.*, **81**, 4915 (1959).

(5) W. D. Kumler, *ibid.*, **62**, 3292 (1940).

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

$$P_{2_0} = \frac{3\alpha v_1}{(\epsilon_1 + 2)^2} + (v_1 + \beta)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$

$$\mu = 0.01281 \sqrt{(P_{2_0} - P_{E_a})T}$$

The plots of ϵ_{12} *versus* ω_2 and v_{12} *versus* ω_2 were straight lines within the limits of experimental error. The values of ϵ_1 and v_1 were obtained by the method of least squares. The standard error in the dipole moments were calculated from the equation $\delta \mu = 0.0046 \, M\delta\alpha/\mu^7$ and the standard error in α from the equation[7,8]

$$\delta\alpha = \pm \left\{ \frac{n}{n-2} \left[\frac{\Sigma(\epsilon' - \epsilon_{12})^2}{n\Sigma(\omega_2)^2 - (\Sigma\omega_2)^2} \right] \right\}^{1/2}$$

The errors from scatter of the points for specific volume do not need to be considered since even large errors in β produce only very small errors in the dipole moment.[9] The α-halocamphors and α-haloindanones were from the same samples or were prepared in the same way and had the same melting point as the compounds used in the infrared paper.[4] The 2-bromo-4-phenylcyclohexanone was a carefully purified sample supplied by Professor E. J. Corey to whom we express our thanks. We also wish to than Howard Schultz for making some of the preliminary measurements.

(7) Private communication, Dr. E. W. Randall and Dr. Roger Raab.

(8) C. G. LeFévre and R. J. W. Le Févre, *J. Chem. Soc.*, 404 (1953).

(9) K. B. Everard, R. A. W. Hill and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

TABLE I
DIPOLE MOMENT DATA

Compound	Solvent[a]	ϵ_1	v_1	α	β	$P_{2\infty}$	P_{E_2}[b]	μ
α-Chlorocamphor	H	1.91141	1.48161	6.3734	−0.59549	384.32	47.10	4.11 ± 0.03
	B	2.25683	1.15287	9.8994	− .24074	388.39	47.10	4.12 ± .02
	D	2.19738	0.97842	10.9053	− .08274	386.11	47.10	4.11 ± .04
α'-Chlorocamphor	H	1.90714	1.48186	6.3954	− .59579	386.10	47.10	4.11 ± .01
	B	2.25802	1.15304	9.6369	− .29929	391.11	47.10	4.14 ± .02
	D	2.20667	0.97901	10.8406	− .0688	384.64	47.10	4.10 ± .01
α-Bromocamphor	H	1.90817	1.48170	5.0850	− .73599	382.11	50.00	4.06 ± .01
	B	2.26312	1.15198	7.4965	− .38516	382.01	50.00	4.06 ± .04
	D	2.19974	0.97828	9.10497	− .23928	398.94	50.00	4.17 ± .01
α,α'-Dibromocamphor	H	1.90784	1.48170	4.4598	− .88718	445.33	57.77	4.39 ± .01
	B	2.25966	1.15304	6.0944	− .54809	415.71	57.77	4.22 ± .04
	D	2.20515	0.97826	7.6249	− .41171	442.71	57.77	4.38 ± .06
1-Chloro-2-indanone	H	1.90845	1.48201	6.6582	− .7537	351.04	41.84	3.92 ± .06
	B	2.26339	1.15362	8.9313	− .3739	321.80	51.84	3.73 ± .05
	D	2.21940	0.97814	12.3915	− .2030	377.59	41.84	4.11 ± .02
1-Bromo-2-indanone	H	1.91032	1.48197	4.8689	− .8823	328.26	44.74	3.76 ± .03
	B	2.26398	1.15365	5.9906	− .5088	281.03	44.74	3.43 ± .06
2-Bromo-4-phenylcyclohexanone	H	1.91124	1.48179	2.5380	− .83669	224.75	58.07	2.88 ± .04
	D	2.20221	0.97810	4.0667	− .26987	222.35	58.07	2.86 ± .04

[a] H = heptane, B = benzene, D = dioxane. [b] P_{E_2} values are the molar refractions as calculated from electron group refractions for the D sodium line measurements at 30°.

TABLE II
DIPOLE MOMENT MEASUREMENTS AT 30°

ω_2	ϵ_{12}	v_{11}

α-Chlorocamphor in heptane

ω_2	ϵ_{12}	v_{11}
0.00075387	1.91627	1.48117
.00123400	1.91885	1.48085
.00231863	1.92600	1.48026
.00271089	1.92861	1.47998

α-Chlorocamphor in benzene

0.00038266	2.27141	1.15387
.00082562	2.27534	1.15372
.00114700	2.27874	1.15361
.00145317	2.28179	1.15349

α-Chlorocamphor in dioxane

0.00059632	2.20404	0.97836
.00107703	2.20884	.97833
.00167099	2.21572	.97829
.00242507	2.22383	.97821

α'-Chlorocamphor in heptane

0.0	1.90700	1.48188
.00066867	1.91153	1.48143
.00117683	1.91476	1.48117
.00177145	1.91842	1.48081
.00382650	1.93158	1.47958

α'-Chlorocamphor in benzene

0.00079808	2.26575	1.15280
.00159236	2.27342	1.15257
.00265267	2.28336	1.15225
.00361900	2.29304	1.15196

α'-Chlorocamphor in dioxane

0.0	2.20666	0.97902
.00026698	2.20954	.97899
.00086928	2.21625	.97895
.00128165	2.22052	.97893
.00167250	2.22479	.97889
.00235811	2.23220	.97885

α-Bromocamphor in heptane

0.0	1.90830	1.48166
.00051930	1.91083	1.48132
.00091982	1.91981	1.48106
.00156846	1.91606	1.48055
.00196639	1.91807	1.48026
.00278387	1.92242	1.47963
.00371976	1.92713	1.47895

α-Bromocamphor in benzene

0.0	2.26297	1.15198
.00044104	2.26654	1.15182
.00085916	2.26907	1.15164
.00124438	2.27299	1.15151
.00168031	2.27604	1.15130
.00216123	2.27909	1.15116
.00296150	2.28519	1.15084

α-Bromocamphor in dioxane

0.0	2.19986	0.97830
.00057183	2.20483	.97814
.00084712	2.20736	.97806
.00133713	2.21189	.97794
.00167482	2.21511	.97787
.00219134	2.21956	.97777
.00269206	2.22427	.97763

α,α'-Dibromocamphor in heptane

0.0	1.90796	1.48166
.00064909	1.91049	1.48110
.00112113	1.91293	1.48081
.00178972	1.91589	1.48012
.00239911	1.91859	1.47959
.00272114	1.91990	1.47925
.00379588	1.92478	1.47832

α,α'-Dibromocamphor in benzene

0.00073443	2.26392	1.15263
.00120925	2.26724	1.15240
.00148102	2.26872	1.15221
.00165217	2.26985	1.15214
.00209551	2.27229	1.15190
.00265055	2.27578	1.15159

TABLE II (continued)

ω_2	ϵ_{12}	ν_{12}
α,α'-Dibromocamphor in dioxane		
0.0	2.20509	0.97825
.00044894	2.20857	.97808
.00086532	2.21180	.97791
.0010699	2.21354	.97779
.0013558	2.21528	.97771
1-Chloro-2-indanone in heptane		
0.0013426	1.91885	1.48103
.0017535	1.92111	1.48063
.0022467	1.92416	1.48034
.0030801	1.93035	1.47969
1-Chloro-2-indanone in benzene		
0.00039627	2.26698	1.15349
.00058033	2.26828	1.15336
.00086990	2.27116	1.15329
.00106946	2.27308	1.15323
1-Chloro-2-indanone in dioxane		
0.00049409	2.20003	0.97804
.00079013	2.20395	.97798
.00102110	2.20657	.97793
.00134188	2.21061	.97786
.00164808	2.21441	.97781
1-Bromo-2-indanone in heptane		
0.0012489	1.91623	1.48085
.0015879	1.91824	1.48059
.0020370	1.92024	1.48019
.0033169	1.92643	1.47904
1-Bromo-2-indanone in benzene		
0.00025888	2.26541	1.15353
.00047608	2.26689	1.15340
.00080857	2.26898	1.15323
.00129382	2.27151	1.15301
2-Bromo-4-phenylcyclohexanone in heptane		
0.00093798	1.91362	1.48106
.0015715	1.91536	1.48042
.0020377	1.91623	1.48006
.0033225	1.91972	1.47904
2-Bromo-4-phenylcyclohexanone in dioxane		
0.00045341	2.20395	0.97799
.00076295	2.20526	.97789
.00118178	2.20700	.97779
.00143728	2.20831	.97772
.00281188	2.21354	.97735

Results and Discussion

In a previous paper,[4] it was suggested because the infrared shifts were identical within the experimental error for α- and α'-chlorocamphor, that the chlorine in each case occupies an intermediate,
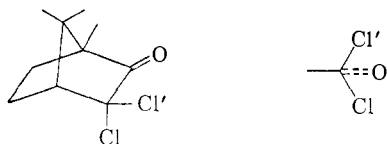
bisectional position between axial and equatorial positions. That the near methyl of the *gem*-dimethyl group in case of the α'-chlorocamphore

did not have an n.m.r. peak[10] that differed from the peak for the far methyl of the *gem*-dimethyl group shows that the α'-chlorine does not interact with the near methyl group and is in agreement with this view of the structure. The α,α'-dibromocamphor, on the other hand, has a different n.m.r. peak for the near methyl of the *gem*-dimethyl group, thus indicating that the α'- bromine is interacting with the near methyl. In Table I it is seen that the moments of the α- and α'-chlorocamphors are identical. This fact is in complete agreement with the previous interpretation that both the α- and α'-chlorine–carbon bonds make the same angle with the carbonyl bond and, therefore, the chlorine atoms are in a bisectional position, half-way between an axial and equational position in these molecules. In the previous paper,[4] it was pointed out that the dipole moment values of the α- and α'-chlorocamphor were nearly identical. The values in Table I and α- and α'-chlorocamphor were redetermined with greater accuracy, and the new values are identical within the experimental error.

There also is no variation of the moment of either of these compounds with change of solvent, which means that there are no interaction forces operating which lead to a different angle between the dipoles when the molecule is placed in a different environment.

The dipole moment of α-bromocamphor has very nearly the same value as the moment for the α- and α'-chlorocamphors. In dioxane, the moment of α-bromocamphor is 0.11 D. larger than in heptane or benzene. It is significant that α-bromocyclopentanone has a larger moment in dioxane, 3.64 D., than it has in heptane, 3.49 D., or benzene, 3.47 D.

α,α'-Dibromocamphor has a higher moment than α-bromocamphor by 0.2–0.3 D., which is the increase expected because of the presence of the additional C–Br dipole. Two dipoles of magnitude 2.0 D. and an angle of 110° have a resultant of 2.3 D. The moment in benzene is 0.17 and 0.18 D. lower than in heptane or dioxane, respectively. This difference is about three times the standard error. The moment of 1-chloro-2-indanone is also lower in benzene than it is in heptane or dioxane, and that of 1-bromo-2-indanone is lower in benzene than it is in heptane. The latter compound decomposed in dioxane, the solutions becoming colored, so it could not be measured in this solvent. It appears from these examples that some halogen compounds have lower moments in benzene than they do in heptane or dioxane, while other halogen compounds, such as α-chlorocamphor α'-chlorocamphor and α-bromocamphor, do not show this effect.

The compounds that have the lower moment in benzene are the ones that show some flexibility, such as the indanones or have given evidence of intramolecular group interaction such as α,α'-dibromocamphor. It is conceivable that the low moment of such compounds in benzene is a consequence of the greater polarizability of this solvent.

(10) W. D. Kumler, J. H. Shoolery and F. V. Brutcher, Jr., J. Am. Chem. Soc., **80**, 2533 (1960).

From the fact that the infrared shift is the same in the α-haloindanones as in the α-halocamphors, one would expect the angles between the carbonyl and the carbon–halogen dipoles to be the same in the two cases, and therefore the dipole moment arising from this part of the molecule to be the same. However, that does not mean the over-all dipole moment will be the same because the phenyl ring in the α-haloindanones would be expected to give rise to a dipole of about 0.4 D. in approximately the opposite direction to that of the resultant of the C=O and C—X dipole, and, therefore, one would expect the α-haloindanones to have lower moments by about this amount. With the exception of the moment of 1-chloro-2-indanone in dioxane, this is the case. The four cases of the two α-haloindanones, measured in heptane and benzene, have lower moments than the corresponding α-halocamphors by from 0.14 to 0.63 D. with an average of 0.37 D.

That the moment of the α-haloindanones differed in the solvents by 0.19, 0.33 and 0.38 D., while the moment of the α-halocamphors differed by only 0.01, 0.01, 0.30, 0.04, 0.00 and 0.11 D. suggests that the α-haloindanone system is not as rigid as the α-halocamphor system. In a previous paper,[10] it was observed that the n.m.r. peak for the two hydrogens on the number 3 carbon in the case of 1-bromo-2-indanone was much broader than in

the case of the corresponding chloro compound, which suggests a change in the ring with the heavier bromine attached, indicating some flexibility.

The fact that 1-bromo-2-indanone has a smaller moment than the corresponding chloro compound while in the camphor series the chloro and bromo compounds have the same moment may result from a larger induction in the more polarizable bromine by phenyl.

The moment of 2-bromo-4-phenyl-cyclohexanone is considerably lower than that of the other compounds and is the same in heptane and dioxane. The fact that the moment does not vary with solvent indicates this is not a mixture of axial and equatorial forms, and the fact that the moment is as small as it is suggests the bromine is in the axial position. The dipole moment of this compound with bromine axial can be calculated from the moment of trans-2-bromo-4-t-butylcyclohexanone of 3.20 D.[2] which is known to have the bromine axial. The phenyl group gives rise to a moment of 0.40 D., which makes an angle of about 140° with the resultant of the C=O and C—Br dipoles. This reduces the resultant by 0.30 D. so the calculated moment of 2-bromo-4-phenyl-cyclohexanone would be 3.20 D. − 0.30 D. = 2.90 D., a value in excellent agreement with the observed moment.

The Synthesis of cis-9-Carbomethoxy-1a-carbomethoxymethyl-8-methyl-cis-1,1a,2,3,4,-4a-Hexahydrofluorene, A Degradation Product of Gibberellic Acid[1]

BY HERBERT O. HOUSE, VASKEN PARAGAMIAN AND DAVID J. WLUKA

The racemate of the title compound has been synthesized and shown to be identical, but for lack of optical activity, with a transformation product of epiallogibberic acid 3, a degradation product of gibberellic acid 1.

The reaction of gibberellic acid (1) with boiling hydrazine hydrate has been found[2] to yield allogibberic acid (2, m.p. 196–198°) and epiallogibberic acid (3, m.p. 244°) via the intermediate gibberellenic acid 4. Subsequent transformations[2,3] furnished the keto diesters 5 (m.p. 205–207°) and 6 (m.p. 168–169°) and demonstrated[2] the epimeric relationship at position 4a between the hexahydrofluorenes 5 and 6. Both these studies[2] and other work[4] has supported the stereochemistry indicated in structures 2, 3, 5 and 6.

We have reduced each of the keto esters 5 and 6[5] to the corresponding diesters 7 (m.p. 118.5–119.5°) and 8a (m.p. 101° or 124°) by the reaction of the ketones with 1,2-ethanedithiol and then desulfurization with Raney nickel.

As confirmation of the aforementioned structural and stereochemical assignments we have synthe-

sized the racemate of structure 8. Our synthesis utilized the previously described[6] hydroxy ester 9 which was converted by reaction with hydrogen bromide in ether to a mixture of the crude bromo ester 10 and the crystalline lactone 11. As noted previously,[6] saponification of the lactone 11 followed by acidification of the corresponding salt of the hydroxy acid resulted in immediate formation of the starting lactone.

Reaction of the crude bromide 10 with sodium cyanide in dimethyl sulfoxide afforded a mixture of cyano esters isolated as the cyano acids 12 and 13. Each of these cyano acids 12 and 13 was converted to the corresponding amide acids 14a and 14b which were converted to the esters 15a and 15b by reaction with diazomethane. Heating the amide acid 14 or reaction of the ester 15b with sodium methoxide afforded the imide 16. Hydrolysis of this imide 16 followed by esterification of the resulting acid mixture with diazomethane yielded the ester 15a and a new ester 17. Inspection of molecular models leaves no doubt that the

(1) This research has been supported by National Science Foundation Grant, No. G9486.

(2) J. F. Grove and T. P. C. Mulholland, J. Chem. Soc., 3007 (1960).

(3) T. P. C. Mulholland, ibid., 2693 (1958).

(4) G. Stork and H. Newman, J. Am. Chem. Soc., 81, 3168 (1959).

(5) We are indebted to Dr. J. F. Grove for supplying us with a sample of this substance.

(6) H. O. House, V. Paragamian and D. J. Wluka, ibid., 82, 2561 (1960).