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CONFORMATIONAL EQUILIBRIA OF 8-HALOGENO-8,9,10,11-TETRAHYDRO-7*H*-CYCLOOCTA(*de*)NAPHTHALEN-9-ONES[1]

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The titled α-haloketones (**1**-**3**) were prepared and the conformations were studied based on the NMR spectra. It was found that **1**-**3** exist as an equlibrium mixture of axial-boat (**ab**) and equatorial-boat (**eb**) conformers in solution with the **ab** overwhelmingly predominant ($-\Delta G°(101^{o}C)=-1.6$ kcal/mol). The conformation **ab** is in a puckered form in all of **1**-**3** as a result of steric compression effect.

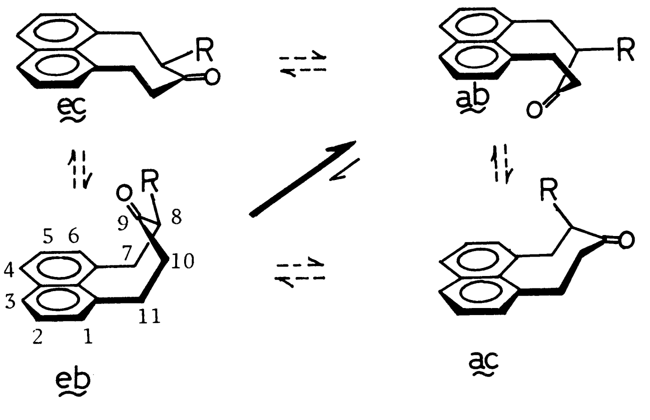
Recently, we have studied the conformations of the eight-membered peri rings in some derivatives of 8,9,10,11-tetrahydro-7*H*-cycloocta(*de*)naphthalene, the stereochemistry of which is very interesting because they are strained owing to the peri interaction.[2-5] Here, we studied the conformational equilibria of α-haloketones (**1**-**3**)[6] of this series of compounds and found that the *axial* isomers in these compounds were unusually stable compared to those in the cyclohexane system.

The reaction of ketone (**4**) with bromine in acetic acid gave 8-bromoketone (**2**), from which the chloride (**1**) and the iodide (**3**) were obtained by the usual halogen exchange reactions employing lithium chloride and sodium iodide, respectively.

At -31.8^{0}, the ^{1}H-NMR spectrum of 8,10,10-trideuterated bromoketone (**2**-*d*$_3$) in the high field region consists of two AB quartets of equal intensities arising from the H_7- and H_{11}- protons, respectively. As the temperature is elevated, these signals broaden and show again two AB patterns above 60^{0}. On the other hand, the proton decoupled ^{13}C-NMR spectrum of **2** shows only a single line for each of the peri ring carbons of **2** at low temperature. Thus it became clear that **2** exists predominantly in one conformation at low temperature, which undergoes ring inversions at ambient temperature. A similar result was obtained for **1** and **3**. Analysis of the low-temperature spectra gives chemical shifts and coupling constants of all the peri ring protons of **1**-**3**, which are summarized in Table 1.

As can be seen in the table, the H_7-*interior* proton of **1**-**3**, which is greatly deshielded as a result of the steric compression,[2-5,7] is coupled strongly with an adjacent H_8 methine proton (12.0-13.5Hz). Thus it is suggested that the conformation of **1**-**3** is *axial*-boat (**ab**), because the *interior* benzyl proton of the boat conformation is situated in a position *trans* to an adjacent *equatorial* proton and thus a strong coupling is expected between these protons.[2-5] The strong vicinal coupling between the H_{11}-*interior* and H_{10}-*equatorial* protons (13.2-13.9 Hz) together with the long range coupling between the H_8- and H_{10}-*equatorial* protons (2.0 Hz) also clearly suggests the **ab** conformation. Moreover, it is supported by the fact that the H_{10}-*axial* proton of **1**-**3** resonates at a field much lower than that of the halogen-free ketone (**4**)[3] ($\Delta\delta$0.63-0.98). Marked

1, R = Cl
2, R = Br
3, R = I
4, R = H



shieldings of C-10 carbon in **1**-**3** compared to that in **4**[3] result from γ-effect, which is well explained by the **ab** conformation as was observed in 8-alkylketones[4] (Table 2).

On the other hand, the IR C=O absorption bands of **1**-**3**, the shift values of which ($\Delta\nu$) are also consistent with the **ab** conformation[8] (Table 2), are unsymmetrical, somewhat broader on higher frequency sides. This indicates that a small fraction of each compound of **1**-**3** assumes also the *equatorial* conformation at ambient temperature. It is most likely that this conformation is boat (**eb**) rather than chair (**ec**), because the chair, bearing *eclipsed* strains about the C_7-C_8 and C_{10}-C_{11} bonds, is much less favored for the peri-8 ring system as described before.[2-5] Consequently, **1**-**3** exist as an equilibrium mixture of the **ab** and **eb** conformers in solution at room temperature with the **ab** overwhelmingly predominant.

The populations of the minor isomer (**eb**) in **1**-**3** can be estimated from the high-temperature averaging spectra in the usual manner,[9] by considering that the interchange of the conformational isomers between **ab**$\rightleftharpoons$**eb** is accompanied by an exchange of the vicinal couplings between $J_{in,eq}$ and $J_{ex,ax}$ in the peri-8 ring system.[3] This shows that the conformational isomer ratios (**eb**/**ab**) are ~1/9 for both **2** and **3** at 101°, which corresponds to the free energy difference ($-\Delta G^0$) of ~-1.6 kcal/mol.[10] The unusually greater stability of the *axial* isomers in **1**-**3** as compared to those in α-halocyclohexanones[11] seems quite reasonable, because steric interactions in **ab** are only one half of those in the *axial* isomers of the cyclohexane rings, whereas the *equatorially* substituting group in **eb** bears a *gauche* arrangement with the C_7-peri bond which is absent in the cyclohexane system.[4] The interconversion between **ab** and **eb** in **1**-**3** is explained most reasonably by a process with pseudorotations of the peri bonds as in the parent ketone (**4**)[3] and in related compounds.[4,5]

Although the conformation **ab** seems most favored for **1**-**3** from both steric and electrostatic points of view, it still involves a severe steric repulsion due to the great proximity of the *interior* benzyl protons (distance 0.63 A).[12] Thus it is expected that the **ab** is in a distorted form in all of **1**-**3** by the compression of the *interior* protons. Table 1 shows that the vicinal coupling constants, $J_{10ax,11ex}$ is very small compared to $J_{10eq,11ex}$, though the *exterior* proton in **ab** almost bisects the angles between the *axial* and the *equatorial* protons. This fact is adequately explained by the ring distortion described above, by which the dihedral angle of H_{10ax}/H_{11ex} is increased ($\phi > 60^0$), while that of H_{10eq}/H_{11ex} is decreased ($\theta < 60^0$).

In addition, the distortion of **ab** is also clearly indicated by the R-values for the C_{10}-C_{11} bond shown in Table 1, which are rather small compared to those of the normal *staggered* conformation.[13] However, this distortion is puckering, not flattening, in contrast with the case of

Table 1. ^{1}H-NMR Data of 1-3 in $CDCl_3$.[a]

	H_{7in}	H_{7ex}	H_{8eq}	H_{10ax}	H_{10eq}	H_{11in}	H_{11ex}	$\Delta\delta$[e]	R-value[f]
1[b]	4.71	3.53	4.34	3.80	2.51	~4.60	3.13	0.63	1.3
(R=Cl)	13.8	13.8	12.0	13.2	13.2	~15	~15		
	12.0	6.5	6.5	5.5	13.2	13.2	6.5		
			2.0	2.8	6.5	5.5	2.8		
					2.0				
2[c]	4.83	3.51	4.33	3.91	2.52	4.52	3.08	0.74	1.3
(R=Br)	14.3	14.3	13.0	14.0	14.0	15.2	15.2		
	13.0	6.3	6.3	6.0	13.9	13.9	6.5		
			2.0	2.5	6.5	6.0	2.5		
					2.0				
3[d]	4.99	3.45	4.53	4.15	2.58	4.52	3.06	0.98	1.3
(R=I)	14.2	14.2	13.5	14.2	14.2	~15	~15		
	13.5	6.0	6.0	6.0	13.4	13.4	6.6		
			2.0	2.4	6.6	6.0	2.4		
					2.0				

[a] Underlined values denote chemical shifts (δ) from TMS and the values below them denote coupling constants (J) in Hz. [b] At -28.8°. [c] At - 31.3°. [d] At -25.6°. [e] Chemical shifts of the H_{10ax} proton relative to that of 4. [f] The trans/cis ratios of the vicinal coupling constants for the C_{10}-C_{11} bond.

Table 2. IR[a] and ^{13}C-NMR[b] Data of 1-3.

	C-7	C-8	C-9	C-10	C-11	ν(C=O)	$\Delta\nu$[g]
1[c]	43.8	62.4	206.5	40.1	33.4	1714	11
2[d]	43.9	52.4	206.9	40.1	33.4	1707	4
3[e]	45.4	30.6	207.5	39.6	33.4	1698	-5
4[f]	34.1	46.0	213.9	46.0	34.1	1703	

[a] In $CHCl_3$ at room temperature. [b] δ from internal TMS in $CDCl_3$. [c] At -40.5°. [d] At -68.7°. [e] At -44.6°. [f] Ref. 4 and 5. [g] Frequency shift from 4.

the previously investigated compounds such as six-membered rings[13] or benzocycloheptene systems.[14] This is ascribable to the difference in the ring system, and is a unique feature of the peri-8 ring system of naphthalene.

Comparison of the vicinal coupling constants between 1-3 and the halogen-free ketone (4) reveals that the $J_{ax,ex}$ value in 1-3 is larger (2.4-2.8 Hz) than that in 4,[15] while the $J_{eq,ex}$ value in 4 is large (7.5 Hz)[3] compared to those in 1-3 (6.5-6.6 Hz). Thus, by considering the relation between the ring distortion and the dihedral angle mentioned above, it is apparent that the peri rings of 1-3 are less distorted than that of 4. This may be caused by the 1,3 -diaxial interaction between the hydrogen and the halogen atoms in 1-3, because as is shown in the molecular model, the *axial* positions at C_8 and C_{10} are compressed by the van der Waals repulsion between the *interior* benzyl protons in **ab**. Then this is a novel type "Reflex effect" observed in the rings other than the cyclohexane system.[8]

It is of interest to note that the shift values ($\Delta\delta$) of the H_{10}-*axial* protons in **1**-**3** are proportional to the van der Waals radii as well as to the electronegativity of the substituting halogen atoms. It may be expected that the van der Waals forces and/or the paramagnetic anisotropy effects are the most important factors in determining the shift of the proton when it occupies the 1,3-*diaxial* position with respect to the substituting group in the molecule.

References and Footnotes

(1) Part V of studies on 8,9,10,11-tetrahydro-7*H*-cycloocta(*de*)naphthalenes; part IV, ref. 5; part III, ref. 4; part II, ref. 3.

(2) T. Kamada, N. Wasada and O. Yamamoto, *Bull. Chem. Soc. Japan*, **49**, 275 (1976).

(3) T. Kamada and O. Yamamoto, *Chem. Lett*. 843 (1976).

(4) T. Kamada and O. Yamamoto, *Tetrahedron Lett*. 691 (1977).

(5) T. Kamada and O. Yamamoto, *ibid*, 1341 (1977).

(6) All new compounds gave satisfactory spectral data and elemental analysis. **1**, mp 193-194°; **2**, mp 169-170°; **3**, mp 138-139°.

(7) P. T. Lansbury, *Accounts. Chem. Res*., **2**, 210 (1969), and references cited therein.

(8) E. L. Eliel, N. L. Allinger, S. T. Angyal, and G. A. Morrison, "*Conformational Analysis*", Interscience Publishers, New York (1965).

(9) The population of **eb** (P_e) is obtained from the relationship: $P_e = (J_{av} - J_{7in,8eq})/(J_{10ax,11ex} - J_{7in,8eq})$, where J_{av} is the averaged coupling constant.

(10) The (**eb**/**ab**) value was not obtained for **1** because of the overlapping of signals.

(11) Y. H. Pan and J. B. Stothers, *Can. J. Chem.* **45**, 2943 (1967).

(12) Interatomic distances were calculated according to the literature; E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.* **77**, 2505 (1955).

(13) J. B. Lambert, *Accounts Chem. Res.* **4**, 87 (1971).

(14) M. St-Jacque and C. Vaziri, *Org. Magn. Resonance*, **4**, 77 (1971); L. Canuel and M. St-Jacque, *Can. J. Chem.* **52**, 3581 (1974).

(15) The $J_{ax,ex}$ value of **4** is small enough not to be obtained; ref. 3.

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