## Intramolecular Hydrogen Bonds. IX.<sup>1)</sup> Intramolecular Hydrogen Bonding in $\omega$ -Haloalkanols

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Some infrared spectroscopic investigations have been reported on intramolecular hydrogen bonding in a number of haloalkanols in non-polar However, the alkanols investigated solvents. have been confined to those with the halogen in the position 2 or 3 relative to the hydroxyl group in both acyclic<sup>2-8</sup>) and alicyclic systems.<sup>9,10</sup>) While 2-haloethanols<sup>4,8</sup>) and alicyclic 1, 3-diaxial halohydrins<sup>9</sup>) are internally bonded, 3-chloropropanol<sup>3)</sup> is internally unbonded. However, it has not yet been determined whether other 3-halopropanols and higher  $\omega$ -haloalkanols are internally bonded, especially when the halogens are higher

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in proton-accepting ability than chlorine.\*1 This problem has now been solved by means of infrared spectroscopy.

Table 1 summarizes the haloalkanols examined and the data on the apparent OH-stretching bands of their dilute carbon tetrachloride solutions. The two, partially-resolved bands of the 2-haloethanols, due to the free and the bonded OH groups respectively, are essentially the same in both peakfrequency and band-shape as those reported in the literature.<sup>4,8</sup> The four 3-halopropanols show only one band with a maximum at  $3640 \text{ cm}^{-1}$ ; this band is somewhat broadened on the lower frequency side. This general shape of the band is characteristic of ordinary free primary hydroxyl

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<sup>\*1</sup> The ability increases with the halogen in the order: F < Cl < Br < I, as is indicated by the numerical differences  $(\Delta \nu)$  between the frequencies of the in-ternally-bonded and unbonded hydroxyl groups of 2-haloethanols<sup>4,8</sup>) and of *o*-halophenols.<sup>11</sup>) However, it is not related to the enthalpy of the formation of the hydrogen bond.8,11)

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$X-(CH_2)_n-OH$		Вр		1	4	
n	x	°C/mmHg	$n_{\mathrm{D}}^{20}$	$\nu_{OH}, cm^{-1}$	$\Delta \nu_{1/2}  \mathrm{cm}^{-1}$	ε
2	Cl	67/47	1.4408	3603 3631	ca. 30 ca. 30	56 23
2	Br	58/24	1.4933	3590 3632	ca. 20 ca. 30	46 25
3	$\mathbf{F}$	128	1.3843	3640	30	63
3	Cl	60/11	1.4443	3642	27	68
3	Br	81/21	1.4836	3642	26	68
3	I	73/3	1.5693	3640	23	55
4	Cl	74/9	1.4525	3641	28	65
5	Cl	99/18	1.4537	3642	30	66
6	Br	114/10	1.4817	3641	29	68

TABLE 1. PHYSICAL CONSTANTS AND INFRARED DATA OF  $\omega$ -haloalkanols

groups.<sup>12</sup>) The simple graphical separation<sup>13</sup>) of the broadened part from the band shows that it is centered at about  $3625 \text{ cm}^{-1}$  and has a relative intensity of about one-fourth. The other higher  $\omega$ -haloalkanols show the same results.

From the above findings it can be concluded that no halogen atom has proton-accepting ability enough to form a six-membered or a larger ring through the intramolecular hydrogen bonding. The fact that even the 3-halopropanols are internally unbonded seems to indicate that the enthalpy of the intramolecular hydrogen bond formation is too small compared with the loss in entropy associated with it. When the loss in entropy, which is due to the decrease in rotational degrees of freedom around all the single bonds pertaining to the ring formation, is relatively small, the hydrogen bonding is possible. In fact, the hydrogen bonding occurs in  $5\beta$ ,  $6\alpha$ -dibromocoprostan- $3\beta$ ol<sup>9)</sup> where the 5 $\beta$ -bromine and the 3 $\beta$ -hydroxyl are fixed in a 1, 3-diaxial configuration convenient for forming the hydrogen bond; in this case, the loss in entropy should be due to only the decrease in rotational degrees of freedom around the C-O bond.

## Experimental

Haloalkanols. The 2-haloethanols were commercial products, while the others were prepared by the methods described in the literature, though in some cases with some modifications. 3-Chloropropanol was obtained by treating trimethyleneglycol with acetyl chloride14) and by refluxing the resultant mixture of chloropropanol and chloropropyl acetate for one hour in a 1.5% methanolic solution of hydrogen chloride. 3-Fluoropropanol was prepared from chloropropanol

and potassium fluoride in ethyleneglycol.<sup>15</sup>) The other 3-halopropanols were synthesized by the reaction of trimethyleneglycol with hydrogen halides.14) 4-Chlorobutanol was obtained from tetrahydrofuran by treating it with hydrogen chloride.<sup>16</sup>) 5-Chloropentanol was derived from chloropentyl acetate, which had been prepared by the method described in the literature,17) by treating it with a 1.5% methanolic hydrogen chloride. 6-Bromohexanol was obtained from hexamethyleneglycol and hydrobromic acid.<sup>18</sup>) In all cases the crude product was dissolved in ether, washed with water to remove a trace of the starting diol, dried with anhydrous potassium carbonate, and evaporated, after which about 10 g of the residue was redistilled twice in a modified Claisen flask equipped with a 10-cm column packed with small glass beads. The rectified samples, except for the iodopropanol, were colorless and had nearly the same physical constants as those reported in the literature. The iodopropanol, however, seemed to be contaminated with 1, 3-diiodopropane, turning pale-brown in color because of its sensitivity to light. None of their OH spectra showed any absorption corresponding to the internally-bonded OH bands of diols.19)

Infrared Measurements. These were carried out at about 25°C by the method previously reported,13) using a Perkin-Elmer 21 single-beam spectrophotometer equipped with a lithium fluoride prism and a cell of 3 cm long. The concentrations were about 0.005 mol/l in carbon tetrachloride, at which concentration intermolecular hydrogen bonding was negligible.

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