Intramolecular Hydrogen Bonding and Conformations of α,α-Dialkyl- and α-Alkyl-*o*-methoxybenzyl Alcohols

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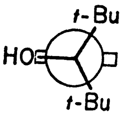
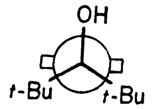
The stable conformations of α-alkyl- and α,α-dialkyl-*o*-methoxybenzyl alcohols were deduced by measurement of their infrared and PMR spectra. Population of these conformations was estimated from the intensities of the O–H stretching bands of the free and the hydrogen-bonded species. The O–H chemical shifts at infinite dilution (δ_{OH}^{∞}) of the free and the hydrogen-bonded species were determined by plotting the δ_{OH}^{∞} values against population obtained from the infrared spectra. An anomalous behavior was observed with the α-alkyl-α-*t*-butyl alcohols, which might be due to a buttressing effect.

α,α-Di-*t*-butylbenzyl alcohol consists of a highly overcrowded molecule in which the rotation of the di-*t*-butylhydroxymethyl group around the $C_{sp^3}—C_{sp^2}$ bond is so slow as to make it possible to observe the hydrogen atoms of the 2 and 6 positions of the aromatic nucleus separately by PMR measurement.[1,2] This suggests that conformer I or a similar one predominates over conformer II.



(I)



(II)

In relation to studies on the accelerating effect of the methoxy group upon the Grignard reaction between *o*-methoxyphenylmagnesium bromide and crowded ketones,[3] the conformations of the α,α-dialkyl-*o*-methoxybenzyl alcohols obtained were investigated by means of infrared and PMR spectroscopic measurements.

The two bulky *t*-butyl groups are expected to force the hydroxyl group nearer to the oxygen atom of the methoxy group than those of the unhindered dialkyl- and monoalkyl-benzyl alcohols in conformation I, causing a larger hydrogen bond shift of the O–H stretching absorption and a low field shift of the O–H proton signal.

Experimental

Preparation of Materials. All the α,α-dialkyl- and α-monoalkyl-benzyl alcohols were prepared by the addition of *o*-methoxyphenylmagnesium bromide to the corresponding ketones in tetrahydrofuran under nitrogen atmosphere. Some of the alcohols are new compounds and identified by elementary analyses, infrared and PMR spectra. The physical constants and the results of elementary analysis are given in Table 1.

Results and Discussion

The O–H stretching frequencies and molar absorptivities of α,α-dialkyl-*o*-methoxybenzyl alcohols[4] are given in Table 2, together with those of the monoalkyl substituted ones. A typical spectrum is illustrated in Fig. 1.

The strength of the O–H···O hydrogen bond in these alcohols can be evaluated from the hydrogen bond shift $\Delta\nu$. The $\Delta\nu$ values are correlated with the length of hydrogen bond H···O by the following equation in which d is the H···O distance in cm.[5]

TABLE 1. PHYSICAL CONSTANTS AND ELEMENTARY ANALYSES OF NEW *o*-METHOXYBENZYL ALCOHOLS (o-$CH_3OC_6H_4CR_1R_2OH$)

R_1	R_2	Boiling point (°C/mmHg)	Calcd C(%)	Calcd H(%)	Found C(%)	Found H(%)
Me	Et	95/4	73.30	8.95	73.28	8.97
Me	*i*-Pr	110/5	74.19	9.34	74.07	9.11
Me	*t*-Bu	143.5/14	74.96	9.68	74.85	9.48
Et	Et	135/16.5	74.19	9.34	74.31	9.46
Et	*i*-Pr	112/6	74.96	9.68	74.74	9.60
Et	*t*-Bu	123/3	75.63	9.97	75.90	9.85
i-Pr	*i*-Pr	122/6	75.63	9.97	75.58	10.04
i-Pr	*t*-Bu	133/5	76.22	10.24	76.50	9.96
t-Bu	*t*-Bu	155/5	76.75	10.47	76.64	10.21

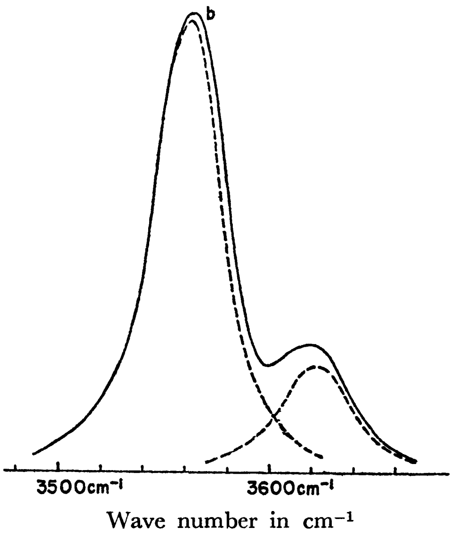


Fig. 1. The O–H stretching absorption of α,α-dimethyl-*o*-methoxybenzyl alcohol. The broken lines in this figure show the dissolved absorption bands of the free and the hydrogen-bonded species. Thus the corrected absorptivity values were employed for calculating the $\varepsilon_b/(\varepsilon_f+\varepsilon_b)$ values when the overlap of the bands is serious.

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Table 2. O-H stretching absorptions and O-H chemical shifts of *o*-methoxybenzyl alcohols

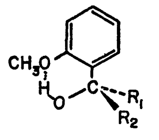
No.	Substituent		O-H Stretching frequency in cm^{-1}			δ_{OH}^{∞} (ppm)	$\frac{\varepsilon_b}{\varepsilon_f+\varepsilon_b}$
	R_1	R_2	$\nu_f(\varepsilon_f)^{a)}$	$\nu_b(\varepsilon_b)^{a)}$	$\Delta\nu$		
1	H	Me	3620.3(50.9)	3583.5(36.8)	38.5	1.98	0.415
2	H	Et	3624.1(53.6)	3576.3(30.4)	47.8	1.70	0.375
3	H	*i*-Pr	3622.2(52.1)	3580.0(28.2)	42.2	1.72	0.355
4	H	*t*-Bu	3627.5(60.2)	3566.7(25.1)	60.8	1.80	0.310
5	Me	Me	3620.0(21.3)	3562.5(78.0)	57.5	3.37	0.821
6	Me	Et	3617.5(19.9)	3564.6(60.9)	52.9	3.15	0.813
7	Me	*i*-Pr	3620.9(16.6)	3560.1(66.8)	60.8	3.17	0.853
8	Me	*t*-Bu	3609.7(9.0)	3532.1(74.2)	77.6	—	0.943
9	Et	Et	3620.2(32.0)	3555.9(57.9)	64.3	2.84	0.734
10	Et	*i*-Pr	3621.4(28.4)	3550.1(53.5)	71.3	2.72	0.670
11	Et	*t*-Bu	3606.8(9.9)	3536.3(120.0)	70.5	5.24	0.942
12	*i*-Pi	*i*-Pr	3627.6(26.6)	3544.7(71.8)	82.9	2.74	0.730
13	*i*-Pi	*t*-Bu	3603.5(10.5)	3532.1(105.0)	71.4	5.60	0.951
14	*t*-Bu	*t*-Bu	3608.0(17.4)	3532.3(113.7)	75.7	5.57	0.947

a) Molar absorptivity in $l\cdot mol^{-1}\cdot cm^{-1}$.

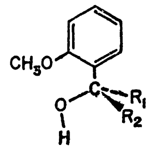
$$\Delta\nu = \frac{250\times10^{-8}}{d} - 74$$

The larger $\Delta\nu$ value indicates that the stronger hydrogen bond exists in the methoxy-alcohol. Except for the case of *t*-butyl substituted ones, the $\Delta\nu$ value increases with the increase in the bulkiness of the alkyl group, indicating that the hydrogen bond is stronger when the α-alkyl groups are bulkier.** However, the population of hydrogen-bonded species is not proportional to the bulkiness of the substituent.

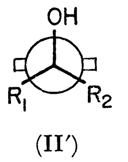
The free O–H bands of the tertiary alcohols of this class generally lie near 3620 cm^{-1}, and the O–H bands arising from the O–H⋯π hydrogen-bonded forms are located near 3600 cm^{-1}.[6,7] Thus, the higher frequency band might be assigned to the free hydroxyl group and the lower frequency one to the O–H⋯O hydrogen-bonded hydroxyl group, at least with the *o*-methoxybenzyl alcohols without *t*-butyl substituent at the α-position. No absorption band due to O–H⋯π interaction could be detected. The O–H⋯π hydrogen-bonded conformation might be rather unfavorable. This conclusion is apparently contrary to the findings on benzyl alcohols without *o*-methoxy substituent.[6,7] However, it can be rationalized in the following way. α,α-Dialkyl-*o*-methoxybenzyl alcohols exist as the equilibrium mixture of the hydrogen-bonded and the free O–O *syn-periplanar* conformer represented by III and IV, respectively. Thus, the II′ conformation of the *o*-methoxy-alcohols is by far less stable than the corresponding conformation of the parent benzyl alcohols due to the steric repulsion between the α-alkyl (R_1 in II′) and the *o*-methoxy groups. Thus, its contribution to the conformational equilibrium is not predominant. It is not certain whether IV or IV′ conformation gives rise to the free O–H absorption. However, the O–O *syn-periplanar* conformation IV seems somewhat less crowded when both of two substituents (R_1 and R_2) are alkyl groups. This is true especially when the alkyl groups are isopropyl and *t*-butyl.



(III)



(IV)



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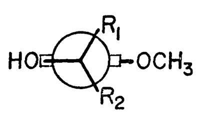
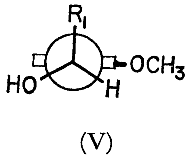


(IV′)

In the alcohols of α-monoalkyl series (Compounds 1—4), the proportion of the hydrogen-bonded species is lower even when the alkyl group is *t*-butyl. In these molecules, the H_α-OCH_3 *syn-periplanar* conformation V might be a stable conformation, since the benzyl hydrogen atom is much less bulkier than the alkyl substituent in the dialkyl series. This conformation would have a free O–H stretching absorption, if the bulkiest alkyl group occupies a position nearly perpendicular to the aromatic nucleus as shown in V.



(V)

If we assume that the O–H chemical shift at infinite dilution δ_{OH}^{∞} is not affected by the nature of the alkyl substituent, the observed chemical shift (δ_{OH}^{∞}) should be linear with respect to the percentage of the hydrogen-bonded species. Hence, the chemical shift (δ_{OH}^{∞}) of the O–H⋯O hydrogen-bonded species and the free species might be obtained by extrapolating the observed δ_{OH}^{∞} *vs.* percentage plot. The O–H chemical

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** The hydrogen-bonded O–H frequencies of the *t*-butyl substituted derivatives are lower than those of the other alcohols investigated, but the $\Delta\nu$ values are smaller because of their lower free O–H frequencies.

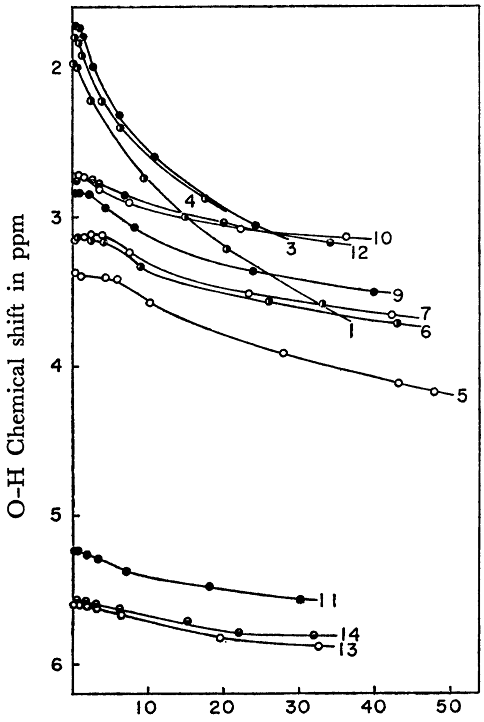

Fig. 2. The concentration dependence of the O–H chemical shifts of the *o*-methoxybenzyl alcohols.

values for the methoxy-benzyl alcohols were obtained from the O–H chemical shift *vs.* molality plot (Fig. 2) by extrapolating the δ_{OH}^{∞} values to zero concentrations. The δ_{OH}^{∞} values should be weighted mean values of the δ_{OH}^{∞}'s of the free and the intramolecularly hydrogen-bonded species of the alcohols. The proportion of the hydrogen-bonded species in these methoxy-alcohols, in turn, was estimated from the infrared spectral data. Thus, the intensity ratio $\varepsilon_b/(\varepsilon_f+\varepsilon_b)$ is taken as a measure for the proportion of the hydrogen-bonded species. Strictly speaking, the integrated intensities for the free and the hydrogen-bonded species should be estimated first, and the proportion should be derived with these values. However, the total molar absorptivity $(\varepsilon_f+\varepsilon_b)$ is constant through the series of alcohols without *t*-butyl group. Thus, the ratio $\varepsilon_b/(\varepsilon_f+\varepsilon_b)$ might be a suitable measure for the abundance of the intramolecularly hydrogen-bonded species. The plot δ_{OH}^{∞} *vs.* $\varepsilon_b/(\varepsilon_f+\varepsilon_b)$ is illustrated in Fig. 3 for the alcohols given in Table 2. Because of the broadening of the O–H signal in PMR spectra at lower concentrations, the δ_{OH}^{∞} value for α-methyl-α-*t*-butyl-*o*-methoxybenzyl alcohol could not be determined. The extrapolation gives the δ_{OH}^{∞} values for the free and the hydrogen-bonded species to be 0.63 ppm and 3.67 ppm, respectively. The δ_{OH}^{∞} value for the free form is lower than those reported by Ōki and Iwamura[8)] for benzyl alcohols. The lower δ_{OH}^{∞} value can be interpreted by conformation IV in which the hydroxyl proton lies in the plane of the aromatic nucleus, opposite to the methoxy oxygen atom.

The plots of the alkyl-*t*-butyl alcohols (11, 13 and 14 in Fig. 3) deviate to the lower fields in the δ_{OH} scale from the line obtained by the mean square calculation excluding the plots of the *t*-butyl derivatives. The anomalous behavior of the *t*-butyl derivatives can be attributed to the buttressing effect which bends the aromatic carbon-benzyl carbon bond towards the methoxy group and forces the hydroxyl and methoxy oxygen atoms to approach closer than normal. Lowering of the free O–H frequencies in the *t*-butyl derivatives was not observed with α,α-di-*t*-butylbenzyl alcohol, and is peculiar to *o*-methoxybenzyl alcohols. The O–H···π interaction would not appear to be persistent in these alcohols carrying bulky alkyl groups. The lower O–H frequencies in overcrowded molecules have been observed in several cases.[9,10)] Anet and Bavin[9)] reported a similar frequency shift with some alcohols. However, the reason for it remains still unclarified.

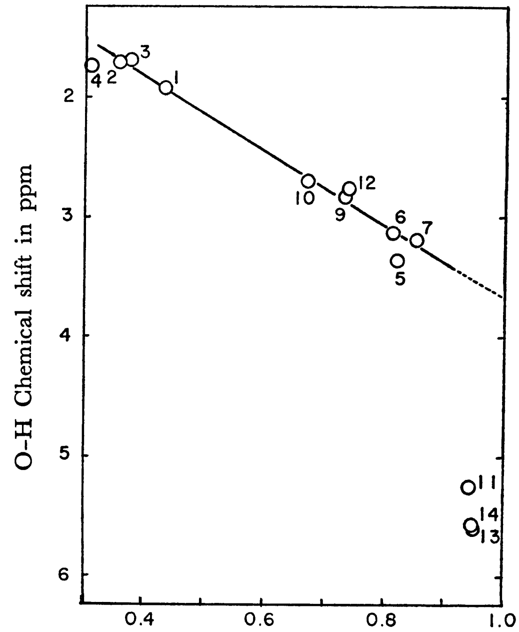

Fig. 3. The O–H chemical shift (δ_{OH}^{∞}) *vs.* the population of the hydrogen-bonded species $(\varepsilon_b/(\varepsilon_f+\varepsilon_b))$ plot.

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