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O–H Stretching Absorption and Conformation of the β-Methyl Derivatives of 1-Tetralol, 4-Chromanol, 4-Thiochromanol, and 4-Thiochromanol 1,1-Dioxide*

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Synopsis. The conformation of eight benzyl alcohol derivatives has been examined by the measurements of OH stretching absorptions. Preference of the OH quasi-axial structure was shown.

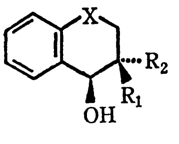
The measurements of the OH stretching absorption bands of epimeric 1-tetralol, 4-chromanol, 4-thiochromanol, and 4-thiochromanol 1,1-dioxide were found to be useful for elucidation of their conformations and for estimation of their conformational free energies ($\Delta G°$).[1,2] A further study concerning OH conformation has been carried out for the epimers of the β-methyl derivatives of these compounds in carbon tetrachloride. The results are reported in this paper.

Results and Discussion

Table 1 shows the OH stretching absorption maxima of the β-methyl derivatives of 1-tetralol (**1**), 4-chromanol (**2**), 4-thiochromanol (**3**), and 4-thiochromanol 1,1-dioxide (**4**) together with their half-widths and intensities. We see that the OH absorption of the *cis*-epimers **1a**, **2a**, **3a**, and **4a** each shows a singlet band and the *trans*-epimers **1b**, **2b**, **3b**, and **4b** a doublet band. The lower frequency bands are stronger than the higher ones for the *trans*-epimers **1b** and **4b**, but weaker for **2b** and **3b**.

TABLE 1. ν_{OH} ABSORPTION MAXIMA OF THE β-METHYL DERIVATIVES OF 1-TETRALOL, 4-CHROMANOL, 4-THIOCHROMANOL, AND 4-THIOCHROMANOL 1,1-DIOXIDE

Compound[a)]	ν_{OH} (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	ε
1a	3620	18	69
1b	3617	22	37
	3598	11	59
2a	3617	19	80
2b	3613	18	84
	3593	12	31
3a	3614	17	67
3b	3611	15	98
	3590	14	17
4a	3613.5	21	76
4b	3611	25	59
	3586	16	97



a) **1a** : $X=CH_2$, $R_1=CH_3$, $R_2=H$
1b : $X=CH_2$, $R_1=H$, $R_2=CH_3$
2a : $X=O$, $R_1=CH_3$, $R_2=H$
2b : $X=O$, $R_1=H$, $R_2=CH_3$
3a : $X=S$, $R_1=CH_3$, $R_2=H$
3b : $X=S$, $R_1=H$, $R_2=CH_3$
4a : $X=SO_2$, $R_1=CH_3$, $R_2=H$
4b : $X=SO_2$, $R_1=H$, $R_2=CH_3$

Referring to the preferred conformations of OH groups in 1-tetralol and 4-chromanols and their ν_{OH} bands,[2)] the following consideration is given on the conformational equilibrium shown in Fig. 1. Since only a singlet band due to the axial OH group was observed for compounds **1a**, **2a**, **3a** and **4a**, it can be assumed that conformation A with the axial OH and equatorial CH_3 groups is decisively predominant over B.

Measurements for compounds **1b**∼**4b** with *trans*-relation between the OH and CH_3 groups might be explained as follows. The axial OH conformation is usually predominant in such compounds if there is no other factor governing the conformation. The axial OH conformation, however, leads to the axial conformation of the CH_3 group as D, which will be unstable when X is a bulky group because of the steric repulsion with the CH_3 group. Thus, the 1,3-diaxial interaction between CH_3 and X would cause the preferential existence of the stable conformation C for **1b** and **4b** with bulky X. This is in line with the fact that a CH_3 group is more bulky than an OH group and has a larger conformational free energy than that of OH group in such a compound.[3)] The "volume requirement" of the lone-paired electrons either on the oxygen atom in **2b** or the sulfur in **3b** will not cause sufficient 1,3-diaxial interaction for conversion of conformation.
Such a small 1,3-diaxial interaction has been pointed out by Eliel and Knoeber[5)] in their stereochemical study on *cis*-2-alkyl-4-butyl-1,3-dioxane, in which the axial conformation of the *t*-butyl group with a chair form was

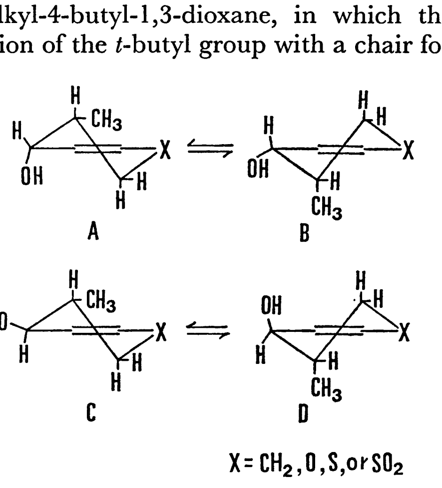


Fig. 1. Conformational equilibria for the β-methyl derivatives of 1-tetralol, 4-chromanol, 4-thiochromanol, and 4-thiochromanol 1,1-dioxide.

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* A part of the study was presented at the 24th Annual Meeting of the Chemical Society of Japan, April, 2, 1971, Osaka.

Table 2. Temperature dependence of the OH stretching absorption band for *trans*-3-methyl-4-chromanol

Temperature °C	ν_{OH} cm^{-1}	ε_h	ν_{OH} cm^{-1}	ε_l	$\varepsilon_l/\varepsilon_h$
−20	3616	98	3588	35	0.35
0	3611	93	3588	35	0.37
23	3613	84	3592	31	0.37
55	3613	76	3591	32	0.42

Table 3. Temperature dependence of the OH stretching absorption band for *trans*-3-methyl-4-thiochromanol

Temperature °C	ν_{OH} cm^{-1}	ε_h	ν_{OH} cm^{-1}	ε_l	$\varepsilon_l/\varepsilon_h$
−23	3609	118	3588	18	0.15
0	3610	119	3588	22	0.19
23	3611	98	3590	17	0.17
55	3612	83	3591	17	0.21

predominant. They also suggested a small interaction between the *t*-butyl group and the sulfur atom in 5-*t*-butyl-4,6-dimethyl-1,3-dithiane on the basis of small conformational free energy.[6)]

In order to confirm the conformational equilibrium (Fig. 1), the temperature dependence of the OH absorption was examined for **2b** and **3b** in the temperature range —23—55 °C. The results (Tables 2 and 3) indicate that the intensity of the lower frequency band increased with a rise in temperature for both **2b** and **3b**. This indicates that the stable form holds an axial OH conformation, supporting the above view. The $\Delta H°$ values were estimated to be 1.0 and 3.5 kcal·mol^{-1} for **2b** and **3b**, respectively.

Experimental

Materials. *cis*- and *trans*-2-Methyl-1-tetralols,[7)] *cis*- and *trans*-3-methyl-4-chromanols[8)] were prepared as reported. *cis*-3-Methyl-4-thiochromanol, *cis*- and *trans*-3-methyl-4-thiochroman ol1,1-dioxides were prepared by reduction with sodium borohydride or the Meerwein-Ponndorf reduction of the corresponding ketones. *trans*-3-Methyl-4-thiochromanol was prepared by the hydroboration-oxidation of 3-methyl-3-thiochromene.[9)] *cis*-3-Methyl-4-thiochromanol (**3a**): mp 78—80 °C (lit.[9)] 78—80 °C). *trans*-3-Methyl-4-thiochromanol (**3b**): mp 73—75 °C. Found: C, 66.40; H, 6.85%. Calcd for $C_{10}H_{12}OS$: C, 66.65; H, 6.71%. *cis*-3-Methyl-4-thiochromanol 1,1-dioxide (**4a**): mp 173—174.5 °C.

Found: C, 56.75; H, 5.61%. Calcd for $C_{10}H_{12}O_3S$: C, 56.60; H, 6.70%. *trans*-3-Methyl-4-thiochromanol 1,1-dioxide (**4b**): mp 117—118 °C (lit.[10)] 117—118 °C).

Instrumentation. The infrared spectra were measured with a Perkin-Elmer 125 or a JASCO DS-403G double beam grating high resolution infrared spectrophotometer. A KCl cell of 30 mm in optical length was used. The concentration of the solutions was *ca.* 0.005 mol/l in carbon tetrachloride, purified by distillation over phosphorus pentoxide. The band due to intermolecular hydrogen bonding was not observed at this concentration.

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