The Hydrogen-stretching Absorptions and Conformations of Tetralin-1-ol, Chroman-4-ol, Thiochroman-4-ol, and Indan-1-ol Derivatives

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The conformations of 1-alkyl (or phenyl)tetralin-1-ols, 4-alkylchroman-4-ols, 4-alkylthiochroman-4-ols, and some secondary and tertiary indan-1-ols have been examined by measurement of the OH stretching absorptions in carbon tetrachloride. For these alcohols, the conformations can be characterized by the following frequencies; quasi-equatorial 3 614—3 628 (free OH) and 3 597—3 610 (OH ··· π hydrogen bonded); quasi-axial, 3 610—3 620 cm^{-1} (OH ··· π hydrogen bonded).

INTRAMOLECULAR OH ··· π bonding has been extensively studied by i.r. spectroscopy which can be successfully applied to conformational and structural studies of various systems containing both a hydroxy-group and a π-source.[1-4] In previous papers,[5] we reported that the axial and equatorial OH groups of secondary αβ-unsaturated six-membered cyclanols such as tetralin-1-ols and chroman-4-ols show π-bonded OH stretching absorptions at *ca.* 3 618 and 3 600 cm^{-1}, respectively, and the axial OH conformation is predominant in these alcohols. These results can be adapted to the conformations of more complex analogous molecules. This paper deals with the conformations of tertiary αβ-unsaturated six-membered and secondary or tertiary αβ-unsaturated five-membered cyclanols. The OH stretching absorptions of the tertiary tetralin-1-ols, chroman-4-ols, thiochroman-4-ols, and the epimeric indan-1-ols have been examined.

RESULTS AND DISCUSSION

The observed ν_{OH} and their intensities measured for the six- and five-membered cyclanols are summarized in Tables 1 and 2, respectively.

Conformations and ν_{OH} *Absorptions of Tertiary Tetralin-1-ols, Chroman-4-ols, and Thiochroman-4-ols.*—It can be readily recognized from Table 1 that compounds having a substituent γ to the tertiary hydroxy-group show absorptions at positions close to those of the secondary alcohols [(1a and b)]. This fact permits similar discussion on the conformations to that for the secondary alcohols. In a series of alcohols with a substituent γ to the hydroxy-group, (2a)—(6a) have each two bands at 3 597—3 607 and 3 614—3 619 cm^{-1}, while (2b) and (3b) have one band at 3 618—3 620 cm^{-1}. This indicates that the OH groups in the former prefer a quasi-equatorial orientation and those in the latter a quasi-axial one. In view of these assignments, the main products in the reactions of the γ-substituted 1-tetralones, chroman-4-ones, or thiochroman-4-ones with Grignard reagents involved a *cis*-relationship between the methyl or phenyl group and the OH group. This is consistent with the formation of *cis*-isomers as the main product in the reduction of γ-substituted 1-tetralones and chroman-4-ones with metal hydride complexes.[6]

TABLE 1

The OH-stretching frequencies (ν_{OH}) and the molar absorption coefficients (ε) for tetralin-1-ols, chroman-4-ols, and thiochroman-4-ols

Compound	ν_{OH}/cm^{-1}	ε
(1a)	3622	37
	3600	66
(1b)	3617	88
(2a)	3619	26
	3607	91
(2b)	3618	76 *
(3a)	3619	33
	3604	99
(3b)	3620	106 *
(4a)	3617	40
	3607	84
(5a)	3614	17
	3602	71
(6a)	3614	22
	3597	70
(7)	3616.5	62
	3604.5	59
(8)	3616.5	82
	3601.5	37
(9)	3614.5	54
	3599	55
(10) †	3615	15
	3604	57
(11)	3620	35
	3607	76
(12)	3616.5	94
(13)	3610	68

* This value was estimated approximately, because the compound was not isolated in pure form. † Different intensities of the bands from those reported by Mori *et al.*, probably caused by different temperatures (20 °C in Mori's work; 25 °C in the present work).

The bands at 3 614—3 619 cm^{-1} of the *cis*-epimers (2a)—(6a) are easily assigned to the free OH groups. The bands at 3 597—3 607 cm^{-1} in the *cis*-epimers and the bands at 3 618—3 620 cm^{-1} of the *trans*-epimers both correspond to OH groups hydrogen-bonded to the π-electrons of the benzene ring.

In Table 1, the 1- and 4-methyl derivatives (7)—(11) exhibit two OH absorptions, in which the lower band is stronger than the higher band for (10) and (11) but

TABLE 2

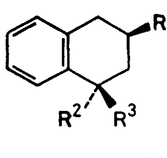
The OH stretching frequencies (ν_{OH}) and the molar absorption coefficients (ε) for indan-1-ol derivatives

Compound	ν_{OH}/cm^{-1}	ε
(14a)	3628	30
	3618	11
	3604	44
(14b)	3620	
(15a)	3628	25
	3617	15
	3604	46
(15b)	3619	58
(16a)	3615	17
	3581	85
(16b)	3622	39
	3601	49
(17a)	3617	80
(17b)	3620	10
	3603	48
(18)	3628 [a]	sh
	3618	33
	3604	55
(19)	3625 [b]	sh
	3616	11
	3604	36
(20)	3602 [c]	123
(21)	3606	81
(22)	3604 [d]	135

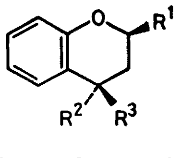
[a] Reported: 3594, 3610 sh (W. R. Jackson and G. H. McMullen, *J. Chem. Soc.*, 1965, 1170); 3605, 3620 (J. M. Brewster and J. G. Buta, *J. Am. Chem. Soc.*, 1966, **88**, 2233); 3601, 3616, 3627 (ref. 4). [b] Reported: 3607, 3615 (ref. 4). [c] Reported: 3601, 3620 (ref. 4). [d] Reported: 3599 (ref. 4).

weaker or almost equal to the other for (7)—(9). The previous study showed that tetralin-1-ol or chroman-4-ol epimers with a quasi-axial OH group each displayed one band at *ca.* 3 618 cm^{-1} while the quasi-equatorial group showed two bands at 3 622 and 3 600 cm^{-1}.[5] It is therefore assumed that the higher frequency band in (7)—(11) is due to the quasi-axial OH group and the lower one to the quasi-equatorial OH group. Accordingly, the quasi-axial OH conformation is predominant in (7)—(9) and the quasi-equatorial one is predominant in (10) and (11). The singlet bands observed in (12) and (13) are readily assigned to their quasi-axial OH groups.

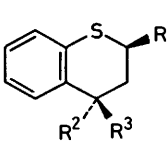
Considering the conformational equilibrium between A and B (Scheme 1), compounds (7)—(11) presumably exist in both A and B forms and compounds (12) and (13) exist overwhelmingly in the A form. It is assumed that the *peri*-interaction[4,5,7] between the equatorially oriented R group and the aromatic hydrogen atom parallel to R is almost equal for (7)—(9). The *peri*-interaction between the quasi-equatorial methyl group at position 1 or 4 and the methyl group at position 8 or 5 in compounds (10) and (11) may be larger than one 1,3-*syn*-diaxial interaction between the methyl group and the hydrogen atom. In the case of (12) and (13), one 1,3-*syn*-diaxial interaction between the quasi-axial isopropyl group and the hydrogen atom would be more serious than the steric interaction between the quasi-equatorial isopropyl group and the hydrogen atom in position 5.



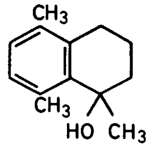
(1a) R^1 = Ph, R^2 = H, R^3 = OH
(1b) R^1 = Ph, R^2 = OH, R^3 = H
(2a) R^1 = Ph, R^2 = CH$_3$, R^3 = OH
(2b) R^1 = Ph, R^2 = OH, R^3 = CH$_3$
(4a) R^1 = R^2 = Ph, R^3 = OH
(5a) R^1 = R^2 = CH$_3$, R^3 = OH
(7) R^1 = H, R^2, R^3 = OH, Pr^i



(3a) R^1 = Ph, R^2 = CH$_3$, R^3 = OH
(3b) R^1 = Ph, R^2 = OH, R^3 = CH$_3$
(8) R^1 = H, R^2, R^3 = OH, CH$_3$
(12) R^1 = H, R^2, R^3 = OH, Pr^i



(6a) R^1 = CH$_3$, R^2 = CH$_3$, R^3 = OH
(9) R^1 = H, R^2, R^3 = OH, CH$_3$
(13) R^1 = H, R^2, R^3 = OH, Pr^i



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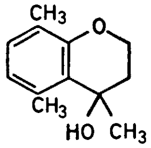

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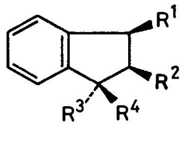
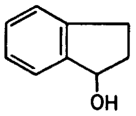


(14a) R^1 = Ph, R^2 = R^3 = H, R^4 = OH
(14b) R^1 = Ph, R^2 = R^4 = H, R^3 = OH
(15a) R^1 = CH$_3$, R^2 = R^3 = H, R^4 = OH
(15b) R^1 = CH$_3$, R^2 = R^4 = H, R^3 = OH
(16a) R^1 = R^3 = H, R^2 = Ph, R^4 = OH
(16b) R^1 = R^4 = H, R^2 = Ph, R^3 = OH
(17a) R^1 = R^3 = H, R^2 = CH$_3$, R^4 = OH
(17b) R^1 = R^4 = H, R^2 = CH$_3$, R^3 = OH



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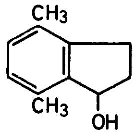

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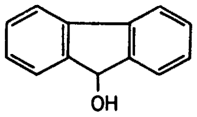

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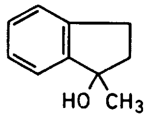

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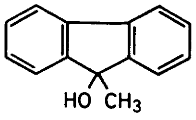
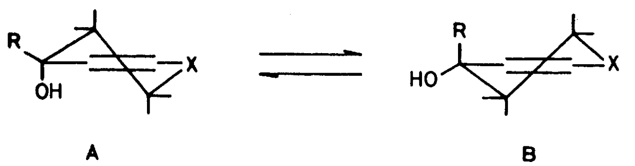


(22)

Conformations and OH *Absorptions of Some Secondary and Tertiary Indan*-1-*ols*.—The configurations of the indan-1-ol derivatives have been established on the basis of the dependence of the vicinal proton coupling constant on the dihedral angle given by the Karplus-type equation, as well as from consideration of the mechanism of their formation.[8] By reference to the relationship observed for tetralin-1-ols,[5] the following characteristics in the OH stretching absorptions of indan-1-ols are evident from Table 2. (i) In alcohols with a substituent γ to the OH group [(14) and (15)], the *cis*-epimer shows two ν_{OH}

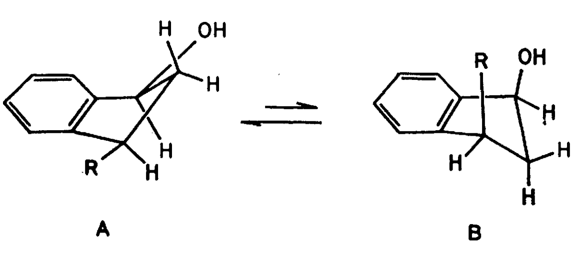
bands at *ca.* 3 628 and 3 600 cm^{-1}, being accompanied by a shoulder at 3 617—3 618 cm^{-1}, while the *trans*-epimer shows a band at 3 619—3 620 cm^{-1}. (ii) In the pair (17a and b), the above correlation is reversed, the singlet band being observed at 3 617 cm^{-1} for the *cis*-isomer. (iii) In the pair (16a and b), both isomers showed two bands at different frequencies. (iv) Appearance of a triplet band in both (14a) and (15a) which have a *cis*-γ-substituent is similar to the case of indan-1-ol (18).



SCHEME 1 Conformational equilibria for 1-alkyltetralin-1-ols, 4-alkylchroman-4-ols, and 4-alkylthiochroman-4-ols. X = CH_2, O, or S; R = CH_3 or $CH(CH_3)_2$

It is known that the alicyclic ring in indanes is usually non-planar and puckered, and the extent of puckering depends on the type of substituent.[9,10] Studies on secondary six-membered cyclanols elucidated that the tetralin-1-ol or chroman-4-ol epimers with a quasi-axial OH group show only one band at *ca.* 3 618 cm^{-1} and those with a quasi-equatorial group give a doublet at 3 622 and 3 600 cm^{-1}, as represented by (1a and b) in Table 1.[5] It is therefore considered that the OH groups in (14a), (15a), and (17b) prefer the quasi-equatorial orientation and those of (14b), (15b), and (17a) the quasi-axial orientation. The bands at 3 628 cm^{-1} of (14a) and (15a) are assigned to the free OH groups. The bands at 3 603—3 604 cm^{-1} in (14a), (15a), and (17b) and at 3 617—3 620 cm^{-1} in (14b), (15b), and (17a) all correspond to OH groups hydrogen-bonded to the π-electrons in the benzene ring. The band at 3 620 cm^{-1} of (17b) is probably an unresolved overlap of both bands due to a free and to a weakly hydrogen-bonded OH group in another isomer formed by rotation of the OH group about the C–O bond.[5]

The *cis*-isomers with a substituent γ to the OH group [(14a) and (15a)] exhibit a shoulder at 3 617—3 618 cm^{-1} in contrast to the corresponding tetralin-1-ol (1a).



SCHEME 2 Conformational equilibria for 3-substituted indan-1-ols

Considering the non-planar structure of the five-membered ring in indanols, it can be assumed that the less stable conformation B exists in equilibrium with the stable form A (Scheme 2). The shoulder thus may be assigned to the OH group in B. In alcohols (16a and b), the internal hydrogen bonding of the OH group with the π-electrons of the aryl group has to be taken into account in addition to the above-mentioned benzylic interaction. As a result of the preferentially equatorial disposition of the aryl group on the cyclopentene ring, the OH group is quasi-axial in the *cis*-isomer. The two bands at 3 615 and 3 581 cm^{-1} in (16a) thus probably arise from OH $\cdots$ π bonding to the benzo-ring and the aryl group, respectively. In the *trans*-β-aryl substituted alcohol (16b), the low ν_{OH} (3 601 cm^{-1}) is attributed to the interaction beween the quasi-equatorial OH group and the benzo-ring or the *trans*-β-aryl group, and the band at 3 622 cm^{-1} can be interpreted as similar to that at 3 620 cm^{-1} in (17b).

The appearance of two ν_{OH} bands in tetralin-1-ol and 5,8-dimethyltetralin-1-ol[11] at *ca.* 3 618 and 3 600 cm^{-1} has been ascribed to the coexistence of the isomers with quasi-axial and quasi-equatorial OH groups, the former conformation being predominant.[5] In contrast to this, the strongest band in (18) showed a frequency close to that of (14a), demonstrating the predominance of quasi-equatorial OH conformation, as reported by Mori *et al.*[4] The OH absorption of (18) is practically unchanged by the introduction of the *peri*-methyl group [compound (19)].

The singlet bands appearing in (20)—(22) at 3 602, 3 606, and 3 604 cm^{-1}, respectively, are assigned to the equatorial OH groups. Since the equatorial OH group and the *peri*-substituent are less eclipsed than in tetralin-1-ols, the *peri*-interaction will be correspondingly less.[4] The energy differences in the *peri*-interactions of indan-1-ols and tetralin-1-ols will be attributed to the difference of the bond angle (θ) C(1)–C(7a)–C(7) in indan-1-ol and of C(1)–C(8a)–C(8) in tetralin-1-ol. It seems likely that the angle in the former is larger than that in the latter.

EXPERIMENTAL

Instrumentation.—The i.r. spectra were measured with Perkin-Elmer 125 or JASCO DS-403G spectrophotometers. A KCl cell of 30 mm in optical length was used. The concentrations of solutions were *ca.* 0.005 mol dm^{-3} in carbon tetrachloride, which was purified by distillation over phosphorus pentaoxide. The band due to intermolecular hydrogen bonding was not observed at this concentration.

Materials.—1-Methyltetralin-1-ol (8),[11] 1,5,8-trimethyltetralin-1-ol (11), 4-methylchroman-4-ol (9),[12] 2- and 3-substituted indan-1-ols,[8] indan-1-ol (18),[13] 4,7-dimethylindan-1-ol (19),[14] fluoren-9-ol (20),[15] 1-methylindan-1-ol (21),[16] and 9-methylfluoren-9-ol (22)[17] were prepared by standard procedures. All other six-membered tertiary alcohols were prepared by a Grignard reaction on the corresponding ketones. The products were chromatographed on silica gel and then examined by i.r. and n.m.r. spectra. 1-*Methyl*-cis-3-*phenyltetralin*-1-*ol* (2a) had m.p. 75—75.5 °C (Found: C,. 85.9; H, 7.65. $C_{17}H_{18}O$ requires C, 85.65; H, 7.6%), 4-*methyl*-cis-2-*phenylchroman*-4-*ol* (3a) m.p. 88—90 °C (Found: C, 79.9; H, 6.8. $C_{16}H_{16}O_2$ requires C, 79,95; H, 6.7%), 1-*phenyl*-cis-3-*phenyltetralin*-1-*ol* (4a) m.p. 107—109 °C (Found: C, 87.6; H, 6.7. $C_{22}H_{20}O$ requires C, 87.95; H, 6.7%), 1,cis-3-*dimethyltetralin*-1-*ol* (5a) m.p. 77—78.5 °C (Found: C, 81.6; H, 9.45. $C_{12}H_{16}O$ requires C, 81.75; H, 9.15%), 4,cis-2-*dimethylthiochroman*-4-*ol* (6a) m.p. 72—74 °C (Found: C, 67.9; H, 7.2. $C_{11}H_{13}SO$ requires C, 68.0; H, 7.25%), *4-methylthiochroman-4-ol* (9) m.p. 111.5—112.5 °C (Found: C, 66.5; H, 6.85. $C_{10}H_{12}SO$ requires C, 66.65; H, 6.7%), 4,5,8-trimethylchroman-4-ol (11) m.p. 84—86 °C (Found: C, 75.05; H, 8.6. $C_{12}H_{16}O_2$ requires C, 74.95; H, 8.4%), 4-isopropylchroman-4-ol (12), oil (Found: C, 74.6; H, 8.2. $C_{12}H_{16}O_2$ requires C, 74.95; H, 8.2%), and 4-isopropylthiochroman-4-ol (13), oil (Found: C, 69.45; H, 7.95. $C_{12}H_{16}SO$ requires C, 69.2; H, 7.75%).

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