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A Hydroxyl Proton Magnetic Resonance Study of 2-Cyclohexen-1-ols, 1-Tetralols, 4-Chromanols, and 4-Thiochromanols in Dimethyl Sulfoxide

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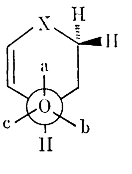
Synopsis. The proton magnetic spectra in dimethyl sulfoxide of 2-cyclohexen-1-ols, 1-tetralols, 4-chromanols, and 4-thiochromanols have been determined. In all cases, the pseudoaxial OH proton resonates at a higher field than the pseudoequatorial one. The spin-spin coupling between the hydroxyl and carbinyl protons is found to be greater for the pseudoequatorial epimer.

Dimethyl sulfoxide (DMSO) is known to be an excellent solvent for the facile observation of H–C–O–H splitting.[1] Recently two studies of the OH proton chemical shifts and coupling constants for a series of epimeric saturated cyclic alcohols have been reported.[2,3] The axial and equatorial hydroxyl groups in a saturated cyclanols can be clearly distinguished from the equatorial hydroxyl resonance at a lower field and a larger coupling constant.

However, no systematic study of the PMR spectra of α,β-unsaturated cyclanols in DMSO has yet appeared in the literature. In order to examine whether or not a relationship similar to those found in the case of the saturated cyclanols exists between the chemical shifts, coupling constants, and conformations of α,β-unsaturated cyclanols, we investigated the ^{1}H NMR spectra in DMSO of epimeric 2-cyclohexen-1-ols, 1-tetralols, 4-chromanols, and 4-thiochromanols in the low-concentration region, in which the chemical shift has been established as invariant. The results are summarized in Table 1. Table 1 shows the clear correlation that, in each epimeric set, the pseudoaxial OH proton resonates at a significantly higher field than its pseudoequatorial counterpart, as has previously been noted for the saturated cyclanols.[2,3] The chemical shift difference between the epimeric alcohols may be related to the solute-solvent hydrogen bonding. Hydrogen bonding is known to influence profoundly the chemical shift of a participating proton.[3] The coupling constant data in Table 1 also lend themselves to ready correlation with the conformation. In each set of epimers, the pseudoequatorial OH coupling constant is greater than that of its pseudoaxial epimers. The difference between the hydroxyl-carbinyl proton coupling constants for epimeric α,β-unsaturated cyclanols may be understood from a consideration of the conformational equilibria resulting from rotation about the C–O bond.[2–4] The contribution of the **a**-type conformation, in which the OH bond is directed towards the center of the cyclohexene, dihydropyran, or dihydrothiopyran ring, may be smaller in the OH pseudoaxial epimer because of the 1,3-diaxial interaction.[5] Assuming that the H–C–O–H coupling constants vary with the dihedral angle in a manner similar to that for the H–C–C–H system, Rader *et al.*,[2] Sehgal *et al.*,[3] and Fraser *et al.*[6] were led to the conclusion that an equatorial alcohol should have a larger coupling constant than its axial epimer because of the greater contribution of the anti conformer, **a**, in the former.



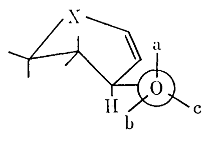
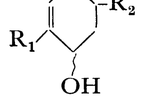
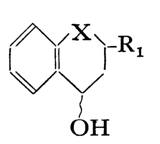


TABLE 1. HYDROXYL PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS OF EPIMERIC α,β-UNSATURATED CYCLANOLS IN DMSO

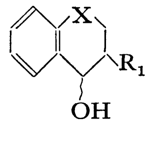
	Pseudoaxial alcohol		Pseudoequatorial alcohol	
Compound	Chemical shift τ	Coupling constant J(Hz)	Chemical shift τ	Coupling constant J(Hz)
1	5.54	6.0	5.45	6.9
2	5.32	4.7	5.24	5.4
3	4.86	5.3	4.63	7.1
4	5.04	5.4	4.81	7.1
5	5.14	6.2	5.13	7.9
6	4.54	5.0	4.47	6.7
7	4.72	5.3	4.61	6.9
8	4.66	6.6	4.52	7.5
9	4.83	5.7	4.65	6.6
10	4.68	5.4	4.49	6.3
11	4.79	5.8	4.04	7.8
12	4.12	6.0	3.89	7.3
13	4.26	5.9	4.05	8.1



1 $R_1=CH_3$, $R_2=t$-Bu
2 $R_1=H$, $R_2=C_6H_5$



3 $X=CH_2$, $R_1=C_6H_5$
4 $X=CH_2$, $R_1=CH_3$
6 $X=O$, $R_1=C_6H_5$
7 $X=O$, $R_1=CH_3$
10 $X=S$, $R_1=CH_3$
12 $X=SO_2$, $R_1=CH_3$



5 $X=CH_2$, $R_1=C_6H_5$
8 $X=O$, $R_1=C_6H_5$
9 $X=O$, $R_1=CH_3$
11 $X=S$, $R_1=CH_3$
13 $X=SO_2$, $R_1=CH_3$

From the present study, it is significant that, in view of the characteristic chemical shift differences and coupling constants, the NMR technique in DMSO can be used to distinguish not only the epimers of saturated cyclanols, but also those of α,β-unsaturated cyclanols. These observations appear to provide direct experimental evidence for the configuration and conformations of these epimers.

Experimental

Materials. All the compounds employed in this work have been previously reported: **1**,7) **2**,8) **3**,9) **4**,9) **5**,10) **6**,11) **7**,12) **8**,13) **9**,14) and **10**—**13**.15) The conformations of 2-cyclohexen-1-ols,7) 1-tetralols,5,16,17) 4-chromanols,5,12,13,15,16) and 4-thiochromanols15) were examined by means of their ^{1}H NMR, ^{13}C NMR, and IR spectra.

NMR Spectra. All the ^{1}H NMR spectra were taken with either a Hitachi H-60 or R-24B spectrometer at a probe temperature of 30 °C, unless otherwise noted. Tetramethylsilane was used as the internal standard; the concentrations were *ca.* 2×10^{-2} in the mole fraction.

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