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TRANS DIRECTIVE EFFECT OF AN ALLYLIC HYDROXYL IN HYDROBORATION. A METHOD FOR PREPARATION OF DIEQUATORIAL DIOLS.

By

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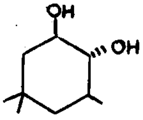
Several methods are known for the preparation of *trans*-diaxial and *cis*-1,2,-diols. No specific procedure is available for the preparation of *trans*-1,2-diols in equatorial conformation. Recently, the preparation of 3β, 4α-cholestanediol by hydroboration of cholestenone (1) was reported. This result was expected, since the ketone is reduced first (2) and should give the more stable equatorial alcohol (3). The subsequent hydroboration is determined by the steric effect of the axial methyl group (4,5) and gives the second hydroxyl in the 4α position.

It was now found that *trans* diequatorial diols are obtained even when *cis* diols are expected for steric reasons.

Hydroboration of isophorone yields a single 1,2-diol I, m.p. 93° in 65% yield. The same diol was obtained from the corresponding allylic alcohol. This diol is different from the *trans*-diaxial isomer, obtained by performic acid hydroxylation of 3,5,5-trimethylcyclohexene and also different from the *cis*-isomer, obtained from the same olefin by silver acetate-iodine treatment.

The additional cis, cis-isomer is excluded as a possibility for the diol obtained by the steric requirements of the hydroboration reaction and by the spectrum of the diol.



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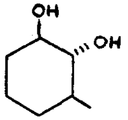

II

The NMR spectrum of diol I shows one proton α to a hydroxyl group as a triplet (7,12τ, J = 9 cps) and a second α proton as a broad multiplet (6,48τ). The infrared spectrum in dilute carbon-tetrachloride solution shows two hydroxyl bands at 3636 and 3599 cm^{-1}. The separation between the hydrogen bonded and free hydroxyl (37 cm^{-1}) is less than for the cis-diol (53 cm^{-1}).

This result is different from the one obtained in the hydroboration of 3,5,5-trimethylcyclohexene, where the axial geminal methyl directs the boron attack preponderantly cis to the methyl in the 3-position (6). On steric grounds, a cis dihydroxy derivative is therefore expected. Moreover, a cis directive effect of a hydroxyl was found in hydroboration of cholesterol (7). On the other side, 3-methylcyclohexene yields almost equal amounts of all four possible isomers (8).

A similar result was found in 3-methylcyclohex-2-enone, which on hydroboration yielded also a single 1,2-diol II, m.p. 39-40°. The infrared spectrum showed two bands (3630 cm^{-1}, 3592 cm^{-1}; $\Delta\nu$ = 38 cm^{-1}) and the NMR spectrum - two protons α to hydroxyls, one a triplet (7,20τ, J = 9 cps) and the second a broad multiplet (6,52τ). All these bands were similar to those of I.

This method should not be limited to β-alkyl substituted cyclohexenones. The polar effect of the hydroxyl formed in the first step will direct the boron to a vicinal position and *trans* to itself. Since the first hydroxyl formed by reduction of the ketone group should be equatorial (3), the second will also be equatorial

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