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PERMANGANATE OXIDATION OF OCCIDENTALOL: UNEXPECTED EPOXIDE FORMATION

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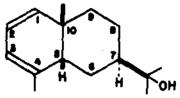
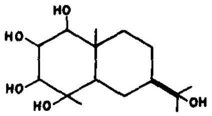
Recently, Klein and Rojahn (1) reported on oxide formation (tetrahydrofuran derivatives) in the permanganate oxidation of acyclic 1,5-dienes. In our studies on the stereochemistry of occidentalol (I) (2,3) we have encountered a similarly unexpected oxide formation during an attempted degradation of occidentalol with the permanganate-periodate reagent (4) (80% tert. butanol as solvent (5)). The oxide is a neutral product, m.p. 152-153°, $[\alpha]_D^{25}$ +5.8° which is formed in 30 to 40% yield when permanganate alone is used as oxidant. The product gives a negative test with tetranitromethane and is not oxidized by periodate (aqueous or alcoholic solutions). Its infrared spectrum is devoid of any absorption in the carbonyl region which shows that an acyloin, the major



I



II

reaction product of an olefin with neutral permanganate (4,6), is not formed. The broad single absorption band at 1375 cm^{-1} indicates that the isopropanol group of occidentalol is not affected by the oxidation. The elementary analyses (C, 66.68, 66.68%; H, 9.87, 9.80%. Calc. for $C_{15}H_{28}O_5$: C, 62.47%, H, 9.79%; for $C_{15}H_{26}O_4$: C, 66.63%, H, 9.69%) are not in accord with the pentol II, which would be the expected hydroxylation product at higher pH (4,6). The results indicate rather that the product contains one molecule of water less than the pentol II. Hence, oxide formation was suspected. Absorption bands (3040, 1245 and 925 cm^{-1}) which may be attributed to a cis-epoxide function (7,8) are present in the infrared spectrum, but such assignments are uncertain without other corroborative data (8). However, the n.m.r. spectrum of the oxidation product is consistent with such a structure. Table I lists the n.m.r. signals of the oxide in chloroform solution, using a Varian HA-100 high-resolution spectrometer. Of the 5 single proton signals at low field, the doublet at τ7.18 and the singlet at τ6.65 disappeared on shaking with deuterium oxide, as did the signal attributable to the isopropanol hydroxyl proton at τ8.64. Under these conditions the quartet at 6.22 collapses to a doublet (spacing = 0.8 c.p.s.); hence this signal must be derived from the proton of the secondary carbinol group. The signals at τ7.00 and τ6.56* were assigned to the two protons of a cis-epoxide, both having a spacing of 2 c.p.s. The spacing of 0.8 c.p.s. of the signal at τ7.00 indicates that

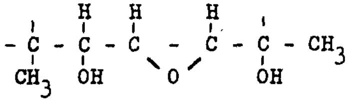
*At present, the only explanation of the additional coupling of 1.0 c.p.s. of this quartet is that long range coupling may be operative.

Table I

Signal	Protons	τ (p.p.m.)	Spacings (c.p.s.)	Assignment
Triplet	1	9.17	12	(C_5-H)
Singlet	6	8.86	-	$-C(OH)(C\underline{H}_3)_2$
Singlet	3	8.79	-	$-C\underline{H}_3$ (at C_{10})
Singlet	3	8.72	-	$-C\underline{H}_3$ (at C_4)
Singlet	1	8.64	-	$-C(O\underline{H})(CH_3)_2$*
Complex	Approx. 7	8.6-8.2	-	($3 \times CH_2$ and C_7-H)
Doublet	1	7.18	5	$>CH-O\underline{H}$ (at C_1)
Quartet	1	7.00	2 and 0.8	$\underline{H}-C_2-O-C_3$
Singlet	1	6.65	-	$\geq C-O\underline{H}$ (at C_4)
Quartet	1	6.56	2 and 1	$\underline{H}-C_3-O-C_2$
Quartet	1	6.22	5 and 0.8	$>C\underline{H}-OH$ (at C_1)

*α-terpineol gives a similar signal in chloroform solution

one of the epoxide protons is coupled with the proton of the secondary carbinol group. Hence, the 1,4-diene system of occidentalol is oxidized by permanganate to



$$-\underset{CH_3}{\overset{|}{C}}-\underset{OH}{\overset{H}{C}}-\overset{H}{C}\underset{\diagdown O \diagup}{-}\overset{H}{C}-\underset{OH}{\overset{|}{C}}-CH_3$$

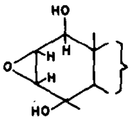
or a similar dihydroxy-oxide system.

Chapman and King (9) have shown that dimethyl sulfoxide (DMSO) is a useful solvent for the classification of hydroxyl functions. When the oxide was dissolved in hexadeuterated DMSO, the n.m.r. signals were similar to those shown in Table I, except that the signals due to the hydroxylic protons were at lower field (singlets at τ 6.33 and τ 5.66;

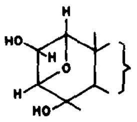
doublet at τ 4.98) and that the six-proton signal of the isopropanol methyl groups was partially resolved into two component signals. These data show clearly that the hydroxylic functions introduced by oxidation with permanganate take the form of one secondary and one tertiary hydroxyl group, which is in agreement with the above formulation.

All the assignments of the signals at low field could be confirmed by double resonance. Also, when spin decoupling was applied to examine the triplet at τ 9.17, changes occurred in the spectrum near τ 8.3. Thus, it is likely that this signal is due to the quaternary (axial) proton at C_5 and that coupling occurs with the signals of the C_6-methylene group.

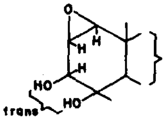
Since the oxide is stable towards periodate the presence of a cis-1,2-diol group may be excluded. Hence, only three structural formulae which contain an oxide, a secondary, and a new tertiary hydroxyl function are possible:



III



IV



V

Of these only III is consistent with the analytical and spectral data. Structure IV may be ruled out on the basis of the proton-proton coupling found in the n.m.r. spectra. Since hydroxylation with permanganate is known to give exclusively cis-1,2-diols, structure V is also improbable. Formation of a 1,4-oxide may be ruled out, as this requires the presence of two secondary hydroxyl groups, as well as different proton-proton coupling.

The present data do not allow any conclusions as to the stereochemistry of the introduced oxygen functions. Models indicate that the β-side of occidentalol is more open to attack by a permanganate anion. Klein and Rojahn (1) suggest that a co-ordination complex between a 1,5-diene and a single permanganate ion is an intermediate in the oxide formation they described. For the hydroxylation of a double bond by permanganate a π-complex is assumed to be the first stage which then rearranges to a cyclic permanganate ester intermediate (10,11). If both the double bonds of a 1,5- or a 1,3-diene form such intermediates simultaneously the two permanganate complex ions are in close proximity and it is possible that an interaction takes place which gives rise to oxide formation, rather than the more normal formation of a tetrol or di-ketol (4,6). The reaction of occidentalol with permanganate (in 80% tert. butanol) was also tried at pH 10 and 11. Instead of the expected tetrol II, the oxide III was again isolated, indicating that the normal hydroxylation mechanism is not predominant. This lends further support to the view that the unusual oxide formation with permanganate oxidation of occidentalol may be the result of such a proximity effect. The permanganate oxidation of occidentalol, as well as simpler 1,3-dienes, is being studied further.

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