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THE STEREOCHEMISTRY OF THE OXYMERCURATION OF SUBSTITUTED CYCLOHEX-2-ENOLS

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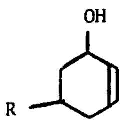
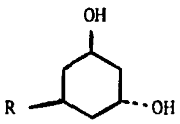
The hydration of double bonds by Brown's procedure[2,3] using oxymercuration and subsequent borohydride reduction was applied recently[4] to cyclohex-2-enol and found to give trans-cyclohexane-1,3-diol. This was attributed to the formation of a complex between the hydroxyl group and mercuric acetate leading to a mercurinium ion cis to this hydroxyl followed by a trans opening of this ion to a trans-diol. Subsequent work[5] detected appreciable amounts (15-25%) of cis-cyclohexane-1,3-diol and small amounts (1% or less) of two 1,2-diols.

We report our results on the oxymercuration reaction[2] of substituted cyclohex-2-enols (I) and (II) existing in solution almost exclusively in one preferential conformation with the substituent in the equatorial position.

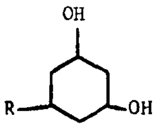
Cis-5-tert. butylcyclohex-2-enol[6] (I) gave in the reported reaction condition[2,3] cis-5-tert. butyl-trans-3-hydroxycyxlohexanol (II) (54% yield) and 4% of its all cis isomer III. These products were identified[7] by their analyses, by the absence of a reaction with periodic acid and by their NMR spectra which showed two bands for the hydrogents on the carbons α to the hydroxyl groups of II, one with a half-width of 10 cps (δ 4,05 ppm from TMS in DMSO-d_6) and another of 27 cps (δ 3,7 ppm) but only one band in III with a halfwidth of 17 cps (δ 3,7 ppm; $CHCl_3$). These diols were different from the 1,2-diols that were prepared by a different method[7].



I:R=$(CH_3)_3C$
IV:R=C_6H_5



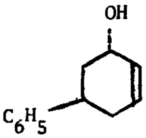
II:R=$(CH_3)_3C$
V:R=C_6H_5



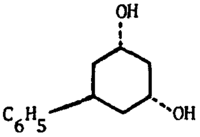
III:R=$(CH_3)_3C$
VI:R=C_6H_5

In a similar manner, cis-5-phenylcyclohex-2-enol[7] (IV) yielded 75% of trans-3-hydroxy-cis-5-phenylcyclohexanol (V) and less than 3% of the all cis-isomer (VI). The same methods as above were used for the assignment of the structures to the obtained products[7] and particularly the NMR spectrum of V which exhibited two bands corresponding to the carbinyl protons at δ 4.01 and 4.20 ppm (from TMS in DMSO-d_6) with corresponding halfwidths of 20 and 10 cps.

It seemed, that the pattern of the reaction, although not totally stereospecific[5] supported the hypothesis of a directing effect exerted by the hydroxyl group[4]. However, oxymercuration-reduction of trans-5-phenylcyclohex-2-enol[7] (VII) gave an excellent yield (60%) of cis-3-hydroxy-trans-5-phenylcyclohexanol (VIII) and only 5% of V. The diol VIII was characterized by the previous methods and by the halfwidth of 8 cps of its carbinyl proton band at δ 4.23 ppm (from TMS in $CDCl_3$).



VII



VIII

This result cannot be reconciled with a mechanism implying cis-mercurinium ion formation by initial complexing of mercuric acetate with the hydroxyl group and subsequent trans opening of this ion. A cis opening of the cis mercurinium ion is consistent with our results in the case of VII. However, such a steric course of this reaction was observed only in strained bicyclic olefins[8] and not in monocyclic compounds[9,10]. It does not conform also to the other hydroxymercurations studied by us. The most probable course taken by the oxymercuration of VII is therefore formation of a mercurinium ion trans to the hydroxyl groups and attack of this ion by water trans to the mercury atom. This is consistent with the reversibility of the mercurinium ion formation[12,13,14,15] and with the second step being the rate- and product-determining one[13].

The steric course of oxymercuration of cyclohexenols is governed by two factors: 1) An inductive effect of the hydroxyl that directs the nucleophile to the 3 position[5] and 2) A conformational effect, favoring trans diaxial opening of the mercurinium ions by the nucleophile in a chair-like transition state. The small amounts of the other isomeric diol could be formed through a boat-like transition state or by the intervention of open carbonium ions[15]. The higher amounts of cis-1,3-cyclohexanediols found in the oxymercuration of 2-cyclohexenol relative to I and IV are caused by the conformational equilibria, favoring a larger proportion of the axial alcohol in cyclohexenol than in I or IV. Trans-diaxial addition to this conformer will give cis-1,3-cyclohexanediol.

The hydroxyl group exerts therefore its influence on the oxymercuration by its inductive effect and by its contribution to the conformational equilibrium - and not by direct intervention in the reaction. This is in agreement with its effect on the rate of this reaction[16].

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