# Stereoselectivity of the Oxymercuration of Cyclohex-2-enol, Cyclohex-2-enyl Methyl Ether, and Cyclohex-2-enyl Acetate

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RECENTLY Moon and Waxman[1] reported that oxymercuration and subsequent borohydride reduction[2] of cyclohex-2-enol yields exclusively *trans*-cyclohexane-1,3-diol. We have re-examined this reaction, and contrary to their report,[1] oxymercuration of cyclohex-2-enol does not occur with a high degree of stereoselectivity. Although *trans*-cyclohexane-1,3-diol is the major product, it is contaminated with 15—25% of *cis*-cyclohexane-1,3-diol, as well as traces of the 1,2-diols. As indicated in the Table, the product distribution appears to be solvent dependent.

Mixtures of the two 1,3-diols proved to be inseparable on silicone oil[1] v.p.c. columns, and analyses were accomplished by conversion into the diacetates, all of which were mutually separable on a Carbowax 20M column. An authentic sample of *trans*-cyclohexane-1,3-diol was prepared by the method of Clarke and Owen,[3] and this was used to establish the identity of the major product from the hydroxymercuration–reduction procedure.

Analogous results were obtained from the methoxymercuration–reduction of cyclohex-2-enol and the hydroxymercuration–reduction of cyclohex-2-enyl methyl ether. In both cases the products, obtained in high yield, consisted of 85 ± 2% *trans*- and 15% of *cis*-3-methoxycyclohexanol.

In a recent kinetic study of hydroxymercuration, Halpern and Tinker[4] found that cyclohex-2-enol reacts approximately ten times slower than cyclohexene. Consequently there is no kinetic basis for anticipating a high degree of stereoselectivity in the reaction of the allylic alcohol. The strong

*Product distribution from hydroxymercuration–reduction of cyclohex-2-enol*

| | | Cyclohexanediol (%) | | | |
|---|---|---|---|---|---|
| Solvent | Yield (%) | *trans*-1,3 | *cis*-1,3 | *trans*-1,2 | *cis*-1,2 |
| $H_2O$ .. .. .. .. .. | 84 | 83·6 | 15·1 | 0·7 | 0·6 |
| 50% aq. THF .. .. .. | 86 | 78·2 | 19·6 | 0·9 | 0·8 |
| 50% aq. THF[a] .. .. .. | 78 | 79·6 | 18·7 | 0·8 | 0·9 |
| 8% aq. THF .. .. .. | 37[b] | 73·5 | 24·6 | 0·9 | 1·0 |

[a] The procedure of Moon and Waxman[1] was followed as closely as possible in this experiment. In other runs, higher yields were achieved by saturation of the aqueous phase after reaction with potassium carbonate, followed by extraction of the diols into ether. [b] 58% of starting material was recovered from this very slow reaction.

positional preference exhibited in oxymercuration can easily be accommodated by consideration of inductive effects.[4]

In contrast to the allylic alcohol and ether, cyclohex-2-enyl acetate gives only *trans*-3-acetoxycyclohexanol (65—75%).

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