

Preparation of *trans*-Cyclohexane-1,3-diol by the Oxymercuration of Cyclohex-2-en-1-ol

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Summary The proportion of *cis*- and *trans*-isomers produced in the oxymercuration of cyclohex-2-en-1-ol depends on the conditions for isolation of the product; under acidic conditions, the *trans*-isomer may be obtained exclusively.

IN 1967 we reported¹ that the oxymercuration of cyclohex-2-en-1-ol proceeded to the *trans*-1,3-diol selectively. Recently, Johnson and Rickborn² repeated our work and reported that yields of 15—25% of the *cis*-isomer accompanied the *trans*-isomer.

We re-examined our product (isolated as the diacetate) which had been obtained prior to our first publication and discovered less than 1% of the *cis*-isomer present (v.p.c. on

ethylene glycol adipate—EGA†), thus confirming our original report. Noting the discrepancy between our results and those of Johnson and Rickborn we re-investigated the oxymercuration of cyclohex-2-en-1-ol.

Cyclohex-2-en-1-ol was treated with mercuric acetate and the product, after reduction with sodium borohydride, was isolated in the exact manner described earlier.¹ This procedure involves neutralizing the product mixture with hydrochloric acid to pH 6.5 and removing the water as an azeotropic mixture with benzene (18 hr.). The benzene is removed under reduced pressure and the solid residue is extracted with hot acetone. The diol is converted into the diacetate by treatment with acetic anhydride in anhydrous pyridine at room temperature. Analysis (v.p.c. on EGA)

† It was shown that authentic samples of *cis*- and *trans*-cyclohexane-1,3-diol diacetate could be readily separated on this column.

showed the product to be essentially pure *trans*-cyclohexane-1,3-diol diacetate, contaminated with 1—2% of the *cis*-1,3-diol and none of the 1,2-diols.

The olefinic alcohol was then treated with mercuric acetate, and the product, after reduction with sodium borohydride, was extracted with ether. The product, isolated as diacetates, contained 84% *trans*- and 15% *cis*-cyclohexane-1,3-diol diacetate in addition to 1% of *cis*- and *trans*-cyclohexane-1,2-diol diacetate. These results were reproducible. The difference in our product ratios and those of Johnson and Rickborn apparently lies in the method of product isolation.

In 1960 Dale³ reported that when a mixture of *cis*-cyclohexane-1,3-diol and boric acid was heated under reflux in benzene, and the water removed as an azeotropic mixture, a borate ester of the diol was formed. We suggest that during neutralization in our isolation procedure of the oxymercuration reaction, a certain amount of boric acid was formed (from sodium borate, a by-product of the reduction of acetoxymethyl diols with sodium borohydride⁴). This material then reacted with any *cis*-1,3-diol

and 1,2-diols present. It is suggested that the *trans*-1,3-diol is esterified much less rapidly.

Support for the above explanation was obtained by the following experiment. A mixture of *cis*- and *trans*-cyclohexane-1,3-diol (in the ratio 44:56) was subjected to reaction conditions and isolation procedures identical to those used previously.¹ The diol thus obtained was shown by v.p.c. analysis of the corresponding diacetates to consist of 99.3% of *trans*-cyclohexane-1,3-diol and only 0.7% of the *cis*-isomer.

In conclusion, the diacetates from oxymercuration-demercuration of cyclohex-2-en-1-ol, when isolated under basic conditions, consist of 10—15% of the *cis*- and 85—90% of the *trans*-isomer. This isomer distribution closely parallels that reported by Johnson and Rickborn.² However, only the *trans*-isomer is obtained when the product is isolated in the manner described in our previous paper,¹ because this isolation procedure selectively removes the *cis*-isomer.

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¹ S. Moon and B. H. Waxman, *Chem. Comm.*, 1967, 1283.

² M. R. Johnson and B. Rickborn, *Chem. Comm.*, 1968, 1073.

³ J. Dale, *J. Chem. Soc.*, 1961, 922.

⁴ H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, 1965, p. 27.