On the Question of Diequatorial Opening of Epoxides. 2,3-Dimethyl-2-octalin Oxide[1]

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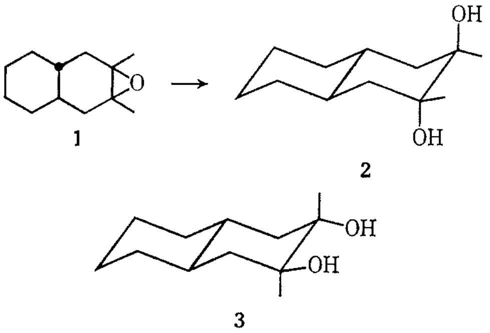
Henbest, Smith, and Thomas[3] have reported that the acid-catalyzed hydration of *trans*-2,3-dimethyl-2-octalin oxide **1** gives a mixture of *trans*-diaxial diol **2** (71%) and *trans*-diequatorial diol **3** (23%).

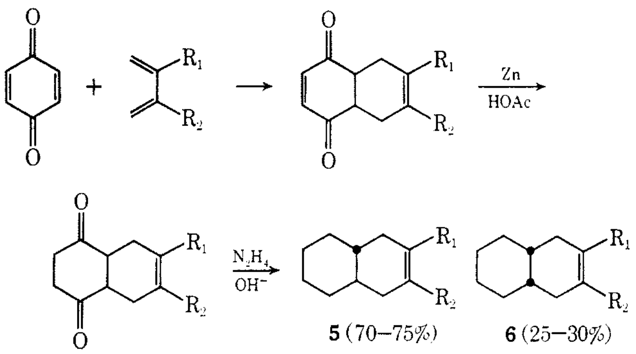


1 2 3

This work has been described without critical comment in at least one review,[4] even though it represents the *only reported example of "diequatorial" opening* of a normal epoxide.[5]

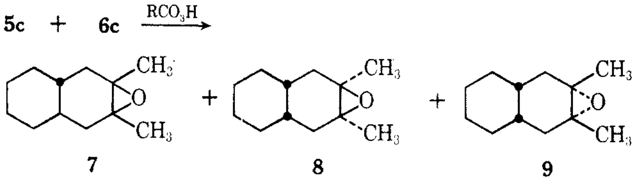
We wish to report that in fact Henbest's observation results from using a mixture of *cis* and *trans* ring-fused olefins (and hence epoxides). While working with 2-octalin[7] and 2-methyl-2-octalin,[6] we first noted the close similarity between the ratio of olefin products and the diol mixture obtained by Henbest. The route to the 2-octalins has been described previously.[3,8]

Henbest[3] subjected the *cis*-hexahydronapthoquinone **4c** to base-catalyzed equilibration and recrystallization to obtain *trans* ring-fused material. As Johnson[8] has pointed out in connection with the synthesis of **5a**, this procedure is unnecessary and fruitless in view of the expected equilibration under the strongly basic Wolff–Kishner reaction conditions. Essentially the same mixture of **5** (*ca.* 75%) and **6** (*ca.* 25%) is obtained by this sequence regardless of the stereochemistry of **4** or the degree of substitution of the double bond (**a**, **b**, or **c**).



4a, $R_1 = R_2 = H$
b, $R_1 = H; R_2 = CH_3$
c, $R_1 = R_2 = CH_3$

Unlike the parent olefin (**5a** + **6a**),[7] the dimethyl derivative (**5c** + **6c**) could not be separated by fractional distillation using a Teflon spinning-band column.[9] Conversion of a mixture (*ca.* 70% **5c**, 30% **6c**; no vinyl proton absorption by nmr) to the epoxide gave a mixture which showed two peaks by vpc (73.6%, 26.4%). Three epoxides should be formed under these conditions, although **6c** should lead predominantly to **8** by analogy with the reaction of *cis*-4,5-dimethylcyclohexene.[10] The percentages indicate that **7** and **8** were separated under the vpc conditions used, with **9** appearing under one or the other of these peaks. Attempted fractional distillation of this epoxide mixture was also unsuccessful, although some enrichment of the major peak component could be accomplished.



7 8 9

Hydration of the same epoxide mixture was carried out with aqueous sulfuric acid in acetone. Two diol products were formed in a ratio of 76.4 to 23.6%; samples were collected by preparative vpc and proved by melting point to be analogous to those obtained by Henbest.[3] It is clear, therefore, that the major diol is the diaxial product **2**, while the minor diol is derived from *cis*-epoxide(s) **8** (and **9**).

Experimental Section

The procedure of Henbest and coworkers[3] was used to prepare the olefin mixture (**5c**, **6c**) except that the dione **4** was not equilibrated and purified. *m*-Chloroperbenzoic acid was used to generate the epoxide mixture (**7**, **8**, **9**); it gave two peaks by vpc, 73.6 to 26.4%.

A sample (0.3 ml) of this mixture was treated with 5 ml of 1% sulfuric acid in 5 ml of acetone for 23 hr at 25°. The product was taken up in ether, washed with water, dried, and evaporated to give a syrup which was separated by vpc using a Carbowax 20M column. The major diol had mp 115–116° (lit.[3] mp 119–121°); the minor product had mp 80–83° (lit.[3] mp 81–85°).

Registry No.—1, 21298-07-7; **2,** 21298-08-8.

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[2] Alfred P. Sloan Fellow, 1967–1969.

[3] H. B. Henbest, M. Smith, and A. Thomas, *J. Chem. Soc.*, 3293 (1958).

[4] A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part One, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1964, p 284.

[5] Several examples of kinetically controlled equatorial product forming reactions of epoxides are known, but these invariably involve conformationally flexible systems with particular substituent effects. We have recently discussed this problem in connection with hydride reduction of substituted cyclohexene oxides.[6]

[6] D. K. Murphy, R. L. Alumbaugh, and B. Rickborn, *J. Amer. Chem. Soc.*, **91**, 2649 (1969).

[7] R. Thummel, unpublished results.

[8] W. S. Johnson, V. J. Baker, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Amer. Chem. Soc.*, **83**, 606 (1961).

[9] Henbest[3] reported only diaxial diol from his sample of **5a**, which apparently was substantially purified by distillation.

[10] B. Rickborn and S. Lwo, *J. Org. Chem.*, **30**, 2212 (1965); this olefin gives 13% *cis*-epoxide, suggesting that only 3–4% **9** would be formed in the above reaction.