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STEREOCHEMISTRY OF THE REARRANGEMENT OF CIS- AND TRANS-1,2-DIVINYL-1,2-CYCLOHEXANEDIOLS

Elliot N. Marvell and William Whalley
Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

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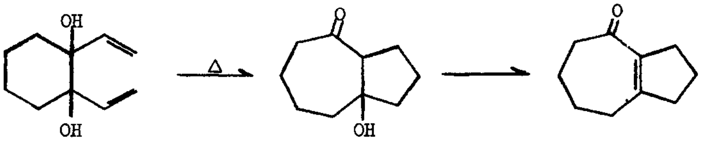
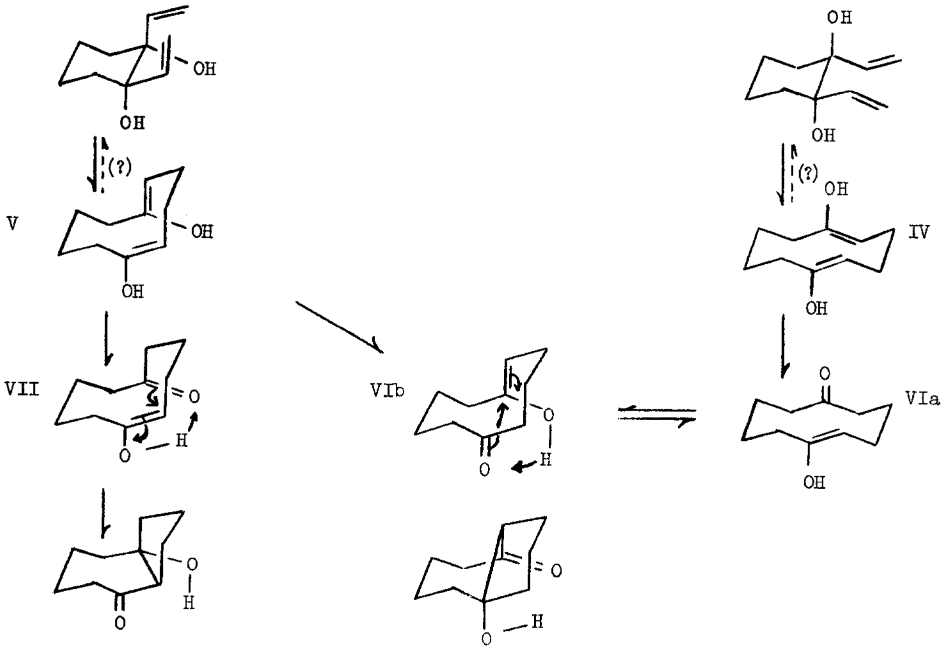
Rearrangement of 1,2-divinyl-1,2-cyclohexanediol (I) was shown by Conia, et al (1) to give 1-bicyclo[5.3.0]decen-2-one (II). We had made the same observation independently (2), but had also found that under milder conditions 7-hydroxybicyclo[5.3.0] decan-2-one (III) can be isolated in good yield. In fact a mixture of cis- and trans-I gave a mixture of the cis- and trans-III. The stereochemical relations involved were not, of course, obvious. We should like to report now some further experiments which reveal the interesting stereochemistry of this rearrangement.



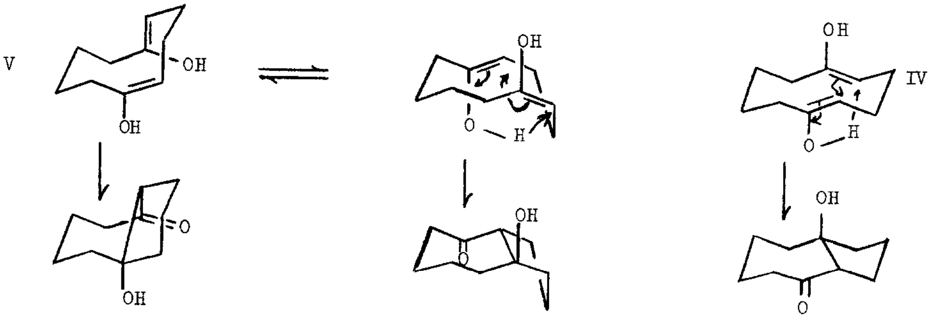
(I) (III) (II)

Treatment of 1,2-cyclohexanedione with four moles of vinyl magnesium bromide in two steps gives a mixture of cis- and trans-I. The isomers were separated by preparative gas chromatography (15 ft. x 1/4 in. 5% FFAP on Chromosorb G at 160°) into a solid, m.p. 47.5-48.5°, and a liquid. Hydrogenation of the solid isomer over platinum gave the known cis-1,2-diethyl-1,2-cyclohexanediol, m.p. 61-63°.[3] Similarly

Scheme 1



Scheme 2



reduction of the liquid isomer gave trans-1,2-diethyl-1,2-cyclohexanediol, m.p. 95.5-96°.[4] Each isomer of I was rearranged as a dilute solution in spectrograde cyclohexane. Glpc analysis (15 ft x 1/4 in. 5% FFAP column at 163°) with cis-decalin as an internal standard was used to follow the rates of rearrangement. The rates are $k_{cis} = 8.0 \times 10^{-4}$ sec.$^{-1}$ at 212° and $k_{trans} = 7.3 \times 10^{-4}$ sec.$^{-1}$ at 212°. In neither case could the presence of the isomeric form of the starting material be detected in the reaction mixture at any stage of the reaction.

The product from the rearrangement of trans-I was a single isomeric form of III, m.p. 95-96.5°, (IIIa) accompanied by a small amount of II. From cis-I there was obtained a mixture of both isomeric forms of III with the ratio of IIIb to IIIa being ca. 2.5. Again small amounts of II were present in the reaction product. The isomers of III are very readily dehydrated and this sensitivity has so far prevented our establishing the stereochemistry of IIIa and IIIb. However the ratio of IIIb to IIIa formed from cis-I remains constant throughout the run, and must therefore reflect a kinetically determined value.

These results clearly eliminate 1,6-cyclodecane-dione as an intermediate under these conditions. If it is presumed that the Cope rearrangement proceeds with its usual stereospecificity,[5] then two mechanisms may be proposed to account for the above observations. In scheme 1 the Cope rearrangement of trans-I gives IV a di-trans-dienol which can convert to only a single mono-enol with a trans double bond, VIa. This cannot react directly but converts to a new conformation VIb,[6] and thus via a stereospecific thermal aldol[7] to trans-III. Similarly cis-I gives V with one trans and one cis double bond, which can give two mono-enols VIb and VII. The latter converts via the aldol reaction to cis-III. Alternatively scheme 2 illustrates the use of an "enolene" process[8] to convert the dienol to the final product. In that case IV gives cis-III regardless of which hydroxyl group reacts, while V gives trans-III readily but requires conversion to another conformation before the final step can give cis-III. This latter appears to be a process which is sterically unfavorable. In any event the steps following the Cope rearrangement must occur rapidly, and there must be no mixing of routes 1 and 2 since they predict the opposite stereochemical results from cis- or trans-I.

The aldol route requires the presence of both hydroxyl groups whereas the "enolene" route makes use of only one. To attempt to distinguish between the two schemes, a sample of <u>cis</u>-I was converted to the monomethyl ether (VIII). Heated for 3 hrs. at 230° VIII gave only II in good yield. Thus the rearrangement does procede where only a single hydroxyl is present. While this may indicate that scheme 2 is a possible route, it does not eliminate scheme 1 from consideration. Further studies on the mechanism of this reaction are underway.

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6. The conformations shown are not intended to illustrate the most favorable, but merely follow more or less directly from the product obtained via a "chair-like" transition state for the Cope rearrangement.
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