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THE OXY-COPE REARRANGEMENT OF 1,2-DIVINYLCYCLOHEXANOL: A NOVEL SYNTHESIS OF 5-CYCLODECEN-1-ONE

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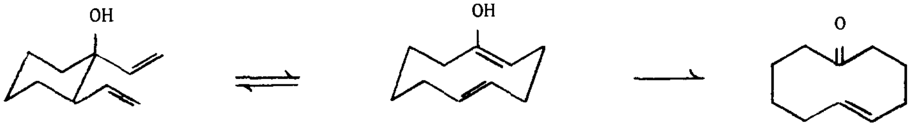
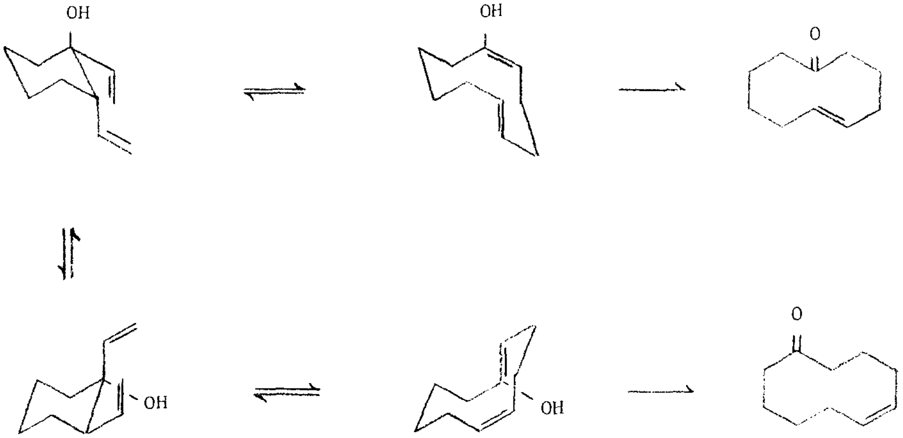
The synthetic value of the Cope rearrangement for ring enlargement by four carbon atoms has been nicely illustrated by the formation of cycloheptadienes from cis-1,2-divinylcyclopropanes[1] and of cyclooctadienes from cis-1,2-divinylcyclobutanes.[2] Recently this preparative utility has been extended to include formation of rings with twelve or more members[3,4] by use of an oxy-Cope rearrangement. All attempts to prepare rings of nine to eleven members have been frustrated by intervention of an aldol-like cyclization following formation of the dienol intermediate.[5,6] We would like to report that the oxy-Cope rearrangement can indeed be used to prepare ten-membered rings in good yield.

A 90% yield of trans-5-cyclodecen-1-one was obtained when a 10% solution of trans-1,2-divinylcyclohexanol was heated 3 hrs. at 220°. The product was identified by its infrared spectrum[7] (1709, 987 cm.$^{-1}$), its nmr spectrum (CCl_4)δ 5.17 (2H), 1.2-2.6 (14 H)



and by preparation of the known[8] semicarbazone, m.p. 178.5-179°. Similarly when *cis*-1,2-divinylcyclohexanol was heated under the same conditions for 2 hrs., a mixture containing 60% of *trans*-5-cyclodecen-1-one and 40% of *cis*-5-cyclodecen-1-one was obtained in ca. 50% yield. The isomers were separated by tlc,[9] and the *cis* isomer was identified by comparison of its infrared spectrum (1706, 703 cm.$^{-1}$) with that of an authentic sample,[10] and preparation of the known[8] 2,4-dinitrophenylhydrazone, m.p. 179-180°. The yields given are for isolated material and these compounds constitute all of the monomeric material in the product.



Oxidation of 2-vinylcyclohexanol[11,12] with chromium trioxide - pyridine complex in methylene chloride[13] gave 2-vinylcyclohexanone[12] in 84% yield. In our hands this oxidation procedure is much superior to the Jones' oxidation used previously.[12] Addition of vinylmagnesium bromide to 2-vinylcyclohexanone gave a mixture of *cis*- and *trans*-1,2-divinylcyclohexanols in 70% yield. The mixture was separated either via glc[14] or tlc[9] to give *trans*-1,2-divinylcyclohexanol (86%); ir (CCl_4) 3610, 1634, 914 cm.$^{-1}$; nmr (CCl_4)δ 6.2-4.7 (m, 6H), 2.3-1.3 (m, 10H), and *cis*-1,2-divinylcyclohexanol (14%), ir (CCl_4) 3620, 1637, 975, 922 cm.$^{-1}$; nmr (CCl_4)δ 6.4-4.7 (m, 6H), 2.3-1.3 (m, 10H).

The stereochemical assignments for the divinylcyclohexanols are based on analogy to the previously demonstrated[15] predominance of trans product in the addition of vinylmagnesium bromide to 2-methylcyclohexanone. It is supported by the chromatographic behavior of the two isomers (trans elutes before cis on both glc and tlc).[15] Assuming that the rearrangement involves a concerted stereospecific Cope reaction via a chair-like transition state[5,16] followed by a rapid ketonization, these assignments permit a ready rationalization of the product stereochemistry (see equations). In view of the readily accessible starting materials, the yields obtained and the stereospecificity, this variant of the oxy-Cope reaction provides a most attractive route to bifunctional cyclodecane derivatives.

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