Tetrahedron Letters No.17, pp. 1341-1342, 1969. Pergamon Press. Printed in Great Britain.

# REARRANGEMENT OF 1,2-DIVINYL-1,2-CYCLOOCTANEDIOL

## A RING EXPANSION BY FOUR CARBONS

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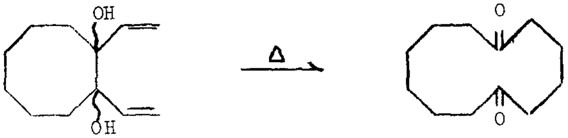
(Received in USA 7 November 1968; received in UK for publication 10 March 1969)

The Cope rearrangement permits the ring expansion or contraction of cycloalkanes containing a suitable 1,5-diene system. Thus cis-1,2-divinylcyclopropanes and cyclobutanes readily form cycloheptadienes[2] and cyclooctadienes[3] respectively. Conversely the cyclodeca-1,5-dienes revert to 1,2-divinylcyclohexanes,[4] a synthetically unfortunate event. Recently attempts to force the reaction of 1,2-divinylcyclohexanes to procede in a synthetically useful direction by employing the oxy-Cope reaction,[5] failed to give the hoped-for 1,6-cyclodecanedione. However, easy and economic access to cyclooctanone[6] suggested that advantage might be taken of the oxy-Cope rearrangement to provide a synthetically valuable ring expansion by four carbon atoms.

A sample of cyclooctanone[6] was oxidized to 1,2-cyclooctanedione by the procedure of Wittig and Krebs.[7] The product contained a number of impurities (glpc analysis on 12 ft. x 1/8 in. 5% FFAP column at 195°) including cyclooctanone and a substance having a strong hydroxyl band in the infrared (hydrate?). Purification proved difficult so the crude



material was dried over calcium chloride and was treated directly with an excess of vinyl magnesium bromide in tetrahydrofuran. The 1,2-divinyl-1,2-cyclooctanediol (I) was isolated from the reaction product by preparative gas chromatography, mp 35-37°; ir ($CCl_4$) 3545, 3096, 1630, 990, 925 cm.$^{-1}$; nmr ($CCl_4$)$\delta$ 4.9-6.3 (m, 6H), 2.1 (s, 2H), 1.1-2.0 (m, 12H).*

The rearrangement of I was carried out by heating a dilute solution in cyclohexane in a sealed tube at 225° for 12 hrs. The product was a crystalline compound, mp 92-93°, identified as 1,6-cyclododecanedione.[8] This product, which was isolated in 40-50% yield, gave an orange bis-dinitrophenylhydrazone, mp 268-272°. Wolff-Kischner reduction of the diketone gave cyclododecane.[9] Work is underway to improve the quality of this synthetic method and to study its application to other ring systems. The present results suggest that the rapid conversion of a cyclic bis-enol to an aldol product is peculiar to the medium rings.

The authors are pleased to acknowledge partial financial support of this work by the National Science Foundation through Grant GP-7830.

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* Analyses for all new compounds were satisfactory.