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REACTIONS OF cis, trans, trans-1, 5, 9-CYCLODODECATRIENE

II. A SIMPLE PREPARATION OF cis-CYCLODODECENE BY SELECTIVE REDUCTION WITH DIIMIDE.

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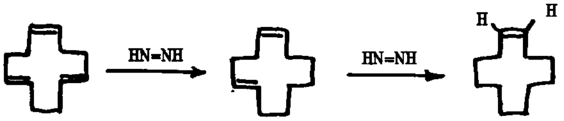
cis, trans, trans-1, 5, 9-Cyclododecatriene (1) is smoothly reduced to cyclododecane by usual catalytic reduction , but the selective hydrogenation to afford cyclododecene was found unsatisfactory[1, 2]. This difficulty diminishes the synthetic utility of the double bonds of cyclododecatriene, and other preparative methods of cyclododecene[3, 4] consist of tedious procedures or afford a mixture of stereoisomers.

In the course of our study on selective reactions of cyclododecatriene[5], we have demonstrated that cis-addition reagents such as osmium tetroxide and potassium permanganate react selectively with a trans double bond affording cis-5, trans-9-cyclododecadiene-trans-1, 2-diol in excellent yields.

Extension of this idea led us to apply diimide reduction to cis, trans, trans-1, 5, 9-cyclododecatriene and a simple synthetic method of cis cyclododecene (III) has been found as shown below.



I II III

Recently, diimide reductions have been investigated extensively by several groups[6]. Corey[7] has clearly established that diimide reacts with olefins in cis manner and Hünig[8] showed that fumaric acid is more rapidly reduced than maleic acid with diimide , although Aylward[6] showed elaidic acid is more slowly reduced than oleic acid.

Since cis, trans, trans-1, 5, 9-cyclododecatriene (I) contains one cis double bond and two trans double bonds in a cyclic system, it is very interesting to clarilfy which double bond is more easily reduced with diimide.

cis, trans, trans, 1, 5, 9-Cyclododecatriene dissolved in ethanol was treated with excess of hydrazine hydrate (10 mole equivalents) in the presence of a catalytic amount of cupric sulfate under vigorous bubbling of air and stirring for 24 - 48 hours. The reaction was found to be highly exothermic and aliquots of the reaction mixture were subjected to spectroscopic and vapor phase chromatograhic analyses at intervals. Their Infrared spectra showed that only the absorption intensity at 980 cm^{-1} for the trans double bond diminished and that at 707 cm^{-1} for the cis double bond remained unchanged during the reaction.

Vapor phase chromatography showed the presence of three components. Two of them were confirmed to be the starting material and cis-cyclododecene (III) judging from their retention time, and another fraction was attributed to cis, trans-1, 5-cyclododecadiene (II). No detectable amount of trans-cyclododecene was identified.

The reaction was continued until the absorption band at 980 cm^{-1} disappeared. The reaction product was extracted with ether and washed with 2N hydrochloric acid. The ethereal solution gave a colorless liquid, b.p. 64 - 65°C/1.0 mmHg, in 82% yield. Vapor phase chromatography using PEG 6000 showed the liquid was consisted of 95% of cis-cyclododecene and 5% of cyclododecane (the ratio depends upon reaction time). Pure cis-cyclododecene was easily obtained by preparative gas chromatography and its infrared spectrum is completely identical with that of authentic sample$^{3)}$. (Calcd. for $C_{12}H_{22}$: C, 86.66 ; H, 13.34. Found : C, 86.48; H, 13.32). It was converted into known cyclododecane-cis-1, 2-diol$^{3)}$, m.p. 157-158°C with osmium tetroxide in 92% yield (Calcd. for $C_{12}H_{24}O_2$: C, 71.95 ; H, 12.08 . Found : C, 72.04 ; H, 12.05). On the other hand, the cyclododecene was subjected to equilibrium by Cope's method$^{9)}$, affording a mixture of trans-cyclododecene and cis-cyclododecene in a ratio of about 2 to 1.

These results clearly show that the attack by diimide takes place at the trans double bonds and there is a considerable difference in reactivities between the cis and trans double bonds enough to control the product.

Such competitive reactivities might resonably be explained by conformational stability at transition state, since the reaction is highly exothermic[10)] and there is no considerable difference in steric approach control between the cis and trans double bonds of the starting material.

Since cis, trans, trans-1, 5, 9-cyclododecatriene is most easily available from butadiene[1)], our results present a simple and valuable synthetic method of cis-cyclododecene.

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