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DIMERIZATION OF 1,3-CYCLOOCTADIENE

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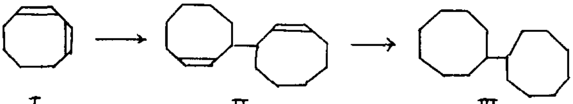
Several complex catalyst systems for the selective dimerization of aliphatic conjugated dienes have been reported. For example butadiene is dimerized with the catalyst which consisted of combinations of transition metal complexes and alkyl aluminium compounds1). Recently, the authors reported that isoprene dimers, 2,6-dimethyl-2,6-octadiene and 2,7-dimethyl-2,6-octadiene, were prepared by the action of lithium naphthalene in tetrahydrofuran2). But the dimerization of cyclic conjugated dienes with metal complex catalysts have not been reported. We have now found that a lithium naphthalene is active for dimerization of 1,3-cyclooctadiene (I).

A catalyst was prepared with 1 mole of metal lithium and 0.5 mole of refined naphthalene in a tetrahydrofuran, and reacted with I (1 mole) at room temperature for three hours. The reaction mixture was decomposed with methanol. Distillation of the reaction products gave a viscous oil (II) (b.p. 140 - 148°C / 8 Torr) in 35 % yield based on the fixed I. This oil could be refined successfully by means of column chromatography using a silica gel column. (d^{16}_{4} 0.9613, n^{16}_{D} 1.5242, molecular refraction 69.54 (calcd. for $C_{16}H_{26}$,F_2 70.75). Anal. C, 88.30 %, H, 11.56 %; Calcd. for $C_{16}H_{26}$ C, 88.00 %, H. 12.00). The results of elemental analysis, molecular weight determination (210) and the bromine value (121) indicated that II was a dimer of I ($C_{16}H_{26}$,F_2) which had isolated double bonds. In the infrared absorption spectrum of II, the absorption of an exo cyclic double bond (760 cm^{-1}) was observed. The nuclear magnetic resonance spectrum indicated the signal of four protons of two exo cyclic double bonds at 4.5τ. The signal at 7.9τ is presumable due to four protons of the cyclic vinylic methylene group ($-C=C-CH_2-$), while the signal at 8.5τ was presumable due to the sixteen protons of the cyclic methylene groups. The ratio of these peak areas was 1 ; 1 : 4. The tetrahydro-compounds (III) (b.p. 145°C / 6 Torr) was prepared by the hydrogenation of II over palladised charcoal under high pressure. The infrared absorption spectrum of III did not show the absorption of an exo cyclic double bond. Nuclear magnetic resonance spectrum of III showed the signal of cyclic methylene groups at 8.5τ. From these results it was considered that the structure of II was 1-(2'-cycloocten-1'-yl)-2-cyclooctene.



I II III

Similarly, dimerization of α-phellandrene gave a dimer in yield of 20 %, (b.p. 120 - 125°C / 6 Torr), the structure of which was not determined. The dimerization of various cyclic conjugated dienes using this method is now in progress at our laboratory.

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