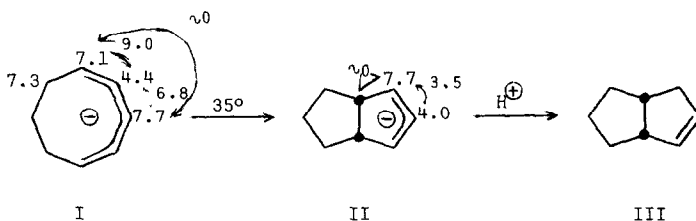


THE PENTADIENYL-CYCLOPENTENYL ANION REARRANGEMENT

R. B. Bates and D. A. McCombs
 Department of Chemistry, University of Arizona
 Tucson, Arizona 85721

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Slaugh observed the high-yield metal hydride-catalyzed isomerization of 1,3- and 1,5-cyclooctadienes to *cis*-bicyclo[3.3.0]oct-2-ene(III) and suggested two possible mechanisms; for one of these, the key step was the cyclization I \rightarrow II.¹ We wish to report the generation and nmr spectral properties of cyclooctadienyllithium (I), and to record its first-order cyclization to II with a half-life of 80 min at 35°. This is the first example of a pentadienyl-cyclopentenyl anion interconversion.



When 0.3 ml of tetrahydrofuran (THF) was added to a solution of 0.2 ml of 1,4-cyclooctadiene and 1.1 ml of 1.6 M *n*-butyllithium in hexane in an nmr tube at -78° and the resulting mixture allowed to warm to room temperature, separation into two layers occurred within a few minutes.² The upper layer (mostly hexane) was discarded, and the nmr spectrum³ of the lower layer revealed it to contain a nearly quantitative yield of I (on the formulas above, chemical shifts are given in τ units and coupling constants-in smaller numbers-in Hertz). On standing in the probe (35°), the signals due to I were observed to decrease, and signals due to II appeared. The reaction, followed by integration of the τ 4.4 quartet of I and the τ 4.0 triplet of II, had a first-order rate constant of $8.7 \times 10^{-3} \text{ min}^{-1}$. When water was added to the lower layer immediately after removal of the upper layer, an equimolar mixture of 1,3- and 1,4-cyclooctadienes containing a few percent of III was formed. On the other hand, the anion II (apparently a stronger base than I) was observed to abstract protons from an unknown source to give III nearly as fast as it formed (pseudo first-order rate constant, $6.1 \times 10^{-3} \text{ min}^{-1}$). The protons did not come from THF, since when the reaction was run in THF- d_8 , the mass spectrum of the resulting III showed no incorporation of deuterium.

Models show that the p orbitals on the 5 sp² hybridized carbons in I cannot possibly be coplanar; the coupling constants show that I is approximately U-shaped,³ but the weakness of the long-range coupling between the central and end carbons of the pentadienyl system indicates considerable deviation from perfect U-shape. The order of chemical shifts for the central and end carbons is reversed in I from what was observed in 4,4-dimethylcyclohexadienyllithium,³ possibly suggesting a large difference in electron density distribution. The protonation results, however, gave similar amounts of 1,3- and 1,4-dienes; this may be largely due to steric hindrance to protonation at the end carbons of 4,4-dimethylcyclohexadienyllithium.

It seems extremely likely that the I → II conversion is indeed the cyclization step in Slaugh's reactions¹; the 190° temperature Slaugh used is clearly not necessary for this step but was probably required for proton abstraction from the initial dienes. The suggestion¹ that a metal hydride surface facilitates the rearrangement is probably incorrect; in t-butoxide-catalyzed isomerizations of cyclooctadienes, the anion I simply does not exist long enough to cyclize to II.

The disrotatory I to II cyclization is thermally favored,⁴ and is related to the thermal (100°) conversion of cis-cis-cis-1,3,5-cyclononatriene to cis-bicyclo[4.3.0]nona-2,4-diene⁵ and the pentadienyl-cyclopentenyl carbonium ion rearrangement.⁶ Anion I can be kept for at least a week at -78° in daylight, indicating the thermal rather than photochemical nature of its conversion to II.

From our results, II is at least 1.5 kcal/mole more stable than I. The equilibrium may lie in this direction only in cyclooctadienyl systems; we are currently investigating other ring sizes and preparing cyclopentenyl systems to look for cleavage to pentadienyl systems.

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