

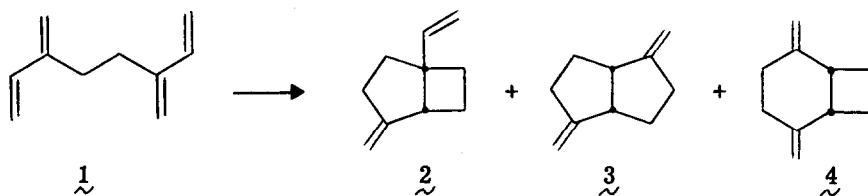
THERMAL REARRANGEMENT OF 3, 6-DIMETHYLIDENE-1, 7-OCTADIENE.  
AN INTRAMOLECULAR CYCLOADDITION REACTION

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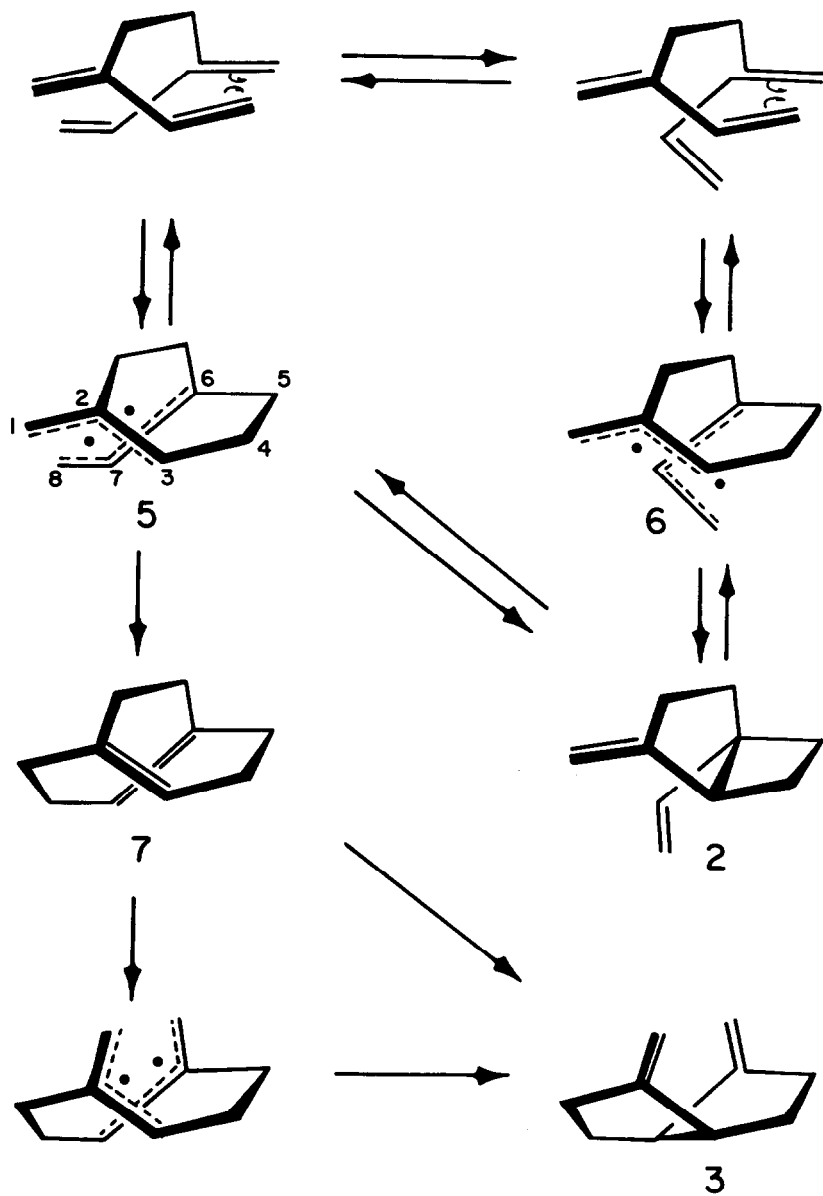
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Thermal  $\pi 2 + \pi 2$  cycloaddition reactions leading to four-membered rings are orbital symmetry allowed when they proceed via a single inversion pathway at one of the reacting centers.<sup>1</sup> In practice, the single inversion pathway is difficult to realize. Diradical<sup>2</sup> or dipolar<sup>3</sup> intermediates are believed to be involved in many instances; indeed, alkene dimerizations often involve reactants that bear substituents capable of stabilizing diradical or dipolar intermediates. It is anticipated that thermally induced intramolecular  $\pi 2 + \pi 2$  cycloaddition reactions will be similarly influenced by orbital symmetry constraints; examples of these reactions however are rare.<sup>4</sup> We report here that simple aliphatic polyenes undergo thermal rearrangement to products that result from a "formal"  $\pi 2 + \pi 2$  intramolecular cycloaddition. Three products are observed when dilute (0.01 M) cyclohexane solutions of 3, 6-dimethylidene-1, 7-octadiene<sup>5</sup> (**1**) are heated to 190 °C.<sup>6</sup>



Compounds 3 and 4 are stable to the reaction conditions; under these same conditions compound 2 is converted to 3. The reactions are insensitive to added base and a change in medium from condensed phase to gas phase produces no more than a two-fold difference in rate.

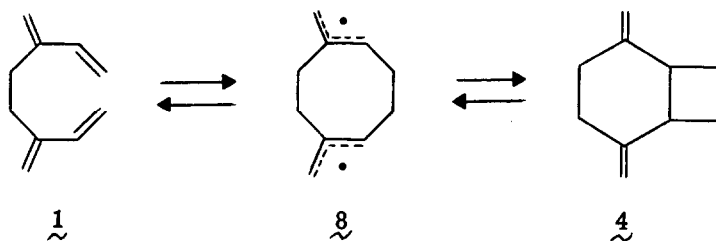
Formation of compound 2 is consistent with an intramolecular cycloaddition reaction, the details of which are outlined in the scheme. Stepwise 1, 7-ring closure of tetraene 1 produces a diastereomeric pair of resonance stabilized diradicals,



$\underline{5}$  and  $\underline{6}$ . These intermediates are analogous to the isomeric bisallyl diradicals proposed in the dimerization of butadiene.<sup>7</sup> Both diradicals ( $\underline{5}$  and  $\underline{6}$ ) can collapse to bicyclic diene  $\underline{2}$  via transannular bond formation across carbons 3 and 6.

Compound  $\underline{3}$  is formed from both  $\underline{1}$  and  $\underline{2}$ ; its formation is most economically accommodated by proposing a common intermediate or intermediates with the necessary symmetry requirement ( $C_2$ ) to accomplish the rearrangement. One such possibility is shown in the scheme. Transannular ring closure of  $\underline{5}$  across carbons 1 and 8 can result in formation of diene  $\underline{7}$ , a 1,5-ethanobridged trans, trans-1,5-cyclooctadiene ( $C_2$  symmetry). Concerted or stepwise rearrangement of  $\underline{7}$  to  $\underline{3}$  completes the transformation. We have not yet been able to detect diene  $\underline{7}$ , although it is not anticipated that this compound would accumulate to a significant extent under the reaction conditions.

An extension of the preceding discussion provides an opportunity to explain the formation of  $\underline{4}$ . 1,8-Ring closure of tetraene  $\underline{1}$  can produce bisallyl diradical  $\underline{8}$ ; transannular collapse of  $\underline{8}$  yields  $\underline{4}$  directly.<sup>8</sup>



Experiments are in progress to detect the proposed intermediate  $\underline{7}$  and to explore the scope of these intramolecular cycloadditions.

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### References and Notes

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6. Compound 2: IR ( $\text{CS}_2$ ) 3070, 2970 - 2848, 1659, 1633, 991, 904, 882  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.4 - 1.8 (m, 3H), 1.8 - 2.3 (m, 3H), 2.3 - 3.0 (m, 3H), 4.68 (m, 1H), 4.78 (m, 1H), 4.9 - 5.1 (m, 2H), 6.07 (dd,  $J = 10.4, 17.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 22.58, 27.68, 33.32, 38.37, 48.51, 51.51, 104.22, 110.11, 145.7, 157.2 ppm. Compound 3: IR ( $\text{CS}_2$ ) 3068, 2980-2830, 1657, 878  $\text{cm}^{-1}$ . NMR ( $\text{CDCl}_3$ )  $\delta$  1.43 - 1.92 (m, 4H), 2.2 - 2.4 (m, 4H), 2.94 (m, 2H), 4.81 (m, 2H), 4.87 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 32.54, 38.84, 49.05, 104.80, 157.80 ppm. Compound 4 showed IR ( $\text{CS}_2$ ) 3071, 2975 - 2840, 1642, 887  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.95 - 2.1 (m, 4H), 2.28 (q, 4H), 3.04 (m, 2H), 4.76 (d, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 26.17, 34.16, 41.71, 108.44, 149.86 ppm.
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8. An alternative mechanism also warrants consideration; 1,6-ring closure can produce 1,4-divinylbicyclo[2.2.0]hexane which can be converted to 4 by a sequence of Cope rearrangements.