

A QUANTITATIVE DETERMINATION OF ONE-CENTER VS. TWO-CENTER THERMAL EPIMERIZATION
OF A CYCLOPROPANE¹

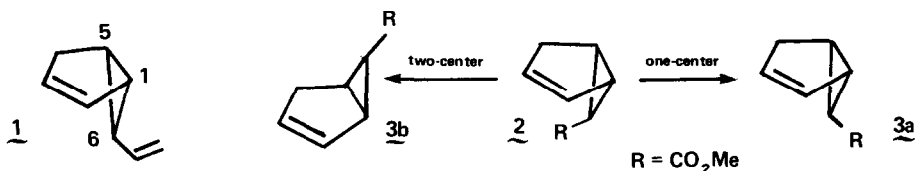
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Baldwin and Gilbert recently reported that the thermal isomerization of 6-exo-vinylbicyclo[3.1.0]hex-2-ene (**1**) to the corresponding endo-isomer occurs exclusively via one-center epimerization at C(6) rather than two-center epimerization at C(1) and C(5).² This was the first example of a one-center epimerization of a cyclopropane predominating over the two-center option when the latter alternative was geometrically feasible.³ We wish to report our results on the thermal epimerization of 6-endo-carbomethoxybicyclo[3.1.0]hex-2-ene (**2**) which demonstrates another example of the occurrence of one-center epimerization without geometric constraints. Moreover, our example is the first to demonstrate that both modes of epimerization can occur competitively.

Flash vacuum pyrolysis⁴ of **2** at 490° gives **3** (45% of isomerized material via glc analysis). At temperatures below 390° no reaction occurs; above 490° the formation of cyclohexadienes predominate. By using optically active **2**, the epimer formed via the two distinctive modes (**3a**, **3b**) can be determined since they have an enantiomeric relationship to each other. Measurement of the optical activity of the product epimer **3** gives the ratio of one-center/two-center epimerization leading to its formation. **3** was isolated from other products and unreacted starting material by sequential preparative glc utilizing both fluorosilicone (QF-1) and FFAP as stationary-phase materials. Proton nmr and glc analyses were used to verify the purity of isolated material; neither isomerization or racemization of **2** occurs in the gas chromatograph under the



conditions employed (column temp. 200°, injection port temp. 235°). In earlier studies, we had obtained the relative rotations of $\underline{3a}$ and $\underline{3b}$ from optically active $\underline{2}$.⁵ Thus, $\underline{2}$ $[\alpha]_D^{+295^\circ}$, via one-center epimerization would lead to $\underline{3a}$, $[\alpha]_D^{+211^\circ}$, via two-center epimerization would lead to $\underline{3b}$, $[\alpha]_D^{-211^\circ}$. The isolated epimer $\underline{3}$ had an observed rotation $[\alpha]_D^{+80.4 \pm 0.1^\circ}$ leading to the conclusion that epimer formation occurs via both modes with one-center epimerization favored by 69:31.⁶

In further experiments, we pyrolyzed two other samples of optically active $\underline{2}$ at 350° and 360°, respectively under a helium gas flow (longer contact time than flash vacuum pyrolysis). Under these conditions, the specific rotations of the isolated epimer $\underline{3}$ gave similar one-center/two-center epimerization ratios (72:28 and 69:31, respectively). A sample of recovered starting material showed no change in optical activity.

Without resorting to detailed mechanistic descriptions, we wish to note that the formation of $\underline{3a}$ cannot occur without cleavage of a bond to C(6) and the formation of $\underline{3b}$ cannot occur without cleavage of the C(1)-C(5) bond. The effect of carbomethoxy substituents in thermal isomerizations of cyclopropanes has been recently discussed.^{3a} However, in the present example, it is well to note that intramolecular H abstraction from C(4) by the carbonyl oxygen would be expected to result either in the formation of cyclopentenylidenes⁷ (which were not present in the pyrolysate in amounts greater than 1%) or, if reversible, in racemization of the starting material (which was not observed). Thus, a comparison of the results from the thermal epimerization of $\underline{1}$ and $\underline{2}$ provides a basis for determining the stabilizing effect of vinyl vs. carbomethoxy substituents on the intermediates and/or transition states involved in one-center and two-center epimerizations of cyclopropanes.

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References and Notes

- 1) Presented in part at the 10th Midwest Regional Meeting of the American Chemical Society, Iowa City, Iowa, October 1974.
- 2) J.E. Baldwin and K.E. Gilbert, *J. Amer. Chem. Soc.*, **98**, 8283 (1976).
- 3) Recent examples of two-center thermal epimerizations of cyclopropanes include: (a) J.J. Gajewski et. al., *J. Amer. Chem. Soc.*, **99**, 816 (1977); (b) J.A. Berson, L.D. Petersen, and B.K. Carpenter, *J. Amer. Chem. Soc.*, **98**, 122 (1976); (c) R.S. Cooke and U.H. Andrews, *J. Amer. Chem. Soc.*, **96**, 2974 (1974).
- 4) H.J. Hageman and U.E. Wiersum, *Chem. Brit.*, **9**, 206 (1973); E. Hedaya, *Acc. Chem. Res.*, **2**, 367 (1969).
- 5) D.L. Garin and D.J. Cooke, *J.C.S., Chem. Comm.*, **33** (1972). The absolute configuration of this compound is not known.
- 6) The ratio is calculated from $2F-1=80.4/211$ where F=mole fraction of the predominant isomer.
- 7) J.C. Gilbert and K.R. Smith, *J. Org. Chem.*, **41**, 3883 (1976).