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# THE CONROTATORY RING OPENING OF cis-BICYCLO[4.2.0] OCT-7-ENE TO cis, trans-1,3-CYCLOOCTADIENE, II. A KINETIC TREATMENT

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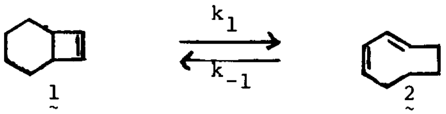
In the preceding paper[1] it was shown that cis-bicyclo[4.2.0] oct-7-ene, 1, does open to cis, trans-1,3-cyclooctadiene, 2, (by trapping the diene) at temperatures as low as 110°. In this paper we present additional evidence including kinetic and equilibrium data for this opening.



The rearrangement of cis, trans cyclooctadiene, 2, to cis-bicyclo[4.2.0] oct-7-ene, 1, at moderate temperatures was only recently observed.[2,3] We have now measured the rate of this isomerization at six temperatures in the range 64-90°. The reactions were carried out in dilute benzene solution and analyzed by g.l.c.[4] Under these conditions the reaction was strictly first order; formation of 1 was quantitative (in more concentrated solution dimerization of the diene was observed while in the neat hydrocarbon, dimer formed the bulk of the product[5]). The results, shown in Table I, produced a typical straight line Arrhenius plot.

TABLE I

Rate of Cyclization of 1,3-cis-trans-Cyclooctadiene

| T(°C) | 64.0 | 70.0 | 73.0 | 77.0 | 86.0 | 90.0 |
|---|---|---|---|---|---|---|
| $k \times 10^5$ ($sec^{-1}$) | 1.795 | 3.715 | 5.18 | 8.45 | 22.8 | 33.7 |

Arrhenius parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by the method of least squares. $\log A = 13.14 \pm .12$ $E_a = 27{,}850 \pm 200$ cal/mole $\Delta H^{\ddagger} = 26.88 \pm 0.18$ kcal./mole $\Delta S^{\ddagger} = -0.70 \pm 0.54$ eu/mole.

It was not practical to directly measure the rate of the reverse reaction 1 → 2 at low temperatures but the position of equilibrium could be determined. Purification of 1, effected by slow distillation on a Nester/Faust Teflon spinning band column, produced product with less than 0.01% impurity by g.l.c. analysis.[4] After portions of this material were heated neat at four temperatures between 90° and 170° and rapidly quenched, g.l.c. analysis[4] showed that a small peak corresponding to 2 rapidly grew and reached a constant value.

In addition a small peak corresponding to cis, cis-1,3-cyclooctadiene 3, grew slowly; initially much smaller than 2, it steadily grew larger eventually surpassing 2 in size and continuing to grow. These results indicate a small amount of 2 in equilibrium with 1, while the appearance of 3 indicates the slow irreversible formation of this more stable isomer. The values for the equilibrium constants (1/2) are given in Table II.

TABLE II

Equilibrium Constants for [1]/[2]

| T(°C) | 89.8 | 115.0 | 140.0 | 170.0 |
|---|---|---|---|---|
| K=[1]/[2] | 3350 | 2040 | 1400 | 805 |

From this data: $\Delta H = -5.60 \pm 0.26$ kcal/mole $\Delta S = 0.73 \pm 0.66$ eu/mole

Thus for the conrotatory opening of cis-bicyclo[4.2.0] oct-7-ene, 1 to the cis, trans-diene, 2, $\Delta H^{\dagger}$ is 32.6 kcal/mole, this is in contrast to the much higher value for apparent disrotatory opening to the cis, cis-diene 3 for which Ea = 43.2 kcal/mole.[7] The enthalpy of activation for the conrotatory opening is approximately 10 kcal/mole lower than for the apparent disrotatory opening, in agreement with the Woodward-Hoffman theory[8] that conrotatory opening should be preferred.

We suggest that the apparent disrotatory opening of 1 to 3 is actually a two step process, proceeding first by an allowed conrotatory opening to 2. The second step of the reaction, isomerization of the cis, trans to the cis, cis diene, then occurs by a 1,5-hydrogen shift. Such hydrogen shifts occur readily at temperatures over 150° in many conjugated dienes, among them cis, cis-1,3-cyclooctadiene[9] and 1,3-cycloheptadiene.[10] If this mechanism were operating, the observed rate constant would be given by: $k_{obs} = k_1 k_2 / k_{-1}$. From published data[7], the extrapolated rate constant, $k_{obs}$, at 150° is $6.8 \times 10^{-9}$ $sec^{-1}$. At this temperature $k_1/k_{-1} = 8.8 \times 10^{-4}$, requiring $k_2$ to be $7.7 \times 10^{-6}$. The rate for a 1,5-hydrogen shift in cis, cis-1,3-cyclooctadiene at 150° is $3.5 \times 10^{-5}$ $sec^{-1}$ [9] so this value for $k_2$ (for the 1,5-hydrogen shift in the cis, trans-diene) is certainly reasonable. Comparison of the rates at which a number of cyclobutenes in the bicyclo[n.2.0] series opens to the cis, cis-diene gives support to the two step mechanistic concept. The overall rates of opening and the equilibrium constant K at 250° for four compounds are shown in Table III.

1 2 3

## TABLE III

Comparison of Equilibrium and Rate Constants
for Isomerization in Bicyclo[n.2.0] series.

| Compound | K at 250° | $k_{obs} \times 10^5 sec^{-1}$ at 250° |
|---|---|---|
| Bicyclo[3.2.0]hept-6-ene | very small | 2.0$^{(11)}$ |
| Bicyclo[4.2.0]oct-7-ene | 0.032 | 12$^{(7)}$ |
| Bicyclo[5.2.0]non-8-ene | 0.5$^{(12)}$ | 30$^{(12)}$ |
| Bicyclo[6.2.0]dec-9-ene | >100$^{(12)}$ | 80$^{(12)}$ |

If the reaction is a one step disrotatory opening, then one would expect the rate of reaction to increase as the strain in the bond which is broken increases (i.e., as the second ring becomes smaller). But this is the reverse of the observed trend. On the other hand, if the reaction is a conrotatory opening followed by a hydrogen shift, the rate would depend on two factors: the equilibrium constant, K (which increases greatly with increasing ring size) and the rate of hydrogen shift, $k_2$ (probably a little faster in smaller rings). The net effect would be an increase in rate with increasing ring size. This in fact, is the experimental observation and supports the analysis. Of course this provides only an indication of, not proof for which of these pathways is correct.[13] Further experiments are necessary and are contemplated on cis and also on trans-bicyclo[n.2.0] olefins.

## REFERENCES

1. J. S. McConaghy, Jr. and J. J. Bloomfield, Tetrahedron Letters, 3719 (1969).
2. K. M. Shumate, P. N. Neuman and G. J. Fonken, J. Am. Chem. Soc., 87, 3996.
3. R. S. Liu, ibid., 89, 112 (1967).
4. A 1/16 inch, 10 foot-long column packed with 3% SE-30 on Aeropak Varian Aerograph) was used at 25 to 50°. The peak areas were determined with a disc integrator. Toluene was used as an internal standard for equilibrium constant measurements.
5. The diene was a mixture of three isomers in the ratio 25:3:72. All had parent ions in the mass spectrum at m/e = 216. The presence of a major ion at m/e = 108 and the known behavior of the diene towards dimethyl acetylenedicarboxylate$^{(1)}$ and tetracyanoethylene$^{(1)}$ suggest dimerization between trans-bonds to form three different cyclobutane derivatives. On hydrogenation three new compounds were formed. This means that the 2+2 cycloaddition in this instance is occurring mainly in a non-concerted manner. Concerted addition would be expected to produce 4 dimers, each of which would produce the same saturated hydrocarbon.
6. Errors given are one standard deviation.

7. G. R. Branton, H. M. Frey and R. F. Skinner, *Trans. Faraday Soc.*, **62**, 1546 (1966).
8. a) R. Hoffmann and R. B. Woodward, *Accounts of Chem. Res.*, **1**, 17 (1968).
   b) Cf. also J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968).
9. D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters* 999 (1966).
10. V. A. Mironov, O. S. Chizhov, Ia. M. Kimelfeld, and A. A. Akhrem, *Tetrahedron Letters*, 499 (1969).
11. G. R. Branton, H. M. Frey, D. C. Montague, and I. D. R. Stevens, *Trans. Faraday Soc.*, **62**, 659 (1966).
12. Either taken directly from or estimated from data in the Ph.D. Thesis of R. M. Shumate, University of Texas (1966).
13. a) A biradical intermediate has been suggested for the apparent disrotatory opening of [n.2.0] systems (n = 1-4); D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).
    b) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).