

$[\alpha]^{25}_D -80.4^\circ$ , and 0.897 g. (4.63 mmoles) of *t*-butyl perbenzoate in 5 ml. of benzene was added 5 mg. of cuprous bromide. The solution was refluxed for 30 min. during which time it turned blue. The reaction mixture was added to 500 ml. of water and the product was isolated by continuous extraction with pentane. The residual bicyclo[3.2.1]oct-3-en-2-yl benzoate was completely inactive.<sup>18</sup>

Saponification of the residual benzoate (methanolic KOH) gave 0.337 g. (57%) of bicyclo[3.2.1]oct-3-en-2-ol which was also completely racemic.<sup>18</sup> This product was shown to be >99.1% *exo* (quasi-axial)-bicyclo[3.2.1]oct-3-en-2-ol (IIIId) and <0.9% of the *endo* isomer IVd by g.c. analysis. No other components were detected.

The bicyclic alcohol was converted to *dl*-*exo*-bicyclo[3.2.1]oct-3-en-2-yl *p*-nitrobenzoate, m.p. 84–85° (lit.<sup>22</sup> 86.2–86.6°). The infrared spectrum was indistinguishable from that of an authentic sample and the melting point was not depressed when mixed with authentic material.<sup>22</sup>

**Control Experiments.**—(–)-*exo*-Bicyclo[3.2.1]oct-3-en-2-ol ((–)-IIIId),  $[\alpha]^{25}_D -143^\circ$ , was converted to the benzoate derivative (–)-IIIa which had  $[\alpha]^{25}_D -66.5^\circ$ .<sup>18</sup>

(22) H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961).

To a solution of 0.615 g. (3.17 mmoles) of *t*-butyl perbenzoate, 1 g. (12.2 mmoles) of cyclohexene, and 5 mg. of cuprous bromide in 3 ml. of benzene was added 0.412 g. of the above (–)-IIIa. After refluxing for 30 min. the mixture was diluted with ether and shaken with cold dilute aqueous acid to remove the copper salts. The ether was removed and the residue diluted to exactly 10 ml. with acetone. The expected observed rotation for a 4-dm. tube is  $-10.962^\circ$  if the (–)-IIIa retains its activity. The observed rotation was  $-10.982^\circ$ . This shows that IIIa is completely optically stable under the conditions of the copper-salt-catalyzed reaction of *t*-butyl perbenzoate with olefins.

In a second control experiment a solution of 0.124 g. (1.15 mmoles) of (+)-I,  $[\alpha]^{25}_D +57.1^\circ$  (*c* 1.1, pentane), 0.043 g. (0.22 mmole) of *t*-butyl perbenzoate, and 5 mg. of cuprous bromide in 2 ml. of benzene was refluxed for 30 min. The reaction mixture was diluted with 4 ml. of pentane and shaken with cold dilute aqueous acid to remove the copper salts. The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and diluted to exactly 10 ml. with pentane. If the excess (+)-I retains its activity completely the expected observed rotation for a 4-dm. tube is  $2.293^\circ$ . The observed rotation was  $2.237^\circ$ . This experiment shows that I is optically stable under the conditions of the reaction with *t*-butyl perbenzoate in the presence of copper salts.

[CONTRIBUTION FROM THE IBM WATSON RESEARCH CENTER, YORKTOWN HEIGHTS, N. Y.]

## Thermal Decomposition Processes in the System Tricyclo[3.3.0.0<sup>2,6</sup>]octane-1,5-Cyclooctadiene<sup>1</sup>

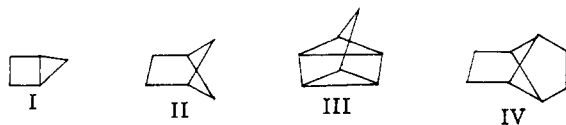
BY R. SRINIVASAN AND A. A. LEVI

RECEIVED MAY 6, 1964

The thermal isomerization of tricyclo[3.3.0.0<sup>2,6</sup>]octane in the gas phase at 1.5-mm. pressure in the temperature range from 327 to 366° is a homogeneous, first-order reaction. The rate of the reaction fitted the equation  $K = 3.22 \times 10^{15} \exp(-55,900 \pm 1400/RT)$ . The addition of propylene had no effect on the kinetics. The products that were observed (in the order of decreasing yield) were 4-vinylcyclohexene, 1,3-butadiene, and 1,5-cyclooctadiene. From separate studies of the pyrolysis of 1,5-cyclooctadiene and 4-vinylcyclohexene, it was concluded that tricyclooctane isomerized to 1,5-cyclooctadiene which in turn isomerized rapidly to 4-vinylcyclohexene. While 1,3-butadiene is a product of the pyrolysis of 1,5-cyclooctadiene, it is not certain that this is the only path by which it is formed from tricyclooctane. The kinetics of the pyrolysis of 1,5-cyclooctadiene was studied over the temperature range from 299.5 to 358.1° at 1.2-mm. pressure. From 299.5 to 327.3° the reaction seemed to be first order, homogeneous, and unaffected by the addition of propylene. Above this range the reaction was complex, although the products remained qualitatively the same.

### Introduction

The thermal decomposition of a great variety of alkyl-substituted cyclobutanes has been investigated by Walters and his co-workers.<sup>2</sup> These reactions, which in every case have been found to be homogeneous, first order, and unimolecular, have activation energies which are affected very little by one or even two alkyl substituents. In view of this fact, it seems reasonable to attribute the diminution in activation energy in going from cyclobutane itself to bridged cyclobutane systems such as bicyclo[2.1.0]pentane (I),<sup>3</sup> bicyclo[2.1.1]hexane (II),<sup>4</sup> and quadricyclene (III)<sup>5</sup> to the



strain energy that the presence of one or more additional ring systems contributes to the energy required

to break the cyclobutane ring. Whether the decrease in activation energy is exactly equal to the strain energy (as it is in the case of I) can be determined only when data on the heats of formation of these strained hydrocarbons become available.

The present study was undertaken to extend these kinetic data to tricyclo[3.3.0.0<sup>2,6</sup>]octane (IV) which is a cyclobutane with two bridges of two carbon atoms each. The formation of this molecule by a photochemical route<sup>6</sup> makes it especially interesting to know the position of the equilibrium in the thermal and photochemical systems.

### Experimental

**Materials.**—Tricyclooctane was prepared by the photochemical isomerization of 1,5-cyclooctadiene in the presence of cuprous chloride.<sup>7</sup> The crude mixture of tricyclooctane and cyclooctadiene that was obtained by a simple distillation after stripping off the ether was fractionated on a spinning-band column. A fraction rich in tricyclooctane was collected. Further purification was carried out on a gas chromatographic column using small samples (0.05 ml.) and conditions of high resolution. The sample that was collected was dried, degassed, and stored at  $-20^\circ$ . The final sample had a refractive index of 1.4709 at  $23.0^\circ$  and contained no detectable impurity when analyzed by gas chromatography. This refractive index agreed with that of a sample that had been prepared by the mercury-sensitized isomerization of 1,5-cyclooctadiene in the gas phase.<sup>6</sup>

(1) Presented at the Third Annual Metropolitan Regional Meeting of the American Chemical Society New York, N. Y., Jan., 1964.

(2) C. T. Genaux, F. Kern, and W. D. Walters, *J. Am. Chem. Soc.*, **76**, 6196 (1953); M. N. Das and W. D. Walters, *Z. physik. Chem.*, **15**, 22 (1958); R. E. Wellman and W. D. Walters, *J. Am. Chem. Soc.*, **79**, 1542 (1957); S. M. E. Kellner and W. D. Walters, *J. Phys. Chem.*, **65**, 466 (1961); H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935, 4884 (1961).

(3) M. L. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962).

(4) R. Srinivasan and A. A. Levi, *ibid.*, **85**, 3363 (1963).

(5) H. M. Frey, *J. Chem. Soc.*, 365 (1964).

(6) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963).

(7) R. Srinivasan, *ibid.*, **85**, 3048 (1963).

1,5-Cyclooctadiene, from K & K Laboratories, was distilled fractionally on a spinning-band column of 24 theoretical plates. The narrow cut, which boiled at 149° (uncor.), was collected, dried, degassed, and used. Gas chromatographic analysis showed that it was only 96.5% pure. The rest was made up of one impurity which was not identified, but was found to decompose more slowly (if at all) even at the highest temperature that was used.

Propylene (Phillips Petroleum Co.) was used as obtained.

**Apparatus.**—The high-vacuum system and furnace that was used has been described before.<sup>4</sup> Stopcocks were lubricated with Dow-Corning silicone grease. The capillary tubing, which contained the dead space, was heated electrically to about 110° to avoid condensation of the organic material. Preseasoning of the reaction vessel was carried out routinely following the admission of air before any runs were made.

Since the reactants had vapor pressures of the order of only 1 to 10 mm. at room temperature, it was found quicker to admit the sample directly from a storage bulb to the reaction cell and then measure the pressure rather than to admit a measured quantity. As a result, the initial pressures of the reactants fluctuated appreciably from run to run.

**Analysis.**—The change in the total pressure of the system was finite but not large enough to help follow the course of the reaction. Hence, the rate of the reaction could be determined only by chemical analysis, each run giving one point on the rate curve. At the end of the run, the pyrolysate was frozen down in liquid nitrogen and a C<sub>4</sub>-fraction was distilled off at Dry Ice-acetone temperature. The rest of the material was sealed in a small tube. The tube was cooled to -195° and cut open, and 0.1 ml. of acetone was added. The solution was injected into a gas chromatographic column (Ucon oil-550X, 8 ft. long) fitted to a F and M programmed gas chromatograph. The column was initially at 50° and after 5 min. was heated to 115° at the rate of 30°/min. A clean separation of the reactant and the products was achieved. The pressure-volume data on the C<sub>4</sub>-fraction and areas under the curves from the C<sub>8</sub>-components in the gas chromatogram were used to calculate the rates of decomposition.

### Results

**Products.**—Pyrolysis of tricyclooctane ( $P = 1.5$  to 7.5 mm.) at 358° to several half-lives leads to a 20% increase in pressure. The products were found to be a C<sub>4</sub>-hydrocarbon and two C<sub>8</sub>-hydrocarbons. The C<sub>4</sub>-hydrocarbon was identified as 1,3-butadiene by mass spectral analysis. The major C<sub>8</sub>-product was identical with an authentic sample of 4-vinylcyclohexene in both its infrared spectrum and the retention time on a gas chromatograph while the minor component was found to be 1,5-cyclooctadiene from its retention time. Quantitative analysis of the C<sub>4</sub>-fraction showed that the increase in pressure during pyrolysis could be wholly accounted for (within the uncertainty of  $\pm 0.05$  mm. in the measurement of pressure) by the over-all process: tricyclooctane  $\rightarrow$  2C<sub>4</sub>H<sub>6</sub>. Pyrolysis of 1,5-cyclooctadiene ( $P = 1.1$  mm.) at 299° to several half-lives showed that the pressure increased by about 20%. The two products which were detected were 4-vinylcyclohexene and 1,3-butadiene. In this instance also, quantitative analysis of the C<sub>4</sub>-fraction showed that the increase in pressure during pyrolysis matched that which can be expected from the process: cyclooctadiene  $\rightarrow$  2C<sub>4</sub>H<sub>6</sub>. A vapor sample of 4-vinylcyclohexene was heated to 358° for 3 hr. There was no detectable change in pressure. A small amount (1%) of volatile product was distillable at Dry Ice-acetone temperature. These results show that the stoichiometry of the decomposition of tricyclooctane is most probably tricyclooctane  $\rightarrow$  1,5-cyclooctadiene + 4-vinylcyclohexene + 2 butadiene.

**Rate Studies.**—The rate of disappearance of tricyclooctane was studied at  $1.5 \pm 0.3$  mm. at five temperatures in the temperature range from 327.4 to 366.3°

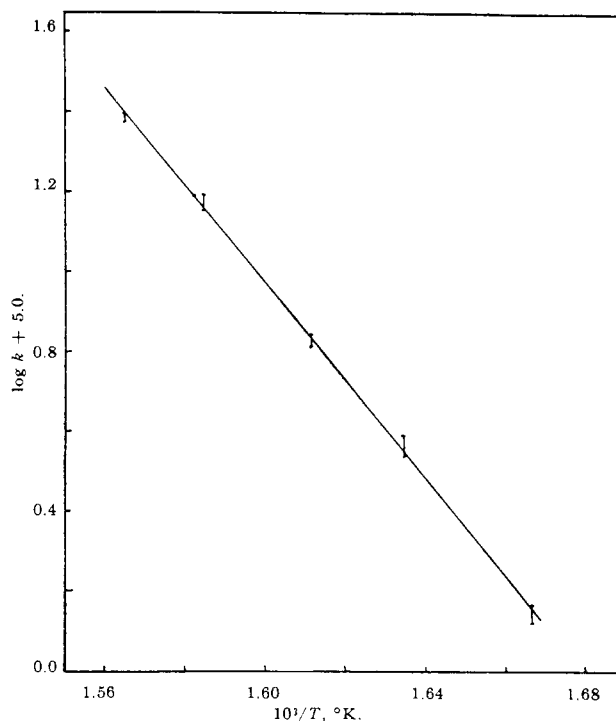


Fig. 1.—Plot of the logarithm of the first-order rate constants vs. the reciprocal of the temperature for the decomposition of tricyclooctane.

The nature of the products did not change over this range, nor did it vary with the conversion. A plot of the logarithm of the per cent of tricyclooctane remaining vs. time was linear up to 74% conversion at 366.3°, and up to 83% conversion at 358.2°. In six runs at two different temperatures the reaction vessel was packed with glass tubing so that the surface-to-volume ratio increased by a factor of 17. This decreased the first-order rate constant by about 13% at both temperatures. But the temperature coefficient of the reaction in the two reaction vessels was not different.

In two runs at 358.7°, propylene gas, at an average pressure of 0.8 mm., was added. This did not change the rate of decomposition detectably. Propylene is known to react efficiently with free-radical species. The lack of any effect due to its presence suggests the absence of free-radical processes in this reaction. Essentially the same conclusion can be drawn from the fact that as the reaction proceeds, since it gives rise to three unsaturated species, no change in the rate constant may be observed.

First-order rate constants at five temperatures have been plotted as a function of temperature in the usual way in Fig. 1. All of the data given in Table I, with the exception of those that were obtained in packed cells or in the presence of propylene, were averaged and included in this plot. The best straight line through all the points as obtained by the least-square method fitted the equation

$$k = 3.22 \times 10^{15} \exp (-55,900 \pm 1400/RT)$$

Since 1,5-cyclooctadiene was a product of the decomposition of tricyclooctane, and since it decomposed at a lower temperature than tricyclooctane, it was thought to be of interest to obtain quantitative data on its decomposition. The rate of disappearance

TABLE I  
THERMAL DECOMPOSITION OF TRICYCLO[3.3.0.0<sup>2,6</sup>]OCTANE

| Temp.,<br>°C. | Initial<br>press.,<br>mm. | Time,<br>min. | % reactant accounted<br>for in prod. |                          |                            |                | <i>k</i><br>× 10 <sup>4</sup> ,<br>sec. <sup>-1</sup> |
|---------------|---------------------------|---------------|--------------------------------------|--------------------------|----------------------------|----------------|---|
|               |                           |               | %<br>reactant<br>remaining           | Cyclo-<br>octa-<br>diene | Vinyl-<br>cyclo-<br>hexene | Buta-<br>diene |   |
| Unpacked Cell |                           |               |                                      |                          |                            |                |   |
| 366.3         | 1.2                       | 30.0          | 63.8                                 | 6.6                      | 72.4                       | 20.9           | 24.9  |
|               | 1.3                       | 60.0          | 41.3                                 | 1.9                      | 76.2                       | 21.9           | 24.5  |
|               | 1.3                       | 90.0          | 27.6                                 | 0                        | 76.8                       | 23.2           | 23.8  |
| 358.7         | 1.4                       | 60.0          | 57.1                                 | 2.7                      | 73.6                       | 23.7           | 15.5  |
|               | 2.8 <sup>a</sup>          | 60.0          | 58.8                                 | 2.7                      | 82.0                       | 15.3           | 14.7  |
|               | 3.4 <sup>b</sup>          | 60.0          | 55.8                                 | 3.4                      | 75.0                       | 21.6           | 16.1  |
| 358.2         | 1.5                       | 30.0          | 76.6                                 | 9.5                      | 71.9                       | 18.6           | 14.7  |
|               | 1.6                       | 60.0          | 57.7                                 | 6.1                      | 72.5                       | 21.5           | 15.2  |
|               | 1.5                       | 60.0          | 57.3                                 | 6.0                      | 75.0                       | 19.0           | 15.4  |
| 347.5         | 1.5                       | 60.0          | 58.0                                 | 3.0                      | 77.5                       | 19.5           | 15.1  |
|               | 3.9                       | 60.0          | 59.5                                 | 4.8                      | 72.3                       | 23.0           | 14.4  |
|               | 1.6                       | 90.0          | 45.1                                 | 2.9                      | 75.6                       | 21.4           | 14.7  |
|               | 1.4                       | 120.0         | 35.0                                 | 1.8                      | 76.4                       | 21.8           | 14.5  |
|               | 1.5                       | 180.0         | 18.2                                 | 0                        | 77.6                       | 22.4           | 15.7  |
|               | 1.6                       | 60.0          | 77.6                                 | 12.5                     | 70.3                       | 17.2           | 7.05  |
|               | 1.6                       | 120.0         | 61.2                                 | 5.0                      | 75.8                       | 19.1           | 6.83  |
|               | 1.3                       | 180.0         | 49.2                                 | 3.2                      | 76.6                       | 20.2           | 6.57  |
| 338.7         | 1.4                       | 60.0          | 86.9                                 | 24.9                     | 66.5                       | 8.6            | 3.89  |
|               | 1.4                       | 120.0         | 77.8                                 | 8.0                      | 75.6                       | 16.4           | 3.48  |
|               | 1.8                       | 150.0         | 71.0                                 | 10.1                     | 72.4                       | 17.6           | 3.81  |
| 327.4         | 1.3                       | 180.0         | 67.9                                 | 7.2                      | 75.4                       | 17.4           | 3.58  |
|               | 1.2                       | 180.0         | 86.6                                 | 23.0                     | 65.1                       | 11.9           | 1.33  |
|               | 1.3                       | 240.0         | 80.6                                 | 12.2                     | 74.9                       | 12.9           | 1.50  |
| Packed Cell   |                           |               |                                      |                          |                            |                |   |
| 358.2         | 1.4                       | 30.0          | 79.5                                 | 0                        | 77.3                       | 22.7           | 12.7  |
|               | 1.3                       | 60.0          | 62.6                                 | 0                        | 80.5                       | 19.5           | 12.9  |
|               | 1.4                       | 60.0          | 62.0                                 | 0                        | 76.4                       | 23.6           | 13.2  |
| 338.7         | 1.3                       | 60.0          | 89.5                                 | 12.7                     | 69.7                       | 17.6           | 3.07  |
|               | 1.5                       | 120.0         | 79.2                                 | 5.4                      | 75.4                       | 19.2           | 3.24  |
|               | 1.4                       | 180.0         | 69.6                                 | 5.0                      | 73.8                       | 21.2           | 3.35  |

<sup>a</sup> Added propylene, 0.9 mm. <sup>b</sup> Added propylene, 0.8 mm.

of 1,5-cyclooctadiene was studied at about 1.2 mm. in the temperature range from 299.3 to 358.1° (see Table II). A plot of the logarithm of the per cent of reactant remaining against time was a straight line up to 60% conversion at 313.3° and 80% conversion at 327.3°. However, at 338.9 and at 358.1°, the plot showed large departures from a linearity at all conversions. In packed reaction vessels, in which the surface-to-volume ratio was 17-fold greater than in the unpacked vessel, the first-order rate constant was nearly the same at 313.2 and 338.7°, but not at 358.2°. Addition of propylene ( $p \sim 0.7$  mm.) had no observable effect on the kinetics at 313.6°.

The logarithm of the first-order rate constant, when plotted against temperature in the usual way, was found to be linear when the data in the range from 299.5 to 327.3° were used. These data were obtained at only three temperatures. The slope of the line corresponded to an activation energy 49 kcal./mole.

The pre-exponential factor was calculated to be  $2.9 \times 10^{14}$  sec.<sup>-1</sup>. It may be noted that very little butadiene is formed in the lower end of the temperature range that was used, and that 4-vinylcyclohexene is the major product.

### Discussion

It is necessary to consider whether tricyclooctane decomposes by a single unimolecular process or by two or more parallel processes. The problem could have

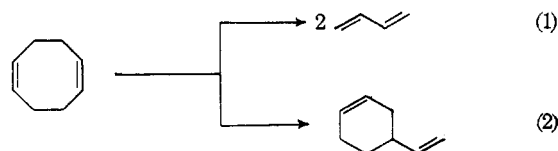
TABLE II  
THERMAL DECOMPOSITION OF 1,5-CYCLOOCTADIENE

| Temp.,<br>°C. | Initial<br>press.,<br>mm. | Time,<br>min. | % reactant accounted<br>for in prod.—        |                            |                |   |
|---------------|---------------------------|---------------|--|----------------------------|----------------|---|
|               |                           |               | %<br>reactant<br>remain-<br>ing <sup>a</sup> | Vinyl-<br>cyclo-<br>hexene | Buta-<br>diene | <i>k</i><br>× 10 <sup>4</sup> ,<br>sec. <sup>-1</sup> |
| Unpacked Cell |                           |               |  |                            |                |   |
| 358.1         | 1.5                       | 15.0          | 18.9   | 76.2                       | 23.8           | 184.9   |
|               | 1.4                       | 30.0          | 11.8   | 76.9                       | 23.1           | 118.7   |
|               | 1.6                       | 60.0          | 10.1   | 77.4                       | 22.6           | 63.7  |
| 338.9         | 1.6                       | 15.0          | 45.6   | 79.2                       | 20.8           | 87.3  |
|               | 1.3                       | 30.0          | 31.7   | 77.2                       | 22.8           | 63.8  |
|               | 1.3                       | 60.0          | 12.8   | 79.5                       | 20.5           | 57.2  |
| 327.3         | 1.1                       | 15.0          | 71.6   | 82.3                       | 17.7           | 37.1  |
|               | 1.0                       | 30.0          | 54.1   | 81.2                       | 18.8           | 34.2  |
|               | 1.1                       | 60.0          | 31.4   | 79.9                       | 20.1           | 32.2  |
| 313.6         | 1.1                       | 90.0          | 18.8   | 80.7                       | 19.3           | 31.0  |
|               | 1.1                       | 60.0          | 60.4   | 82.3                       | 17.7           | 14.0  |
|               | 2.2 <sup>b</sup>          | 60.0          | 52.4   | 84.8                       | 15.2           | 17.9  |
|               | 1.3 <sup>c</sup>          | 60.0          | 59.6   | 84.2                       | 15.8           | 14.4  |
| 313.3         | 1.2                       | 30.0          | 80.1   | 84.0                       | 16.0           | 12.3  |
|               | 1.1                       | 60.0          | 62.5   | 83.9                       | 16.1           | 13.1  |
|               | 1.1                       | 90.0          | 49.5   | 81.4                       | 18.6           | 13.1  |
| 299.5         | 1.0                       | 120.0         | 39.4   | 81.2                       | 18.7           | 12.9  |
|               | 1.0                       | 30.4          | 92.3   | 94.4                       | 5.6            | 4.37  |
|               | 1.1                       | 60.0          | 84.3   | 90.0                       | 10.0           | 4.74  |
|               | 1.1                       | 120.0         | 70.5   | 86.5                       | 13.5           | 4.85  |
|               | 1.0                       | 180.0         | 61.8   | 84.9                       | 15.1           | 4.46  |
| Packed Cell   |                           |               |  |                            |                |   |
| 358.2         | 1.1                       | 15.0          | 23.9   | 72.3                       | 27.7           | 159.0   |
|               | 1.1                       | 30.0          | 19.0   | 73.1                       | 26.9           | 92.3  |
| 338.7         | 0.9                       | 15.0          | 53.5   | 75.3                       | 24.7           | 69.6  |
|               | 1.1                       | 30.0          | 34.9   | 76.3                       | 23.7           | 58.5  |
| 313.2         | 1.2                       | 30.0          | 78.6   | 81.5                       | 18.5           | 13.4  |
|               | 1.3                       | 60.0          | 66.5   | 78.2                       | 21.8           | 11.3  |
|               | 1.3                       | 90.0          | 51.6   | 79.3                       | 20.7           | 12.3  |

<sup>a</sup> Corrected for impurity present. <sup>b</sup> Added propylene, 0.9 mm. <sup>c</sup> Added propylene, 0.4 mm.

been resolved by the mathematical analysis of the data if the analytical accuracy had been an order of magnitude better, or if the rate of decomposition of 1,5-cyclooctadiene was comparable with that of tricyclooctane.

It has been shown that 4-vinylcyclohexene does not decompose readily in the temperature range used in this study. It is also known that 1,3-butadiene is stable in this range.<sup>8</sup> Since the pyrolysis of 1,5-cyclooctadiene yields 4-vinylcyclohexene and 1,3-butadiene, this reaction must involve two parallel paths.

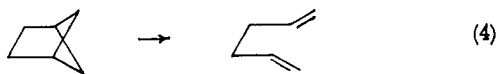


One obvious product in the pyrolysis of tricyclooctane is 1,5-cyclooctadiene. This reaction would be analogous to the decomposition of cyclobutane to two mole-



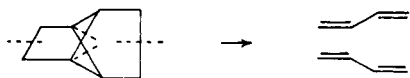
cules of ethylene<sup>2</sup> and the isomerization of bicyclo[2.1.1]-hexane to 1,5-hexadiene.<sup>2</sup> It seems unlikely that tri-

(8) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **32**, 1992 (1964).

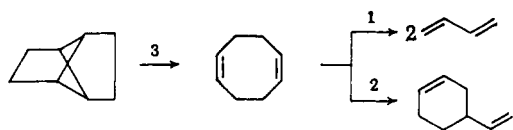


cyclooctane would rearrange to 4-vinylcyclohexene in a single step as a deep-seated rearrangement would be necessary to open the four- and five-membered rings in tricyclooctane and close again to give a six-membered ring. Hence, it is more reasonable to conclude that the 1,5-cyclooctadiene is an intermediate in the isomerization of tricyclooctane to 4-vinylcyclohexene. The data in Table I show that in the decomposition of tricyclooctane the amount of 1,5-cyclooctadiene that remains is a maximum at the shortest time a measurement can be made. It can be calculated from the experimental first-order rate constants (at 327.3°) that the amount of 1,5-cyclooctadiene would go through a maximum at only 98/1000 sec. after the reaction had started, and the ratio of 1,5-cyclooctadiene to tricyclooctane would have been 0.034.

It is much more difficult to decide whether 1,3-butadiene is formed *via* 1,5-cyclooctadiene or directly in the decomposition of tricyclooctane. Mechanistically it can be seen that the pathway which does not involve 1,5-cyclooctadiene as an intermediate requires the simultaneous cleavage of four bonds as is shown.



The breaking of these bonds in a stepwise fashion does not seem to lead to an energetically favored pathway except in the one instance in which 1,5-cyclooctadiene is formed. Hence, it is reasonable to conclude that the sequence of reactions is



In common with the decomposition of cyclobutane,<sup>2</sup> alkyl substituted cyclobutanes,<sup>2</sup> and bicyclo[2.1.1]-

hexane,<sup>4</sup> the isomerization of tricyclooctane appears to be a homogeneous, unimolecular process which is unaffected by the presence of molecules which act as free-radical traps. The activation energy for the reaction is the same as that for bicyclo[2.1.1]hexane within experimental error. While at first sight it may appear that the tricyclooctane is a more strained system than bicyclo[2.1.1]hexane, molecular models show that the addition of a second two-carbon bridge diagonally to a cyclobutane ring can be achieved with little or no additional distortion. The fact that the activation energy remains the same is either due to all of the strain energy not being available for the rupture of the cyclobutane system during pyrolysis, or due to the increase in strain energy being no more than the experimental error in the activation energy. It is surprising that the pre-exponential factor in this instance is larger than for bicyclo[2.1.1]hexane by a factor of 3 which corresponds to a difference of more than 2 e.u. of entropy of activation. Since the isomerization of bicyclo[2.1.1]hexane involves a reaction from a bicyclic to an open-chain system while the isomerization of tricyclooctane involves a reaction from a tricyclic to a monocyclic system, a smaller ratio of pre-exponential factors would have been predicted.

In view of the complexity in the decomposition of 1,5-cyclooctadiene, very little can be said about the mechanism of this process. The ratio of 4-vinylcyclohexene to 1,3-butadiene is seen to decrease with an increase in temperature. From a plot of the logarithm of this ratio *vs.* the reciprocal of this temperature, it can be calculated that the difference in the activation energies for the formation of these products ( $E_1 - E_2$ ) equals 6.2 kcal./mole. If the activation energy of the first-order process from 299.5 to 327.3° is identified with reaction 2, then the activation energy for reaction 1 is probably  $(49 + 6) = 55$  kcal./mole. This value is of the same order of magnitude as the activation energy of 61.8 kcal./mole for the unimolecular decomposition of 4-vinylcyclohexene to two molecules of 1,3-butadiene.<sup>9</sup>

(9) N. E. Duncan and G. J. Janz, *J. Chem. Phys.*, **20**, 1644 (1952).

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## The Addition of Nitrones to Olefins. Fused Bicyclic Isoxazolidines<sup>1</sup>

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The oxidation of N-methyl-N-5-hexenylhydroxylamine with mercuric oxide and the condensation between 5-hexenal and N-methylhydroxylamine afforded *cis*-N-methyl-3-oxa-2-azabicyclo[3.3.0]octane (2). Other bicyclic isoxazolidines have been synthesized by the condensation reaction employing unsaturated aldehydes and *unsaturated ketones*. The structures of these compounds were proved by hydrogenolysis and, in some cases, independent synthesis of the amino alcohols. The mechanism of the cyclization reactions are postulated as intramolecular 1,3-additions of an unsaturated nitron intermediate. The scope of this preparative route to fused bicyclic isoxazolidines is discussed in terms of reactivity, orientation, and stereochemistry.

The pyrolysis of a mixture of the isomeric N-methyl- $\alpha$ -pipecoline oxides produced, in addition to the predicted unsaturated hydroxylamine, an unexpected bicyclic base.<sup>2</sup> This product was identified as N-

methyl-3-oxa-2-azabicyclo[3.3.0]octane (2), and was postulated as having arisen from an unsaturated nitron intermediate (1). The nitron may have been produced from N-methyl-N-5-hexenylhydroxylamine by an oxidation-reduction reaction. However, this unsaturated hydroxylamine was obtained in good

(1) A preliminary communication concerning a part of this work has appeared: *J. Am. Chem. Soc.*, **81**, 6334 (1959). This work was reported in part: Abstracts, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960, p. 85-O.

(2) A. C. Cope and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 4656 (1960).