

**The Thermal Decomposition of Cyclobutanes:
6,7-Dimethylbicyclo[3,2,0]heptane**

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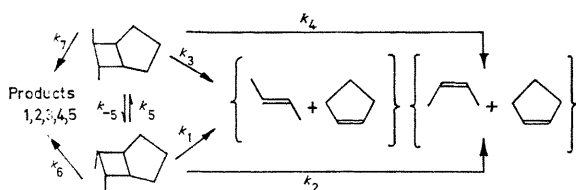
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Two essentially distinct mechanisms have been suggested for the thermal unimolecular decomposition of cyclobutane and alkylcyclobutanes to olefins. One involves the formation of a tetramethylene biradical intermediate and can be considered as a two-stage process; the other, a symmetrical stretching of two (opposite) carbon-carbon

bonds in the ring to yield the olefins by a one step, concerted process. Until recently it appeared remarkable that this concerted process was energetically so difficult, as shown by the experimental values for E_a (60 to 65 kcal. mole⁻¹). The Woodward-Hoffmann rules provide a rationale for this; the simple concerted mechanism is in

fact an orbital-symmetry-forbidden process. There is however, an allowed concerted process which involves a very twisted transition complex and which results in inversion taking place at one of the ring carbon atoms. Such a process might well be expected to have a high energy of activation. To date all the substituted cyclobutanes that have been studied, have been such, that they contained centres at which inversion would be undetectable in the products, and hence no definite test of this concerted mechanism has been possible. We now report some results obtained from the thermal decomposition of *trans*- and *cis*-(*exo*)-6,7-dimethylbicyclo[3,2,0]heptane which do provide such a test. The pyrolyses of these compounds were studied in the gas phase, under conditions where they were homogeneous, molecular, and kinetically first order. The reaction scheme is fairly complex but unambiguous.



The reaction has been studied starting from both isomers at 414.3, 428.7, and 452.7° and several runs for different times were carried out at each temperature. The rates of *cis*-*trans*-isomerization of the starting materials (k_5 and k_6) were found to be slow compared with the other rate constants. The reactions of major interest for the purpose of deciding on the nature of the transition complex are

those leading to cyclopentene and but-2-ene. The following ratios of rate constants were determined from the analytical results:

Temperature	k_1/k_3	k_3/k_4	k_3/k_1	k_2/k_4
414.3°	1.11	3.09	1.28	2.18
428.7°	1.12	3.05	1.22	2.22
452.7°	1.03	3.04	1.24	2.38

Thus *trans*-6,7-dimethylbicyclo[3,2,0]heptane yields but-2-ene with about 75% retention of configuration and the *cis*-(*exo*)-isomer gives approximately equimolar amounts of the two but-2-ene isomers. Since inversion at either C(1) or C(5) would result in the formation of cyclopentene with a *trans*-double bond we may rule out this possibility on energetic grounds. Thus if the decomposition were to proceed by an allowed concerted process 100% inversion of the but-2-ene would be necessary. The experimental results show that this is not the case and indeed the results are quite similar to those obtained for the decomposition of *cis*- and *trans*-1,2-dimethylcyclobutane.¹ The evidence is strongly in favour of a biradical intermediate, though for reasons which we present elsewhere we believe that this biradical is produced by a twisting of the cyclobutane ring.

For completeness we note that products 2, 4, and 5 are the three nona-2,7-dienes (formed by the cleavage of the cyclobutane ring in an opposite sense to that required for the but-2-ene formation) and products 1 and 3 the *trans*- and *cis*-1-ethyl-2-vinylcyclopentanes formed by the isomerization of 2, 4, and 5. (The numbering merely indicates the order of chromatographic elution.)

(Received, March 10th, 1969; Com. 331.)

¹ H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 3935, 4884.