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Thermal Rearrangement of Tricyclo[4.1.0.$0^{2,7}$]heptane (1)

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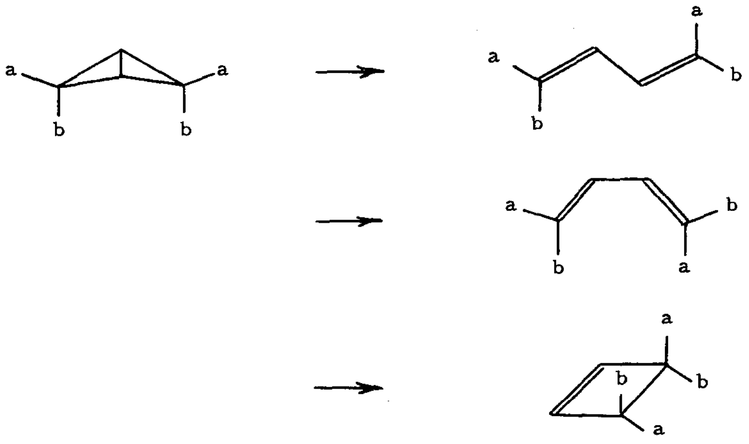
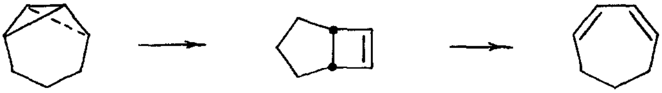
The thermal rearrangement of bicyclobutane to butadiene has been of particular interest to us because although it appears to be a very simple process, seven concerted paths are available as well as two paths involving diradical intermediates. We have recently found that molecular orbital calculations indicate only three of the concerted paths are electronically allowed: (2)



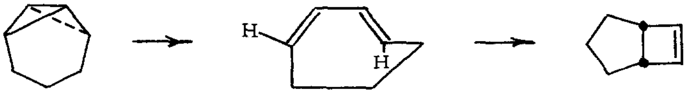
Our previous results on the rearrangement of bicyclobutane-exo-d_1 (3) are consistent with any of the three paths given above. However, they are also consistent with the diradical path which involves initial cleavage of one of the peripheral bonds. In order to obtain further experimental data which might distinguish between a concerted and a diradical path, we have examined the thermolysis of tricyclo[4.1.0.$0^{2,7}$]heptane (I). (4).

At a temperature over 300° in a flow system, I is converted to a mixture of bicyclo[3.2.0]heptene-6 (II) and 1,3-cycloheptadiene (III). The proportion of III in the product decreases from 71% at 400° to 16% at 365° and 9% at 320°. The conversion at temperatures lower than 320° was too small for convenient measurement. Thus, II is the major product of the reaction, and since the proportion of III decreased with decreasing temperature, it appears probable that it is formed by the rearrangement of II. (5)



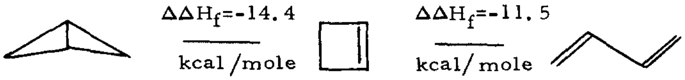
I II III

It seems unlikely that II is formed directly from I, and cis-trans-cycloheptadiene (IV) is a reasonable intermediate. Molecular orbital calculations are in agreement with this conclusion. In analogy with the reactions of the corresponding larger ring dienes (6) IV would be expected to close to II in an allowed thermal conrotatory process:

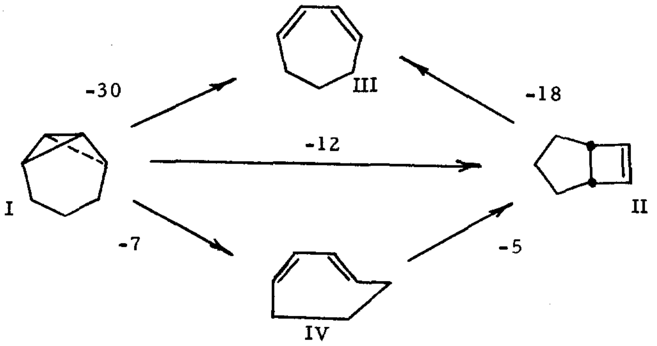


IV

We have determined the heat of combustion of bicyclobutane and of cyclobutene (7) and find the following differences in heats of formation:

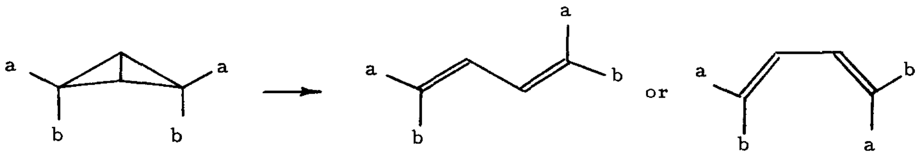


The additional strain energies of I and II have been estimated leading to the approximate values given below in kcal/mole. The heat of isomerization of IV to II was assumed to be at least 5 kcal/mole in view of the fact that the less strained *cis-trans* C_8 and C_9 dienes also undergo conversion to a cyclobutene. (6)



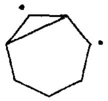
Although the estimates may be in error by several kcal/mole, it seems certain that the conversion of I to III is favored over the conversion to IV by 20 kcal/mole or more.

In view of this estimate, it is clear that thermodynamic factors have been overruled by electronic factors in determining the course of the reaction. Our previous calculations on the course of the concerted process (2) indicate that it is electronically allowed only for the process:



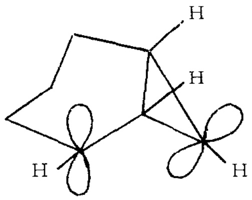
This is in agreement with the observed course of the reaction. One must then consider whether or not a two-step diradical path could be electronically controlled.

The central bond cannot be involved in a two-step process (2) and therefore the intermediate would be:



e ring opening of the cyclopropyl radical has been considered by Longuett-Higgins and Abrahamson (8) and by Woodward and Hoffmann (9). Longuett-Higgins found that both the conrotatory and disrotatory modes of opening were electronically forbidden, and using the CNDO method (10) and our scheme of plotting the bond indices against the angle of rotation, (2) we have obtained the same result.

However, one cannot neglect the second radical center. If the diradical were a true intermediate, the two radical centers could rotate with respect to each other, as, for example, is found in the thermolysis of cyclopropane (11). In order to try to estimate the course of the conversion of the diradical to the diene, we have started with the conformation in which there is minimal overlap between the two radical centers, and maximum overlap between the exocyclic radical center and the cyclopropane ring:



An examination of the conrotatory and disrotatory modes of opening using the CNDO method indicated that both modes were allowed, and the calculated difference in energy between the two paths was very small. Thus, we conclude that the two step process will not readily explain the observed results, and that the concerted process better represents the conversion of bicyclobutane to butadiene.

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