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THE KINETICS OF THE BICYCLO[3.2.0]HEPTADIENE TO CYCLOHEPTATRIENE CONVERSION

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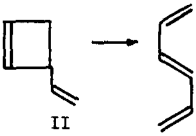
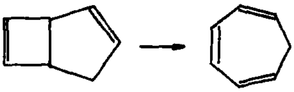
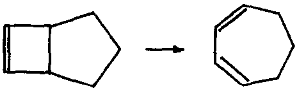
Several kinetic schemes have been discussed for the thermal reorganization of bicyclo[2.2.1]heptadiene to cycloheptatriene and toluene (1). In addition to these rather substantial rearrangements, two much more subtle reactions, the interconversion of non-planar cycloheptatriene (2) and the intramolecular transfer of hydrogen (3), have been directly observed. This communication reports the kinetic parameters which can be used to assess the role of bicyclo[3.2.0]heptadiene in this series of reactions.

Bicyclo[3.2.0]heptane was produced by the photolysis of cycloheptatriene using the Dauben-Cargill procedure (4). The conversion of the bicyclic isomer to cycloheptatriene was carried out in the flow reactor described by Lewis (5). The reaction was found to be kinetically first-order, thereby permitting rates to be determined from a plot of $\frac{(A_0-A)u}{V}$ vs. A where A_0 is the initial amount of cycloheptatriene, A is the final amount, u the flow rate through the reactor, and V is the volume of the reactor. Rates measured at 217, 235 and 255°C were treated in the usual fashion to give the rate expression $k = 10^{14}e^{-39,500/RT}$.

This experimental value of the activation energy can be employed profitably to complement some qualitative statements that have been made concerning bicyclo[3.2.0]heptadiene. For instance, the symmetry considerations codified in the Woodward-Hoffman rules for electrocyclic reactions predict that the cyclobutene to butadiene thermolysis occurs more readily in the conrotary than in the disrotary mode (6), but these rules give no assessment of the difference in activation energy between the two modes of ring opening. Since monocyclic cyclobutenes open exclusively in the conrotary mode it is very difficult to determine experimentally the difference in activation energy for the two modes of ring opening. A bicyclic cyclobutene must open in disrotary fashion if the product is to be the cis-cis 1,3 cyclic diene that is usually observed. It is thus possible to obtain a value of 13 Kcal/mole for the difference in activation energy between the two modes of ring opening from the kinetic parameters for pyrolysis of bicyclo[3.2.0]heptene (III) and cyclobutene (I) (See Table I). The accepted value of the allylic resonance, 13 Kcal/mole (8), leads to estimated values for activation energies of 20 Kcal/mole for 3-vinylcyclobutene (II) and 32.5 Kcal/mole for bicyclo[3.2.0]-heptadiene (IV). Clearly, the full benefit of the allylic resonance is not realized in the bicyclic compound. In fact, the activation energy for bicycloheptadiene reported in this paper can be used to determine the kinetic advantage of breaking an allylic carbon-carbon that is coplanar with the olefinic bond, i.e., arranged so minimum overlap occurs in the allylic radical. The lower activation energy of bicycloheptadiene (IV) (39.5 Kcal/mole) reactive to bicycloheptene (III) (45.5 Kcal/mole) suggests a value of about 6 Kcal/mole for this minimal type of allylic stabilization.

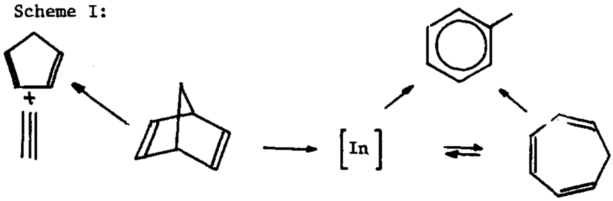
TABLE I

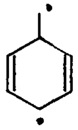
REACTIONS USED TO DERIVE ESTIMATE OF ALLYLIC STABILIZATION IN BICYCLO[3.2.0]HEPTADIENE PYROLYSIS

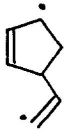
	log A	E_a Kcal/mole	Ref.
 I	13.	32.5	(7)
 II		20 (estimated)	(7,8)
 IV	14.	39.5	This work
 III	14.3	45.5	(9)

Critical commentary concerning thermal pathways connecting bicyclo[2.2.1]-heptadiene, cycloheptatriene, cyclopentadiene, acetylene and toluene has been provided by Woods (10) and by Chesick (11). Herndon cites this work and his own kinetic information proposes that the reaction scheme shown is consistent with all observations (1). Even though the structure of the intermediate is not easily determined, a carefully constructed rationale leads Herndon to favor the diradical V as the intermediate. It is clear from Herndon's arguments that the diradical VI should not participate in this reaction. However, two structures with completely developed bonding, norcaradiene (VIII) and bicyclo[3.2.0]heptadiene, are also kinetically reasonable intermediates. The activation energies of the observable reactions in scheme A are 50 Kcal/mole or greater. If formation of bicyclo[3.2.0]heptadiene was the rate determining step, its conversion to cycloheptatriene would be so rapid that bicyclo[3.2.0]heptadiene would be a non-observable intermediate. The same reasoning applies to norcaradiene. We therefore conclude that the kinetic parameters that are now available do not distinguish which intermediate is involved. More experimental evidence must be gathered to establish the remaining details of these thermal reorganizations.

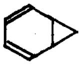
Scheme I:




V


VI


IV


VIII

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