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EVIDENCE CONCERNING PARTICIPATION OF CYCLOBUTYL BONDING ELECTRONS IN THERMOLYSIS OF AZO COMPOUNDS

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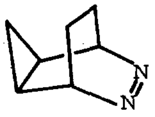
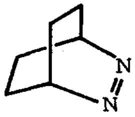
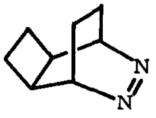
The extensive affect of edge participation of cyclopropyl electrons on chemical reactivity is now well established.[1-6] For example, I is more reactive than II by the astonishing factor of 10^{17}.[4] However, until recently there has been no evidence that there might be similar "edge" participation by the electrons of a cyclobutane ring.[4,7,8]



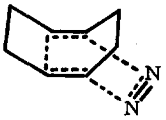
I



II



III

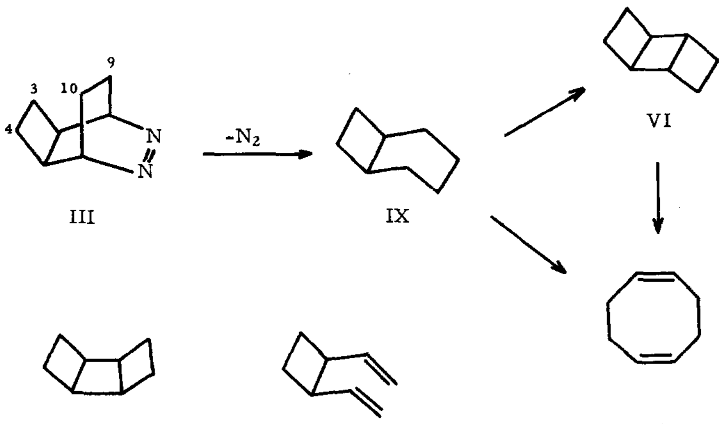


IV

In an earlier paper we reported that incorporation of a cyclobutane ring in II to give system III causes an impressive increase $(>10^4)$ in the thermal decomposition rate.[4] This suggests the possibility that cyclobutyl bonding electrons participate in a concerted loss of nitrogen and carbon-carbon double bond formation <u>via</u> transition state IV similar to the process described for I.[4] However, the differences in entropy of activation values of I ($\Delta S^{\ddagger} = -21$ eu), II ($\Delta S^{\ddagger} = +10.5$ eu), and III ($\Delta S^{\ddagger} = +11$ eu) suggests that II and III decompose by a different mechanism than I. We now have additional data which bear on the question of the mechanism for III.

Previously we reported that gas phase thermolysis of III at 150° produced 1,5-cyclooctadiene (V) and nitrogen as products.[4] By carrying out g.p.c. analysis in the early stages of decomposition we have found formation of another product VI. At 22% decomposition the ratio of VI:V is *ca.* 1:12. As decomposition proceeds VI gradually disappears. Compound VI has been identified as *trans*-tricyclo[4.2.0.$0^{2,5}$]octane[9] by comparison of its g.p.c. retention times with those of an authentic sample[10] on four columns of widely different separation characteristics. In agreement with this, the mass spectra of VI and authentic *trans*-tricyclo[4.2.0.$0^{2,5}$]octane were identical. C_8H_{12} isomers VII and VIII are also conceivable products, but they were not observed. A consideration of the reported isomerization kinetics for VII[11] and VIII[12] indicate that neither would have been detected.

In the formation of VI from III the cyclobutane ring remains intact and VI cannot be a consequence of involvement of cyclobutyl bonding electrons. Instead, VI clearly is a product of the closure of a diradical intermediate IX.[13-16] Kinetic analysis[17] based on the rates of



III IX VI V VII VIII

decomposition of III[4] and isomerization of VI to V[11] shows that ca. 20% of V arises from VI. The substantial formation of VI and the correspondence in entropy of activation values for III and II demonstrate that III decomposes by a diradical pathway. Molecular models show serious steric interaction between the C_3C_9 and C_4C_{10} hydrogens of III. Relief of this interaction is the most probable cause of the enhanced rate of decomposition.

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