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THE THERMOLYSIS OF BICYCLO[3.2.1]OCTA-2,6-DIENE AND OF BICYCLO[3.2.2]NONA-2,6-DIENE

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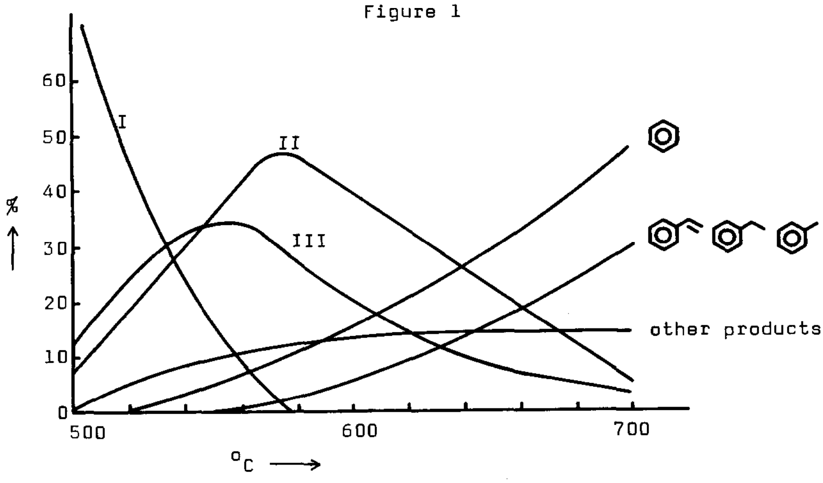
Thermolysis of bicyclo[3.2.1]octa-2,6-diene (I) in a flow-system at 550 - 600°, 2 Torr, and a reaction time of about 1 second[1] yields cis-bicyclo[3.3.0]octa-2,6-diene (II) in about 45% yield together with 1-vinylcyclohexadiene-1,3 (III, 35%) and several unknown minor products.

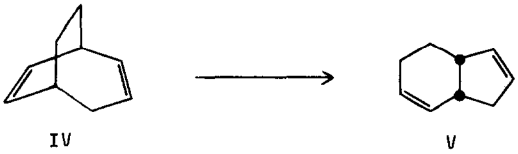
I II III

The structures of II and III were assigned after comparison of their IR and NMR-spectra with those of authentic samples[2]. Subjecting II and III to the thermolysis conditions did not lead to their interconversion. At 650° III was completely transformed into benzene and a small amount of ethyl benzene, whereas II was converted for 30% into benzene. The product distribution obtained from I at various temperatures is shown in figure 1.

Figure 1



Very similar behaviour is observed with bicyclo[3.2.2]nona-2,6-diene (IV). At 550 - 600° a single product is formed, which on the basis of its hydrogenation to cis-hydrindane and its NMR-spectrum [100 MHz, CCl_4-TMS, ppm (δ): 5.6, broad singlet, 4H; 2.6, singlet superimposed on multiplet, 3H; 1.9, multiplet, 4H; 1.3, multiplet, 1H] is assigned the structure of cis-bicyclo[4.3.0]nona-2,7-diene (V).



The transformations I ⟶ II and IV ⟶ V are new examples of thermal 1.3-carbon shifts. Considering the broad range of mechanisms that have been invoked for such and related transformations[3a-e] elucidation of their mechanism is an attractive goal, which is being pursued in this laboratory[4].

The formation of III has also been observed in the thermolysis of other C_8H_{10} hydrocarbons[2a] and it is possible that these hydrocarbons together with I are parts of the same energy surface.

References

1. The apparatus used was similar to the one described by R.F.C. Brown and R.K. Solly, Austr. J. Chem., 19, 1045 (1966).
2. a. W.R. Roth and B. Peltzer, Ann., 685, 56 (1965).
   b. W. von E. Doering and W.R. Roth, Tetrahedron, 19, 715 (1963).
   We are grateful to Professor Roth for providing copies of the spectra of III.
3. a. "Woodward-Hoffmann-controlled" reactions, cf.: N.T. Anh, Die Woodward-Hoffmann-Regeln und ihre Anwendung, Verlag Chemie, 1972.
   b. Step-wise reactions via diradicals, e.g., D. Hasselmann, Tetrahedron Letters, (1973) 3739.
   c. Subjacent orbital controlled reactions, cf.: J.A. Berson and R.W. Holder, J. Amer. Chem. Soc., 95, 2037 (1973) and earlier papers cited therein.
   d. Continuous diradicals as transition states: W. von E. Doering and K. Sachdev, J. Amer. Chem. Soc., 96, 1168 (1974).
   e. Least-motion controlled reactions: F.-G. Klärner, Angew. Chem., 86, 270 (1974).
4. Recently II was found as the product of the Rh(I) catalyzed rearrangement endo-6-vinylbicyclo[3.1.0]hex-2-ene: V. Aris, J.M. Brown, and B.T. Golding, Chem. Comm., 1972, 1206.