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THERMAL 1,4- AND 1,2-ELIMINATION OF HYDROGEN FROM CYCLOPENTENE

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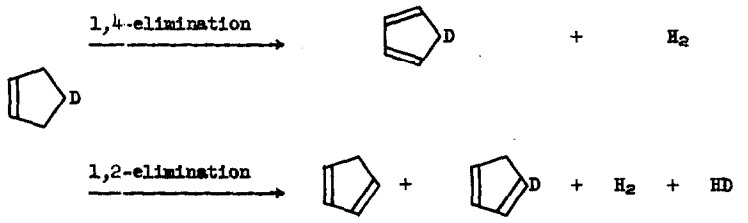
A fundamental mechanistic ambiguity in the thermal conversion of cyclopentene to cyclopentadiene and hydrogen has been recognized but unresolved for over twenty years (1-3): Are the hydrogen atoms which become molecular hydrogen in a 1,4- or a 1,2-relationship in cyclopentene? Does the reaction occur through a 6-centered or a 4-centered transition state?

Recent theoretical developments have sharpened the issue. Application of the proposals of Woodward and Hoffmann (4) based on molecular-orbital symmetry relationships would suggest that the 1,4-elimination could be concerted, while the calculations of Benson and Haugen (5) based on an electrostatic model for 4-centered reactions would seem to favor a 1,2-elimination through a polar transition state.

The experimental results now reported implicate both 1,4- and 1,2-elimination of hydrogen from cyclopentene, with the 1,4-process being favored.



4-Deuteriocyclopentene (6) (4% $\underline{d}_0$, 96% $\underline{d}_1$ (7)) was pyrolyzed at 550° and the products were analyzed by mass spectrometry: the recovered cyclopentene was 4% $\underline{d}_0$, 96% $\underline{d}_1$ and the cyclopentadiene produced was 11% $\underline{d}_0$, 89% $\underline{d}_1$. The isotopic compositions of cyclopentene and cyclopentadiene after four separate runs at 550° lasting 4 to 16 minutes were indistinguishable. Thus the observed differences in isotopic composition between starting material and product originate during the elimination of H_2 or HD, and both 1,4- and 1,2-processes are operative.

If no important kinetic isotope effect for the 4-deuterio or 4-protio substituents is involved at 550° (8) then the ratio of H_2 to HD elimination corresponds to $(k_{1,4} + k_{1,2})/k_{1,2}$, where $k_{1,4}$ and $k_{1,2}$ are the intrinsic rate constants for the two modes of reaction, and the symmetry corrected ratio $k_{1,4}/k_{1,2}$ is approximately 12.

These results underscore the dominant role played by the presumably concerted 1,4-elimination of hydrogen from cyclopentene, yet demonstrate that the 1,2-elimination is not quite negligible.

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REFERENCES

1. F. O. Rice and M. T. Murphy, J. Am. Chem. Soc., 64, 896 (1942).

2. A. Eucken, Die Chemie, 56, 342 (1943).

3. D. W. Vanas and W. D. Walters, J. Am. Chem. Soc., 70, 4035 (1948).

4. R. B. Woodward and R. Hoffmann, ibid., 87, 395 (1965); ibid., 87, 2046 (1965); see also H. C. Longuet-Higgens and E. W. Abrahamson, ibid., 87, 2045 (1965).

5. S. W. Benson and G. R. Haugen, ibid., 87, 4036 (1965).

6. Prepared from Δ^3-cyclopentenyl tosylate and lithium aluminium deuteride. The tosylate had m.p. 44-45° (Anal. Found: C, 60.67; H, 5.87; S, 13.25). E. L. Allred, J. Sonnenberg, and S. Winstein, J. Org. Chem., 25, 26 (1960), report this tosylate as having m.p. 53.4-54.6°. The identity and purity of the labeled cyclopentene were fully verified by n.m.r. and mass spectrometric criteria. The only peak in the n.m.r. spectrum of the labeled hydrocarbon not in full accord with expectations was a small sharp absorption at 8.49τ ascribed to a trace of partially deuterated cyclopentene (cf. K. B. Wiberg and B. J. Nist, J. Am. Chem. Soc., 83, 1226 (1961)). At low electron energies, this impurity did not contribute to the observed mass spectral ion peaks.

7. Deuterium analyses were obtained mass spectrometrically on an Atlas Ch-4 instrument using low electron energies, and were reproducible to ± 1%.

8. Cf. L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Company, New York, 1960, p. 44.