

KINETICS OF THE THERMAL ISOMERIZATION OF
cis,anti,cis-TRICYCLO[3.1.0.0^{2,4}]HEXANE¹

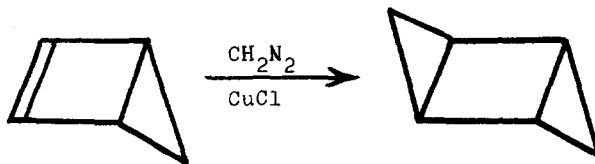
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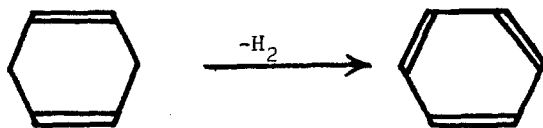
The cis,anti,cis isomer of tricyclo[3.1.0.0^{2,4}]hexane,²⁻⁵ first secured by Allred and Hinshaw in 1968, may be obtained directly in 85% conversion through reaction of a solution of bicyclo[2.1.0]pent-2-ene⁶ in tetrahydrofuran with diazomethane in the presence of powdered cuprous chloride.⁷



After purification by preparative glpc on a 1-m 7.5% Apiezon L on 1:1 Anakrom:Chromosorb W column at 45° and vacuum transfer, the tricyclic hydrocarbon had the reported nmr spectral characteristics² and no contaminants detectable by analytical glpc. The temperature dependent vapor-pressure of the tricyclohexane could be summarized through the equation $\log_{10} P(\text{mm}) = -1.559 \times 10^3 T^{-1} + 7.357$, corresponding to bp 75.1° (760 mm) and heat of vaporization $\Delta H_v = 7.13 \text{ kcal mol}^{-1}$.

Thermolyses of the hydrocarbon were done in a 300-ml Pyrex vessel connected to a vacuum system, with pentane as a diluent bringing the pressure to 10 mm. Temperatures were measured with a chromel-alumel thermocouple. After each run, starting material and products were condensed and analyzed by glpc on a 3-mm x 6-m 5% TCEP on 60/80 chromosorb P column at 65°. Only two products were detected: cyclohexa-1,4-diene, and benzene (6-11% of the product mixtures). Both were identified by glpc, mass spectral, and nmr spectroscopic comparisons with authen-

tic samples. At 10 mm pressure, some further reaction of the initially formed vibrationally excited and thus chemically activated⁸ cyclohexa-1,4-diene to give benzene and hydrogen is not at all surprising.^{9,10}

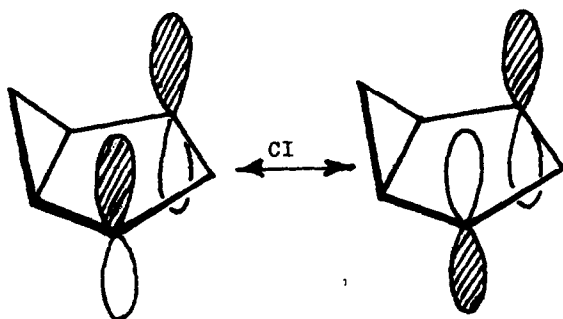


Rate Constants for the Thermal Isomerization of
cis,anti,cis-Tricyclo[3.1.0.0^{2,4}]hexane

T(°C)	k(s ⁻¹)x10 ⁴
169.8	0.375 ± 0.007
180.5	1.02 ± 0.010
190.0	2.29 ± 0.016
200.2	5.53 ± 0.052

The Arrhenius parameters derived from the tabulated rate constants are log A 13.70 ± 0.01, E_a 36.75 ± .03 kcal mol⁻¹, sufficiently different for those measured for many other cyclobutane pyrolyses (eg, bicyclo[3.2.0]heptane to 1,6-heptadiene, log A 15.4, E_a 63.97¹¹; bicyclo[2.1.1]hexane to 1,5-hexadiene, log A 15.2, E_a 55.0¹²) to suggest a separate type of mechanistic route.

The activation parameters for the tricyclohexane isomerization are similar to those reported for the isomerization of exo-2-methylbicyclo[2.1.0]pentane to its endo isomer (log A 13.9, E_a 38.65)⁷. (The tentative stereochemical assignments for the exo- and endo-2-methylbicyclo[2.1.0]pentanes made by Chesick⁷ have been verified.¹³) Given this similarity, it is possible that the rate-determining transition states for the two processes both involve extensive mixing of two configurations of the opening bicyclopentane moiety.¹⁴



This mixing of configurations of the same state symmetry would provide a means for achieving an "orbital symmetry inversion,"¹⁵ and make possible an energetically concerted reaction profile for the tricyclohexane to cyclohexa-1,4-diene thermal isomerization.¹⁶

NOTES AND REFERENCES

1. Supported in part by the National Science Foundation and Hoffmann-LaRoche Inc.
2. E. L. Allred and J. C. Hinshaw, J. Amer. Chem. Soc., 90, 6885 (1968).
3. E. L. Allred, J. C. Hinshaw, and A. L. Johnson, ibid., 91, 3382 (1969).
4. H. Tanida and S. Teratake, Tetrahedron Lett., 4991 (1970).
5. A. J. Schipperijn and J. Lukas, ibid., 231 (1972).
6. A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., Org. Syntheses, in press.
7. J. P. Chesick, J. Amer. Chem. Soc., 84, 3250 (1962).
8. For discussions of chemical activation effects see B. S. Rabinovitch and M. C. Flowers, Quart. Rev., 18, 122 (1964); L. M. Stephenson and J. I. Brauman, J. Amer. Chem. Soc., 93, 1988^b (1971); and M. C. Flowers and A. R. Gibbons, J. Chem. Soc., Perkin II, 548^c (1972).
9. R. J. Ellis and H. M. Frey, J. Chem. Soc. A, 533 (1966).
10. S. W. Benson and R. Shaw, Trans. Faraday Soc., 63, 985 (1967).

11. R. J. Ellis and H. M. Frey, J. Chem. Soc., 4184 (1964).
12. R. Srinivasan and A. A. Levi, J. Amer. Chem. Soc., 85, 3363 (1963).
13. J. Ollerenshaw, unpublished result.
14. F. S. Collins, J. K. George, and C. Trindle, J. Amer. Chem. Soc., 94, 3732 (1972).
15. J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., ibid., in press.
16. J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., "Orbital Symmetry Disallowed Energetically Concerted Reactions," manuscript submitted.