Geometrical Orbital Overlap Requirements in Allowed Thermal Reactions: the *trans,trans* Cope Rearrangement of 3,7-Dideuteriobicyclo[3,3,0]octa-2,6-diene

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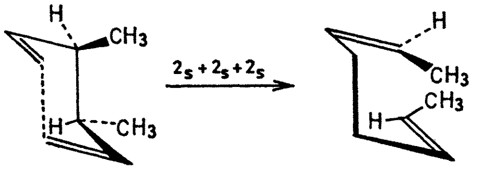
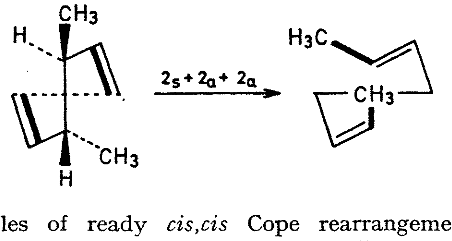
Summary The degenerate *trans,trans* Cope rearrangement of bicyclo[3,3,0]octa-2,6-diene, although a symmetry-allowed process, does not occur appreciably in 85 min. at 450°.

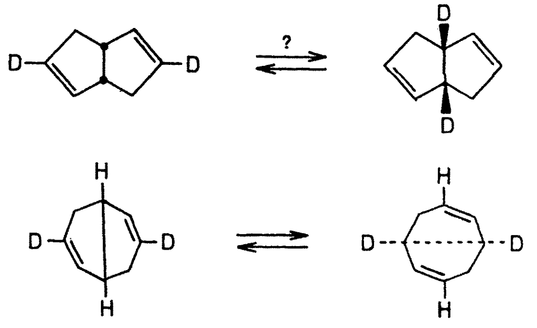
THEORETICAL developments associated with conservation of orbital symmetry during concerted reactions may predict several stereochemical modes for a certain type of thermal cyclo-reaction.[1] Thus a concerted Cope rearrangement, also characterizable as a (2+2+2) cycloaddition or a (3,3) sigmatropic reaction, may in principle occur with each allyl unit being utilized in a *cis* (suprafacial) or *trans* (antarafacial) fashion. For instance, the thermal conversion of *meso*-3,4-dimethylhexa-1,5-diene into *cis,trans*-octa-2,6-diene[2] might satisfy the stereochemical stringencies of orbital symmetry control for concerted processes through either *cis,cis*-reaction with a chair-like conformation in the transition state or *trans,trans*-reaction through the conformation shown. Symbolically, these alternative pathways would be termed $(\sigma^2_s + \pi^2_s + \pi^2_s)$ and $(\sigma^2_s + \pi^2_a + \pi^2_a)$ cyclo-reactions.





Examples of ready *cis,cis* Cope rearrangements are common.[3] Is the other theoretically allowed pathway equally or nearly equally feasible?

A concerted degenerate Cope rearrangement in bicyclo[3,3,0]octa-2,6-diene[4] would be constrained to occur in the *trans,trans*-manner, or not at all. The *cis,cis*-stereochemistry would not be accessible. 3,7-Dideuteriobicyclo[3,3,0]octa-2,6-diene was selected for investigation and synthesized: Cope rearrangement of this molecule would cause the ratio of vinyl to methine protons to grow from 1 : 1 to 3 : 1 as the interconversion went to equilibrium.



Reduction of Vossen's red salt[5] or the condensation of glyoxal with dimethyl acetonedicarboxylate[6] gave, after hydrolysis and decarboxylation, bicyclo[3,3,0]octa-3-7-dione.[5]

Reduction of the dione with lithium aluminium deuteride, followed by dehydration of the resultant diol by way of the dixanthate ester,[7] gave 3,7-dideuteriobicyclo[3,3,0]-octa-2,6,diene together with some of the 2,7-diene. The integrated n.m.r. absorptions for olefinic and methine protons in the labelled 2,6-diene were in a 1 : 1 ratio as expected. This hydrocarbon was heated to 450° at 0·5 atm. for 85 min. with only 10% decomposition to other hydrocarbons. The n.m.r. spectrum of recovered diene was unaltered, indicating that no detectable amount of *trans, trans* Cope rearrangement product, 1,5-dideuteriobicyclo-[3,3,0]octa-2,6-diene, had been formed.

An analogous *cis, cis* Cope rearrangement would have had a half-life of no more than a few msec. at this high temperature.[8] The degenerate Cope rearrangement of the dideuterio-2,6-dienes is thus conspicuously retarded. In spite of a geometrical arrangement which permits the molecule to take an allowed *trans,trans*-pathway yet requires no unlikely molecular distortions,[9] the valence isomerization fails to happen.

In addition to the nodel structure of the orbitals principally involved in a cyclo-reaction, which determines whether a reaction is allowed to be concerted, the relative effectiveness of interorbital overlaps dictated by molecular geometry may be of decisive importance in making an allowed reaction ready or sluggish.

The only reported example of a *trans,trans* Cope rearrangement[10] may occur through another mechanism; further work will be required to settle the issue.

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[2] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1962, **18**, 67.

[3] S. J. Rhoads in "Molecular Rearrangements," Part I, ed. P. de Mayo, Wiley, New York, 1963, ch. 11.

[4] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1963, **19**, 715.

[5] G. Vossen, Doctoral Dissertation, University of Bonn, 1910; E. R. Hanna, K. T. Finley, W. H. Saunders, jun., and V. Boekelheide, *J. Amer. Chem. Soc.*, 1960, **82**, 6342; P. Yates, E. S. Hand, and G. B. French, *ibid.*, 6347.

[6] U. Weiss and J. M. Edwards, *Tetrahedron Letters*, 1968, 4885.

[7] H. R. Nace, in "Organic Reactions," vol. 12, Wiley, New York, 1962, ch. 2.

[8] Estimated from rate data for *trans*-1,2-divinylcyclobutane; G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, 1964, **86**, 899; see also W. D. Huntsman, *ibid.*, 1960, **82**, 6389, for instances of homolytic dissociation of 1,5-alkadienes under less drastic conditions.

[9] A concerted, antarafacial (1,3) sigmatropic hydrogen migration has not been observed, presumably because severe molecular distortions would be necessary in the transition state: J. A. Berson, *Accounts Chem. Res.*, 1968, **1**, 152, and ref. 1.

[10] T. Miyashi, M. Nitta, and T. Mukai, *Tetrahedron Letters*, 1967, 3433.