Tetrahedron Letters No. 13, pp 1131 - 1132, 1973. Pergamon Press. Printed in Great Britain.

THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF TRANS-1,2,6-CYCLONONATRIENE[1]

J. A. Deyrup and M. Betkouski

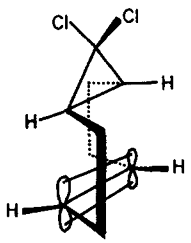
Department of Chemistry, University of Florida, Gainesville, Florida 32601

(Received in USA 16 January 1973; received in UK for publication 22 February 1973)

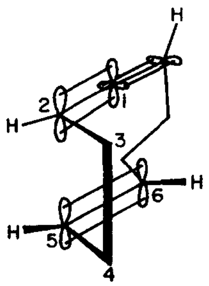
The thermal and photochemical Cope rearrangement of *cis*-1,2,6-cyclononatrience (1) to 2 has been studied and contrasted with acyclic analogs.[2-4] In spite of these studies, questions remain concerning the role of transition state geometry. Neither examination of molecular models nor experiments serve to distinguish between chair (four center) and boat (six center) transitions states. Other ambiguities concern the importance of conformational flexibility and the specific consequences of the cyclic structure.

1 2

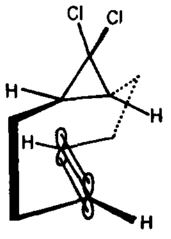
We have recently synthesized the parallel (3) and perpendicular (4) *trans*, *trans*-bicyclo (6.1.0)non-4-enes.[5] The structural and symmetry features of these molecules require that conversion of their gem-dihalocyclopropane moieties to allenes with organo-lithium reagents should result in two previously unknown isomers of *trans* 1,2,6-cyclononatriene, 5 and 6. In contrast to 1, however, 5 and 6 are restricted to (and may attain with less angle deformation) the high energy boat and low energy chair transition states respectively.[6] Thus in principle, a direct verification and measure of energy difference between these two transition states could be made *via* kinetic study.



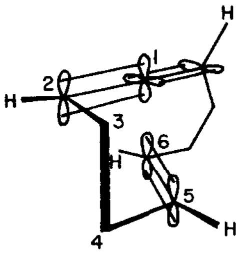
3



5



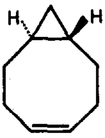
4



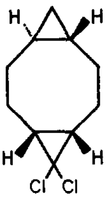
6

A (1:5) mixture of 3 and 4 in ether was reacted with butyllithium and hexane at -78° followed by subsequent warming to room temperature and product (49%) isolation. Examination of the product by nmr spectroscopy and glc chromotography revealed only 2 and no trace of allenic products. Thus both 5 and 6 rearrange rapidly at (or probably below) room temperature. In contrast, 1 has a half life of over 30 minutes at 150°.[2] We believe that this rate enhancement is attributable to those structural features of 5 and 6 which allow C-1 and C-6 to approach each other in the proper orientation with relatively (in comparison to 1) little angle strain. Of equal or greater importance is the relative (again to 1) ease with which bond 3-4 may achieve coplanarity with the p-orbitals on C-1 and C-5.

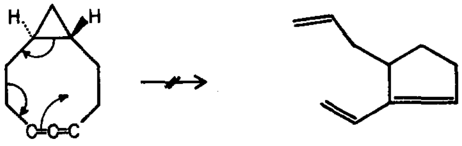
In comparison with other Cope rearrangements which are not driven by small ring rupture, the isomerization of 5 and 6 is unusually facile. This result suggests that other unusually facile Cope rearrangements might be discovered in systems which incorporate similar features. Finally, in this connection, it is interesting to consider the properties of 9 which was prepared from 7 *via* 8. Although this allene is similar in geometry to 5 and 6, it was unchanged after 27 hours at 140°.



7



8



9

FOOTNOTES AND REFERENCES

(1) We wish to thank the National Science Foundation (Grant GP-17642) for support of this research.

(2) K. G. Untch and D. J. Martin, *J. Am. Chem. Soc. 87*, 4501 (1965).

(3) L. Skattebøl and S. Solomon, *ibid.*, 87, 4507 (1965).

(4) H. R. Ward and E. Karafiath, *ibid.*, 91, 522 (1969).

(5) J. A. Deyrup, M. Betkouski, W. Szabo, M. Mathew and G. J. Palenik, *ibid.*, 94, 2147 (1972).

(6) cf discussion in ref. 4.