Tetrahedron Letters No.13, pp. 993-994, 1969. Pergamon Press. Printed in Great Britain.

PHOTOISOMERIZATION OF TETRAMETHYLALLENE DIMER: A FACILE 1,5-HYDROGEN SHIFT

Edgar F. Kiefer and James Y. Fukunaga
Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

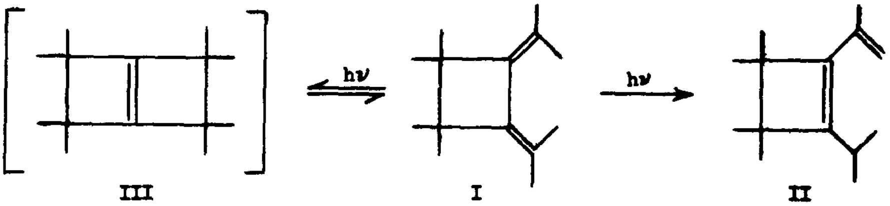
(Received in USA 27 December 1968; received in UK for publication 7 February 1969)

Although thermal 1,5-shifts are well known in both cyclic and acyclic systems, few photochemical analogs have been reported. The reverse is true for 1,7-shifts. These reactions are of considerable interest in view of the alternate stereochemical modes postulated for sigmatropic rearrangements by Woodward and Hoffmann:[1] photochemical 1,5- and thermal 1,3- and 1,7-rearrangements should require antarafacial transfer of the migrating substituent, which in most of the molecules studied to date could not be achieved without prohibitive molecular distortion.[2] Hydrogen atom shifts are of particular significance in this connection, since no antibonding σ-orbital is available to provide a symmetry-allowed pathway for suprafacial transfer.[2] An authentic case of an antarafacial 1,5-shift has yet to be described.

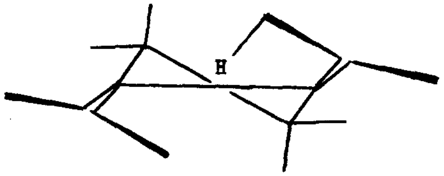
We wish to report an example of a rapid and specific photochemical 1,5-hydrogen shift in a system which uniquely favors antarafacial transfer.

1,2-Diisopropylidene-3,3,4,4-tetramethylcyclobutane (I, prepared by thermal dimerization of tetramethylallene at 145°[3]), on photolysis in dilute ether or benzene solution in a quartz vessel with a ring of low-pressure Hg lamps, is rapidly and cleanly isomerized to II, isolable by glc (20% Carbowax 20M on 60/80 firebrick, 3/8" X 20' column, 130°). The maximum yield is obtained at about 75% conversion, since II itself photolyzes at an appreciable rate to give a complex mixture of products. The nmr spectrum of II shows an allylic isopropyl group (τ 8.90, 6H, doublet; τ 7.16, 1H, septet; J = 7.0 Hz), an isopropenyl group (τ 8.13, 3H, triplet; τ 5.26, 2H, multiplet; J = 1.2 Hz), and two pairs of quaternary methyl groups (τ 8.87, 6H; τ 8.91, 6H, singlets), which, along with ultraviolet (λ_{max} 235, 244 nm) and mass spectra (M^+ 192) are sufficient to establish structure.

The exceptional specificity of this reaction may be ascribed to two factors. (a) The product of the usual electrocyclization reaction of cisoid dienes, III, if formed at all,



undoubtedly is thermally unstable with respect to reopening to I. The analogous degenerate photorearrangement was detected in 1,2-dimethylenecyclobutane by means of deuterium labelling,[4] though efforts to trap the presumed intermediate bicyclohexene were unsuccessful.[4b] (b) The particular combination of steric influences in I forces the diene system to adopt a nearly ideal configuration for antarafacial 1,5-transfer of a hydrogen atom (IV). Serious van der Waals repulsion between the "endo" allylic methyl groups in the planar configuration is most efficiently relieved by a combination of ring puckering and conrotatory torsion of the isopropylidene groups, rather than by widening of the C=C-C bond angle or disrotatory torsion. The presence of two adjacent gem-dimethyl groups on the ring also strongly favors ring puckering to relieve conformational strain. Perhaps most importantly, however, the strained ring itself prevents free rotation which would uncouple the pi bonds and destroy the extended conjugation necessary for excitation and electrocyclic reorganization. The ultraviolet spectra of allene dimers, including I (λ_{max} 253 nm, ϵ 15,300) indicate relatively little distortion from planarity. Analogously substituted acyclic dienes, e.g., hexamethylbutadiene, show no uv absorption above 210 nm.[5]



IV

It seems probable that similar conformational factors are responsible for the anomalous[6] photochemical behavior of β-ionol, which is also reported to undergo a 1,5-hydrogen shift.[7] Rate effects observed in more recent work on the photolysis and thermolysis of dimethylallene dimers support the proposed stereochemistry.[8]

REFERENCES

1. R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc., **87**, 2511 (1965).
2. J. A. Berson, Accounts Chem. Res., **1**, 152 (1968).
3. J. McClenon, Ph.D. Dissertation, University of California at Los Angeles, 1964, (Dissertation Abstr., **25** (1), 101 (1964)).
4. G. J. Fonken, Ann. Report of the Robt. A. Welch Found., 1965-66, p. 81. (b) G. J. Fonken, private communication.
5. W. F. Forbes, R. Shilton, and A. Balasubramanian, J. Org. Chem., **29**, 3527 (1964).
6. W. G. Dauben and W. T. Wipke, Pure Appl. Chem., **9**, 539 (1964).
7. M. Mousseron-Canet, M. Mousseron, and P. Legendre, Bull. Soc. Chim. France, **31**, 50 (1964).
8. E. F. Kiefer and C. H. Tanna, results to be published.