Tetrahedron Letters No.44, pp. 3905-3907, 1969. Pergamon Press. Printed in Great Britain.

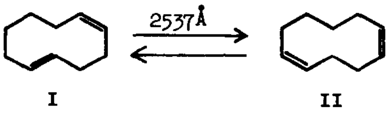
PHOTOISOMERIZATION OF CIS,TRANS-1,5-CYCLODECADIENE. RELATIVE REACTIVITIES OF CIS,TRANS- AND CIS,CIS-1,5-CYCLODECADIENES.[1]

James G. Traynham and H.H. Hsieh
Coates Chemical Laboratories, Louisiana State University
Baton Rouge, Louisiana 70803

(Received in USA 21 July 1969; received in UK for publication 19 August 1969)

Photoisomerizations of several cyclooctadienes[2] and cyclodecadienes[3] have been reported. In some cases, geometrical and/or positional isomerization of one or both C=C occur;[2b,c,3] in some, intramolecular cycloaddition to form cyclobutane derivatives occurs;[2c,d,3d,e] and with cis,cis-1,5-cyclooctadiene, intramolecular cycloaddition occurs in a "crossed" fashion to produce tricyclo[3.3.0.0^{2,6}]octane.[2a,b,e] The structural features responsible for the rather individual behavior of each cyclic diene have not been clearly identified.

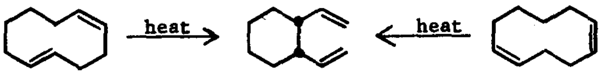
Some but not all radical additions to cis,cis-1,5-cyclooctadiene yield substituted bicyclo[3.3.0]octanes as products.[4] These processes involve transannular C-C bond formation resembling that in the photoisomerizations of the same diene. Radical (and ionic) additions to cis,trans-1,5-cyclodecadiene apparently occur exclusively by transannular (1,6) C-C bond formation;[5] that is, the tendency for such a transannular process is much greater with cis,trans-1,5-cyclodecadiene (I) than with cis,cis-1,5-cyclooctadiene. Therefore, we considered the possible photoisomerization of I to be of interest. In spite of the strong driving force for substituted cis-decalin formation in addition reactions, however, we have been unable to find any evidence for intramolecular cycloaddition-- "straight" or "crossed"[3e]-- in the photoisomerizations. Instead, I is photoisomerized cleanly to the previously unreported isomer, cis,cis-1,5-cyclodecadiene (II).



Irradiation (2537Å, quartz flasks, nitrogen atmosphere) of solutions of I[5a,6] in ethyl ether containing small amounts of copper(I) chloride or xylene produces a mixture of I and II.[7] After about 100 hr, the relative amounts of I and II do not change further (I:II $\simeq$ 1:4). Prolonged irradiation leads to the diversion of the dienes to some high-boiling, yet unidentified materials, but gas chromatographic analysis of a solution (xylene sensitizer) after 8 hr irradiation revealed II as the only product from I. The photostationary state is more rapidly established from II as starting diene (less than 30 hr with xylene sensitizer).

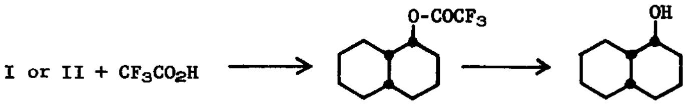
I and II are conveniently separated by preparative gas chromatography on a Carbowax 20M column, $\frac{1}{4}$ in. x 12 ft., heated at 80°; II has a longer retention time than I. The isomeric dienes are readily distinguished by their infrared and nmr spectra. The infrared spectrum of II includes absorptions at 13.52 and 14.0μ (cis C=C) but none at 10.02 and 10.43μ (trans C=C), which are in the spectrum of I. The nmr spectrum of II is consistent only with the 1,5-diene assignment; it consists of four multiplets of equal area centered at -5.38 ($C{=}C\underset{\sim}{H}$), -2.34 $[(C{=}C\underset{\sim}{H_2})_2]$, -2.16$[(C{=}C\underset{\sim}{H_2}CH_2)_2]$, and -1.50 ppm $[(CH_2C\underset{\sim}{H_2})_2]$. (Chemical shifts are relative to internal tetramethylsilane.) Association of the absorptions with the protons indicated was confirmed by decoupling experiments.

II undergoes thermal rearrangement to <u>cis</u>-1,2-divinylcyclohexane (III) but, in contrast to photoconversion of I and II, at a much slower rate than I does. The conversion of I to III[5a,6] was more than 99% complete after 44.5 hr of heating at 125° (17% complete after 1 hr), but only 3% of II was converted to III by the same heating.



I III II

Both I and II react rapidly with trifluoracetic acid without external heating to form <u>cis</u>-1-trifluoroacetoxy-<u>cis</u>-decalin, bp 99-100.5° (9 mm), which was hydrolyzed by 2<u>M</u> aqueous sodium hydroxide to <u>cis</u>,<u>cis</u>-1-decalol,[5a] mp 90-91°, in quantitative yield. A qualitative estimate of the relative rates of reaction of the dienes was made by noting the times for disappearance of olefinic proton absorptions in the nmr spectra of the dienes in trifluoroacetic acid solutions. After 6 min, the reaction of I appeared to be about 90% complete, and that of II to be about 50% complete. These reactions are very convenient sources of <u>cis</u>,<u>cis</u>-1-decalol.



REFERENCES

1. This research was supported in part by a grant from the National Science Foundation (NSF GP-8228).

2. (a) R. Srinivasan, J. Am. Chem. Soc., **85**, 819, 3048 (1963); (b) R. Srinivasan, ibid., **86**, 3318 (1964); (c) R.S.H. Liu, ibid., **89**, 112 (1967); (d) S. Moon and C.R. Ganz, Tetrahedron Letters, 6275 (1968); (e) G.M. Whitesides, G. L. Goe, and A.C. Cope, J. Amer. Chem. Soc., **91**, 2608 (1969).

3. (a) P. Radlick and W. Fenical, Tetrahedron Letters, 4901 (1967); (b) J. Dale and C. Moussebois, J. Chem. Soc., (C), 264 (1966); (c) P. Heimbach, Angew. Chem. Internat. Ed. Engl., **5**, 595 (1966); (d) A. Soni, Tetrahedron Letters, 5175 (1968); (e) J.R. Scheffer and M.L. Lungle, ibid., 845 (1969).

4. (a) R. Dowbenko, J. Am. Chem. Soc., **86**, 946 (1964); (b) J.M. Locke and E.W. Duck, Chem. Commun., 151 (1965); (c) W.H. Mueller, J. Am. Chem. Soc., **91**, 1223 (1969).

5. (a) J.G. Traynham, G.R. Franzen, G.A. Knesel, and D.J. Northington, Jr., J. Org. Chem., **32**, 3285 (1967); (b) H.H. Hsieh and J.G. Traynham, Abstracts, 1968 Southwest Regional Meeting of the American Chemical Society, Austin, Texas, paper no. 189.

6. G. Wilke, Angew. Chem. Internat. Ed. Engl., **2**, 105 (1963).

7. Ultraviolet irradiation of a solution of $Fe(CO)_5$ in I produces cis,cis- and trans,trans-1,6-cyclodecadienes, products of C=C migration; see reference 3c.