Tetrahedron Letters No. 19, pp 1857 - 1860, 1972. Pergamon Press. Printed in Great Britain.

COMPETITIVE PATHWAYS IN ALLYLIDENECYCLOPROPANE PHOTOCHEMISTRY

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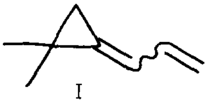
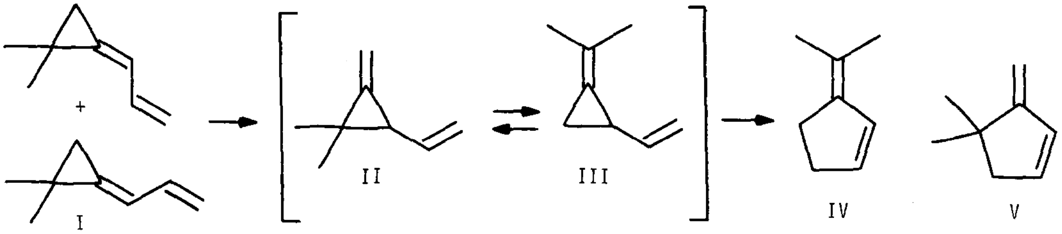
(Received in USA 21 February 1972; received in UK for publication 30 March 1972)

The direct photolysis of linear conjugated dienes has provided a wealth of information bearing on the nature and reactivity of excited singlet states in organic molecules. Elegant studies by Srinivasan[1] and other workers[2] have revealed that alkyl-substituted 1,3-butadiene singlets undergo three principal reactions in solution: cyclobutene formation, cyclopropene (or methylenecyclopropane) formation by hydrogen transfer, and cis-trans isomerization. We wish to report that solution photolysis of diene I leads to new singlet photochemistry wherein ${}_{\sigma}2 + {}_{\pi}2$ pericyclic rearrangements involving ring cleavage play a major role.



I

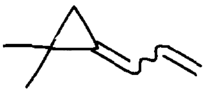
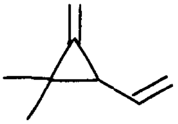
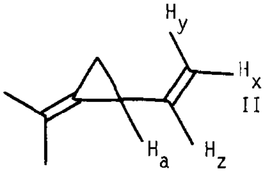
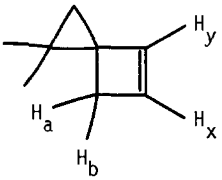
Recent work[3] in our laboratories has demonstrated that thermolysis of diene I[4] leads to formation of the two methylenecyclopentene isomers IV and V. The ratio of IV to V remains 2.3 to 1.0 regardless of the stereochemistry of I, and this observation was rationalized in terms of a "conducted tour mechanism" involving two successive methylenecyclopropane rearrangements:



In order to compare the photochemical fate of I with the thermal pathway we have carried out the direct (in quartz) photolysis of a 0.11 M acetonitrile solution of diene I (1:1 mixture of cis and trans isomers) at 0-10° using a low pressure mercury vapor lamp. The three C_8H_{12}

photoisomers thus formed in a 5:1:1 ratio were isolated by preparative glc at 70° using a 25' x 1/4" column of 15% Carbowax 20M on Chromosorb P. The major product was identified as 1-isopropylidene-2-vinylcyclopropane (III)[5] by 100 MHz decoupling studies which established the chemical shifts and coupling constants in Table I. The two minor isomers were similarly identified as 1-methylene-2,2-dimethyl-3-vinylcyclopropane (II) and 1,1-dimethylspiro[2.3]-hex-4-ene (VI).

Table I. Nmr Chemical Shifts and Coupling Constants[a]

	I	1.02(2H,m);1.18(3H,s);1.23(3H,s);5.1(2H,m);6.4(2H,m)
	II	1.09(3H,s);1.21(3H,s);1.8(1H,m);4.8-5.7(5H,m)
	III	0.95(2H,m);1.79(3H,s);1.81(3H,s);2.07(1H,m);4.42(H_x,dd,J_{xy}=2.5,J_{xz}=9.5);5.00(H_y,dd,J_{yx}=2.5,J_{yz}=17);5.72(H_z,m,J_{za}=7.5,J_{zx}=9.5,J_{zy}=17)
	VI	0.62(2H,s);1.09(6H,s);2.40(1H,d,J_{ab}=12.8); 2.72(1H,d);6.02(1H,d,J_{xy}=2.6);6.22(1H,m)

[a] All nmr spectra were taken in $CDCl_3$ with a TMS internal standard; chemical shifts are in parts per million relative to TMS, coupling constants in hertz.

Accompanying the C_8H_{12} photoisomers were significant amounts of C_4 primary photofragmentation products identified as vinylacetylene (VII) and isobutylene (VIII) by glc and ms comparison with authentic samples. Analogy with earlier work suggests that these fragments arise by cheletropic[6] fragmentation of excited singlet I to olefin and allylidenecarbene. Indeed, benzophenone-sensitized photolysis of I produced neither C_8H_{12} isomers nor fragments

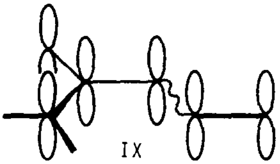
VII and VIII, but led largely to polymerization. Quantum yields for the direct photolysis of I are given in Table II; no methylenecyclopentenes (IV, V) were detected.

Table II. Quantim Yields[7] for Products from Direct Photolysis of I (1:1 *cis-trans*)

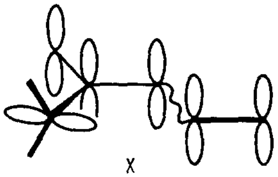
Compound	Φ
Vinylacetylene (VII)	0.029
Isobutylene (VIII)	0.038
Cyclopropane II	0.046
Spirohexene VI	0.048
Cyclopropane III	0.232

Despite moderate loss of I by photopolymerization, the data of Table II suggest an efficient "hidden" energy-dissipating step to account for the fate of over half of the excited singlets formed. By employing a sample of I kinetically enriched[8] in the thermally more stable geometric isomer we have been able to show (nmr) that rapid *cis-trans* isomerization occurs during photolysis, Φ_{ct} being 0.55 ± 0.04.[7] Thus approximately 91% of the diene singlets formed undergo unimolecular photochemistry.

We conclude that ring-opening reactions in I compete effectively with the conventional pericyclic reactions of singlet butadienes. In addition, it is remarkable that the major photoisomerization of I, which gives III, involves *migration of the less substituted ring carbon*. This selectivity is the reverse of that observed in the corresponding thermal methylenecyclopropane rearrangement[9] and could suggest a planar singlet vinyltrimethylenemethane intermediate (IX) in the photochemical process in contrast to the orthogonal species (X) previously invoked[3,10] in the thermal rearrangement. A stereochemical test of this hypothesis is in progress.



IX



X

Acknowledgements. We thank George Kraus for the preparation of intermediates in the synthesis of 2,2-dimethylallylidenecyclopropane. Partial support of this research by the Petroleum Research Fund, administered by the American Chemical Society, and by the U. S. Public Health Service is gratefully acknowledged.

FOOTNOTES AND REFERENCES

1. R. Srinivasan, *Advances in Photochemistry*, Vol. 4, W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., eds., Interscience, New York, 1966, p. 113. Recent investigations are discussed in S. Boue and R. Srinivasan, *J. Amer. Chem. Soc.*, *92*, 3226 (1970).
2. *E.g.*, J. Saltiel, L. Metts and M. Wrighton, *ibid.*, *92*, 3227 (1970); R. S. H. Liu and G. S. Hammond, *ibid.*, *89*, 4936 (1967), and references therein.
3. A. S. Kende and E. E. Riecke, "The Allylidenecyclopropane-Methylenecyclopentene Energy Surface: Evidence for a 'Conducted Tour' Mechanism," *ibid.*, in press.
4. T. C. Shields, W. E. Billups and A. R. Lepley, *ibid.*, *90*, 4749 (1968); T. C. Shields and W. E. Billups, *Chem. and Ind.*, 619 (1969).
5. All photolysis products showed the correct parent peaks in their mass spectra. Moreover, the C_8H_{12} isomers I, II, III and VI gave substantially identical mass spectra with major fragments at m/e 93(base peak), 91, 79, 77, 65, 41 and 39.
6. J. C. Gilbert and J. R. Butler, *J. Amer. Chem. Soc.*, *92*, 7493 (1970); A. S. Kende, Z. Goldschmidt and R. Smith, *ibid.*, *92*, 7606 (1970).
7. Quantum yields were determined at low conversions in acetonitrile or deuteroacetonitrile at 2537 Å using cyclopentanone-4-pentenal actinometry (J. C. Dalton, P. A. Wriede and N. J. Turro, *ibid.*, *92*, 1318 (1970); P. Dunion and C. N. Trumbore, *ibid.*, *87*, 4211 (1965)). Product composition was determined by glc using a 10' x 1/8" column of 15% Carbowax 20M on Chromosorb P employing p-dioxane as an internal standard; controls established the absence of thermal isomerization during analysis. *Cis-trans* isomerizations were followed by nmr and corrected for back-reaction by assuming $\Phi_{ct} = \Phi_{tc}$. The photostationary state for *cis-trans* isomerization gives a 1:1 mixture of *cis* and *trans* I.
8. Glc-recovered I from a 68 minute pyrolysis at 163° contained 76 and 24% of isomers having δ_{Me} 1.18 and 1.23, respectively.
9. W. R. Dolbier, Jr., K. Akiba, M. Bertrand and M. Santelli, *Chem. Comm.*, 717 (1970).
10. W. E. Doering and H. Roth, *Tetrahedron*, *26*, 2825 (1970); J. J. Gajewski, *J. Amer. Chem. Soc.*, *93*, 4450 (1971); W. R. Roth and H. Schmidt, *Tetrahedron Lett.*, *39*, 3639 (1971).