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Electronic excited states of small ring compounds. Cyclopropene, vinylcarbene, and vinylmethylene

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desoxy derivative of **6**. The nmr spectrum of **7** showed signals for a vinyl methyl group (τ 8.44 (3 H, br s)) and vinyl proton (τ 4.50 (1 H, br d, $J = 10$ Hz)) instead of the signals for the 4-methyl and 5-H protons of the 4,5-epoxide system of **6** and a downfield shift of the C-2 and C-3 protons relative to **6**. The structure of **7** was supported also by the bathochromic shift of its uv and ir carbonyl absorption peaks in comparison with those of **6**. Chemical interrelation was effected by reductive elimination of the epoxide of **6** with chromous chloride in acetic acid to give maytensine (**7**).¹¹

The X-ray crystallographic structural elucidation of maytansine bromopropyl ether (**3**) revealed that the two longer sides of the 19-membered ring are roughly parallel and separated by about 5.4 Å, so that there is a hole in the center of the ring.^{4,12} The two faces of the ring have a different character; the lower surface, opposite the ester residue, is predominantly hydrophobic, while the upper face is more hydrophilic. Furthermore, the ester residue is oriented in a manner which would hinder sterically the approach of reactants to the hydrophilic face. The ester function in the antileukemic maytansinoids may play a key role in the formation of highly selective molecular complexes with growth-regulatory biological macromolecules. Such molecular complex formation may be crucial for the subsequent selective alkylation of specific nucleophiles by, e.g., the carbinolamide and epoxide functions.¹³ In this connection, it is noteworthy that maytansine ethyl ether (**2**),⁴ in which the reactive carbinolamide is no longer available as a potential alkylating function, shows no antileukemic activity. Structural studies of additional active principles are in progress, to elucidate further the requirements for biological activity among the antileukemic maytansinoids.

(11) W. Cole and P. L. Julian, *J. Org. Chem.*, **19**, 131 (1954).

(12) R. F. Bryan, C. J. Gilmore, and R. C. Haltiwanger, *J. Chem. Soc., Perkin Trans. 2*, 897 (1973).

(13) Cf. S. M. Kupchan, *Intra-Sci. Chem. Rep.*, **8**, 57 (1973).

(14) NIH Postdoctoral Fellow, 1972-1974.

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Electronic Excited States of Small Ring Compounds: Cyclopropene, Vinylcarbene, and Vinylmethylene¹

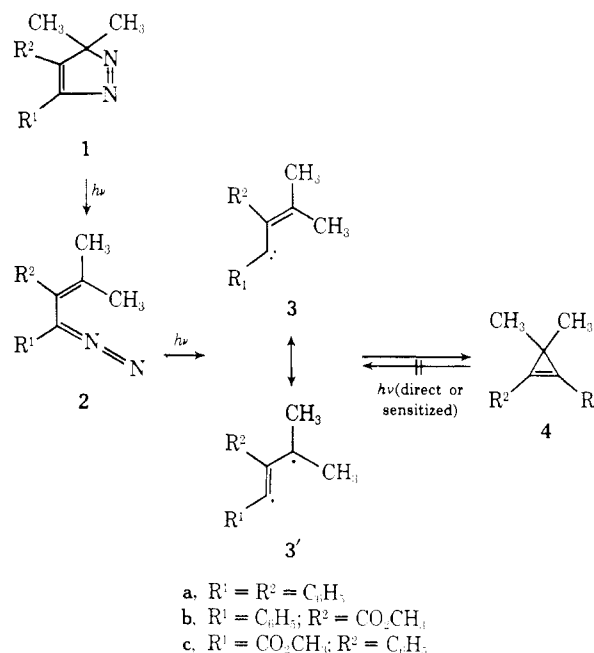
Sir:

The mechanism(s) for the interconversion, and the relative energies of, three-membered rings and the corresponding heterolytic and homolytic bond-cleaved species continues to be of both theoretical and experimental interest.² In this communication we report the

(1) Contribution No. 99 from the Photochemistry Unit.

(2) For cyclopropene, for example: experimental (a) J. A. Pincock, R. Morchat, and D. R. Arnold, *J. Amer. Chem. Soc.*, **95**, 7536 (1973); (b) E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *ibid.*, **95**, 5680 (1973); (c) W. J. Baron, M. E. Hendrick, and M. Jones, Jr., *ibid.*, **95**, 6286 (1973); (d) M. F. Neumann and C. Buchecker, *Tetrahedron Lett.*, 2875 (1973); (e) L. Schrader and W. Hartmann, *ibid.*, 3995 (1973); (f) R. S. Streeper and P. S. Gardner, *ibid.*, 767 (1973); (g) O. L. Chapman, J. Pacansky, and R. Roth, unpublished results; theoretical, (h) R. Hoffmann, G. D. Leiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968); (i) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); (j) L. Salem and W. D. Stohrer, unpublished results.

esr spectral characterization of the triplets, vinylmethylenes, **3a** and **3b**, formally derived from the cyclopropenes (**4a**, **b**).³ These species were obtained by irradiating the vinyl azo compounds (**2a**, **b**).



The 3H-pyrazoles (**1a-c**) have been reported previously.^{2a,4} Treatment of methyl phenylpropiolate with diazoisopropane gives the isomeric adducts **1b** (mp 41°) and **1c** (mp 84°). The structure assigned to the major product (**1b:1c**, 2.5:1) was based on expectation of polar factors directing the cycloaddition. Since this reasoning is not compelling, we sought additional proof for these structures. Irradiation^{5a} of the 3H-pyrazoles (**1a-c**) in benzene solution, brings about formation of the vinyl azo compounds (**2a-c**) in good yield. These vinyl azo compounds are stable for hours in benzene solution at room temperature. The spectral evidence, summarized in Table I, shows the pertinent uv and ir

Table I. Spectral Properties of the Vinyl Azo Compounds

Vinyl azo com- pound	Ir (CCl ₄), cm ⁻¹	Uv (C ₆ H ₆), nm (ε)	Nmr (CCl ₄)	
			δ(CH ₃)	δ(CO ₂ CH ₃)
2a	2040	512 (80)	1.87, 1.92	
2b	2043	510 (75)	1.93, 2.27	3.58
2c	2083	420 (115)	1.82, 1.92	3.68

absorption bands of **2a** and **b** are similar to one another and are significantly different from **2c**; this provides additional support for structures **1b** and **c**. Irradiation^{5b} of benzene solutions of the vinyl azo compound **2a-c**, at room temperature, leads to good yields of the cyclopropenes **4a** and **b**.^{2a,4}

(3) Closs has reported the esr detection of a triplet vinylmethylene for a "phenyl-substituted" case; however, no details have appeared. G. L. Closs, W. A. Boll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968); see footnote b, Table II.

(4) M. F. Neumann and C. Buchecker, *Tetrahedron Lett.*, 15 (1969).

(5) (a) 2 cm, 1.0 M CuSO₄·7H₂O and 0.1 M NiSO₄·6H₂O in 5% H₂SO₄ and 1 cm, 0.4 M SnCl₂·2H₂O in 10% HCl. (b) 1 cm, 4 × 10⁻³ M BiCl₃ in 10% HCl. (c) Corning filter CS 7-51 or CS 7-59.

Irradiation^{5c} of **1a** and **1b** in methylcyclohexane:isopentane (4:1) glasses at *ca.* 5°K, in Supersil tubes in the cavity of an esr spectrometer,⁶ generated strong, stable signals typical of triplet species⁷ to which we assign structure **3a** and **3b**. Free radicals were also produced as evidenced by a strong signal at *g* \sim 2. Similar irradiation of **1c** produced the yellow color characteristic of **2c** and the signal due to the free radical(s); however, no signal due to a triplet (**3c**) could be detected. No signal due to **3a** was observed upon irradiation, direct or triplet-sensitized (benzophenone), of **4a** under these low temperature conditions.

The zero-field splitting parameters derived from the observed spectra are summarized in Table II along with

Table II. Zero-Field Splitting Parameters for Some Vinyl Methylenes and Model Compounds

Methylene	<i>D</i> / <i>hc</i> (cm ⁻¹)	<i>E</i> / <i>hc</i> (cm ⁻¹)	Ref
3a	0.3580	0.0206	<i>a</i>
3b	0.3643	0.0166	<i>a</i>
(CH ₃) ₂ C=CHC \ddot{C} C ₆ H ₅	0.357	0.0194	<i>b</i>
C ₆ H ₅ CO \ddot{C} C ₆ H ₅	0.3815	0.0489	<i>c</i>
C ₆ H ₅ C \equiv C \ddot{C} H	0.541	0.0035	<i>d</i>

^a This work. ^b J. L. Riemenschneider, Ph.D. Thesis, University of Chicago, 1969. ^c A. M. Trozzolo and S. R. Fahrenholtz, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., 1966, No. k23. ^d R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **43**, 196 (1965).

values reported for some model systems. The *D* value indicates a major contribution of the vinylmethylene valence bond structure (**3**) to the resonance hybrid. Assuming the electron-electron interaction is predominantly dipolar, the observed *D* values are equivalent to a mean separation of the electrons of *ca.* 2 Å, considerably smaller than in other trimethylenes.⁸

The stability of the triplet at 5°K indicates either that the triplet is the lowest energy state of the acyclic species (**3**) or is close enough in energy to the lowest singlet to be in thermal equilibrium with it at this low temperature. An analysis of the temperature dependence of the esr signals can distinguish between these possibilities.

For a constant concentration of triplets, the signal intensity due to the triplet will vary with temperature the same as the signal due to the free radical; thus, a plot of signal intensity *vs.* *T*⁻¹ will be linear (Curie law)⁹ and will extrapolate to zero intensity at infinite temperature. Plots of the observed intensities of the doublet signal and of the signals due to **3a** and **3b** exhibit Curie law dependence¹⁰ over the range 5–45°K. For a triplet arising through thermal population from a singlet of lower energy, an estimate of the energy difference ΔE , of

the two states is available from the relationship¹¹ between the signal intensity, *I*, and the temperature for a given energy difference

$$I = \frac{1}{T} \frac{3e^{-\Delta E/RT}}{1 + 3e^{-\Delta E/RT}}$$

These data indicate that either the triplets are the lowest energy states or are separated from singlets of lower energy by less than 4 cal mol⁻¹.

The lack of a triplet signal from the irradiation of **2c** may indicate that the singlet is the lowest energy state in this case and that the singlet-triplet separation is too large to maintain a significant concentration of triplets at these temperatures.

Acknowledgment. The authors wish to thank Dr. E. Wasserman for helpful discussions concerning the interpretation of these results and Professor G. L. Closs for permission to cite unpublished data.

(11) R. Breslow, R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, **86**, 5349 (1964).

(12) Visiting Professor (1973), on leave from the Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, Canada.

(13) Alfred P. Sloan Fellow, 1972–1974.

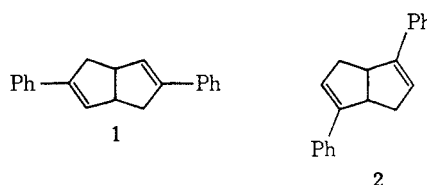
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Received January 21, 1974

The Mechanism of Certain Intramolecular [$\pi 2 + \pi 2$] Cycloadditions

Sir:

We present here evidence, not yet conclusive but strongly suggestive, that certain intramolecular photochemical cycloadditions which on the surface appear to be of the [$\pi 2 + \pi 2$] type in fact occur in two steps; these are a di- π -methane rearrangement,¹ followed by a [$\sigma 2 + \pi 2$] cycloaddition. Examples are to be found in molecules which contain a di- π -methane moiety, but whose molecular geometry conspires, both with regard to bond distance and orbital dihedral angle, to make a direct [$\pi 2 + \pi 2$] process unfavorable.

It was recently reported² that neither **1** nor **2** under-



goes intramolecular photocycloaddition.³ In contrast, we find that **3**⁴ on irradiation (ether, Vycor) gave an essentially quantitative yield of the crystalline isomer **4**, whose structure corresponds to that of a cycloaddition of the two endocyclic π bonds. The structure of **4**

(1) For a recent review, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

(2) G. Kaupp and K. Krieger, *Angew. Chem., Int. Ed. Engl.*, **11**, 719 (1972).

(3) The double bonds in **1** and **2** are separated by about 3.5 Å.

(4) M. Kuzuya and H. Hart, *Tetrahedron Lett.*, 3891 (1973); see also erratum, *ibid.*, 4206 (1973).