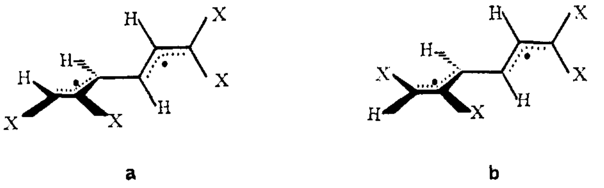
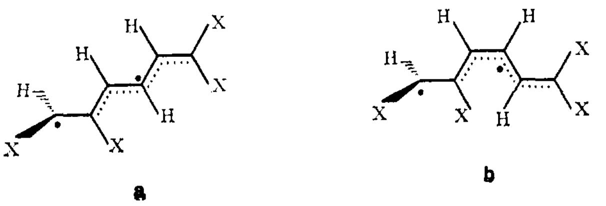


I



II

$X = CH_3$

centrations.[9] Also, quenching processes involving triene triplets have been observed.[10] Quantitative studies on these bimolecular processes will be the subject of a future communication.

Data in Tables I and II also show that excited state bond orders cannot be used reliably in predicting the direction of isomerization, *i.e.*, whether preferentially around the central or the terminal double bond. Calculations on 1,3,5-hexatriene give significantly lower central bond orders as compared with that of the terminal bond in both the S_1 and T_1 states,[11] thus suggesting that isomerization was favored around the central double bonds. Experimentally, such a trend is not evident and, in fact, if anything the results are more consistent with isomerization favored around the terminal double bond. Surely the observed differences are partly due to the methyl groups which not only perturb the π system but also, more significantly, add considerable nonbonded interactions (methyl–methyl and methyl–vinyl H). Furthermore, considering that the excited bond order can only be a kinetic factor in determining the initial distribution of the relaxed intermediates, and that the final product composition should further be affected by the thermal stability of these intermediates and the magnitude of individual decay rate constants from these intermediates, the inadequacy in predicting the direction of isomerization is perhaps not surprising.

Acknowledgment. This work was partially supported by a University of Hawaii Biomedical Grant and by the Sloan Foundation. Discussions with Dr. H. E. Simmons on properties of polyenes have been most helpful.

[9] Unpublished results of S. Arslanian and R. S. H. Liu; also ref 1e.

[10] Unpublished results of Y. Butt and R. S. H. Liu.

[11] See, *e.g.*, calculations based on SCF-CI methods by H. E. Simmons, *Progr. Phys. Org. Chem.*, 7, 1 (1970). We wish to thank Dr. Simmons for a copy of the manuscript prior to its publication.

[12] Alfred P. Sloan Fellow, 1970–1972.

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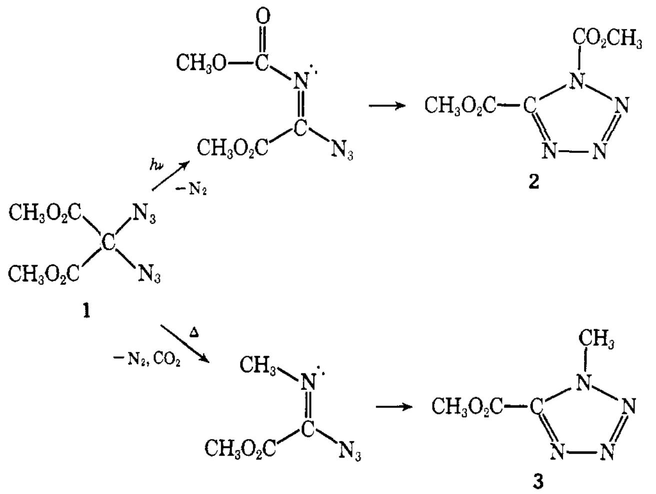
Thermal Decomposition of Geminal Diazides

Sir:

Earlier we reported that photolysis of dimethyl diazidomalonate (**1**) proceeds with loss of one molecule of nitrogen, followed by migration of the carbomethoxy group from carbon to nitrogen to yield an azomethine azide which cyclizes to the tetrazole (**2**). Separate irradiation of the tetrazole (**2**) caused loss of nitrogen and intramolecular cyclization to the oxadiazole (**4**).[1]

We now report that the thermal pathway is strikingly different.[2–4] The analogous loss of nitrogen is observed but the resulting intermediates follow different product-forming pathways. Thermolysis causes loss of both nitrogen and carbon dioxide to yield the *N*-methyl azomethine azide which cyclizes to **3**. Photolysis and thermolysis are compared in Scheme I.

Scheme I



Each pathway is completely specific; there is no crossover in products. Importantly, thermolysis of **2** does not yield **3**. While photolysis of **2** yielded only oxadiazole (**4**), thermolysis yields oxadiazolone (**5**) (Scheme II).[4]

The dichotomy in behavior of geminal diazides upon photolysis relative to thermolysis was found to hold generally for other derivatives.[5]

Photolysis of **6a** or **6b** proceeded with loss of one molecule of nitrogen and migration of the carboxamido and *N*-methylcarboxamide groups, respectively. Pyrolysis followed the fragmentative pathways trans-

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[1] R. M. Moriarty, J. M. Kliegman, and C. Shovlin, *J. Amer. Chem. Soc.*, **89**, 5958 (1967).

[2] A strong precautionary note concerning the explosive nature of the geminal diazides is in order. We have already referred to this property[3] but more recent experiences reveal that they are more hazardous than formerly believed. Under no circumstances should pure neat samples be heated above 100°. A pure neat 0.500-g sample heated to 130° evolved nitrogen briskly prior to a brisant explosion which shattered a heavy safety shield, badly damaged a fume hood, and startled the experimentalist. No explosive decompositions were observed in the course of thermolyses carried out in dilute tetralin.

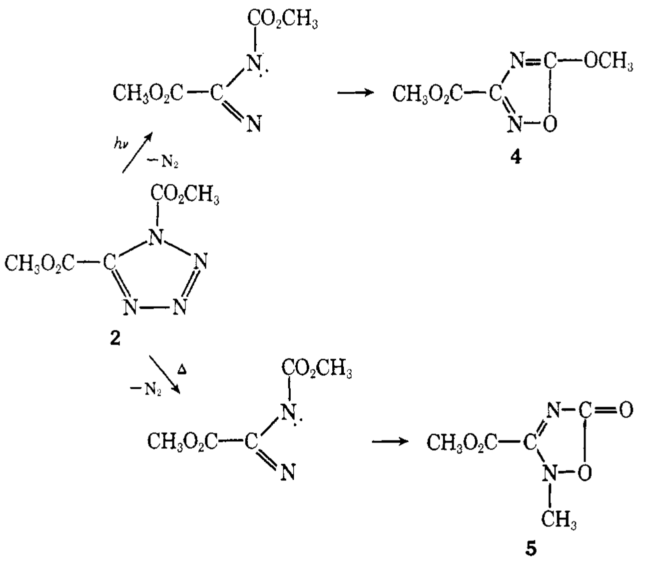
[3] R. M. Moriarty, J. M. Kliegman, and C. Shovlin, *J. Amer. Chem. Soc.*, **90**, 5947 (1968).

[4] Thermolyses were carried out in tetralin solution at 185°. All new compounds gave correct microanalyses. Tetrazole **3** had: mp 108–109°; ν_{CO} 1745 cm^{-1}; nmr ($CDCl_3$, TMS) δ 4.50, 4.10 ppm (singlets); *m/e* 114 (P − 28). 2-Methyl-3-carbomethoxy-1,2,4-oxadiazolin-5-one (**5**) obtained in 50% yield had: mp 77–78°; ν_{CO} 1790 cm^{-1}; nmr ($CDCl_3$, TMS) δ 5.70, 5.97 ppm (singlets); *m/e* 158, 114 (P − CO_2).

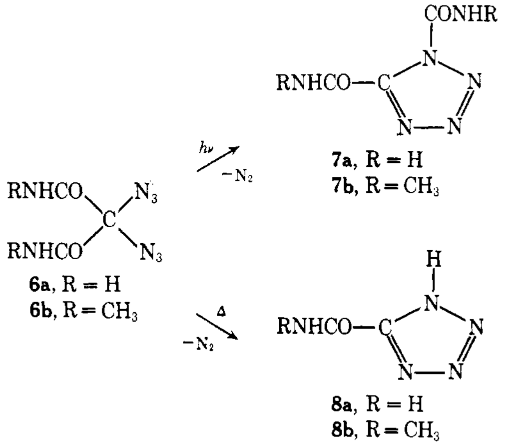
[5] Diazidomalonamide (**6a**) has mp 157–158°, lit.[6] mp 162°. 5-Carboxamidotetrazole (**8a**) obtained in 94% yield has mp 231–232°. Base hydrolysis yielded tetrazole in 80%. Photolysis of **6a** in acetonitrile using a water-cooled Hanau Q81 high-pressure mercury vapor lamp yielded 1,5-dicarboxamidotetrazole (**7a**), 53%, mp 200° dec. Treatment with 30% ammonium hydroxide yielded 5-carboxamidotetrazole as its ammonium salt. *N,N*-Dimethyldiazidomalonamide (**6b**) had mp 104–105°; pyrolysis yielded **8b** in 90% yield, mp 235–236°, ν_{CO} 1665 cm^{-1}.

[6] M. O. Forster and R. Muller, *J. Chem. Soc.*, 126 (1910).

Scheme II



ferring hydrogen to nitrogen in the case of both **6a** and **6b** to yield **8a** and **8b**, respectively.



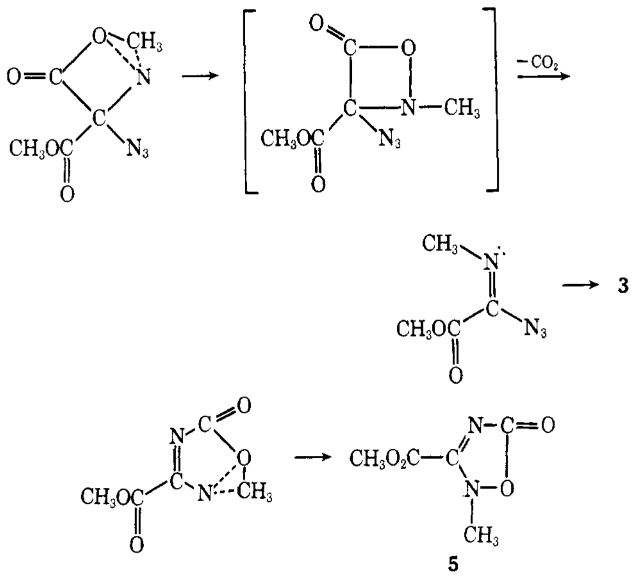
This is the first example of a unique and exclusive difference in the two modes of decomposition of azides. The pattern which emerges is that the photochemical reaction of either the diazides or tetrazoles[7,8] involves migration, whereas the thermal decomposition shows a preference for insertion.

Our view of the photochemical decomposition of alkyl azides is that migration of the α substituent is concerted with loss of nitrogen. The discrete nitrene has no real existence and the group which migrates is determined by ground-state conformational structures. Concisely, rotational equilibration is slower than the Franck–Condon controlled photoexcitation. The thermal reaction is characterized by the adoption of a transition state in which insertion of the nitrenoid nitrogen into the carbon–oxygen bond may occur.

The two thermal reactions may be represented by the following intermediates or transition states for the thermal decomposition of **1** and **2**, respectively (Scheme III).

The thermal loss of nitrogen from the tetrazole proceeds through a $4n + 2\pi$ electron transition state which is isoconjugate with the cyclopentadienate anion. This process should be concerted and lead directly to a singlet nitrene. The photoreaction proceeds *via* an excited state which is antiaromatic. The five atomic orbitals of the excited state possess a phase discontinuity and therefore it is isoconjugate with the cyclobutadiene system. This process is therefore nonconcerted and may yield the triplet state of the nitrene by a stepwise path.

Scheme III



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[7] P. A. S. Smith and E. Leon, *J. Amer. Chem. Soc.*, **80**, 4647 (1958).

[8] T. Bachetti and A. Alemagna, *Rend. Ist. Lomb. Sci. Lett. A*, **94**, 247, 351 (1960); *Chem. Abstr.*, **55**, 16527 (1961).

Nuclear Magnetic Resonance Studies of Long-Range Fluorine Spin Couplings

Sir:

The relative importance of "through-space" and "through-bond" interactions in determining the overall magnitude of long-range ^{1}H–^{19}F spin–spin coupling has not been convincingly established.[1–3] Detailed studies of the five-bond F–F coupling in a series of substituted 4,5-difluorophenanthrenes[4] led to the firm conclusion that through-space interaction of the fluorine nuclei predominates in long-range F–F coupling.[5,6] A similar approach to the study of long-range H–F coupling did not appear attractive because of the expected much smaller magnitude of the long-range H–F coupling

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[1] (a) M. Takahashi, D. R. Davis, and J. D. Roberts, *J. Amer. Chem. Soc.*, **84**, 2935 (1962); (b) A. D. Cross and P. W. Landis, *ibid.*, **84**, 1736 (1962); (c) P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *ibid.*, **88**, 2459 (1966); (d) A. B. Foster, R. Hems, L. D. Hall, and J. F. Manville, *Chem. Commun.*, 158 (1968); (e) C. W. Jefford, D. T. Hill, L. Ghosez, S. Toppet, and K. C. Ramey, *J. Amer. Chem. Soc.*, **91**, 1532 (1969).

[2] R. K. Harris and V. J. Robinson, *J. Magn. Resonance*, **1**, 362 (1969).

[3] M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969).

[4] K. L. Servis and K.-N. Fang, *ibid.*, **90**, 6712 (1968).

[5] (a) R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, **26**, 71 (1970); (b) R. D. Chambers, L. H. Sutcliffe, and G. J. T. Tiddy, *Trans. Faraday Soc.*, **66**, 1025 (1970).

[6] As expected for through-space interaction, the signs of these long-range F–F coupling constants are found to be positive.[5b]