Table IX. Refinement Details

method used to solve struct	Patterson method
type of refinement	full matrix least-squares method
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
H atoms	geometrically located
variables refined	180
a,b values in the weight function:	
$w = 1.0/(a + F_o + bF_o)$	0.068; 0.0108
final *R* (isotropic), %	10.19
final R_w (isotropic), %	15.56
final *R* (anisotropic), %	5.01
final R_w (anisotropic), %	7.75
goodness of fit, *s*	0.40

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. H atoms were idealized (C–H = 1.0 Å); each H atom was assigned the *B* value of parent C atom and allowed to ride on it. Details of the refinement procedure are given in Table IX. The final difference Fourier map, with a root-mean-square deviation of electron density of 0.14 e Å^{-3}, showed a pair of peaks with values exceeding 3.0 times the estimated standard deviation located near Br atoms, which, however, are not of chemical significance. Atomic scattering factors were taken from ref 38. The program used was SIR CAOS,[39] on the Data General MV8000/II of Istituto di Strutturistica Chimica CNR.

Acknowledgment. This work was supported by a grant from the Consiglio Nazionale delle Ricerche and from the Ministero della Pubblica Istruzione. We thank Clara Marciante for technical assistance in the X-ray diffraction measurements.

Supplementary Material Available: Tables of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(38) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV.

(39) Camalli, M.; Capitani, D.; Cascarano, G.; Cerrini, S.; Giacovazzo, C.; Spagna, R. Italian Patent No. 35403c/86, 1986. SIR CAOS user guide, Istituto di Strutturistica Chimica CNR, CP No. 10, 00016 Monterotondo Stazione, Roma.

Rapid, Multistep Rearrangements of Hydrocarbon Triplet Biradicals at 4 K. A Possible Example of Hot Molecule Effects in Frozen Organic Solvents

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Abstract: Photolysis of 2,3-diazabicyclo[2.2.1]hept-2-enes with spirocyclopropyl groups at the 7-positions (e.g., **1** and **8**) in organic matrices at 4–35 K produces triplet 2-alkylidene-1,3-cyclopentanediyls (e.g., **2** and **9**, respectively). The products were identified by comparing EPR spectra—including both zero-field splitting parameters and interpretable hyperfine coupling patterns in the $\Delta m_s = 2$ region—with those obtained from authentic samples. The proposed mechanism involves several unusual features, including hot molecule effects in a condensed phase and quantum mechanical tunneling. An important component in the analysis is the substantial thermodynamic stability of trimethylenemethane compared with other hydrocarbon triplets.

In the present work we describe a remarkable series of transformations that occur at 4 K in frozen organic solvents upon photolysis of members of a class of polycyclic azoalkanes typified by structure **1** (Scheme I). The final products are triplet trimethylenemethane (TMM) derivatives such as **2**. These products have been identified by EPR spectroscopy, including comparison of zero-field splitting parameters with those of authentic samples. In addition, interpretable hyperfine splittings have been seen in the $\Delta m_s = 2$ transitions of the product EPR spectra, and these lead to an unambiguous structural assignment.

The proposed route to **2** is necessarily complex and somewhat speculative. It involves two, sequential biradical-to-biradical rearrangements. The first step (I in Scheme I) is consistent with the conventional thermal chemistry of such structures but would be expected to have a barrier that cannot be surmounted by normal thermal activation at 4 K. We propose that this is an example of hot molecule effects in a condensed phase at 4 K. The second step (II) represents an unprecedented departure from the chemistry these structures display under conventional conditions, and we believe quantum mechanical tunneling is involved. Our mechanistic analysis emphasizes the substantial thermodynamic driving force for obtaining a TMM-like structure, indicating that for hydrocarbon triplets, TMM is a thermodynamic sink.

Scheme I

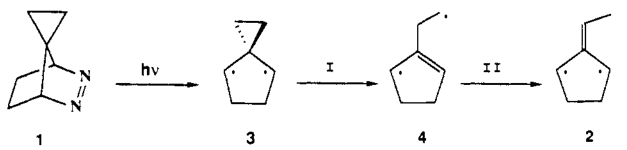

Table I. Zero-Field Splitting Parameters

azoalkane precursor	biradical	$\lvert D/hc\rvert^a$	$\lvert E/hc\rvert^a$
1	**2**	0.0264	0.0035
6^b	**7**^{c}	0.025^b	0.004^b
8	**9**	0.0255	0.0030
10	**2**	0.0264	0.0035
11	**9**	0.0255	0.0030
21	**23**^{c}	0.0256	0.0045
24	**26**^{c}	0.0271	0.009

^{a} In cm^{-1}. ^{b} Reference 4. ^{c} Tentative assignment.

Identification of TMMs as the Reaction Products

Zero-Field Splitting Parameters and Thermal Stability. Photolysis (304–388 nm or monochromatic 334 ± 2 nm) of 2,3-diazabicyclo[2.2.1]hept-2-ene-7-spirocyclopropane (**1**)[2] in a glassy

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(1) (a) Present address: Department of Chemistry, Stanford University. (b) Camille and Henry Dreyfus Teacher-Scholar, 1984–1989.

(2) Roth, W. R.; Enderer, K. *Justus Liebigs Ann. Chem.* **1969**, *730*, 82–90; **1970**, *733*, 44–58. See also: Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3303–3312.

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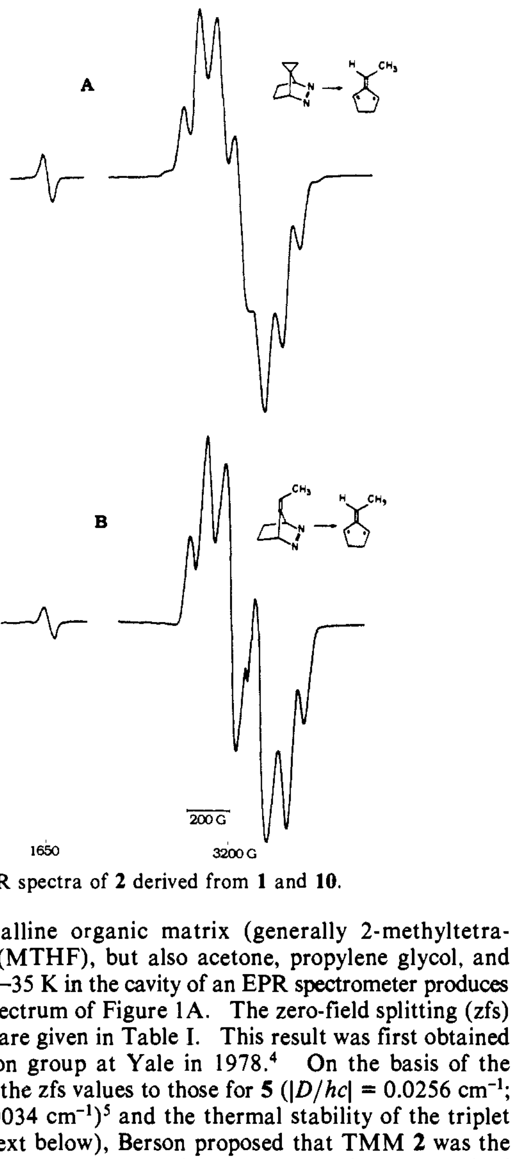
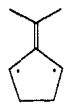


Figure 1. EPR spectra of **2** derived from **1** and **10**.

or polycrystalline organic matrix (generally 2-methyltetrahydrofuran (MTHF), but also acetone, propylene glycol, and heptane) at 4–35 K in the cavity of an EPR spectrometer produces the triplet spectrum of Figure 1A. The zero-field splitting (zfs) parameters[3] are given in Table I. This result was first obtained by the Berson group at Yale in 1978.[4] On the basis of the similarity of the zfs values to those for **5** ($|D/hc| = 0.0256\ \mathrm{cm}^{-1}$; $|E/hc| = 0.0034\ \mathrm{cm}^{-1}$)[5] and the thermal stability of the triplet signal (see text below), Berson proposed that TMM **2** was the carrier of the signal. A mechanism was suggested, as summarized in Scheme I. In Scheme I, and throughout this work, all biradicals shown are triplet states, unless explicitly denoted otherwise. The Berson group obtained a similar spectrum from **6**, presumably due to **7**.[6] Since there were no data to corroborate the assignments, and since many biradicals have zfs values similar to those for **2**, Berson's hypothesis remained just that. We have now been able to show that Berson's intuition was correct.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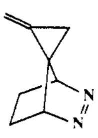

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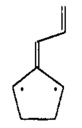
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In 1981, we conducted a similar experiment with diazene **8**, which we had prepared as a possible tetraradical precursor.[7] The spectrum we observed (Figure 2A; Table I) was very similar to that obtained from **2**. The EPR signals from both **1** and **8** give linear Curie plots over a broad temperature range, indicating the species being observed most likely have triplet ground states. In addition, these triplet signals were quite stable thermally, that derived from **1** being stable to at least 146 K in propylene glycol.

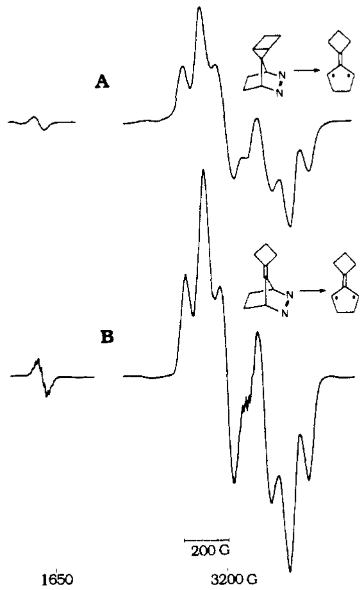
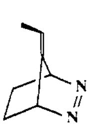


Figure 2. EPR spectra of **9** derived from **8** and **11**.



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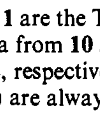
If one accepts Scheme I as a working hypothesis, then the precise conversions implied are **1** → **2** and **8** → **9**. We therefore set out to prepare authentic samples of **2** and **9** by photolysis of diazenes **10**[8] and **11**, respectively. These diazenes were synthesized in a straightforward manner, the key steps being the syntheses of the appropriate fulvenes using the method developed recently by Little.[9] Photolysis of **10** and **11** at 4–77 K does indeed give thermally stable, triplet spectra with zfs parameters (Table I) completely in accord with expectation. On the basis of substantial precedent,[5a] one can assert with confidence that the triplets that arise from **10** and **11** are the TMMs **2** and **9**. As shown in Figures 1 and 2, the spectra from **10** and **11** are essentially identical with those from **1** and **8**, respectively. The spectra from the authentic precursors (**10**/**11**) are always more intense and accompanied by fewer radical impurities, which accounts for the minor differences in the central regions of the spectra. There is one important difference between the authentic precursors **10** and **11** and the diazenes **1** and **8**. When photolysis is conducted at 77 K, only **10** and **11** give TMMs. No triplet signal is seen when **1** or **8** is photolyzed at 77 K, even though photolysis at 4–35 K produces biradicals that are quite stable when warmed to 77 K or higher (see text above).



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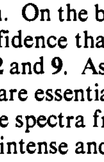

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(3) For a discussion of triplet ESR spectroscopy, see: Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972; pp 223–257. Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763–1772.

(4) Lokensgard, D. M.; Hilinski, E. F.; Berson, J. A., Yale University, 1978;, unpublished results.

(5) (a) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446–453. Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 151–194. (b) The parent TMM shows a similar zfs: Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587–2589.

(6) Lokensgard, D. M.; Dougherty, D. A.; Hilinski, E. F.; Berson, J. A. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3090–3094.

(7) McElwee-White, L.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 3466–3474.

(8) Little, R. D.; Carroll, G. L. *J. Org. Chem.* **1979**, *44*, 4720–4722.

(9) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849–1853.

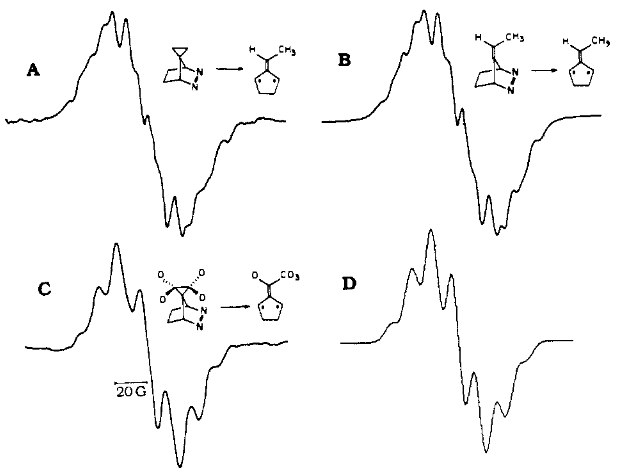


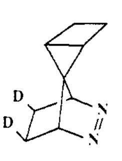
Figure 3. Hyperfine structure in $\Delta m_s = 2$ region of spectra for **2** and **17** and simulation for **17**.

Hyperfine Coupling. While the results of Figures 1 and 2 support the general route in Scheme I, they can hardly be considered compelling. One can imagine a wide range of biradical structures that might have zfs values in the range observed. An especially attractive alternative is an "allyl + p" biradical (e.g., **4**). Fortunately, in many of the spectra we have observed, there is additional information besides just the zfs parameters.

All of the spectra we have recorded clearly show the half-field ($\Delta m_s = 2$) transition that is diagnostic of a triplet spectrum.[3] Distinctive hyperfine patterns are observable on these transitions. Figure 3 shows the $\Delta m_s = 2$ transitions in the spectra from diazenes **1** and **10**. The pattern is complex, but it is clear that the two spectra are essentially superimposable.

More importantly, diazenes **8** and **11** give well-defined, *interpretable* hyperfine patterns that are, again, identical, as shown in Figure 4. Nine fairly evenly spaced lines separated by ca. 13.5 G are clearly visible. A detailed analysis of these hyperfine patterns will be presented in the Discussion. The most important point is that the spectra are dominated by couplings to the hydrogens that are β to the radical centers, with some contribution from the two protons that are α (on the radical centers).

Obtaining identical spectra from different precursors again provides support for our structural assignment. However, the fact that the hyperfine patterns of Figure 4 can be related to a specific structural feature of the biradicals involved provides a much more powerful tool. In particular, we can observe the changes in hfc patterns that result when precursor **8** is specifically deuteriated to give **12** and **13**.[7] According to Scheme I, diazene **12** should produce biradical **14** with two deuteriums in β-positions. Since $a_D = a_H/6.514$, this substitution should reduce the number of hfc lines by 2. The spectrum shown in Figure 4C is completely in accord with expectation. Although the lines are broadened by deuterium coupling, the basic pattern is unchanged and there are two fewer lines.



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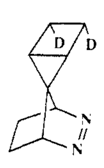

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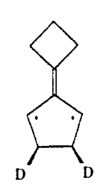

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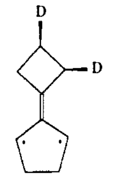

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The more convincing case is provided by diazene **13**. Scheme I predicts that **13** should produce **15**, in which only one of the two deuteriums ends up in a β-position. Figure 4D clearly bears out this expectation. There is an important difference between Figure 4D and all the other hyperfine patterns we have shown. In Figure 4D, when the signal crosses the base line in the center of the spectrum, it is going from lower left to upper right. This indicates that the true spectrum (i.e., not the first derivative) has a minimum in the center. The actual absorption spectrum, obtained by integration, confirms this (Figure 5). This requires an even number of lines in the spectrum and thus coupling to an odd number of protons. In Figure 4A–C, the crossing is upper left to lower right, indicating a maximum (see Figure 5). This requires an odd number of lines and thus an even number of protons. The fact that Scheme I predicted that this sort of parity change would result from incorporation of deuteriums that are quite remote from where one might have expected radical character provides compelling support for the scheme.

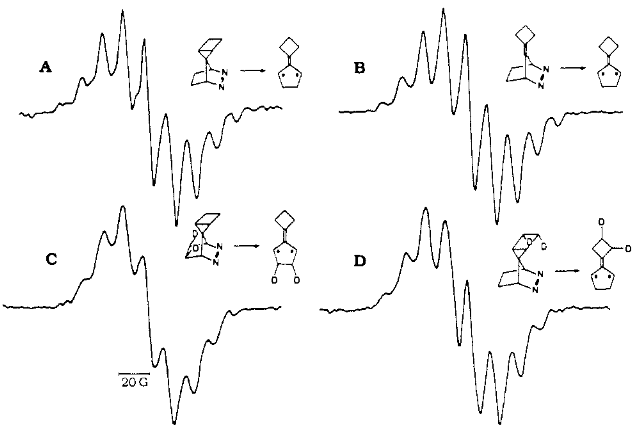


Figure 4. Hyperfine structure in $\Delta m_s = 2$ region of spectra for **9**, **14**, and **15**.

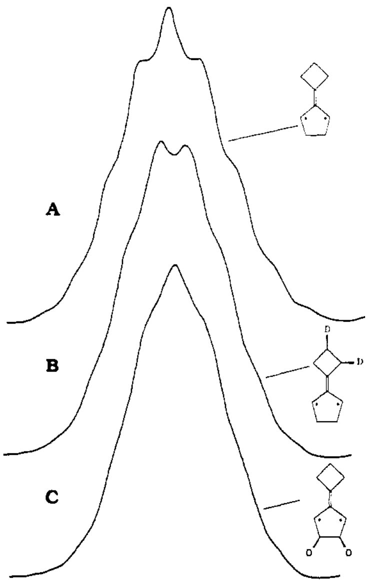
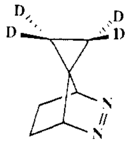


Figure 5. Absorption spectra, obtained by integration of analogous spectra from Figure 4, for $\Delta m_s = 2$ region of **9**, **14**, and **15**.

Given these results, we reasoned that the complex hfc pattern for **2** arose from the protons in the methyl group. Assuming methyl rotation is frozen, these protons could all have different orientations[3] (θ values) and would contribute hfc constants that are not the same as those for the ring β protons. To circumvent this problem, we prepared the tetradeuterio diazene **16** as a precursor to biradical **17**. As shown in Figure 3C, the $\Delta m_s = 2$ pattern is now an easily interpretable seven-line spectrum with ca. 13.5-G spacings. Our interpretation of these spectra, including complete simulation (Figure 3D) will be presented in the Discussion.



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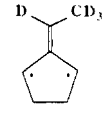

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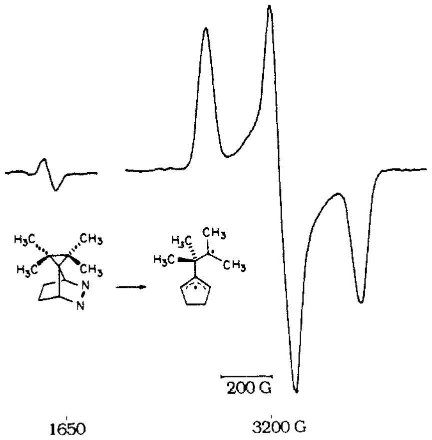
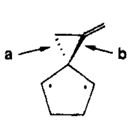


Figure 6. EPR spectrum from **24**, tentatively assigned to biradical **26**.

Other Possible Examples. We consider the above data as irrefutable proof that diazenes **1** and **8** give rise to TMMs **2** and **9**, respectively, upon photolysis in a matrix at 4–35 K. The observation of two examples suggests that this remarkable rearrangement could be general. In particular, the conversion of **6** to **7** seems quite feasible, but there is neither interpretable hyperfine nor generation from an authentic precursor in this case, so the assignment must still be considered tentative. If correct, however, this would represent another example of "wrong bond cleavage".[6] One would expect biradical **18** to cleave bond a to give the doubly allylic biradical **19**, rather than the presumably stronger bond b to give **20** and, ultimately, **7**. Of course, cleavage a could still be the dominant path if it produces EPR-silent products. Our data simply indicate that cleavage b is operative to some extent, as it is under conventional conditions.[6]



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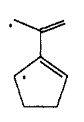

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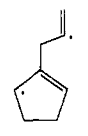

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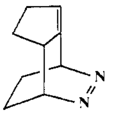
The results for **1** and **8** also suggest that attempts to directly prepare allyl + p biradicals from appropriate precursors should lead to TMMs. Diazene **21**[7] is such a precursor, in that loss of N_2 should produce allyl + p biradical **22**. Direct photolysis of **21** under matrix isolation conditions produces no EPR signal. However, when benzophenone is included as a sensitizer, a triplet signal is seen.[10] Again, the zfs parameters (Table I) are completely consistent with a TMM structure. Additionally, the EPR signal is stable to at least 100 K in propylene glycol. These attributes seem to be more consistent with TMM **23** than with allyl + p **22**. It should be recognized, however, that the ring closure pathway that has been suggested as the thermal decomposition path for other allyl + p systems (see below) is much less viable for **22** due to ring strain. In fact, the preferred decomposition path for **22** is presumably C–C bond cleavage to give 2,3-divinylcyclopentene.[7] Thus, it is difficult to predict the thermal stability of **22**.



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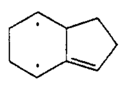

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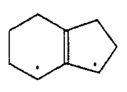

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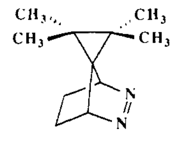
An Attempt To Prepare an Authentic Allyl + p Biradical. Having established that TMMs are the carriers of the EPR signals, we prepared to evaluate whether Scheme I is the actual route to these structures, probing in particular the intermediacy of biradicals **3** and **4**. We therefore prepared tetramethyl diazene **24**. Our goal was to suppress the hydrogen migration (step II of Scheme I) and perhaps directly observe the allyl + p biradical. Photolysis of **24** in MTHF at 4–35 K produces the spectrum shown in Figure 6. The *D* value is slightly larger than those for the TMMs we have observed, and the *E* value is very much different (Table I). The fact that $D \approx 3E$ gives the spectrum its unusual appearance.



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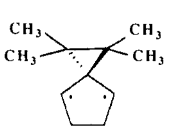
Unlike all the other triplet spectra we have described, the signal of Figure 6 is not thermally stable over a broad temperature range. It decays at temperatures as low as 35 K, although it is indefinitely stable at 4 K. The thermal instability combined with the large *E* value establishes that the carrier of the signal in Figure 6 is not an alkylidenecyclopentanediyl (TMM) of the sort we have observed previously.

The two most likely carriers are biradicals **25** and **26**. The cyclopropyl-1,1-dicarbinyl type structure **25** can be ruled out on the basis of its *D* value. The parent 1,3-cyclopentanediyl (**27**) displays[11] a value of $|D/hc| = 0.084$ cm^{-1}, much larger than the 0.027 cm^{-1} seen here. One could argue that delocalization through the Walsh orbitals of the cyclopropane could substantially diminish *D*. However, we have previously evaluated this effect computationally using ab initio wave functions and a complete numerical evaluation of the zfs integrals.[12] The calculations predict a decrease in *D* of less than 20% upon incorporation of a spirocyclopropyl ring.



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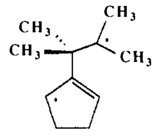

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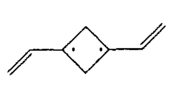
Further, we have found that we can photochemically destroy the EPR signal. Varying the irradiation wavelength reveals that only light between 350 and 420 nm or below 300 nm leads to bleaching of the EPR signal. This is effectively a photochemical "action spectrum", and it implies that the biradical absorbs light in these regions.[13] The UV spectrum for matrix-isolated allyl radical consists of a weak transition between 350 and 410 nm and a strong transition at 213 nm, which tails out above 300 nm,[14] in good agreement with our observations. Also, a similar action spectrum is seen for triplet 1,3-divinyl-1,3-cyclobutanediyl (**28**), another biradical with an allyl moiety.[15]



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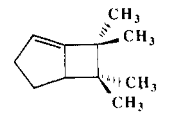

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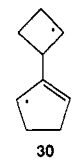

30

We therefore tentatively assign biradical **26** as the carrier of the signal in Figure 6. The *D* value is quite consistent with a partially delocalized 1,4-biradical. The thermal instability pre-

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(10) It is not surprising that direct photolysis is not successful with **21**. This diazene is a derivative of diazabicyclo[2.2.2]octene, a ring system known to be relatively photoinert.

(11) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688–4693.

(12) Goldberg, A. H. M.S. Thesis, California Institute of Technology, 1982.

(13) Synder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 299–300.

(14) Maier, G.; Reisenauer, H. P.; Rohde, B.; Dehnicke, K. *Chem. Ber.* **1983**, *116*, 732–740.

(15) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A., manuscript in preparation. Snyder, G. J.; Dougherty, D. A., manuscript in preparation.

Table II. Product Compositions from Photolysis of **1**

solvent	phase	temp, K	**31**:**32**
ether[a]	fluid	298	9:1
acetone-d_6	fluid	298	8:1
acetone-d_6	fluid	195	6.5:1
acetone-d_6	solid	148	1:1
acetone-d_6	solid	77	1:25

[a] Reference 2.

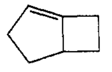
sumably indicates a relatively facile ring closure to the bicyclo[3.2.0]hept-1-ene **29**, a well-precedented process for biradicals of this type.[2,16]

We have occasionally seen shoulders on the outer lines of the spectra generated when diazenes **8**, **12**, and **13** are photolyzed at 4 K. Because they are shoulders it is not possible to determine their separation accurately. We estimate it as 600–625 G, implying a value of $|D/hc|$ between 0.028 and 0.029 cm^{-1}, if the shoulders are the outer lines of a triplet spectrum. On warming to 8 K, these lines irreversibly decay over a period of ca. 20 min. We tentatively ascribe these signals to allyl + p structure **30**.

Discussion

Background—Room-Temperature Chemistry and Thermochemistry. Before discussing our matrix isolation results, we briefly review the chemistry of these azoalkanes under conventional conditions. For the parent system **1**, it has been shown[2] that both thermolysis (140 °C) and photolysis (20 °C) give predominantly the spiropentane derivative **31**. Sensitized photolysis, however,

31



32

gives predominantly olefin **32**. This result was rationalized by invoking cyclopropyl-1,1-dicarbinyl biradical **3**. In the triplet state (sensitized photolysis), **3** cannot ring close to **31** but instead undergoes ring cleavage to biradical **4**. Diazene **8** also shows the same general reactivity pattern,[7] although the sensitized photolysis is more complex and involves pathways in addition to the cleavage route analogous to **3** → **4**.

Under the conditions of the present study, we assume that after excitation from S_0 to S_1 of the diazene, intersystem crossing (ISC) to T_1 occurs. Loss of singlet N_2 then produces a triplet hydrocarbon directly. While such ISC in diazenes is relatively rare under conventional conditions, there is precedent for it becoming more important at lower temperatures.[17] This is because there are generally small thermal barriers to N_2 loss on S_1. As the temperature is lowered, such barriers become more difficult to cross, and ISC, the rate of which is generally considered to be independent of temperature, becomes competitive. Studies we have performed that are summarized in Table II support this conclusion. As the temperature is lowered in the photolysis of **1**, the yield of triplet product **32** does increase at the expense of singlet product **31**.

Photolysis at 4 K produces slightly different results. After 7 h of photolysis with a focused 1000-W Hg/Xe arc lamp at 4 K in acetone-d_6, less than 10% of azoalkane **2** decomposed. Products were barely detectable by 400-MHz NMR. This illustrates the remarkable sensitivity of EPR, since the spectra shown throughout this paper typically required less than 1 min of photolysis. From the 4 K experiments, the **31** to **32** ratio is 1:2. In addition, many new ^1H NMR peaks appear in the olefinic region that were not present in the 77 K (or higher) photolysates. On thawing a 4 K sample, one would expect that TMM **2** would dimerize or would be trapped by reactive "diylophiles".[5a] We have prepared the authentic TMM dimers from azoalkane **10**, and their NMR spectra are somewhat different than those obtained from an EPR sample. The concentration of triplets in our EPR samples is so low that we feel trapping is a much more likely reaction. Strained olefin **32** is an obvious trapping candidate. In addition, bicyclopentanes react rapidly with radicals,[18] and so **31** should also trap **2** efficiently. Thus, the **31**:**32** ratio from the EPR experiment most likely does not reflect the initial product ratio.

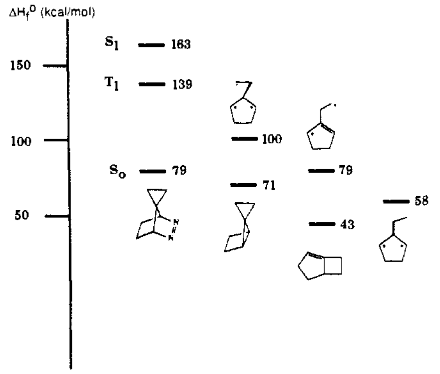


Figure 7. Energy diagram relevant to Scheme I. All biradical structures are in triplet states.

The important point is that, on going from 77 to 4 K, *new products appear*. Remember that at 77 K no TMM is seen. From the NMR intensities, the amount of new material is comparable to the amount of **31** and **32** formed. Thus, at 4 K, the TMM route is *not* a trivial side reaction that is detected only because EPR is so sensitive. Rather, it competes with all other reactive modes and so must be considered as a significant reaction component.

Another important reference point for our discussion is the thermochemistry of the processes involved. There is a significant amount of relevant experimental data that can be combined with standard group increments and strain energies to arrive at the overall scheme of Figure 7.[19] This scheme can only be considered to be semiquantitatively accurate, but it does lead to important conclusions concerning the viability of the stepwise mechanism of Scheme I. All the reactions proposed, i.e., **1** (T_1) → **3** → **4** → **2** are substantially exothermic and, of course, spin-allowed. All alternative reactions are spin-forbidden, a factor that should significantly slow their rates.

Stepwise Mechanism. Step I. Cyclopropylcarbinyl Cleavage. We now consider whether Scheme I is in fact a viable mechanistic route to TMMs such as **2**. As discussed above, the first step **3** → **4**, is the observed path in solution at room temperature.[2] It has also long been considered as an important component of the rearrangement of spiropentanes to methylenecyclobutanes and has been observed in other systems.[16] Thus, it is perhaps not surprising that it should occur in a matrix at low temperatures.

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(16) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981; pp 90–106.

(17) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333–2334; Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *Ibid.* **1976**, *98*, 4320–4322.

(18) Jamieson, C.; Walton, J. C.; Ingold, K. U. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1366–1371.

(19) (a) $\Delta H_f(\mathbf{1})$: Standard group increments (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976) were used to add a cyclopropyl ring to 2,3-diazabicyclo[2.2.1]hept-2-ene (ΔH_f = 49.6 kcal/mol) (Kao, J.; Huang, T.-N. *J. Am. Chem. Soc.* **1979**, *101*, 5546–5557). Spiro strain (5 kcal/mol) and ring strain (29 kcal/mol) were also added. The S_1 and T_1 excited states were placed 84 and 60 kcal/mol higher (Engel, P. S.; Steel, C. *Acc. Chem. Res.* **1973**, *6*, 275–281). (b) $\Delta H_f(\mathbf{3})$: The known energy barrier for the bridge-flip process of **31** (29 kcal/mol[2]) was added to $\Delta H_f(\mathbf{31})$ obtained by addition of a cyclopropyl ring and spiro strain (10 kcal/mol) to the known ΔH_f for bicyclo[2.1.0]pentane (37 kcal/mol) (Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109–3118). (c) $\Delta H_f(\mathbf{4})$: Molecular mechanics was used to obtain $\Delta H_f(\mathbf{32})$ = 43 kcal/mol. The activation energy for the degenerate rearrangement of methylenecyclobutane (49.5 kcal/mol) (Doering, W. v. E.; Gilbert, J. C. *Tetrahedron, Suppl. N7*, 397–414) was added. The additional release of strain due to the bridgehead olefin was estimated at 15 kcal/mol by molecular mechanics calculations on **32** and its saturated analogue. This put $\Delta H_f(\mathbf{4})$ at roughly 79 kcal/mol. (d) $\Delta H_f(\mathbf{2})$: $\Delta H_f(\mathbf{39})$ = 38.3 + ΔH_f(1,3-butadiene) = 64 kcal/mol (Feller, D.; Davidson, E. R.; Borden, W. T. *Isr. J. Chem.* **1983**, *23*, 105–108; and Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970). Addition of an ethano bridge, a methyl group and strain energy (7 kcal/mol) gives $\Delta H_f(\mathbf{2})$ as roughly 58 kcal/mol.

However, it is surprising that the cleavage is so rapid ($k > 1\ s^{-1}$) at 4 K that **3** never accumulates to an extent sufficient for EPR detection.

The reaction is the biradical version of the much-studied cyclopropylcarbinyl-to-3-butenyl rearrangement (**33** → **34**).[20] The activation parameters for this monoradical process (log $A = 12.5$; $E_a = 5.9$ kcal/mol; $k(25\ °C) = 1.3 \times 10^8\ s^{-1}$) show that such a reaction would be expected to be extremely slow at 4 K. In the biradical version there is a greater thermodynamic driving force for the rearrangement due to the development of allylic resonance, and this should lead to a decrease in E_a.[21] Product studies suggest[2] that in triplet biradical **3** the rate of cleavage to **4** is ca. 10 times faster than the rate of closure to **31** at room temperature. Closure to **31** is a spin-forbidden process in a hydrocarbon with a constrained geometry and would be expected to have a rate no greater than $10^9\ s^{-1}$.[23] Thus, the upper limit to the cleavage rate is ca. $10^{10}\ s^{-1}$. If log $A = 12.5$, this implies a barrier of 3.4 kcal/mol, which would be completely insurmountable at 4 K. Only barriers on the order of 0.2 kcal/mol or less can be overcome rapidly by thermal activation at 4 K. It seems unlikely that developing allylic resonance could almost completely eliminate E_a. In addition, such a small barrier would require an anomalously low log A value (ca. 10) in order for the cleavage rate to be $10^{10}\ s^{-1}$ at room temperature. It is hard to imagine why a spin-allowed, unimolecular, bond-cleavage reaction would have such a low log A. We do note that the stereoelectronics for cleavage may not be perfect in this case, since the optimal arrangement appears to be one in which a cyclopropyl C–C bond is aligned with a radical p orbital.[20] We, of course, cannot rule out the possibility that the monoradical cleavage is simply a poor model for the biradical cleavage and that a combination of stereoelectronics, allylic stabilization, and perhaps other effects conspire to give the reaction **3** → **4** remarkably low log A and E_a values.

33 **34**

There are, however, alternatives to thermal activation. One is quantum mechanical tunneling.[24] In fact, the closely related biradical **27** is believed to undergo ring closure (to bicyclo[2.1.0]pentane) via heavy-atom tunneling.[11] The key to achieving tunneling when heavy- (i.e., non-hydrogen) atom motions are involved (as in **3** → **4**) is to have a small, *narrow* barrier.[25] It is possible that the ring opening **3** → **4** has such a small, narrow barrier through which tunneling can occur at 4 K. However, it is difficult to imagine that the cleavage barrier is very much smaller and narrower than that for closure of **27**.[11] The ring closure of **27** is more exothermic than the conversion **3** → **4**. Additionally, it appears that more substantial heavy-atom motions are involved in the cleavage of **3**. Yet, the tunneling of **27** is slow enough that the biradical can be detected easily by EPR under the same conditions as the present work. On the basis of these observations we cannot rule out tunneling, but we consider it to be unlikely.

Table III. Unimolecular Rate Constants for **3** → **4** from RRKM Calculations

E_a	$k_2{}^a$	$k_4{}^a$	$k_{10}{}^a$	$k_{50}{}^a$
4.0	1.8×10^{10}	3.5×10^{10}	9.2×10^{10}	3.5×10^{11}
6.0	2.18×10^{9}	5.2×10^{9}	2.0×10^{10}	1.6×10^{11}
10.0	5.5×10^{7}	1.8×10^{8}	1.2×10^{9}	3.6×10^{10}

[a] k_E = Rate constant when total energy content is E kcal mol^{-1} above E_a.

Another way to get over an "insurmountable" barrier is chemical activation ("hot" molecule effects). Figure 7 shows that ca. 39 kcal/mol of excess vibrational energy is available after N_2 loss from T_1 of **1**. It is now generally accepted that when such deazetations are accomplished thermally or photochemically (S_1), most of the excess energy is localized within the hydrocarbon fragment, rather than the N_2.[26] If this is also true (or even nearly so) in the present case, the initial energy of **3** is well above the small (<6 kcal/mol) barrier for its rearrangement to **4**. Then, if the rate of rearrangement is competitive with that of vibrational cooling, the **3** → **4** reaction becomes quite viable under the reaction conditions.

Chemical activation is well-known in the gas phase, where collisional deactivation of hot molecules can be quite slow. It has been proposed only rarely in condensed media, and only when the chemically activated process has a relatively small barrier (<25 kcal/mol).[27] In recent years, picosecond spectroscopic techniques have provided a wealth of information on the rates of vibrational energy redistribution and vibrational cooling in molecules.[28] At best, these processes occur on the time scale of molecular vibrations, often requiring tens or hundreds of picoseconds for complete relaxation. This sets an upper limit for the rate of cooling of vibrationally excited **3**. It is not certain how effective a frozen organic solvent at 4 K would be at "collisional deactivation". It seems possible that vibronic coupling would be less effective under these circumstances than in fluid media, but in any event it cannot be any faster than the processes discussed above.

To estimate the unimolecular rate constant, we have modeled this reaction using RRKM theory.[29] The vibrational spectrum of bicyclo[2.1.0]pentane[30] was used as a starting point to obtain the frequencies for **3**, and some low-frequency modes were incorporated for the biradical. Since the reaction is spin-allowed but may face some stereoelectronic constraints, we have chosen $A = 4.4 \times 10^{11}$. Of course, there are many approximations in this process. However, the calculations should be able to indicate whether a molecule the size of **3** with an energy content consistent with Figure 7 can undergo a rearrangement at a rate that could be competitive with vibrational relaxation.

The results of the RRKM calculations are presented in Table III. It is evident that for small barriers the reaction is essentially controlled by the Arrhenius preexponential factor. Note that a very rapid reaction can occur even when there is <10 kcal/mol of excess energy, i.e., even if the matrix withdraws a substantial part of the available energy. This is because the unimolecular rate depends not only on how far above the barrier the molecule is but also on the absolute magnitude of the barrier. In other

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[20] Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed., Academic: New York, 1980; Vol. I, pp 161–310.

[21] An additional factor that could affect E_a is through-bond coupling.[22] In **27** the CH_2 group is an effective through-bond coupler that precisely cancels the through-space interaction and leads to a near degeneracy of the NBMOs. In **3** a filled Walsh orbital is the through-bond coupler, which could alter the magnitude of the interaction. Preliminary ab initio calculations indicate a 1.5 kcal/mol triplet preference in **3**, much larger than that for **27**.[22]

[22] Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284–290. Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *Ibid.* **1982**, *104*, 6533–6542.

[23] See, for example: Reference 11. Wilson, R. M.; Geiser, F. *J. Am. Chem. Soc.* **1978**, *100*, 2225–2226. Wilson, R. M.; Rekers, J. W. *Ibid.* **1981**, *103*, 206–207. For an alternative analysis, see: Adam, W.; Hannemann, K.; Hössel, P. *Tetrahedron Lett.* **1984**, *25*, 181–184.

[24] Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: New York, 1980.

[25] (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700–1701. Huang, M.-J.; Wolfsberg, M. *Ibid.* **1984**, *106*, 4039–4040. (b) Dewar, M. J. S.; Merz, K. M., Jr.; Stewart, J. J. P. *J. Chem. Soc., Chem. Commun.* **1985**, 166–168.

[26] (a) Chang, M. H.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 4211–4217. (b) Holt, P. L.; McCurdy, K. E.; Adams, J. S.; Burton, K. A.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1985**, *107*, 2180–2182. Adams, J. S.; Burton, K. A.; Andrews, B. K.; Weisman, R. B.; Engel, P. S. *Ibid.* **1986**, *108*, 7935–7938.

[27] Farneth, W. E.; D'Amore, M. B.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 5546–5552. A possible example in a frozen matrix is the loss of 4 equiv of N_2 upon absorption of one photon in a tetrakis(diazo) compound: Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147–2156.

[28] In rare-gas matrices vibrationally excited states of small molecules can be quite long-lived. See: Bondybey, V. E.; English, J. H.; Miller, T. E. *J. Phys. Chem.* **1983**, *87*, 1300–1305. Bondybey, V. E.; English, J. H. *J. Chem. Phys.* **1980**, *73*, 87–92.

[29] Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: New York, 1972.

[30] Bragin, J.; Guthals, D. *J. Phys. Chem.* **1975**, *79*, 2139–2144.

words, a molecule that is 4 kcal/mol above a 4 kcal/mol barrier will react *much* faster than a molecule that is 40 kcal/mol above a 40 kcal/mol barrier.

Qualitatively, then, the calculations indicate that it is quite possible for the rearrangement to compete favorably with deactivation of hot **3**. Biradical **3** reacts faster than it can be cooled by the medium and thus never accumulates to an extent that would allow detection. It is tempting to conclude that hot **3** preferentially cleaves to **4** rather than closes to **31** because of the spin-allowedness of the cleavage, or perhaps because of some dynamic effect. However, we hasten to add that we cannot detect the process **3** → **31**, and thus we cannot rule out the possibility that ring closure is also an important reactive mode for hot **3**.

Stepwise Mechanism. Step II. Hydrogen Shift. Unlike step I, the hydrogen shift reaction **4** → **2** is, to our knowledge, completely unprecedented. It is formally a 1,2-shift in a free radical, a reaction that is completely unknown in solution.[20] Such shifts are important in certain biradical systems (see below), but extensive studies of a variety of reactions thought to involve allyl + p biradicals such as **4** have failed to uncover any involvement by TMMs.[2,16] It thus appears that the present conditions have opened up a completely new reaction pathway.

For this observation we feel that quantum mechanical tunneling provides an especially suitable explanation. Tunneling is often involved in hydrogen atom and proton transfers at low temperatures. One common aspect of such reactions is very large kinetic isotope effects (KIE), such that ^{2}H tunnels much more slowly than ^{1}H, or perhaps not at all.[31] This reasoning prompted our synthesis of deuterio analogue **16**. However, within our (quite slow) time scale of observation, the deuteriated material rearranges rapidly. This implies that if tunneling is involved, it must be quite efficient. Two factors could be involved in making the tunneling especially effective in the conversion **4** → **2**.

The first effect is the very short distance the hydrogen must move. Most H (and H$^+$) transfers that involve tunneling are not 1,2-shifts, and therefore involve longer migration distances. The shorter distance in the present case implies a narrower barrier, and thus much faster tunneling. The second effect is the possibility that biradical **4**, like **3**, is born in a vibrationally excited state. The thermochemistry (Figure 7) is certainly consistent with this possibility. If so, the conversion **4** → **2** could be an example of vibrationally assisted tunneling (VAT), a notion that is implicit in most tunneling models and that has been explicitly developed recently.[25b]

Tunneling also nicely explains the unusual effect in which photolysis of **1** and **8** at 77 K does not produce TMMs. The expected decay path for a biradical like **4** is ring closure to **32**. This reaction is apparently slow at 4 K and so a new process involving tunneling can compete. As the temperature is raised the rate of the ring closure should increase substantially, but the tunneling rate should increase only slightly. Thus, the ring closure should overtake the H shift at higher temperatures. This would explain why no TMM is seen at 77 K.

Although deuteriation does not measurably slow the H shift, apparently the incorporation of the ethano bridge in **30** (relative to **4**) does to some extent, if the assignment of **30** as the carrier of the outer wings in spectra derived from **8** is correct. While this may at first seem surprising, it does have precedent. A similar 1,2 H shift is often invoked to explain the presence of olefinic products in reactions thought to involve simple 1,3-biradicals. Examples include the conversion of trimethylene (**35**) to propene and **27** to cyclopentene. In contrast, reactions that involve 1,3-cyclobutanediyls (**36**) do not produce cyclobutene.[15,17,26a,32] A stereoelectronic effect has been invoked to explain this result.[26a] The smaller C–C–C angle at the CH_2 group of **36** moves the radical center away from the hydrogens that must migrate. These ring constraints make it more difficult to achieve an arrangement in which a C–H bond is aligned with the radical p orbital. Analogous effects are present in **30**. One might expect that a tunneling reaction would be especially sensitive to stereoelectronic effects. Small changes in barrier height and, more importantly, barrier width can have substantial effects on tunneling rates. Another possible explanation of this result would be that VAT is important. The larger size of **30** vs **4** would make such a "chemically activated" process less efficient. Thus, it seems quite plausible that the H shift reaction should be slower in **30** than in **4**.

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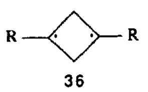

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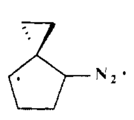
Alternative Mechanisms. In order to consider Scheme I as a viable mechanistic path to the TMMs we observe, some unusual effects must be invoked. However, it is quite difficult to develop alternatives. As always, one could say that diazenyl biradicals such as **37** are involved. However, conversion of **37** to **38** is even less likely than **3** → **4**, since allylic resonance is not developed. Furthermore, there is no direct evidence for the involvement of diazenyl biradicals in the *triplet* chemistry of this or any related system. We have also considered the possibility that step I and/or step II of Scheme I are photochemically induced. Factors that argue against this route include the lack, in both **3** and **4**, of an obvious chromophore that could efficiently absorb 334-nm light. This is especially true for **3**. Thus, if step I is photochemical, it would have to be *much* slower than **1** → **3**, in which case enough **3** should accumulate to allow its direct detection. In addition, we have shown that the rate of production of **2** varies linearly with lamp intensity, which rules out certain types of biphotonic mechanisms.



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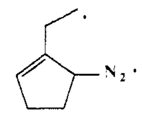

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We have also considered a direct, one-step conversion **3** → **2**. The motions involved are quite unlike anything previously described in the thermal rearrangement literature. It should be recognized, however, that once "hot molecule" effects are considered, the notion of a stepwise mechanism can become fuzzy. One can envision a scenario in which **3** is formed in a vibrationally excited state and is never relaxed, but goes on directly to **4**. Similarly, **4** is vibrationally excited and never relaxes, but goes on directly (VAT?) to **2**, which finally "cools down". In such a process, **3** and **4** can hardly be considered intermediates. Rather, the reaction involves exploration of the high- (vibrational) energy regions of the triplet C_7H_{10} surface. As it is deactivated, the molecule falls into the deepest well—the thermodynamic sink **2**.

Hyperfine Coupling Constants. The observation of interpretable hfc in the $\Delta m_s = 2$ transition of a sample of randomly oriented triplet species is relatively rare.[15,34,35a] Usually complications arise due to the inherent anisotropy of such systems, in that there are four stationary resonant fields (turning points) in this region of the spectrum.[35] Their positions are given by H_{min} (corresponding to the lowest limit of absorption) and H_x, H_y, and H_z (corresponding to orientations in which the external magnetic field is along one of the three principal axes of the electron spin-spin

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(31) See, for example: Brunton, G.; Gray, J. A.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 4197–4200. Platz, M. S.; Senthilnathan, V. P.; Wright, B. B.; McCurdy, C. W., Jr. *Ibid.* **1982**, *104*, 6494–6501.

(32) It is *possible* that such a shift is responsible for the formation of cyclobutene in the 185-nm photolysis of bicyclobutane.[33] However, such excitation could lead to upper electronic (or vibrational) states of **36** (R = H). Also, paths to cyclobutene that do not involve **36** (R = H) are feasible.

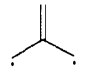
(33) Becknell, A. F.; Berson, J. A.; Srinivasan, R. *J. Am. Chem. Soc.* **1985**, *107*, 1076–1078. Adam, W.; Oppenländer, T.; Zang, G. *Ibid.* **1985**, *107*, 3921–3924.

(34) Muller, J.-F.; Muller, D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629–1630. Snyder, G. J.; Dougherty, D. A. *Ibid.* **1985**, *107*, 1774–1775. Dowd, P.; Chang, W.; Paik, Y. H. *Ibid.* **1986**, *108*, 7416–7417.

(35) (a) Grivet, J.-Ph. *Mol. Phys.* **1970**, *19*, 389–398. (b) Kottis, P.; Lefebvre, R. *J. Chem. Phys.* **1963**, *39*, 393–403. Kottis, P.; Lefebvre, R. *J. Chem. Phys.* **1964**, *41*, 379–393.

coupling tensor). It has also been observed that $H_{\min}$ represents the most intense peak. The positions of the four turning points are determined by the zfs parameters and can be calculated easily. In the present systems the calculated separations between $H_{\min}$ and H_x, H_y, H_z are only 1, 3, and 8 G, respectively. This gives a highly isotropic peak, and all the structure can be interpreted as arising from hfc.

Before providing a detailed interpretation of the hyperfine patterns we have seen, it is instructive to consider the hfc values one would expect for structures such as **2** and **9**. The α (i.e., hydrogens attached directly to the radical centers) hfc constant, a_{α_H}, for the parent TMM (**39**) has been determined to be ca. 9 G.[36] There is no reason to expect a significantly different value in alkylidenecyclopentanediyls, and so one would anticipate that the two α protons of **2** and **9** would contribute a 9-G coupling.



39

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From the number of lines observed (and the spacing) it is apparent that the hyperfine patterns are dominated by the β hydrogens, and one can consider several ways to estimate a_{β_H}. In radicals, a_{β_H} depends on the spin density (ρ) at the adjacent radical center and on θ, the angle between the p-orbital axis at C_α and the plane containing C_α, C_β, and H_β.[37] At the Huckel level, ρ in a TMM should be $^2/_3$, and so we can write[34]

$$a_{\beta_H} = \frac{1}{2}\,\frac{2}{3}\,(\cos^2\theta)C$$

If we assume $C = 42.5$ G and $\theta = 30°$,[37] we obtain $a_{\beta_H} = 10.6$ G.

In TMM-like structures, however, one must also take into account a spin polarization effect, which gives rise to a negative spin density at the central carbon atom.[38] For example, in the parent TMM (**39**), Huckel calculations alone predict a_{α_H} to be ca. 7 G, whereas the experimental value is 9 G.[36] If we scale the calculated value for a_{β_H} in our systems by the same factor ($^9/_7$), a value of 13.6 G is obtained, in remarkable agreement with the major splitting seen in our spectra. Alternatively, one can consider cyclopentenyl **40**, a radical with a similar geometry and similar spin polarization effects to those in **2**. For **40**, $a_{\alpha_H} = 14$ G and $a_{\beta_H} = 22$ G.[39] If we assume that the ratio of a_{β_H} to a_{α_H} should be the same in **40** and **2**, then for a_{β_H} in **2** we obtain $(^{22}/_{14})9 = 14.1$ G, again in good agreement with our major splitting. Of course, these calculations are quite approximate in nature, but they do show that it is reasonable to relate a_{β_H} in these systems to the major splitting seen in the spectra. Note that all the β hydrogens we will consider are part of relatively rigid rings and so θ, and thus a_{β_H}, should be the same for all of them.

One final consideration is the possible influence of various types of anisotropy, since these are rigid media spectra. We have already shown that the intrinsic anisotropy of the $\Delta m_s = 2$ line is not a significant factor for these spectra. This will generally be the case for molecules with small D values, but considerable anisotropy arises if $|D/hc| > 0.06$ cm^{-1}. In addition, the β hfc tensor for organic free radicals is generally quite isotropic,[37] and so the values of a_{β_H} we observe can be directly related to those obtained for free radicals in isotropic media. The α hfc tensor is generally anisotropic.[3] However, several studies have shown that the splitting observed in randomly oriented, nonreorienting samples of planar radical centers are, nevertheless, interpretable as approximately equal to the isotropic a_{α_H}.[40]

Spectral simulations we have performed support this analysis. As described elsewhere,[15] we have developed a series of programs for simulating triplet EPR spectra, including hyperfine coupling. The simulations explicitly consider the anisotropy of the $\Delta m_s = 2$ line but assume isotropic hfc. Figure 3D shows a simulation of the hfc for **17**. The simulation is not the result of a complicated fitting procedure. It is the spectrum obtained by assuming $a_{\beta_H} = 13.5$ G, the major splitting seen, and $a_{\alpha_H} = 9$, the value for TMM.[41] The agreement is excellent, and no further refinement of the parameters was considered to be necessary. Similarly, good fits of the spectra in Figure 4 could be obtained with the same hfc constants.[41]

To summarize, the hfc in **2** and **9** is dominated by a 13.5-G splitting, and several arguments indicate that this is a quite reasonable value for a_{β_H} in such systems. Simulations using this value and a 9-G a_{α_H}, taken from the parent TMM, provide excellent fits to the experimental spectra. We thus conclude that the splittings seen in the $\Delta m_s = 2$ transitions in these structures result from interpretable hfc that can be directly related to specific structural features of the molecules.

Conclusions

Photolysis of 2,3-diazabicyclo[2.2.1]hept-2-enes with spirocyclopropyl groups at the 7-position in glassy matrices at 4–35 K produces triplet 2-alkylidene-1,3-cyclopentanediyls. This is a significant departure from the chemistry seen under conventional conditions and emphasizes the potential for the expression of new reactive pathways in rigid media at cryogenic temperatures. The proposed mechanism involves several novel features, including chemical activation in condensed media, and an especially efficient tunneling reaction. In addition, the hfc constants for alkylidenecyclopentanediyls have been measured and shown to be in complete accord with expectations based on conventional models.

Experimental Section

General Procedures. Varian EM-390 and JEOL-GX400 spectrometers were used for CW and FT NMR spectroscopy (^{1}H and ^{13}C). A Hewlett-Packard 8451A diode array spectrophotometer was used to obtain UV spectra. Synthetic photolyses were performed with a Hanovia 450-W medium-pressure mercury arc lamp. Elemental analyses and mass spectra were obtained by the Caltech Analytical Facility.

Preparation of EPR Samples. Samples were prepared by adding 2–3 mg of the diazene to 0.3 mL of solvent (2-methyltetrahydrofuran was freshly distilled over benzophenone–ketyl). The solutions were placed in quartz EPR tubes equipped with high-vacuum stopcocks. The tubes were then degassed by five freeze–pump–thaw cycles and frozen in liquid nitrogen before being inserted into the precooled EPR cavity.

EPR Experiments. A Varian E-line Century Series X-band spectrometer fit with an Oxford Instruments ESR-900 continuous-flow liquid helium cryostat was used to obtain EPR spectra at low temperatures. The temperature at the sample was measured before and after each experiment with a calibrated carbon–glass thermistor (Lakeshore Cryotronics) placed inside a sample tube and is accurate to within ±0.3 K. During each experiment the temperature was monitored continuously by a gold–chromel thermocouple fixed 1 cm below the sample in the quartz Dewar. Temperature was varied by using either the helium flow rate or the automatic digital temperature controller.

An Oriel 1000-W mercury–xenon or xenon arc lamp was focused into the microwave cavity for photolysis. Various optical filters or an Oriel monochromator were used to obtain narrow bands of light of the desired wavelength range.

Dependence of Signal Intensity on Light Intensity. These studies were performed by measuring the growth of the EPR signal for biradical **2** at 4 K upon photolysis of diazene **1** in an MTHF matrix for 1 min. The intensity of the incident light was varied by using optical filters. A mercury interference filter and a KG-4 or a KG-5 filter (Schott) were used to obtain three different intensities: interference filter, transmittance 1.00; interference filter + KG-4, transmittance 0.70; interference filter + KG-5, transmittance 0.21. The transmittance was measured both by a UV-vis spectrophotometer and a thermopile detector.

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(41) The simulations for **9** and many other triplet biradicals[15] assume a line width of 6 G. For **17**, a line width of 10 G was used to account for small residual couplings from the deuteriums.

2,3-Dicarbethoxy-7-cyclobutylidene-2,3-diazabicyclo[2.2.1]heptane (41). To a sample of 6,6-trimethylenefulvene[9,42] (0.71 g, 6.1 mmol, 1.0 equiv) in 35 mL of dry ether was added diethyl azodicarboxylate (1.15 g, 6.6 mmol, 1.1 equiv). The mixture was stirred under nitrogen for 1 h. Filtration through basic alumina and removal of solvent gave 1.7 g of a pale yellow oil, which was characterized by NMR spectroscopy: ^{1}H NMR ($CDCl_3$) δ 1.04 (t, 6 H), 1.93 (quintet, 2 H), 2.62 (br t, 4 H), 4.20 (quartet, 4 H), 5.18 (br s, 2 H), 6.65 (br s, 2 H). Since attempts at purification resulted in decomposition, the oil was immediately subjected to catalytic hydrogenation[43] (ethyl acetate, 10% palladium on charcoal). Filtration through Celite, removal of solvent and flash chromatography[44] (3:1 ether/petroleum ether; R_f 0.35) afforded **41** (1.11 g) in the form of a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 6 H), 1.64–1.81 (br m, 4 H), 1.94 (quintet, 2 H), 2.62 (br t, 4 H), 4.20 (quartet, 4 H), 4.56 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.8, 17.3, 27.5, 29.6, 58.6, 62.1, 127.7, 128.3, 156.9.

7-Cyclobutylidene-2,3-diazabicyclo[2.2.1]hept-2-ene (11). A solution of potassium hydroxide (3.02 g, 87%, 46.9 mmol, 12.5 equiv) in 3 mL of 2-propanol (previously purged with nitrogen for 15 min) was brought to reflux. Degassed 2-propanol (3 mL) containing carbamate **41** (1.11 g, 3.7 mmol, 1.0 equiv) was added dropwise. Reflux was maintained for 2 h. The reaction mixture was cooled to room temperature, and sodium bicarbonate (2.0 g) was added. After the resultant mixture was stirred for 0.5 h, the suspension was filtered. Yellow mercuric oxide (4.0 g) was added to the filtrate, and the heterogeneous mixtures was stirred at 0° C for 2 h.[45] Filtration through Celite, extraction of the brown solution with pentane, removal of solvent, and flash chromatography (1:1 ethyl acetate/petroleum ether; R_f 0.45) gave 274 mg of a white solid: ^{1}H NMR ($CDCl_3$) δ 1.04 (m, 2 H), 1.58 (m, 2 H), 1.92 (quintet, 2 H), 2.58 (t, 4 H), 5.15 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.4, 21.6, 29.5, 73.6, 127.6, 133.6; UV (pentane) λ_{max} 336 nm (ϵ 73), 341 (ϵ 80).

2,3-Dicarbethoxy-7-ethylidene-2,3-diazabicyclo[2.2.1]heptane (42). 6-Methylfulvene[9,42] (0.95 g, 10.3 mmol, 1.0 equiv) in 40 mL of dry ether was stirred at room temperature with diethyl azodicarboxylate (2.0 g, 11.4 mmol, 1.1 equiv) for 1 h. Filtration through basic alumina and removal of solvent yielded 2.5 g of a pale yellow oil, which was characterized by NMR spectroscopy: ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 6 H), 1.59 (d, 3 H), 4.21 (q, 4 H), 4.61–4.97 (m, 3 H), 6.7–6.9 (br s, 2 H). Without further purification this oil was taken up in 25 mL of ethanol and about 2 mL of hydrazine hydrate was added.[46] Air was bubbled through this solution for 14 h. Solvent was then removed, and the residue was taken up in 50 mL of ether. This solution was repeatedly washed with water until the aqueous layer was neutral by pH paper. The ether layer was dried over magnesium sulfate and filtered through Celite, and solvent was removed. Flash chromatography (3:1 ether/pentane; R_f 0.35) gave 1.04 g of a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.10 (t, 6 H), 1.62 (d, 3 H), 1.75–1.91 (m, 4 H), 4.21 (q, 4 H), 5.12 (br s, 2 H), 6.55 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.9, 14.6, 28.0, 58.8, 61.9, 128.1, 138.7, 157.3. Anal. C, H, N.

7-Ethylidene-2,3-diazabicyclo[2.2.1]hept-2-ene (10). A solution of potassium hydroxide (0.26 g, 87%, 4.0 mmol, 12.0 equiv) in 1 mL of 2-propanol (previously purged with nitrogen for 15 min) was brought to reflux. Degassed 2-propanol (1 mL) containing carbamate **42** (0.09 g, 0.3 mmol, 1.0 equiv) was added and the mixture heated at reflux for 2 h. Solvent was then removed, and the yellow paste obtained was taken up in 5 mL of a saturated sodium bicarbonate solution. This solution was extracted with methylene chloride (5 × 10 mL). The organic layer was dried over magnesium sulfate and filtered. Yellow mercuric oxide (1.0 g) was then added and the mixture stirred at 0 °C for 3 h. Filtration through Celite, removal of solvent, and recrystallization from pentane yielded 12 mg of white crystals. ^{1}H NMR was identical with that reported by Little.[8]

2,3-Dicarbethoxy-2,3-diazabicyclo[2.2.1]hept-5-ene-7-spiro-2′,2′,3′,3′-tetramethylcyclopropane (43). A sample of 1,1,2,2-tetramethylspiro[2.4]hepta-4,6-diene[47] (0.49 g, 3.3 mmol, 1.0 equiv) was dissolved in 20 mL of methylene chloride, and diethyl azodicarboxylate (0.63 g, 3.6 mmol, 1.1 equiv) was added dropwise under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature for 2.5 h. Filtration through basic alumina, removal of solvent, and flash chromatography (2:1 ether/pentane; R_f 0.3) yielded 0.82 g (78%) of pure product in the form of a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 6 H), 1.00 (s, 6 H), 1.09 (t, 6 H), 4.06 (quartet, 4 H), 4.69 (br s, 2 H), 6.62 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.8, 23.3, 23.8, 59.8, 62.1, 66.5, 135.4, 158.4.

2,3-Dicarbethoxy-2,3-diazabicyclo[2.2.1]heptane-7-spiro-2′,2′,3′,3′-tetramethylcyclopropane (44). To a sample of **43** (0.12 g, 0.4 mmol) in 20 mL of ethanol was added about 2 mL of hydrazine hydrate. Air was bubbled through the solution at room temperature for 15 h. The solvent was then removed and the residue taken up in 35 mL of ether. This solution was washed repeatedly with water until the aqueous layer was neutral by pH paper. The organic layer was dried over magnesium sulfate, filtered through basic alumina, and flash chromatographed (2:1 ether/pentane; R_f 0.33) to yield 89 mg of a white crystalline solid: ^{1}H NMR ($CDCl_3$) δ 1.01 (br s, 12 H), 1.24 (t, 6 H), 1.65–1.83 (m, 4 H), 4.10–4.22 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.5, 18.6, 19.1, 22.2, 22.9, 28.3, 48.5, 61.5, 61.9, 157.3. Anal. C, H, N.

2,3-Diazabicyclo[2.2.1]hept-2-ene-7-spiro-2′,2′,3′,3′-tetramethylcyclopropane (24). A solution of potassium hydroxide (0.26 g, 87%, 4.0 mmol, 7.6 equiv) in 1 mL of 2-propanol (previously purged with nitrogen for 15 min) was brought to reflux under nitrogen. A solution of carbamate **44** (0.17 g, 0.5 mmol, 1.0 equiv) in 1 mL of degassed 2-propanol was added and the mixture heated at reflux for 3 h. After cooling to room temperature, solvent was removed yielding a yellow paste, which was then taken up in 3 mL of a saturated sodium bicarbonate solution. The aqueous solution was extracted with methylene chloride (5 × 20 mL). The solvent was then removed, and cupric bromide (0.30 g, 1.3 mmol, 2.5 equiv) in 0.5 mL of water was added. The red precipitate formed was filtered and taken up in 15 mL of methylene chloride. The diazene was liberated by the addition of 5 mL of 1 N ammonium hydroxide. The organic layer was separated and dried over sodium sulfate. Filtration and removal of solvent yielded 0.12 g of a yellow solid. Recrystallization from ethyl acetate gave **24** as a white crystalline solid: mp 101–102 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 6 H), 0.95 (s, 6 H), 1.01 (m, 2 H), 1.53 (m, 2 H), 4.76 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.57, 19.05, 21.07, 21.38, 21.54, 51.00, 76.68; UV (ethanol) λ_{max} 334 nm (ϵ 74), 342 (ϵ (74); mass spectrum, *m/e* 150 (M − 28), 135, 121, 107, 28 (100).

2,3-Diazabicyclo[2.2.1]hept-2-ene-7-spiro-2′,2′,3′,3′-tetradeuteriocyclopropane (16). **16** was prepared by following the procedure of Roth and Enderer.[2] 1,2-Dibromotetradeuterioethane was used to incorporate the deuterium into spiro[2.4]hepta-1,3-diene.[48] Addition of diethyl azodicarboxylate and hydrolysis-oxidation then afforded the desired product.

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