was rotated around the S_4 axis by an angle $\theta = 10°$. The other distortion mode involved a pyramidalization at each carbon in such a way as to produce structure **8**. Such pyramidalization does distort the molecule toward **5**, but the carbon atoms are not moved any closer to one another. The pyramidalization was accomplished by moving one hydrogen at each carbon of **4a** out of plane, such that its C-H bond made at 30° angle with the original C-C-H plane. Both **7** and **8** have D_2 symmetry, which serves to remove all the degeneracies present in **4a**.

The results of the calculations on **7** and **8**, which were performed at the CI-VDZ level, are summarized in Figure 4. Both distortions are destabilizing for **4a**, and both lead to only minor perturbations of the relative energies of the six covalent states. It would thus appear that **1** cannot significantly stabilize itself by a second-order Jahn-Teller distortion.

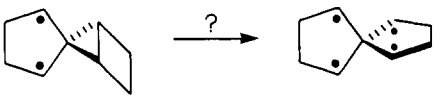
The alternative closed-shell form of **1**, 5,5′-spirobi[bicyclo-[2.1.0]pentane] (**9**, C_2 symmetry), arises by a double, disrotatory ring closure of **1**. This structure should have ca. 125 kcal/mol of strain energy, but we have recently prepared it and found it to be a stable, isolable molecule.[2] Pursuing the analogy between **1** and cyclobutadiene further, **9** corresponds to tetrahedrane. While the cyclobutadiene-tetrahedrane interconversion is forbidden by orbital symmetry, this is formally not the case for the interconversion of **1** and **9** because of the low symmetry of **9**. However, inspection of the orbitals of Figure 1 reveals that it is the e pair which on disrotation correlates with the σ-bonding orbitals of **9**. Both the b_1 and a_2 orbitals lead to σ^* interactions. Thus, the **1**-**9** interconversion is forbidden in the sense of the "natural orbital correlations",[25] and one might anticipate a barrier to the double ring closure of **1** to **9**.

Conclusions

Our calculations indicate that **1** possesses six low-lying states that correspond to the covalent states of a tetraradical. Thus, the spiroconjugative interaction predicted on the basis of qualitative MO arguments (Figure 1) is not strong enough to convert **1** into a biradical. However, the relative energies of the six tetraradical states are influenced strongly by spiroconjugation.

We believe the present results are relevant to our ongoing experimental effort to characterize **1**.[2] One of our goals is to observe **1** spectroscopically, under cryogenic, matrix-isolation conditions. The prediction of a singlet ground state rules out ESR detection of **1** (unless the $^3A_2$ state can be thermally populated), leaving IR and UV spectroscopy as the best candidates. The prediction of a significant, although relatively small, stabilization in **1** due to spiroconjugation suggests that **1** lies in a potential energy minimum. Distorting the molecule toward closed shell isomer **5** destabilizes the molecule (Figure 4), while ring closure to **9** goes against the "natural orbital correlations". Thus, one might expect potential energy barriers to closure of **1** to **5** or **9**, and **1** could well represent an absolute potential energy minimum. Given that biradical **2** is directly observable at temperatures below 40 K,[26] it seems quite possible that tetraradical **1** will also be observable.

Another goal of our experimental work has been to determine whether a structure such as **1** could be considered as a viable reactive intermediate in solution chemistry at ambient temperatures. One of the several approaches we are studying involves the ring opening of biradical **10** to give tetraradical **1**. Such a



10 1

reaction would relieve over 50 kcal/mol of strain energy[22] and would turn on all of the spiroconjugative stabilization of **1**. As discussed above, there is some uncertainty as to the magnitude of the calculated stabilization energy of **1**, due to uncertainties in the choice of reference state and best geometry for **1**. As such, we do not feel that the present results allow for a clear-cut prediction concerning the viability of such a reaction. Until more complete calculations on **1**, **10**, and related structures become feasible, such questions will have to be addressed experimentally.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-8024664) for support of this work. Technical assistance and helpful discussion from John J. Low, Arthur F. Voter, and Marvin M. Goodgame are gratefully acknowledged, as are the helpful comments of a referee.

Registry No. 1, 82482-44-8; **4**, 89556-20-7.

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Concerning the Viability of 1,4,6,9-Spiro[4.4]nonatetrayl as a Reactive Intermediate. New Biradical-to-Biradical Rearrangements

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Abstract: Direct photolysis of 7,7′-spirobi[2,3-diazabicyclo[2.2.1]hept-2-ene] (**6**) leads to loss of 1 equiv of N_2 and ring closure of the resulting biradical to 2,3-diazabicyclo[2.2.1]hept-2-ene-7,5′-spirobicyclo[2.1.0]pentane (**8**). Generation of the triplet biradical by sensitized photolysis results in a competition between ring closure to **8** and a 1,2-alkyl shift to 8,9-diazatricyclo[5.2.2.$0^{2,6}$]undeca-2,8-diene (**14**). While direct photolysis and thermolysis of **8** yield primarily ring closure product, sensitized photolysis leads to a series of biradical-to-biradical rearrangements that ultimately produce 2,3-divinylcyclopentene (**15**). Deuterium labeling studies indicate competing mechanistic pathways for this reaction. Rationalization of the label distribution requires one of two unprecedented processes: front-side radical attack on a C-C bond or intermediacy of 1,4,6,9-spiro[4.4]nonatetrayl (**1**), an organic tetraradical whose four radical centers are predicted to be stabilized via spiroconjugation.

There has been considerable recent interest in biradicals and related structures,[2] in part because of the important role such structures are thought to play in a variety of thermal and photochemical reactions.[3] Since biradicals are generally highly

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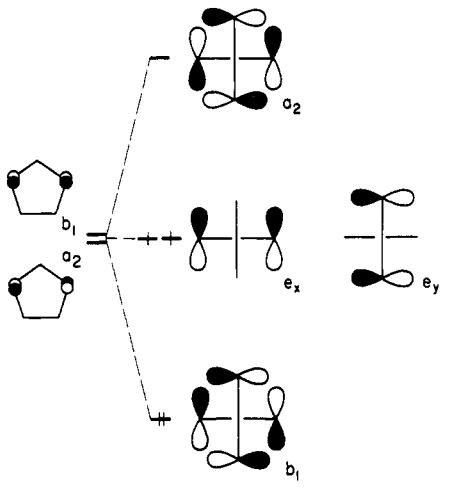

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Figure 1. Orbital mixing diagram for **1**. Orbitals of **1** are pictured as Newman projections down the S_4 axis.

reactive species, direct observation and characterization pose a formidable challenge to the experimentalist. One strategy for designing experimentally observable biradicals has been to destabilize any closed shell isomers by introducing high strain energies and to stabilize the biradical by delocalization of the nonbonding electrons. The most successful example of this approach has been Berson's elegant studies of trimethylenemethane derivatives.[4]

We have been investigating the extension of this strategy to the organic tetraradical 1,4,6,9-spiro[4.4]nonatetrayl (**1**). A

1

detailed theoretical analysis of **1** has been presented elsewhere,[5] so we will present only a brief summary of those results here. As shown in Figure 1, the four radical centers of **1** interact extensively through spiroconjugation.[6] This leads to a significant energy gap between the b_1 and a_2 orbitals and a stabilization in **1** relative to a "typical" tetraradical. The two closed-shell isomers of **1**, i.e., **3**[7] and **4**, are both very highly strained, while **1** is essentially strain

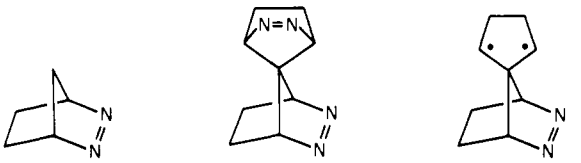
3 4

free. Also, ab initio calculations[5] suggest possible kinetic barriers to the ring closures of **1** to **3** or **4**.

Since the half-molecule of **1**, 1,3-cyclopentanediyl (**2**, Figure 1), has no spiroconjugative interaction but is observable by ESR in a matrix at temperatures below 40 K,[8] we felt that **1** also could be amenable to direct spectroscopic observation under cryogenic, matrix-isolation conditions. We have also considered the possibility that evidence for the intermediacy of **1** under conventional conditions (ambient temperatures, solution phase) could be obtained. The present work addresses this second issue and describes our initial efforts to evaluate the viability of **1** as a reactive intermediate.[9] Our results thus far have uncovered new and interesting biradical-to-biradical rearrangements and suggest, but do not require, the intervention of tetraradical **1**.

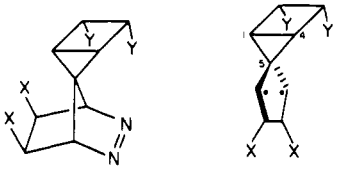
Potential Precursors to Spirononatetrayl (1)

The thermal and photochemical deazetations of cyclic and polycyclic 1,2-diazenes (azoalkanes) have often been used to generate biradicals.[2,10,11] Given the successful use of diazene **5**[12,13]



5 6 7

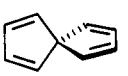
to generate biradical **2**,[8] the most obvious precursor to tetraradical **1** was the bisdiazene 7,7′-spirobi[2,3-diazabicyclo[2.2.1]hept-2-ene] (**6**). The primary issue with bisdiazene **6** is whether one can induce a loss of two N_2 molecules, either simultaneously by using a very intense light source or by first producing biradical **7** and having it lose a second N_2 prior to ring closure. Monodiazene **8** is also a potential precursor to **1**. Loss of N_2 could produce



8 a X = Y = H 9
b X = D ; Y = H
c X = H ; Y = D

biradical **9**. Cleavage of the C1–C4 bond in **9** would release ca. 50 kcal/mol of strain energy and allow the full spiroconjugative stabilization of **1** to develop. Thus, if this stabilization is large enough, the novel biradical-to-tetraradical rearrangement **9** → **1** seems possible.

Synthesis. A quite feasible route to bisdiazene **6** would begin with the known[14] 1,3,6,8-spiro[4.4]nonatetraene (**10**). The



10

standard synthetic sequence[12] by which, for example, cyclopentadiene is converted to **5** should be applicable to **10**. In fact, at the time we started this work, the crucial first step of this sequence, the double Diels–Alder addition of dimethyl azodi-

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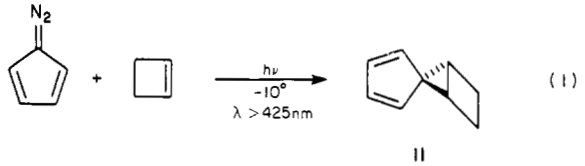
carboxylate to **10**, had been accomplished. However, the synthesis of **10** is lengthy and proceeds in relatively low overall yield,[14] and the tetraene is a relatively reactive molecule.[14,15]

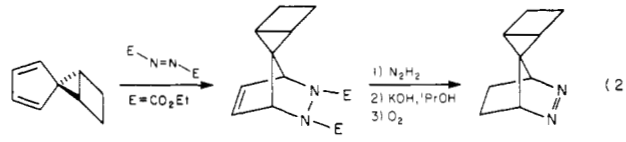
We therefore developed an alternative synthetic approach to **6** and **8**. As shown in eq 1, photolysis of diazocyclopentadiene



(1)

11

in cyclobutene produces spiro[bicyclo[2.1.0]pentane-5,1′-cyclopenta-2′,4′-diene] (**11**). Although the yield of this reaction is low, it does produce in one step a molecule that, for the present purposes, is a complete functional equivalent of tetraene **10**. Conversion of diene **11** to monodiazene **8** (eq 2) follows the usual

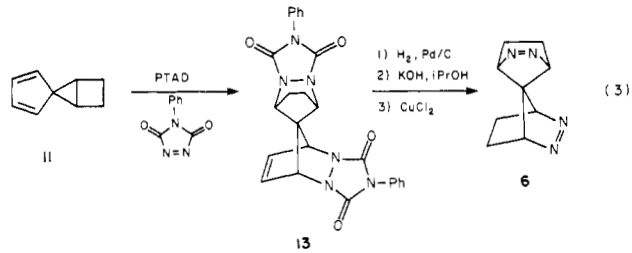


(2)

11 **12** **8**

sequence,[12] with two minor modifications. Because of the presence of a reactive bicyclo[2.1.0]pentane moiety in Diels–Alder adduct **12**, diimide reduction was used in place of catalytic hydrogenation, and air oxidation of the hydrazine precursor was used to produce **8**.

Bisdiazene **6** can also be prepared readily from **11** (eq 3), the



(3)

11 **6**

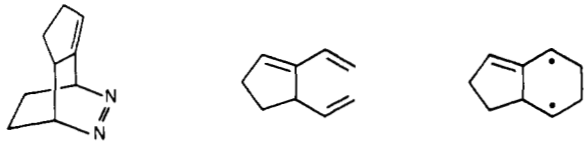
13

key step being the reaction of **11** with *N*-phenyltriazolinedione (PTAD). PTAD is a highly reactive dienophile, and it can also add across strained C–C single bonds.[16,17] In the present case, bisadduct **13** is produced in one step in acceptable yield. Conversion of **13** to **6** follows the standard sequence.[18]

Results and Discussion

Direct Photolysis of 6. Photolysis of bisdiazene **6** using a 450-W Hanovia lamp results in N_2 loss and closure to **8** as the sole primary photoproduct. Diazene **8** then undergoes secondary photolysis, as described below.

Sensitized Photolysis of 6. Photolysis of **6** in the presence of benzophenone as a triplet sensitizer results in three major products: biradical closure product **8**, the rearranged diazene 8,9-diazatricyclo[5.2.2.0^{2,6}]undeca-2,8-diene (**14**),[19] and the hydrocarbon



14 **15** **16**

product 2,3-divinylcyclopentene (**15**). The changing relative ratios

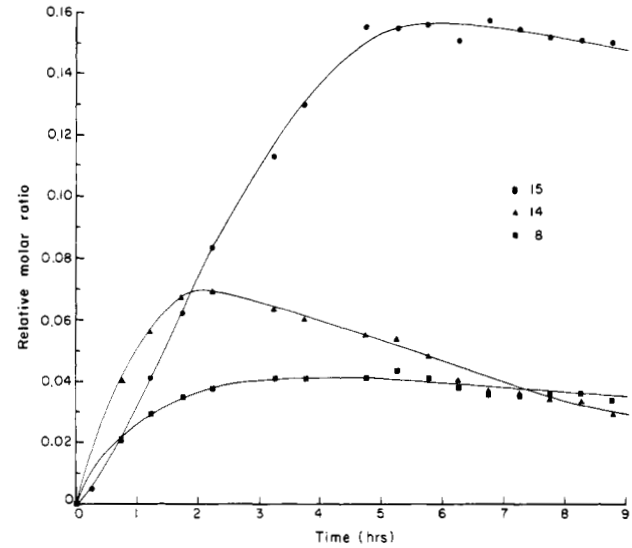


Figure 2. Relative molar ratios of products from the sensitized photolysis of **6**.

Table I. Quantum Yields[a] for Sensitized Photolysis of Azo Compounds

compd	$^3\phi_{N_2}$[b]	$^3\phi_{dis}$[c]
6	0.97	0.95
8	0.50	
14		0.65

[a] Values are ±10%. [b] For N_2 evolution. [c] For compound disappearance.

of these products with time are shown in Figure 2.

Diazene **14** arises from a 1,2-alkyl shift in biradical **7** analogous to the trimethylene-to-propene H-shift observed in many other 1,3-biradicals.[20] However, olefin formation is usually observed in singlet 1,3-biradicals (thermolysis or direct photolysis of diazenes) rather than triplets (sensitized photolysis). Ab initio calculations on the singlet and triplet surfaces of trimethylene have led Doubleday and McIver to propose that intersystem crossing from the triplet to the singlet is most favorable at geometries from which closure to cyclopropane proceeds without a barrier.[20] Thus, triplet biradicals would yield almost entirely cyclopropanes. However, due to the ring constraints, biradical **7** cannot achieve the preferred intersystem crossing geometries and will necessarily come onto the singlet surface in the vicinity of (0,0)-trimethylene. The transition state for the 1,2-H shift to propylene has not been located computationally,[20] but it seems likely that it is near the (0,0) geometry. If so, olefin formation would be more favorable for **7** than for acyclic systems. It is interesting to note that sensitized photolysis of bicyclic diazene **5** does produce ca. 10% of the H-shift product, cyclopentene.[13]

The origin of triene **15** is less straightforward. One would expect that sensitized photolysis of **14** would produce triplet 1,4-biradical **16**, which could then cleave to two olefins, producing **15**. Indeed, we have found that **15** is the sole product of sensitized photolysis of **14**. As described below, triene **15** is also the major product of sensitized photolysis of monodiazene **8**. Thus, it was possible that **15** arose entirely through sensitized photolysis of the primary photoproducts **8** and **14**. However, formation of spirononatetrayl (**1**) from **6** would also be expected to result in the formation of **15** through the rearrangement pathways described below. Formation of **1** from **6** requires loss of 2 equiv of N_2 from a single sensitization event, as the lifetime of triplet **7** would undoubtedly be too short for a second sensitization to occur. As a test for this possibility, we determined two sensitization quantum yields for **6**: one for N_2 evolution (equivalents of N_2 released per sensitization) and one for compound disappearance (equivalents of **6**

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(18) We have also developed another synthetic route to **6** which is longer but more amenable to large scale. Anderson, J. A., M.S. Thesis, California Institute of Technology, 1983.
(19) ^{1}H (90 MHz) and ^{13}C (50 MHz) NMR and capillary GC of diazene **14** indicate the presence of only one diastereomer, suggesting stereoselectivity in the 1,2-alkyl shift.
(20) Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533–6542.

Scheme I

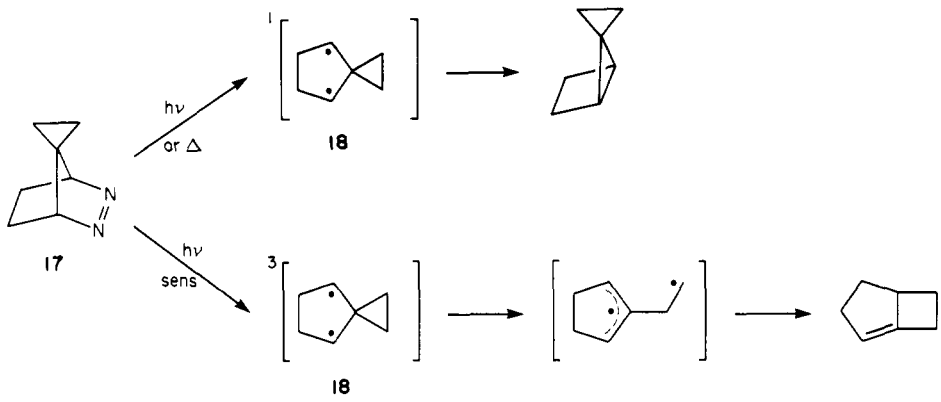


Table II. Product Yields from 8 and 14

precursor	cond	3	15	other
8	140 °C, 4 h	70.6[a]	29.4[a]	
8	*hν* direct	86.7	9.6	3.6
8	*hν*, Ph_2CO sensitized	2.3	84.6[b]	13.0[b]
14	*hν*, Ph_2CO sensitized		100.0	

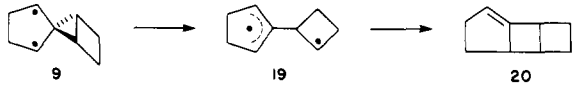
[a] Control experiments indicate that 3 → 15 under these conditions. Values are for 90% conversion of 8. [b] These products decompose slowly under the reaction conditions. Values are for 90% conversion of 8.

destroyed per sensitization). Formation of **1** would be evidenced by a greater quantum yield for nitrogen evolution than for diazene disappearance. As can be seen in Table I, both quantum yields are equal within experimental error. Therefore, each sensitization causes loss of a single N_2 to give biradical **7**, which undergoes either ring closure to **8** or a 1,2-alkyl shift to **14**. Initial product ratios indicate that the kinetic ratio of these two processes is greater than 2:1, favoring the alkyl shift. Triene **15** must be entirely the product of secondary photolysis, as was also suggested by the sigmoidal nature of its appearance curve (Figure 2). An interesting sidelight of this study is the surprisingly high quantum yield for sensitized photolysis of **14** (Table I) compared to the parent system 2,3-diazabicyclo[2.2.2]octene.[21]

Thermolysis and Direct Photolysis of 8. Both thermolysis and direct photolysis of monodiazene **8** lead to a mixture of biradical closure product **3** and 2,3-divinylcyclopentene (**15**) (Table II). Control experiments reveal that hydrocarbon **3** does rearrange to triene **15** under the thermolysis conditions, and thus **15** could be entirely a secondary product in this reaction. Direct photolysis also produces another C_9H_{12} isomer that we have not been able to identify and that appears to be thermally labile.

Sensitized Photolysis of 8. Benzophenone-sensitized photolysis of **8** yields triene **15** as the major product (Table II). The overall results for **8** thus parallel Roth's studies on 2,3-diazabicyclo-[2.2.1]hept-2-ene-7-spirocyclopropane (**17**) (Scheme I).[22] Roth found that ring closure was the dominant mode of reaction for singlet diyl **18** but that the triplet underwent C–C cleavage to give, ultimately, an olefin product. Such a cleavage of a cyclopropane-1,1-dicarbinyl biradical to an "allyl-plus-p" biradical is well-precedented as the second step of the much-studied thermal rearrangement of spiropentanes to methylenecyclobutanes.[3a]

By analogy, one would expect triplet biradical **9** to cleave at the C1–C5 bond to give biradical **19** and, ultimately, olefin **20** (eq 4). Bicyclo[2.2.0]hexane derivative **20** is highly strained and



(4)

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(22) Roth, W. R.; Enderer, K. *Justus Liebigs Ann. Chem.* **1970**, *733*, 44–58.

Table III. Distribution of ^2H in 15

precursor	15-A:15-V	15-T:15-C[a]
8b	4.0:1.0	1.0:1.0
8c[b]	1.0:3.3	2.3:1.0

[a] Deuterium cis or trans with respect to the proton on C3. [b] 4.0:1.0 endo:exo.

should be thermally labile.[23] The expected rearrangement of **20** would involve ring opening to biradical **16** and subsequent cleavage of the cyclohexanediyl to product **15**. Thus, the deep-seated rearrangement of biradical **9** to triene **15** can be rationalized by invoking well-precedented, biradical rearrangement chemistry.

As described above, another rearrangement of biradical **9** seemed feasible, namely C1–C4 cleavage to give spirononatetrayl. One can also envision a rational conversion of tetraradical **1** to triene **15**. One surprising feature of the chemistry of spirononatetraene (**10**) is the ease with which a 1,5-sigmatropic shift of a vinyl group occurs to give, after a hydrogen shift, indene.[15] This result was rationalized by invoking stabilizing, secondary orbital interactions among the formerly spiroconjugating centers. The analogous process in **1** is a 1,2-alkyl shift reaction (eq 5) like that

(5)

described above for biradical **7**. In **1** the migrating center is itself a radical, but the transition state could be stabilized by the same type of secondary orbital interactions as in the rearrangement of **10**. The product of such a rearrangement (eq 5) is biradical **16**, which we have already invoked as a logical precursor to triene **15**. In fact, we already know that triplet **16** produces **15**, since **15** is the sole product from sensitized photolysis of diazene **14**.

In order to differentiate these two possible pathways to **15**, we prepared diazene **8b** with completely stereospecific exo deuterium labeling. Synthesis involved simply substituting N_2D_2 for N_2H_2 in eq 2. Should the rearrangement to **15** proceed by C1–C5 cleavage only (eq 4), the cyclopentanediyl ring of **9b** would maintain its integrity throughout the rearrangement and end up as the cyclopentene ring of **15**. Thus, the deuterium label of **8b** would appear entirely in the aliphatic CH_2's of **15**. However, if tetraradical **1** should intervene, all four CH_2 groups would become equivalent due to the D_{2d} symmetry of **1**. Thus, any **15** derived

(23) Starting from the conversion of bicyclo[2.2.0]hexane to 1,5-hexadiene (log A = 13.4, E_a = 36 kcal/mol)[24] and diminishing E_a by 11.5 kcal/mol (the difference between cyclobutane and methylenecyclobutane stereomutations)[25] and then by 6 kcal/mol (the approximate difference between the methylenecyclobutane rearrangements of the parent and of bicyclo[3.2.0]hept-1-ene)[22] for inclusion of the five-membered ring give an estimate of log A = 13.4, E_a = 18.5 kcal/mol, and $t_{1/2}$(298 K) = 1 s for **20** → **15**.

(24) Steel, C.; Zand, R.; Hurwitz, P.; Cohen, S. G. *J. Am. Chem. Soc.* **1964**, *86*, 679–684.

(25) Doering, W. von E.; Gilbert, J. C. *Tetrahedron Suppl.* **1966**, *7*, 397–414.

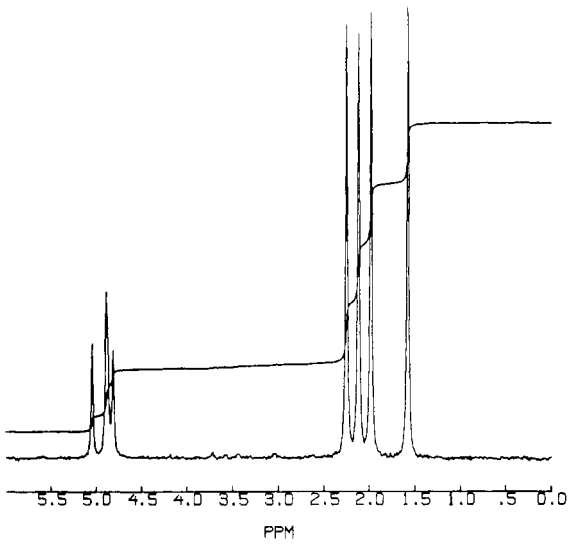


Figure 3. ^2H NMR of **11** derived from the sensitized photolysis of **8b**.

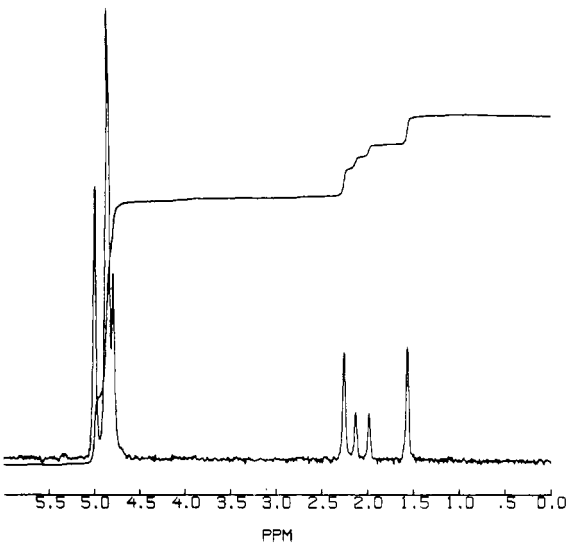


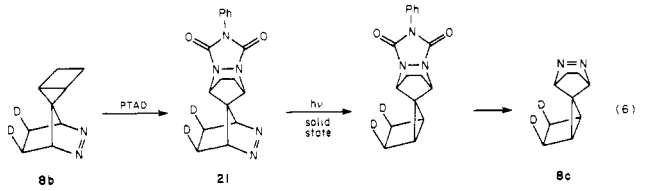
Figure 4. ^2H NMR of **11** derived from the sensitized photolysis of **8c**.

from the tetraradical would contain an equal mixture of aliphatic (A) and vinylic (V) deuterium label.

Figure 3 shows the ^2H NMR spectrum of **15** produced from the sensitized photolysis of **8b**. The spectrum clearly shows the presence of both aliphatic and vinylic label, but in a 4.0:1.0 ratio (Table III).

The excess of **15**-A (aliphatic ^2H) over **15**-V (vinylic ^2H) from **8b** indicates that the C1–C5 cleavage (eq 4) does occur in **9**. However, the observation of **15**-V *requires another mechanism* that makes the two five-membered rings of **9** equivalent. Such a process must also produce **15**-A, and so a significant portion of the **15**-A evidenced in Figure 3 arises from the new mechanism.

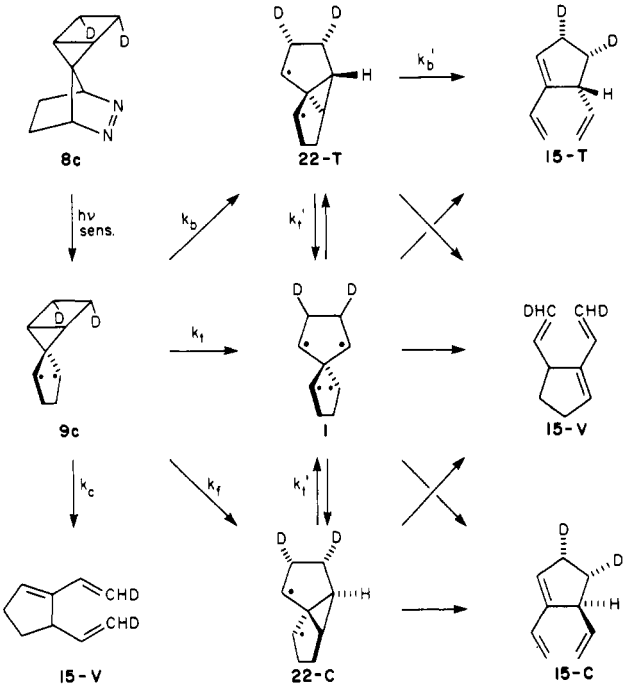
If tetraradical **1** is involved in the scrambling mechanism, not only do the two five-membered rings become symmetry equivalent but both faces of both rings are indistinguishable as well. Thus, there is a second stereochemical test for **1**. In diazene **8b**, the ^2H labeling has differentiated the two five-membered rings and the two faces of the labeled ring, since ^2H incorporation is 100% exo. However, the face differentiation is lost because the first-formed biradical **9b** has a mirror plane of symmetry (disregarding the ^2H label). Thus, the four aliphatic deuteriums in **15** from **8b** are in a 1:1:1:1 ratio (Figure 3). Such facial scrambling does not occur in biradical **9c**, which would be formed from diazene **8c**. As shown in eq 6, **8c** can be prepared from **8b** by an "azo transposition"



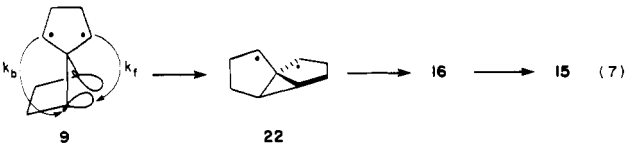
sequence. The key step is the *solid-state* photolysis of **21**, using the lattice constraining forces to produce stereospecificity.[26] By use of this sequence, **8c** is ultimately produced with the ^2H 80% endo and 20% exo (only the endo isomer is shown).

Figure 4 shows the ^2H NMR of **15** obtained from sensitized photolysis of **8c**. Again one sees a mixture of **15**-A and **15**-V. In this case, though, it is the vinylic ^2H that arise from the conventional mechanism (eq 4) and the excess of **15**-V over **15**-A (Table III, Figure 4) that signals its operation. The probe of the new mechanistic route to triene **15** is in the aliphatic region. The aliphatic ^2H can be either cis (**15**-C) or trans (**15**-T) to the proton on C-3 (see Scheme II). The preferential formation of **15**-T vs. 15-C (Table III) requires a *partial* scrambling of ring faces. This

Scheme II



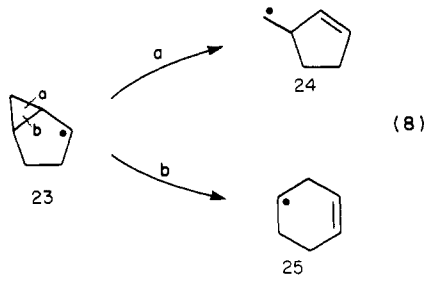
result requires a new reaction path that interconverts the five-membered rings of biradical **9** but does not lead to complete equivalence of the ring faces.[27] A possible intermediate that would produce such a labeling result is biradical **22** (eq 7), which has



only C_2 symmetry. It can arise from **9** by an intramolecular S_H reaction, with either stereochemical inversion (back-side attack, k_b) or retention (front-side attack, k_f) (eq 7). The conversion of **22** to **15** has good precedent in free radical rearrangement chemistry. The bicyclo[3.1.0]hex-2-yl radical (**23**) is known to rearrange readily by paths a and b (eq 8).[28] The two paths are

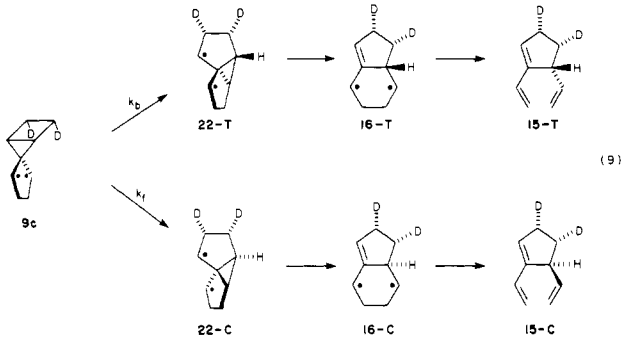
(26) Roth, W. R.; Enderer, K. *Justus Liebigs Ann. Chem.* **1969**, *730*, 82–90. Roth, W. R.; Martin, M. *Ibid.* **1967**, *702*, 1–7. Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 6766–6775.

(27) Control experiments reveal that **3** is stable to the sensitized photolysis conditions and that **8c** does not rearrange to **8b** or scramble stereochemistry during the reaction.



(8)

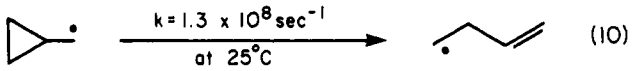
equivalent in **22** and give rise to the previously discussed biradical **16**. This is also another example of the cyclopropyldicarbinyl to allyl-plus-p rearrangement.[30] As shown in eq 9, the k_b and k_f



(9)

mechanisms have different stereochemical consequences with respect to formation of **15**-A.

A complete overview of our mechanistic model for the current system is presented in Scheme II.[32,33] The scrambling of the ^2H label between the two five-membered rings is incomplete starting from either **8b** or **8c**, as shown by the **15**-A:**15**-V ratios. We interpret this to mean that the C1–C5 cleavage mechanism (eq 4, k_c in Scheme II) must be operative. This is the biradical version of a cyclopropylcarbinyl-to-allylcarbinyl ring opening.[29b] In the parent free radical (eq 10), such a process is quite facile. One



(10)

might expect that in the biradical case the reaction would be further accelerated by the developing allylic stabilization of the other radical site. As discussed above, the k_c process is also well-known in biradical chemistry, being the second step of the spiropentane rearrangement.[3a] Nevertheless, our labeling results require other, somewhat unusual, processes to be competitive. Perhaps the k_c reaction in the present system is retarded by stereoelectronic factors, since the radical p orbitals in the preferred conformation are not directly aligned with the cleaving bond.[29b,34] Further work is under way to investigate this possibility.

Table IV. Relative Rates for Biradical-to-Biradical Rearrangements Leading To **15**

source of **15**-C from **8c**	k_c	rel rate k_b	rel rate k_f	rel rate k_t
k_f	1.0	0.72	0.15	
k_t	1.0	0.57		0.30
k_t'[a]	1.0	0.89		

[a] For this mechanism k_b'/k_t' must be 0.57/0.30.

The ring scrambling pathways can best be discussed in terms of the **15**-C to **15**-T ratio from **8c**. Within the framework of the current model (Scheme II), the preferential formation of **15**-T from **8c** *requires the operation of the back-side attack* (k_b) *mechanism* (see eq 9).[35] The stereochemical alignment for this back-side attack is far removed from the 180° angle which is strongly preferred in related reactions.[36] However, the unusual steric constraints of this system and the high strain of the C1–C4 bond in **9** must conspire to make this process competitive with k_c.

In order to rationalize the formation of **15**-C from **8c**, we must invoke either front-side attack in **9** (k_f) or tetraradical formation (k_t or k_t'). Front-side free radical attack on a C–C bond (stereochemical retention) is unprecedented, and a variety of studies has found a strong preference for back-side attack.[36] Again, however, the unusual stereoelectronic features of our system and the high strain of the C1–C4 bond could facilitate the k_f process.

Alternatively, the formation of **15**-C could signal the intervention of tetraradical **1**. One can envision two pathways to **1** (Scheme II), and once formed, the tetraradical must produce **15**-V, **15**-C, and **15**-T in a 2:1:1 ratio. The first route to **1** assumes that only the k_b process is competitive with k_c. Once formed, biradical **22**-T (Scheme II) undergoes both cleavage to biradical **16** (eq 9, k_b', in Scheme II), leading to **15**-T, and interconversion with **22**-C via tetraradical **1** (k_t', Scheme II). Due to its high symmetry, **1** cannot be a transition state for the interconversion of **22**-T and **22**-C and thus seems likely to be a reactive intermediate.[37]

The other route to **1** involves the previously discussed direct conversion of **9** to **1** (k_t, Scheme II), in competition with both k_b and k_c. Ring opening of the bicyclopentane moiety in **9** must be disrotatory, and the back lobes of the C1–C4 σ-bonding orbital would come into a much more favorable position for bonding with the cyclopentanediyl radical centers as the bond is cleaved. Thus, one would have a competition between complete scission of the C1–C4 bond (k_t) and intramolecular back-side trapping of the incipient cyclopentanediyl (k_b). Table IV shows the relative rates that would be necessary to reconcile each mechanistic scenario with the observed product ratios.

Once formed, **1** could lead to products through a **1** → **22** → **16** → **15** pathway or through the previously discussed **1** → **16** → **15** route, or by a return to **9** followed by k_b and k_c pathways. Our labeling studies only indicate that some symmetrization has occurred and thus do not allow distinctions among these pathways to be made.

(28) No products derived from the 5-bicyclo[2.1.0]pentylmethyl radical

26

26 were observed, suggesting that the conversion of **22** to **16** is irreversible.[29a]

(29) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P. D., Ed.; Academic Press: New York, 1980; Vol. 1, (a) p 180, (b) pp 227–235.

(30) Another possible path to **15** would begin with a direct conversion of **22** to *trans*-1,2,6-cyclononatriene, a reaction similar to the reverse of a carbene addition to an olefin. The triene would be expected to, and apparently does,[31] undergo a Cope rearrangement to **22**. This route would also be stereospecific and thus would in no way alter our stereochemical analysis. Given the strong precedent, we think the route mentioned in text is much more likely, but we thank Professor Orville Chapman (UCLA) for this elegant, alternative sequence.

(31) Connell, A. C.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1983**, 989–994.

(32) The fact that **15**-A/**15**-V from **8b** does not equal **15**-V/**15**-A from **8c** suggests a kinetic isotope effect. However, we cannot at present assign the effect to any particular microscopic event(s).

(33) We have no data concerning the spin states of the various species in Scheme II. However, it seems certain that **9** is initially formed as a triplet and it seems likely that any biradical in Scheme II that is long-lived enough to undergo rearrangement is also a triplet. We have also ignored the possibility that loss of N_2 from **6** and **8** occurs via diazenyl radicals as their intervention would not affect our stereochemical arguments. Note also that there are no experimental data that suggest the intervention of a diazenyl radical in the sensitized photolysis of a pyrazoline.

(34) Suzuki, M.; Murahashi, S.-I.; Sonoda, A.; Moritani, I. *Chem. Lett.* **1974**, 267–270.

(35) One could envision a scheme to produce **15**-A from **8c** involving only the k_c path, by first interconverting **9c** and **9b** via **22**. However, such a path must produce a 1:1 ratio of **15**-C to **15**-T, as the facial distinction is lost in **9b**.

(36) Porter, N. A.; Nixon, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7116–7117. Porter, N. A.; Cudd, M. A.; Miller, R. W.; McPhail, A. T. *Ibid.* **1980**, *102*, 414–416.

(37) McIver, J. W., Jr. *Acc. Chem. Res.* **1974**, *7*, 72–77.

Conclusions

The present work describes our initial efforts at determining the viability of an organic tetraradical as a reactive intermediate. The chemistry of bisdiazene **6** gives no indication that **1** is involved under conventional conditions. Sensitized photolysis of **6** does lead to the novel rearrangement product **14**. Still to be probed is the potential for two-photon photochemistry in **6**. Similarly, thermolysis and direct photolysis of diazene **8** are relatively straightforward.

In contrast, the stereochemical labeling studies of the sensitized photolysis of **8** unambiguously indicate the operation of new biradical-to-biradical rearrangement pathways. Biradical-to-biradical rearrangements are relatively uncommon and could provide a wealth of valuable information on these reactive species. Our work and the work of others[38] demonstrate the value of preparing *triplet* biradicals, for which ring closure is spin forbidden, in studies of biradical rearrangements. Our current mechanistic scheme (Scheme II) requires at least three biradical rearrangement pathways. The first is the precedented cleavage of biradical **9**, k_c (eq 4), a process consistent with the accepted mechanism of the spiropentane rearrangement.[3a] In addition, we propose the novel, back-side, intramolecular S_H reaction, k_b (eq 7), which is unique in its substantial deviation from the usual alignment for radical additions. The third process involves completely unprecedented chemistry, either in the form of a front-side radical attack on a C–C bond (k_f) or in the formation of tetraradical **1**. Thus, our suspicion that new and interesting chemistry would occur on the C_9H_{12} potential energy surface[3b] in the vicinity of tetraradical **1** was confirmed, although we have thus far found only permissive rather than compelling evidence for the direct involvement of **1**. Work is in progress to further characterize the novel biradical rearrangements uncovered in the present work and to investigate the viability of **6** and **8** as precursors to **1** under cryogenic, matrix-isolation conditions.

Experimental Section

General. Photolyses were performed with a Hanovia 450-W medium-pressure mercury arc lamp. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer. Fourier transform NMR spectra (^{1}H and ^{13}C) were recorded on a JEOL FX-90Q or a Varian XL-200 spectrometer. ^{2}H NMR (77.8 MHz) and 500-MHz ^{1}H NMR spectra were recorded on a Bruker WM500 spectrometer. Ultraviolet spectra were recorded on a Beckman Model 25 spectrophotometer. Mass spectra were obtained by the Caltech Analytical Facility. Elemental analysis was performed by Spang Microanalytical Laboratory, Eagle Harbor, MI, or by the Caltech Analytical Facility. Analytical gas chromatography was performed on a Hewlett-Packard 5840A or 5880A chromatograph equipped with a flame ionization detector. Preparative gas chromatography was performed on a Varian Aerograph Model 920 chromatograph with a thermal conductivity detector. Columns for gas chromatography were as follows: column A, 5 ft × $^1/_4$ in. 15% OV-101 on Chrom G mesh size 100/120; column B, 10 ft × $^1/_4$ in. 10% UCW-982 on Chrom WAW-DMCS mesh size 80/100; column C, 8 ft × $^1/_4$ in. 15% SE-30 on Chrom WAW-DMCS mesh size 80/100; column D, 20 in. × $^1/_8$ in. 10% UCW-982 on Chrom WAW-DMCS mesh size 80/100; column E, 30 m × 0.032 mm DB-1 25-μm film on fused silica; column F, 30 m × 0.032 mm DB-5 25 μm film on fused silica.

Cyclobutene. Cyclobutene was made by the method of Cope.[39]

Tosyl Azide. Sodium azide (71.5 g, 1.10 mol) was dissolved in 300 mL of 95% ethanol. To this solution was added 190.5 g (1.00 mol) of *p*-toluenesulfonyl chloride in 800 mL of reagent grade acetone. A precipitate of NaCl formed immediately and the supernatant liquid turned orange. The reaction mixture was stirred for 15 h and then filtered. Acetone was removed by rotary evaporation and the organic phase separated and diluted with 100 mL of CH_2Cl_2. The solution was washed three times with distilled water and dried over Na_2SO_4. Removal of the solvent left 185.0 g of tosyl azide (92% yield, 98.6% pure by NMR analysis).

Diazocyclopentadiene. Diazocyclopentadiene was made by a modification of the method of Weil and Cais.[40] Tosyl azide (50.1 g, 0.250 mol) was placed in a flask cooled to 0 °C. Ethanolamine (13.5 mL, 0.223 mol) was added and stirring begun. Cyclopentadiene (20.0 mL, 0.243 mol) was then added and the mixture left to stir at 0 °C for 4.5 h. The brick-red slurry was washed with pentane until the washings were light yellow and the pentane solution extracted with distilled water until the aqueous phase was neutral by pH paper. Pentane was removed and the crude diazocyclopentadiene stored in the freezer. Samples were trap to trap distilled at room temperature and 0.5 torr and collected at −78 °C immediately before use.[41]

Spiro[bicyclo[2.1.0]pentane-5,1′-cyclopenta-2′,4′-diene] (11). Cyclobutene (11.5 g, 0.213 mol) was vacuum transferred into a tube equipped with a stopcock and a side arm closed with a serum cap. Diazocyclopentadiene (0.750 mL, 8.62 mmol) was added by syringe. The solution was irradiated for 6 h at −10 °C through a Corning 3-73 filter (cutoff 415 nm). The remaining cyclobutene was recovered by vacuum transfer and the procedure repeated until all cyclobutene was consumed. The combined photolysis products were purified by flash chromatography[43] on silica gel (EM Silica Gel 60, 230–400 mesh), eluting with petroleum ether. Total yield was 778 mg of spirodiene **11**. Analytical samples were purified by preparative gas chromatography on column A (oven temperature 75 °C, gas flow 23 cm^3 of He/min): ^{1}H NMR ($CDCl_3$) δ 1.85–2.09 (m, 2 H), 2.32–2.56 (m, 2 H), 2.62 (br d, 2 H), 5.64–5.79 (m, 1 H), 6.23–6.38 (m, 1 H), 6.48–6.73 (m, 2 H); ^{13}C NMR (CCl_4) δ 24.63, 30.28, 48.41, 128.41, 131.72, 132.24, 137.44; UV max (EtOH) 201 nm (ε 5040), 229 (ε 6660), 254 (ε 2190); mass spectrum (EI), *m/e* (rel intensity) 118 (66.1%, M), 119 (5.36%, M + 1), 117 (100%, M − 1). Anal. (C_9H_{10}) C, H.

2,3-Bis(ethoxycarbonyl)-2,3-diazabicyclo[2.2.1]hept-5-ene-7,5′-spirobicyclo[2.1.0]pentane (12). A sample of **11** (124 mg, 1.06 mmol) was dissolved in 3 mL of dry benzene and 0.183 mL (1.16 mmol) of diethyl azodicarboxylate added. The mixture was refluxed under N_2 for 12 h and the solvent removed. The reaction mixture was dissolved in CH_2Cl_2 and filtered through basic alumina. Removal of solvent gave 240 mg of **12** (78% yield): ^{1}H NMR ($CDCl_3$) δ 1.30 (2 t, 6 H), 1.39–1.68 (m, 2 H), 1.68–1.95 (m, 2 H), 2.00–2.24 (m, 2 H), 4.01–4.42 (m, 5 H), 5.00–5.36 (br s, 1 H), 6.52–6.87 (br s, 2 H). ^{13}C NMR ($CDCl_3$) δ 14.49, 19.43, 20.60, 24.50, 56.54, 62.45, 63.49, 67.33, 159.09; mass spectrum (EI), *m/e* (relative intensity) 292 (0.750%, M), 293 (0.125%, M + 1), 294 (0.0625%, M + 2), 116 (100%, M − 176).

2,3-Bis(ethoxycarbonyl)-2,3-diazabicyclo[2.2.1]heptane-7,5′-spirobicyclo[2.1.0]pentane (27a). A sample of **12** (295 mg, 1.01 mmol) was dissolved in 5 mL of absolute ethanol and 0.400 mL (8.15 mmol) of hydrazine hydrate added. The mixture was heated to 55 °C and left open to the atmosphere with stirring for 18 h. Ethanol was removed by rotary evaporation and the product taken up in ether. The solution was extracted with distilled water until the aqueous layer was neutral by pH paper. The organic layer was then filtered through basic alumina and the solvent removed to give 221 mg (74% yield) of **27a**: ^{1}H NMR ($CDCl_3$) δ 1.29 (t, 6 H), 1.40–1.63 (m, 2 H), 1.91 (br s, 6 H), 2.07–2.30 (m, 2 H), 3.64 (br s, 1 H), 4.16 (q, 4 H), 4.54 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.42, 20.27, 20.79, 21.11, 45.55, 58.28, 61.99, 62.90; mass spectrum (EI), *m/e* (relative intensity) 294 (14.0%, M), 295 (2.38%, M + 1), 296 (5.00%, M + 2), 117 (100%, M − 177).

2,3-Diazabicyclo[2.2.1]hept-2-ene-7,5′-spirobicyclo[2.1.0]pentane (8a). A solution of 1.40 g (25.0 mmol) of potassium hydroxide in 10 mL of 2-propanol was brought to reflux under argon. Degassed 2-propanol (12 mL) containing carbamate **27a** (661 mg, 2.24 mmol) was added dropwise. Reflux was maintained for 2 h. The solution was concentrated down to a light yellow paste which was taken up in 50 mL of saturated sodium bicarbonate solution and extracted 5 times with methylene chloride. The organic layers were dried over sodium sulfate and left overnight in the dark in the presence of oxygen, after which solvent was removed. The crude diazene was sublimed at 85 °C and 0.1 torr then recrystallized from pentane: yield 162 mg (49%); ^{1}H NMR (C_6D_6) δ 0.58–1.33 (m, 8 H), 1.50–1.69 (m, 2 H), 3.84 (s, 1 H), 4.75 (s, 1 H); ^{13}C NMR (C_6D_6) δ 19.91, 20.43, 21.21, 21.40, 21.53, 22.44, 48.24, 74.37, 78.79; UV max (EtOH) 207 nm (ε 501), 331 (ε 80.1), 338 (ε 79.1). Anal. ($C_9H_{12}N_2$) C, H.

Decomposition Studies of 8a. Compound **8a** (ca. 12 mg, 0.08 mmol) was dissolved in 0.5 mL of benzene-d_6 and placed in an NMR tube. The solution was degassed by five freeze–pump–thaw cycles and the tube sealed under vacuum. NMR spectra were taken at 15-min intervals during the reactions. Analysis of the products was performed by gas

(38) Engel, P. S.; Keys, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 6860–6861.
(39) Cope, A. C.; Stevens, C. L.; Hochstein, F. A. *J. Am. Chem. Soc.* **1950**, *72*, 2510–2514. Cope, A. C.; Haven, A. C., Jr.; Ramp, F. L.; Trumbull, E. R. *Ibid.* **1952**, *74*, 4867–4871.
(40) Weil, T.; Cais, M. *J. Org. Chem.* **1963**, *28*, 2472.
(41) An explosion during the distillation of diazocyclopentadiene has been reported,[42] but this occurred at 47 °C and 48 torr. We have encountered no difficulties during trap-to-trap distillations as described.
(42) Ramirez, F.; Levy, S. *J. Org. Chem.* **1958**, *23*, 2036–2037.
(43) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

chromatography on column D (oven temperature 60–120 °C, flow rate 50 cm³ N_2/min). GC/MS analysis confirmed that all products were C_9H_{12} isomers. Thermolysis: The tube was heated to 140 °C in an oil bath for 3 h. Direct photolysis: The tube was irradiated for 3 h through a Pyrex filter. Sensitized photolysis: Sample was made up as above but also containing 41.8 mg of benzophenone. The solution was photolyzed for 5.5 h through a Corning LP-30 filter (cutoff 365 nm).[44]

5,5′-Spirobi[bicyclo[2.1.0]pentane] (3). Product mixtures from direct photolysis of **8a** were separated by preparative gas chromatography on column B (oven temperature 100 °C, gas flow 75 cm³ of He/min) to obtain a pure sample of **3**: ^{1}H NMR (C_6D_6) δ 1.45–1.73 (m, 4 H), 1.94 (br s, 4 H), 2.00–2.22 (m, 4 H); ^{13}C NMR (C_6D_6) δ 18.22, 22.22, 22.31, 23.52, 35.59; mass spectrum (EI), *m/e* (relative intensity) 120 (8.1%, M), 121 (1.2%, M + 1), 91 (43.4%, M − 29).

2,3-Divinylcyclopentene (15). 2,3-Divinylcyclopentene (**15**) was isolated from the sensitized photolysate of **8** by preparative gas chromatography on column B (oven temperature 110 °C, gas flow 75 cm³ of He/min). Spectral properties were identical with those reported in the literature.[31,45]

Reduction of 12 with Diimide-d_2. A solution of carbamate **12** (140 mg, 0.478 mmol) and hydrazine-d_6 hydrate (0.250 mL, 5.09 mmol) in EtOD was stirred at 60 °C in the presence of oxygen for 16 h. The solvent was removed and the residue taken up in ether. The organic layer was extracted with distilled water until the aqueous layer was neutral to pH paper. Filtration through basic alumina and removal of the solvent gave 139 mg of **27b** (98% yield): ^{2}H NMR (C_6H_6) δ 1.41 (br s).

Synthesis of 8b. Carbamate-d_2 (**27b**, 501 mg, 1.69 mmol) was subjected to the hydrolysis–oxidation procedure described above to yield 123 mg of **8b** (48% yield): ^{2}H NMR (CCl_4) δ 1.52 (s, exo).

Addition of PTAD to 8b. *N*-Phenyltriazolinedione (250 mg, 1.43 mmol) was added to a solution of **8b** (109 mg, 0.725 mmol) in 5 mL of benzene. The reaction mixture was stirred under argon at 50 °C for 2 days, and then H_2O was added and the solution reheated until the red color of PTAD disappeared. The resulting yellow solution was extracted 3 times with saturated sodium bicarbonate solution and then with distilled water until neutral to pH paper. After drying with sodium sulfate, the solvent was removed to give 226 mg of adduct **21** (96% yield): ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 2 H), 1.49 (s, 1 H), 1.87 (s, 3 H), 3.89 (s, 1 H), 4.07 (s, 1 H), 4.73 (s, 1 H), 4.96 (s, 1 H), 7.39 (s, 5 H).

Solid-State Photolysis of 21. Adduct **21** (226 mg, 0.692 mmol) was divided into 10–5-mm o.d. Pyrex tubes and photolyzed under argon for 6 days. ^{1}H NMR confirmed that the reaction had reached >95% completion. Yield of **28c** was 198 mg (96%): ^{2}H NMR (C_6H_6) δ 0.88 (endo), 1.43 (endo), 1.62 (exo), 1.77 (exo). Solution phase thermolysis and photolysis both lead to complete ^{2}H scrambling.

Synthesis of 8c. A solution of 0.37 g (6.6 mmol) of potassium hydroxide in 6 mL of 2-propanol was brought to reflux under argon, and a suspension of 198 mg (0.665 mmol) of urazole **28c** in 40 mL of degassed 2-propanol was added dropwise. Reflux was maintained for 2.5 h and the solvent removed to give a brown paste which was taken up in saturated sodium bicarbonate solution and extracted five times with methylene chloride. After drying with sodium sulfate the solution was allowed to stand overnight, in the dark, in the presence of oxygen. Evaporation of solvent gave a yellow oil from which **8c** was purified by preparative gas chromatography on column A (oven temperature 90 °C, gas flow 100 cm³ of He/min). The yield of **8c** was 44.2 mg (44%): ^{2}H NMR (CCl_4) δ 1.24 (0.80D, endo), 1.39 (0.80D, endo), 1.95 (0.20D, exo), 1.98 (0.20D, exo).

2,3-Divinylcyclopentene-d_2. 2,3-Divinylcyclopentene-d_2 was isolated from the sensitized photolysate of **8b** or **8c** as described above for unlabeled material: ^{2}H NMR (CCl_4) δ 1.56 (D4, trans),[46] 1.98 (D4, cis), 2.13 (D5, cis), 2.25 (D5, trans), 4.78 (vinyl), 4.85 + sh (vinyl), 4.99 (vinyl). Deuterium is labeled as cis or trans with respect to the proton on C3 (see Figures 3 and 4). Relaxation (T_1) studies ensured that the integrals were reliable. Signal assignments for **15** were based on extensive decoupling and NOE experiments using 500-MHz ^{1}H NMR.

Addition of PTAD to 11. Diene **11** (471 mg, 3.98 mmol) was dissolved in benzene and 2.09 g (11.9 mmol) of *N*-phenyltriazolinedione added. The solution was heated to 60 °C and reaction followed by TLC until complete after 6 days. The solvent was removed, and the products were chromatographed on silica gel (EM Silica Gel 60, 70–230 mesh), eluting with 10% EtOAc/$CHCl_3$ to give 590 mg of bisurazole **13** (32% yield): ^{1}H NMR ($CDCl_3$) δ 1.81–2.07 (m, 4 H), 4.08 (s, 1 H), 4.62 (s, 1 H), 4.82 (s, 1 H), 5.13 (s, 1 H), 6.57 (qt, 2 H), 7.39 (s, 5 H), 7.45 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.40, 26.51, 60.62, 64.91, 78.43, 78.95, 125.35, 125.36, 125.48, 128.54, 129.25, 130.29, 130.94, 131.33, 132.63, 155.18, 155.31, 157.91, 158.30.

Reduction of 13. A solution of 360 mg (0.769 mmol) of bisurazole **13** in 200 mL of ethyl acetate was hydrogenated at atmospheric pressure using palladium on carbon as catalyst. The yield was 290 mg of **29** (80%): ^{1}H NMR ($CDCl_3$) δ 2.08 (br s, 8 H), 4.32 (s, 2 H), 4.55 (s, 2 H), 7.48 (br s, 10 H); ^{13}C NMR ($CDCl_3$) δ 26.77, 26.90, 59.98, 60.31, 71.62, 125.36, 128.61, 129.33, 131.38, 155.32, 155.78.

7,7′-Spirobi[2,3-diazabicyclo[2.2.1]hept-2-ene] (6). A solution of 0.49 g (8.73 mmol) of potassium hydroxide in 30 mL of 2-propanol was brought to reflux under argon and a suspension of 197 mg (0.419 mmol) of bisurazole **29** in 125 mL of degassed 2-propanol added dropwise. Reflux was maintained for 3 h and the solvent removed to yield a yellow paste which was taken up in 95% ethanol. Saturated copper(II) chloride solution was added until a dark brown precipitate formed. The precipitate was collected and dissolved in ca. 50 mL of 25% ammonium hydroxide, which was extracted 6 times with methylene chloride. Drying over sodium sulfate and removal of solvent gave a yellowish solid from which the bisdiazene **6** was sublimed at 0.5 torr and 100 °C. The yield was 65.5 mg (89%). The compound was further purified by recrystallization from methylene chloride/hexane: ^{1}H NMR (C_6D_6) δ 0.32–1.11 (m, 8 H), 3.93 (m, 2 H), 4.17 (m, 2 H); ^{13}C NMR (CD_2Cl_2) δ 19.42, 20.33, 74.14, 76.09, 76.94; UV max (EtOH) 224 nm (ε 520), 334 (ε 84), 342 (ε 86). Anal. ($C_9H_{12}N_4$) C, H, N.

Direct Photolysis of 6. A solution of **6** (1.00 mg, 0.00567 mmol) in 0.5 mL of benzene-d_6 was degassed by bubbling argon through it for 15 min and capped with a septum.[47] The sample was irradiated through a Pyrex filter. Aliquots were removed at 15-min intervals and analyzed by gas chromatography on column D (oven temperature 50–120 °C, gas flow 75 cm³ of N_2/min).

Sensitized Photolysis of 6. Compound **6** (0.75 mg, 0.00426 mmol) was dissolved in 0.075 mL of 0.250 M benzophenone in benzene. *n*-Undecane (0.3 μL) was added as an internal standard. The solution was placed in a 3-mm o.d. Pyrex tube, degassed by bubbling argon through for 15 min, and capped with a septum. The sample was irradiated through a Corning 0–52 filter[44] and aliquots taken every 30 min for analysis by gas chromatography on column D (oven temperature 50–150 °C, gas flow 75 cm³ of N_2/min).

8,9-Diazatricyclo[5.2.2.0^{2,6}]undeca-2,8-diene (14). Diazene **6** (14.0 mg, 0.0795 mmol) was dissolved in 1.00 mL of 0.250 M benzophenone in benzene and placed in an 8-mm o.d. Pyrex tube. The sample was degassed by four freeze–pump–thaw cycles and irradiated for 2.5 h through a Corning 0–52 filter.[44] The products were isolated by preparative gas chromatography on column C (oven temperature 120 °C, gas flow 100 cm³ of He/min). The isolated yield of **14** was 0.60 mg (5.1%): ^{1}H NMR (C_6D_6) δ 0.65–2.20 (m, 9 H), 4.94 (br s, 1 H), 5.15 (br s, 1 H), 5.49 (br s, 1 H); ^{13}C NMR (C_6D_6) δ 13.94, 28.46, 29.27, 34.12, 45.41, 65.36, 68.05, 120.79, 143.83; UV max (EtOH) 227 nm (ε 1230), 375 (ε 51); mass spectrum (EI) *m/e* (relative intensity) 120 (27.7%, M − N_2), 121 (2.3%, M − N_2 +1).

Sensitized Photolysis of 14. Compound **14** (0.17 mg, 0.00115 mmol) was dissolved in 0.125 mL of 0.250 M benzophenone in benzene, degassed by bubbling argon through for 10 min, and capped with a septum. The sample was photolyzed for 20 min through a Corning 0–52 filter[44] and analyzed by gas chromatography on column E (oven temperature 50–150 °C, H_2 carrier gas, linear velocity 40 cm/s).

Quantum Yields. The azo compound (0.075 mmol) was dissolved in 1.00 mL of 0.250 M benzophenone in benzene and placed in one of a set of three labeled 8-mm o.d. Pyrex tubes. One sample in each run consisted of 2,3-diazabicycloheptene[12,13] (**5**) as an actinometer. Solutions were degassed by five freeze–pump–thaw cycles and placed in a merry-go-round where they were irradiated to ca. 10% conversion through a Corning 0–52 filter. Control experiments confirmed that the sample tubes had identical optical properties and that no direct photolysis occurred under the experimental conditions. Nitrogen produced upon irradiation was measured by pumping the gas into a calibrated gas buret by using a Toepler pump. Disappearance of the azo compound was measured by gas chromatography on column E or F (oven temperature 50–150 °C, H_2 carrier gas, linear velocity 40 cm/s) using the benzophenone sensitizer as an internal standard. If both nitrogen measurement and GC analysis were required, separate runs were performed for each.

(44) Control experiments confirmed that direct photolysis did not occur through the filters used in sensitization experiments.

(45) Untch, K. G.; Martin, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 4501–4506. Skattebol, L.; Solomon S. *Ibid.* **1965**, *87*, 4506–4513.

(46) Deuterium cis or trans to proton on C3.

(47) There has been a recent criticism of deoxygenation by bubbling inert gas through solvents.[48] In our hands, samples degassed by several freeze–pump–thaw cycles and those deoxygenated with argon have given identical results. However, we have indicated in this section which method was used for each experiment.

(48) Skell, P. S.; Tlumak, R. L.; Seshadri, S. *J. Am. Chem. Soc.* **1983**, *105*, 5125–5131.

The exception to the above procedure was compound **14**, for which 0.94 mg (0.00634 mmol) of **14** and 0.98 mg (0.00661 mmol) of **8a** were dissolved together in 0.250 mL of 0.250 M benzophenone in benzene and the solution degassed by five freeze–pump–thaw cycles. Irradiation was performed as described above and analysis done by gas chromatography on column F (conditions above) using **8a** as an internal actinometer and the benzophenone as an internal standard.

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Registry No. 3, 82482-48-2; **6**, 89597-60-4; **8a**, 82482-45-9; **8b**, 82482-46-0; *endo*-**8c**, 82482-47-1; **11**, 82494-77-7; **12** (E = EtOCO), 82482-51-7; **13**, 89597-58-0; **14**, 89597-61-5; **15**, 3641-77-8; **15-T**, 89597-57-9; **15-C**, 89673-94-9; **21**, 82494-76-6; **27a**, 89597-54-6; **27b**, 89597-55-7; **28c**, 89597-56-8; **29**, 89597-59-1; 5-diazo-1,3-cyclopentadiene, 1192-27-4; *p*-toluenesulfonyl chloride, 98-59-9; tosyl azide, 941-55-9; 1,3-cyclopentadiene, 542-92-7; cyclobutene, 822-35-5; diethyl azodicarboxylate, 1972-28-7; *N*-phenyltriazolinedione, 4233-33-4; *exo*-**8c**, 89673-95-0.

A Novel, Dinuclear Mechanism for Catalytic Olefin Dimerization. Photochemical Reactivity of (μ-Hydrido)(μ-alkenyl)dirhenium Octacarbonyl Compounds[1]

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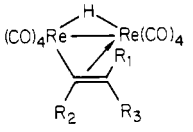
Abstract: UV photolysis of (μ-hydrido)(μ-ethenyl)dirhenium octacarbonyl, (μ-H)(μ-CH=CH$_2$)Re$_2$(CO)$_8$ (I), in the presence of ethylene affords (μ-hydrido)(μ-butenyl)dirhenium octacarbonyl complexes. A mechanism is proposed in which the initial step is photodissociation of CO from I, as photolysis of I in the presence of ^{13}CO or PPh$_3$ results in CO substitution. Subsequent steps in the formation of the μ-hydrido μ-butenyl species are coordination of ethylene, insertion of ethylene into the Re–H or Re–ethenyl σ bond, recoordination of CO, C–C or C–H reductive elimination to yield Re$_2$(CO)$_8$(1-butene), and oxidative addition of a vinylic C–H bond of coordinated butene. Slow catalytic production of 1-butene and *trans*-3-hexene occurs in the photochemical reaction of I with ethylene; butene formation is the result of thermal reaction of the (μ-hydrido)(μ-butenyl)dirhenium octacarbonyl species with ethylene, while hexene results from photochemical reaction. Removal of photodissociated CO from the system via an ethylene purge during photolysis results in subsequent catalytic production of butene and hexene under thermal (25 °C) conditions. Photolysis of (μ-hydrido)(μ-propenyl)dirhenium octacarbonyl, (μ-H)(μ-CH=CHCH$_3$)-Re$_2$(CO)$_8$, in the presence of propylene yields 2-hexene. A general mechanism for dimerization of olefins is proposed in which a dinuclear metal catalyst effects the insertion of one olefin into a vinylic C–H bond of another. Additionally, cis–trans photoisomerization of the bridging alkenyl ligand of (μ-H)(μ-CH=CHR)Re$_2$(CO)$_8$ complexes is discussed.

We recently reported the synthesis of (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyl compounds (I–III) via UV photolysis of Re$_2$(CO)$_{10}$ in the presence of simple olefins.[2,3] Analogues to



I, $R_1 = R_2 = R_3 = H$
IIa, $R_1 = R_2 = H$; $R_3 = CH_3$
IIb, $R_2 = R_3 = H$; $R_1 = CH_3$
IIIa, $R_1 = R_2 = H$; $R_3 = C_2H_5$
IIIb, $R_2 = R_3 = H$; $R_1 = C_2H_5$
IIIc, $R_1 = R_3 = H$; $R_2 = C_2H_5$
IV, $R_1 = R_2 = H$; $R_3 = OCH_3$
V, $R_1 = R_2 = H$; $R_3 = CH_2CH_2OCH_3$

these compounds exist in osmium cluster chemistry; reactions of olefins (and acetylenes) with H$_2$Os$_3$(CO)$_{10}$ and H$_4$Os$_4$(CO)$_{12}$ yield μ-hydrido μ-alkenyl tri-[4] and tetraosmium[5] products, respectively. Additionally, dirhodium μ-hydrido μ-alkenyl complexes have been prepared by the reaction of ((μ-H)Rh[P(O-*i*-C$_3$H$_7$)$_3$]$_2$)$_2$ with dialkyl- and diarylalkynes.[6]

We have found the dirhenium compounds to be remarkably reactive, both thermally and photochemically. Treatment of I–III with a variety of substrates (CO, pyridine, phosphorus nucleophiles, olefins, terminal acetylenes, H$_2$, etc.) under mild thermal conditions results in elimination of olefin and production of a substituted dirhenium octacarbonyl complex.[2] A very interesting and novel photochemical reaction pathway was first manifested by the formation of μ-hydrido μ-butenyl species III upon UV photolysis ($\lambda > 297$ nm) of I in the presence of ethylene.[2] We thus initiated a thorough investigation of the photochemical reactivity of the dirhenium hydrido alkenyl compounds with olefins and other substrates. We now report the results of these studies, most notably the identification of a mechanism for olefin dimerization which requires a dinuclear metal catalyst.

Experimental Section

General. Dirhenium decacarbonyl was purchased from Pressure Chemical Co. and used without further purification. Hexane and toluene

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