be hindered by the highly metastable nature of the $(Fe_6S_6(SPh)_6)^{3-}$ clusters and their rapid conversion to $(Fe_4S_4(SPh)_4)^{2-}$.

Note Added in Proof. In a recent publication, Cleland and Averill reported on the isolation of a new iron–sulfur cluster with phenoxide ligands.[19] They propose that this compound is a trianionic, $[Fe_6S_6(OR)_6]^{3-}$ cluster that has a *diamagnetic*(!) ground state and a structure similar to that shown in Figure 1. In view of the demonstrated[5b] paramagnetic ($S = {}^1/_2$) ground state for *I*, we submit that the cluster described by Cleland and Averill does not exist as such.

Supplementary Material Available: Tables of structure factors, positional and thermal parameters, and data reduction and structure solution protocol (15 pages). Ordering information is given on any current masthead page.

(19) Cleland, W. E., Jr.; Averill, B. A. *Inorg. Chim. Acta* **1985**, *106*, L17–L19.

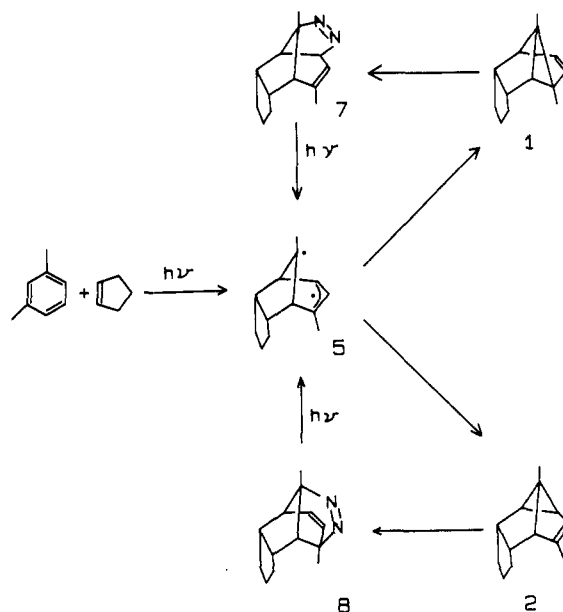## Independent Generation of Arene Meta Photoaddition Biradicals

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The meta photoaddition of aromatic compounds to olefins continues to fascinate mechanistic[1] and synthetic chemists.[2] Although the general regiochemistry of addition has been rationalized on the basis of frontier orbital overlap in exciplex intermediates,[3] subsequent mechanistic details are less clear.[1] Initial olefin meta photoaddition to give bicyclo[3.2.1]octenyl biradicals has been suggested,[1,6] yet independent proof of this assertion is lacking. Moreover, the intimate behavior of these biradicals, including substituent effects, etc., has not been explored. We now wish to report direct evidence for intermediacy of biradicals in these reactions and an initial exploration of factors controlling ring closure. A novel wavelength-dependent photochemical effect is also described.

Irradiation (254 nm) of *m*-xylene and cyclopentene (1 mM each in cyclohexane) gave meta photoadducts **1** and **2** in a 1:1.0 ± 0.1 ratio.[4,5] Because of product photolability, it was necessary to assay the reaction mixture at very low conversions. This point has not been stressed in previous meta photoaddition investigations, and literature data may not reflect meaningful product ratios (see ref

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(3) Houk, K. N. *Pure. Appl. Chem.* **1982**, *54*, 1633.
(4) Assayed on linked 24-m BP-1 and 25-m BP-20 (Scientific Glass Engineering Inc.) fused silica capillary columns with splitless injection and FID detection. This combination of two columns was necessary to completely separate **1** and **2** from minor products. Analysis of the azo irradiations was through a 10-m SE-30 fused silica capillary column with split injection. Both analysis methods gave identical results on standard mixtures. Irradiation of starting materials in the presence of known amounts of products showed the products to be stable under these conditions.
(5) Sheridan, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5140.
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2, however). Although at least four other photoadducts are observed by capillary GC, **1** and **2** account for ca. 80% of volatile products. Similarly, short-term irradiation of *o*-xylene and cyclopentene gave a 1:1.36 ± 0.02 ratio of **3** and **4**.[4,6,7] Only trace amounts of other adducts were observed by GC.
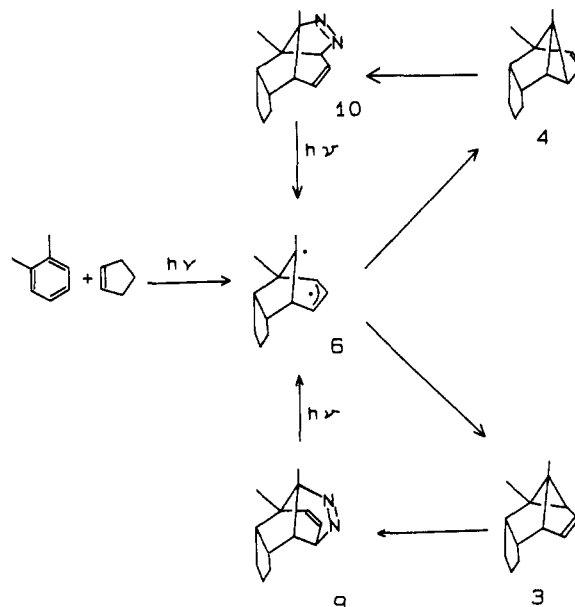
The above results suggest that if biradicals **5** and **6** are involved, substituent perturbations on ring closure are minimal. Moreover, allylic substitution as in **5** surprisingly appears to have less influence than bridgehead substitution as in **6**. As one approach to these questions, we recently reported a potential alternate route to biradicals such as **5** and **6**.[5] Thus, azo compounds **7** and **8** can be synthesized from **1** and **2**.[5] Similarly, treatment of **3** and **4** with 4-methyl-1,2,4-triazoline-3,5-dione, followed by hydrolysis and oxidation, gave regioisomeric **9** and **10**.[7]

Our previous results indicated that thermolyses of **7** and **8** are dominated by concerted $[\sigma^2s + \sigma^2s + \pi^2s]$ cycloreversions.[5,8] Analogously, at 75 °C **9** gives a 10:1 ratio and **10** gives a 1:17 ratio of **3** to **4**. These "memory" effects, leading to predominant closure away from N_2, obscure the role of biradicals in the den-

(7) Structures were confirmed by ${}^1H$ NMR. Extensive proton–proton decoupling was used to support the regioisomeric assignments.
(8) Askani and co-workers have recently reported similar elegant results on optically active compounds: Askani, R.; Hornykiewytsch, T.; Müller, K. M. *Tetrahedron Lett.* **1983**, *24*, 513.

Table I. Azo Compound Photolyses[a]

compd	prod	prod ratio ± 0.04[b]		
		350 nm	254 nm	³sens
7	1/2	1:1.06	1:1.04	1:1.02
8	1/2	1:1.20	1:1.01	1:1.05
9	3/4	1:1.10	1:1.34	1:1.33
10	3/4	1:1.77	1:1.32	1:1.33

[a] 254-nm irradiations in cyclohexane with Rayonet photochemical reactor. 350-nm irradiations in cyclohexane and sensitized irradiations in benzene with 300-W Xe lamp and cutoff filter ($\lambda > 340$ nm). Triplet sensitizer is 4,4-bis(dimethylamino)benzophenone, at concentrations calculated to absorb greater than 99% of the light. No other products were detected by capillary GC or ^{1}H NMR. [b] All numbers represent the average of at least eight separate analyses at several different irradiation times short enough to ensure negligible product rearrangement. The error limit represents two standard deviations, which was approximately the same for all the reported numbers.

itrogenations. Photolyses of the azo compounds, in contrast, are more informative. Results of direct and sensitized irradiations are listed in Table I.[9] The photoproducts are stable to direct irradiation at 350 nm, but the product ratios change slowly under sensitized conditions or at 254 nm. The reported ratios were obtained by GC at short irradiation times where the photoproducts were independently shown to be stable.

Under all irradiation conditions the denitrogenations approach the ring-closure ratios exhibited in the corresponding meta photoadditions. Direct 350-nm irradiation shows some memory effects, albeit smaller than in the analogous thermolyses. The sensitized and direct 254-nm irradiations are more clear-cut. Under these excitation conditions ring-closure ratios are independent of azo position (i.e., **7** and **8** give the same product ratio, as do **9** and **10**). Moreover, the ratios of photoproducts obtained on triplet sensitization and on 254-nm irradiation are identical, within experimental error. Most dramatically, the ratio of **1:2** from **7** and **8** and the ratio of **3:4** from **9** and **10** are identical within experimental error to the ratios obtained in the corresponding arene photoadditions.

We believe that the above results provide direct evidence for the intermediacy of biradicals such as **5** and **6** in meta photoadditions. The ground-state multiplicity of such biradicals is unknown. Although meta photoadditions have been shown to be singlet reactions,[1] the same regioselectivity is exhibited in the triplet denitrogenations. Triplet pyrazolines have been shown to generate triplet 1,3-biradicals, whose chemistry can be correlated with triplet biradicals from other sources.[10] Triplet 1,3-biradicals, however, often give different product mixtures than the corresponding singlets.[11] In our case the intermediates are rigidly constrained, and major differences between singlet and triplet geometries are not possible. Our results suggest that triplet biradicals **5** and **6**, generated from the triplet azo compounds, intersystem cross to the same singlet biradicals as generated in the photoadditions.

It seems likely that the 350-nm fragmentations proceed mainly via the biradical route. The exhibition of a small memory effect is puzzling, however. A minor $[\pi 2s + \sigma 2s + \sigma 2s]$ component would fit these results, although simple-minded analysis suggests such a process to be orbital symmetry forbidden photochemically. Epiotis and co-workers[12] have discussed various schemes by which such orbital symmetry constraints may be overridden in photochemical reactions, and certain of these suggestions may have relevance here. In the absence of additional data, however, we hesitate to speculate further. It is of note that Berson and Olin have also observed apparent forbidden six-electron concerted cycloreversions from azo $n\pi^*$ states.[13]

Most 1,2-diazenes show only $n\pi^*$ absorption (ca. 360 nm) in the near-UV.[14] Interestingly, **7–10** exhibit an additional transition at ca. 235 nm ($\epsilon \sim 3100$ M^{-1} cm^{-1}). The assignment of this band is not known, although $n_+\pi^*$, $\pi\pi^*$, and $n_-\sigma^*$ are possibilities.[14] Selective excitation at 254 nm gives ring closure ratios identical with those observed on triplet sensitization (Table I). Adam and co-workers[15] have shown that S$_2$ azo excitation (at 185 or 193 nm) in general leads to more efficient biradical formation than S$_1$. Consistent with this, our results suggest that S$_2$ azo gives biradical chemistry without competing concerted cycloreversion. Intersystem crossing to a triplet azo state, e.g., $\pi\pi^*$, cannot be excluded, however.

The reasons behind the substituent effects on ring closure are not known. The greater perturbation of bridgehead substitution suggests that steric interactions may dominate over electronics. Interestingly, similar bridgehead substitution effects are observed in di-π-methane rearrangements.[16] The effects of other substituents are currently being explored.

Supplementary Material Available: Spectral data for **9**, **10**, and corresponding urazoles (1 page). Ordering information is given on any current masthead page.

(9) No evidence for diazo formation was observed under any irradiation conditions,[5] nor was interconversion of azo isomers detected by ^{1}H NMR or HPLC at partial conversion.

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Tetrahydroborate Complexes of Tantalum: Synthesis, Characterization, and Reactivity of Ta(BH$_4$)H$_2$(PMe$_3$)$_4$

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Covalent tetrahydroborate complexes of the group 5 metals are very rare and the only well-characterized examples are Cp$_2$V-(BH$_4$),[2] [V(μ-Cl)(μ-dppm)(BH$_4$)]$_2$,[3] Cp$_2$Nb(BH$_4$),[4] and CpNbH(BH$_4$)(dmpe).[5,6] Here we report the synthesis and characterization of an unusual 8-coordinate tetrahydroborate complex of tantalum, Ta(BH$_4$)H$_2$(PMe$_3$)$_4$ (**1**), and describe our

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