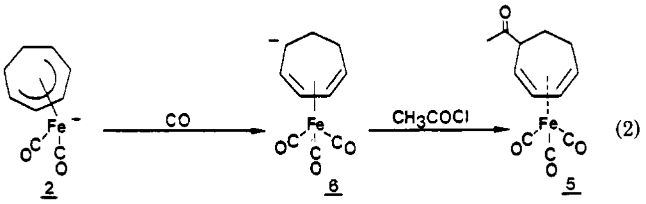
at the coordinated ring; their combined yield is approximately 10%. The final product is the exo (acylidene)iron complex **5** (yellow oil, <10%). The assignment of structure of **5** is based on NMR data. Most telling are one-proton multiplets at δ 5.4 and 5.25, due to the internal protons of the coordinated diene. The external diene protons are also nonequivalent. These data clearly show the coordinated seven-membered ring to be unsymmetrical. The three-proton singlet at δ 2.1 and the IR band at 1722 cm^{-1} indicate the ring to be acyl substituted. The NMR signal at highest field (δ 1.15) is a quartet of doublets assigned to the exo proton on C-6, consistent with a boat conformation for the seven-membered ring.[7,8] In this geometry, the dihedral angle between the outer diene proton (H-4) and an endo proton on C-5 would be close to 90°. Accordingly, we observe only minor coupling (<1 Hz) between H-4 and H-5. An exo proton on C-5 (in the boat conformation) should exhibit a larger value (5-7 Hz) for J_{45}.[9] Complex **5** shows no tendency to isomerize to a symmetrical structure. Thus, after refluxing in THF for 12 h **5** can be recovered in 94% yield. There is no evidence for formation of **3**. Exo substituents at C-5 would have no steric interaction with the metal center. Accordingly, recent studies on the functionalization of cycloheptadienyliron cations with nucleophiles show exo C-5 substituted iron dienes to be configurationally stable.[8]

Isolation of *exo*-acyl **5** is intriguing in that it implies that anion **2** can act as an ambident nucleophile. We felt that it might be possible to control the reduction of **1** such that either the exo or endo (acylidene)iron complex could be prepared selectively. To promote electrophilic attack on the exo face of the dienyl ligand of **2** it was necessary to block reactivity at the metal. This was accomplished by treatment of anion **2** with CO to provide a new species, **6**, which we suggest is *tricarbonyl*iron anion.[10] Acylation of **6** provides **5** in 52% yield. The *endo*-acyl **3** is present in only minor amounts (<5%) (eq 2). Byproducts $(C_7H_{10})Fe(CO)_3$ and $[(C_7H_9)Fe(CO)_3]_2$ are formed in 10% combined yield.



(Diene)Fe(CO)$_3$ complexes can be acylated under Friedel–Crafts conditions.[11] However, such procedures have not been well developed and appear to provide product mixtures. Our dienyliron anions should be much more versatile reagents, reacting with a wide range of organic electrophiles. Further, anions derived from **1** provide the first opportunity for selective control of stereochemistry in the functionalization of iron dienes. Extensive studies to determine the precise nature of anions **2** and **6** and their patterns of reactivity are in progress.

Acknowledgment. Supported by an Atlantic Richfield Foundation Grant of the Research Corporation. We thank Dr. Shoumo Chang for helpful discussions.

Supplementary Material Available: Crystallographic data, an ORTEP diagram, and tables for positional parameters and temperature factors for **3** as well as ^{1}H NMR, ^{13}C NMR, IR, and elemental analyses for **3** and **5** (9 pages). Ordering information is given on any current masthead page.

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(8) Pearson, A. J.; Kole, S. L.; Chen, B. *J. Am. Chem. Soc.* **1983**, *105*, 4483. Pearson, A. J.; Kole, S. L.; Ray, T. *Ibid.* **1984**, *106*, 6060.

(9) Our ^{1}H NMR analysis is in full accord with assignments of (5-*exo*- and (5-*endo*-anilinocycloheptadiene)tricarbonyliron.[7] Becker, Y.; Eisenstadt, A.; Shvo, Y. *J. Organomet. Chem.* **1978**, *166*, 63.

(10) IR (THF, cm^{-1}) 2032 s, 1972 s, 1937 s, 1852 s, 1837 s, sh. Absorptions at 2032 and 1972 are indicative of $(C_7H_{10})Fe(CO)_3$ and $[(C_7H_9)Fe(CO)_3]_2$. The bands at 1937, 1852, and 1837 are consistent with the tricarbonyliron anion shown in eq 2.

(11) Johnson, B. F. G.; Lewis, J.; Parker, D. G. *J. Organomet. Chem.* **1977**, *141*, 319. Johnson, B. F.G.; Lewis, J.; Parker, D. G.; Raithby, P. R.; Sheldrick, G. M. *Ibid.* **1978**, *150*, 118. Birch, A. J.; Raverty, W. D.; Hsu, S.-Y.; Pearson, A. J. *Ibid.* **1984**, *260*, C59.

A New Fe/S Cluster with the $(Fe_6S_6)^{3+}$ Prismatic Core and *p*-Methylphenolate Terminal Ligands. The Synthesis, Structure, and Properties of $(Et_4N)_3Fe_6S_6(OC_6H_4\text{-}p\text{-}CH_3)_6$

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In most of the non-heme iron proteins (NHIP) oligonuclear Fe/S cores, such as Fe_2S_2 or Fe_4S_4, are attached to the protein matrix by coordination to deprotonated cysteinyl S atoms and possess characteristic spectroscopic "signatures".[1] Among these proteins there exist several members that display unusual spectroscopic and magnetic characteristics and consequently do not belong to any of the generally recognized classes. These unusual characteristics have been attributed to either the coordination of common (i.e., Fe_4S_4 or Fe_2S_2) Fe/S cores by ligands other than cysteinyl thiolates or to the presence of unusual Fe/S centers. Examples of these new "unconventional" NHIP include the Rieske proteins which contain Fe_2S_2 cores attached to the protein "backbone" by less than a full complement of non-sulfur ligands[2] and Fe/S proteins that contain the Fe_3S_3[3] or Fe_3S_4[4] cores.

Recently we reported on the synthesis and structural characterization of the $(Fe_6S_6Cl_6)^{n-}$ clusters (n = 3,[5] 2[6]). These clusters contain the Fe_6S_6 prismatic core, which is a new structural unit and belongs in the general class of the oligonuclear $(FeS)_n$ centers. The $(Fe_6S_6Cl_6)^{3-}$ cluster is characterized by a $S = {}^1/_2$ magnetic ground state and is a metastable homologue of the $(Fe_4S_4Cl_4)^{2-}$ cluster. In hot CH_3,cN solution, the transformation shown in eq 1 proceeds readily and quantitatively.

$$2(Fe_6S_6Cl_6)^{3-} \rightarrow 3(Fe_4S_4Cl_4)^{2-} \qquad (1)$$

At ambient (and lower) temperatures, in CH_3CN solution, the reaction represented by eq 1 is slow and the substitution of the terminal Cl$^-$ ligands in the $(Fe_6S_6Cl_6)^{3-}$ cluster with ligands such as RS$^-$ or RO$^-$ (R = aryl groups) can be accomplished by metathetical reactions.[5b]

In this paper we report on the properties and crystal structure of $(Et_4N)_3(Fe_6S_6(OC_6H_4\text{-}p\text{-}CH_3)_6$ (I), which is obtained in 75% yield by the reaction of $(Et_4N)_3(Fe_6S_6Cl_6)$ with the Na$^+$ salt of $p\text{-}CH_3C_6H_4OH$ in CH_3CN at ambient temperature. The conversion of I to the corresponding cubane, by a reaction similar to the one depicted in eq 1, takes place in low yield only after prolonged heating in CH_3CN solution[7] and reveals exceptional stability by comparison to the halide and thiophenolate analogues. The electronic spectrum of I in CH_3CN solution is very similar to but broader than the spectrum of the corresponding $(Fe_4S_4(OC_6H_4\text{-}p\text{-}CH_3)_4)^{2-}$ "cubane"[8] and shows absorptions at 427 (ϵ 19720), 272 (ϵ 42360), and 232 nm (ϵ 62300). This new cluster is quite sensitive to hydrolysis and represents the first example of a nonconventional $(FeS)_n$ core bound exclusively by phenolate terminal ligands.

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(1) Lovenberg, W., Ed. "Iron-Sulfur Proteins"; Academic Press: New York 1977; Vol. III. Spiro, T. G., Ed. "Iron-Sulfur Proteins"; Wiley: New York 1982.

(2) Fee, J. A.; Findling, K. L.; Yoshida, T.; Hille, R.; Tarr, G. E.; Hearshen, D. O.; Dunham, W. R.; Day, E. P.; Kent, T. A.; Münck, E. P. *J. Biol. Chem.* **1984**, *259*, 124 and references therein.

(3) Howard, J. B.; Lorsbach, T. W.; Ghosh, D.; Melis, K.; Stout, C. D. *J. Biol. Chem.* **1982**, *258*, 508.

(4) Beinert, H.; Thomson, A. J. *Arch. Biochem. Biophys.* **1983**, *222*, 333-361.

(5) (a) Kanatzidis, M. G.; Dunham, W. R.; Hagen, W. R.; Coucouvanis, D. *J. Chem. Soc., Chem. Commun.* **1984**, 356. (b) Kanatzidis, M. G.; Hagen, W. R.; Dunham, W. R.; Lester, R. K.; Coucouvanis, D. *J. Am. Chem. Soc.* **1985**, *107*, 953-961.

(6) Coucouvanis, D.; Kanatzidis, M. G.; Dunham, W. R.; Hagen, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 7998.

(7) The integrity of I was monitored by ^{1}H NMR. Only after prolonged heating (ca. 2 h) in CH_3CN solution the characteristic isotropically shifted ^{1}H NMR spectra of the $[Fe_4S_4(OR)_4]^{2-}$ cluster begin to appear.

(8) Cleland, W. E.; Holtman, D. A.; Sabat, M.; Ibers, J. A.; DeFotis, G. C.; Averill, B. A. *J. Am. Chem. Soc.* **1983**, *105*, 6021.

0002-7863/85/1507-3358$01.50/0

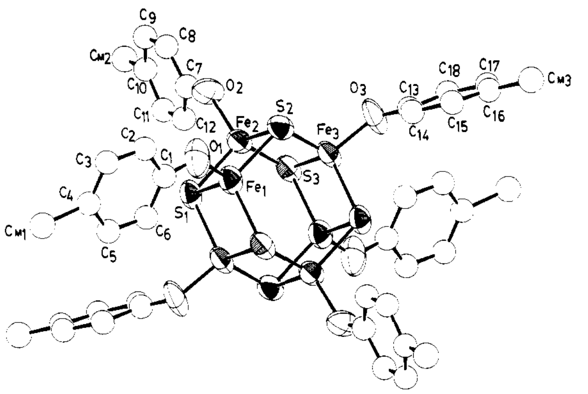

Figure 1. Structure of the $[Fe_6S_6(OC_6H_4\text{-}p\text{-}CH_3)_6]^{3-}$ anion in I. Thermal ellipsoids as drawn by ORTEP (Johnson, C. K., ORNL-4794 Oak Ridge National Laboratory, Oak Ridge, Tn, 1965) represent the 50% probability surfaces. The temperature factors of the carbon atoms of the cresolate ligands were drawn artificially small ($B = 6.0$) for clarity.

Table I. Interatomic Distances[a] (Å) and Angles (deg) in the $[Fe_6S_6(OC_6H_4\text{-}p\text{-}CH_3)_6]^{3-}$ (A), $[Fe_6S_6Cl_6]^{3-}$ (B), and $[Fe_4S_4(OC_6H_5)_4]^{2-}$ (C) Clusters

	A	B[5]	C[7]
	Distances[b]		
Fe–Fe(3)[c]	2.761 (5)	2.765 (3)	2.753 (5)[e]
Fe–Fe(3)[d]	3.80 (4)	3.790 (8)	
Fe–S(3)[c]	2.285 (5)	2.284 (3)	
Fe–S(6)[d]	2.271 (5)	2.272 (2)	
Fe–S(9)[e]	2.276 (5)	2.276 (3)	2.294 (8)[e]
Fe–O or –Cl(3)	1.880 (11)	2.224 (2)	1.865 (8)[e]
S–S(3)[c]	3.624 (8)	3.618 (5)	
S–S(d)[d]	3.77 (4)	3.801 (9)	
S–S(6)[e]			3.619 (24)[e]
	Angles		
S–Fe–S(3)	113.8 (3)[d]	113.7 (3)[d]	
S–Fe–S(6)	105.4 (2)[c]	105.1 (2)[c]	104.1 (4)[e]
Fe–S–Fe(3)	113.8 (2)[d]	113.2 (3)[d]	
Fe–S–Fe(6)	74.6 (2)[c]	74.7 (1)[c]	73.7 (3)[e]
Fe–Fe–Fe(3)	60.0 (1)	60.0 (2)	60.0 (12)[e]
Fe–Fe–Fe(3)	87.1 (1)	86.5 (3)	

[b] The values in parentheses represent the number of independent distances or angles averaged out. [c] Distances or angles outside the Fe_3S_3 hexagonal unit. [d] Distances or angles within the Fe_3S_3 hexagonal unit. [e] Mean value of all distances or angles of this type.

Black crystals of I were obtained by the slow diffusion of diethyl ether into a CH_3CN solution of I kept at ambient temperature and the crystal and molecular structures were determined.[9]

The anion in I is required by space group[9] symmetry to reside on an inversion center and the $(Fe_6(\mu\text{-}S)_6)^{3+}$ core can be described as a hexagonal prism with alternating Fe and S atoms at the apices and nearly exact D_{3d} symmetry (Figure 1). The structural parameters of this core (Table I) are strikingly similar to corresponding values in the $(Fe_6S_6Cl_6)^{3-}$ cluster.[5] The structural parameters within the Fe_3S_3 prism "bases" (Table I) roughly resemble those determined crystallographically for the 3Fe–3S center in FdI from *A. vinelandii*.[3] In the latter, the long Fe–Fe distances of ~4.2 Å and the obtuse Fe–S–Fe angles of ~120° have not been observed previously in the structures of either synthetic or biologically occurring $(FeS)_n$ cores.

The $\overline{\text{Fe–S}}$ bond and $\overline{\text{Fe–O}}$ bond lengths in I at 2.276 (4) and 1.880 (11) Å are within 3σ from corresponding values in the $(Fe_4S_4(OPh)_4{}^{2-}$ "cubane"[8] at 2.294 (8) and 1.865 (8) Å, respectively. The $\overline{\text{Fe–O}}$ bond lengths in I and $(Fe_4S_4(OPh)_4{}^{2-}$ are very similar to the $\overline{\text{Fe(III)–O}}$ bond lengths in the $(Fe(OAr)_4)^-$ complexes[10] (1.847 (13) Å, R = 2,3,5,6-Me_4C_6H; 1.866 (6) Å, R = 2,4,6-$Cl_3C_6H_3$) and somewhat shorter than the $\overline{\text{Fe(III)–O}}$ bond in the $(Fe_2S_2(o,o'\text{-biphenolate})_2)^{2-}$ anion[11] (1.893 (3) Å) and the $\overline{\text{Fe–O}}$ bond in the $[Fe_4S_4(OR)_2Cl_2]^{2-}$ cluster [12] (2.057 (9) Å). The $\overline{\text{Fe–S}}$ bond in I is significantly longer than the Fe(III)–S_b bond in the $(Fe_2S_2(L)_4)^{2-}$ clusters. In the latter this bond is found around 2.21 Å.[1] At this point it is difficult to correlate the Fe–O bond lengths in the $(Fe_{2n}S_{2n}(OAr)_{2n})^{n-}$ and $(Fe(OAr)_4)^-$ complexes with the different Fe formal oxidation states suggested by the ^{57}Fe Mössbauer spectra. The Mössbauer parameters for the $(Fe_4S_4(OPh)_4)^{2-}$ "cubane" (IS = 0.50 (1) mm/s, E_Q = 1.21 (1) mm/s, T = 4.2 K[8]) and the $(Fe_6S_6(OC_6H_4\text{-}p\text{-}CH_3)_6)^{3-}$ "prismane" (IS = 0.476 (1) mm/s, E_Q = 1.016 (1) mm/s, T = 125 K[5]) are unexceptional and as expected for a formal oxidation state of +2.5 for the iron atoms. Similarly, the Mössbauer spectrum[11] of the $(Fe_2S_2(o,o'\text{-biphenolate})_2)^{2-}$ dimer (IS = 0.35 (2) mm/s, E_Q = 1.02 (1) mm/s, 77 K) is similar to those of other $(Fe_2S_2L_4)^{2-}$ complexes[1] that formally contain Fe(III).

The magnetic properties[13] of I indicate a spin-coupled structure ($\mu_{\text{eff}}{}^{\text{corr}} = 4.65\ \mu_B$, 295 K in CD_3CN[13] and the EPR spectrum at 8 K is very similar to that of the $(Fe_6S_6Cl_6)^{3-}$ cluster[5] and consistent with a $S = {}^1/_2$ magnetic ground state. The proton magnetic resonance spectra of I in CD_3CN solution at 293 K show isotropically shifted resonances, relative to the diamagnetic *p*-methylphenol,[12] at 5.52, −5.20, and −6.07 ppm respectively for the *o*-, *m*-, and *p*-CH_3 protons. The shift values are about twice as large as those reported[8] for the corresponding protons in the $(Fe_4S_4(OC_6H_4\text{-}p\text{-}CH_3)_4)^{2-}$ cluster, at 2.33, −2.23, and −2.77 ppm, (295 K), and increase in magnitude with increasing temperature as would be expected for intramolecular antiferromagnetic coupling.

As observed previously[5] for other $(Fe_6S_6L_6)^{3-}$ clusters, I readily undergoes oxidation. This oxidation in CH_2Cl_2 (E_{pa} = −0.102 V) is quasi-reversible[15] by cyclic voltammetric criteria (E = 184 mV) with a i_{pc}/i_{pa} ratio of ~1.0.

The chemical inertness of I, toward a transformation to the $[Fe_4S_4(OR)_4]^{2-}$ analogue may be a derivative of the relative thermodynamic and/or kinetic stability of the former. The apparent stability of I suggests that Fe/S clusters of hitherto unknown structures may be stabilized in proteins in a similar fashion by ligation to non-sulfur terminal ligands (i.e., tyrosine groups).

The unique Fe/Mo/S aggregate of nitrogenase may be such a cluster coordinated to the protein, at least partially, by oxygen and/or nitrogen terminal ligands. Such a proposal finds support in (a) an apparently small number of cysteinyl residues in the Fe–Mo protein of nitrogenase[16] and (b) in the Fe EXAFS analysis on the Fe–Mo cofactor of nitrogenase that shows an average of 1.2 ± 1.0 O (N) atoms at 1.81 (7) Å from the iron atoms.[17]

The chemical reactivity of I also indicates that, if analogous centers were present in certain Fe/S proteins, they would be extruded by thiophenol.[18] However, their identification would

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(9) Crystal data: Space group, $P2_1/a$, a = 13.173 (5) Å, b = 19.848 (10) Å, c = 14.304 (4) Å, β = 98.05 (3)°; Z = 2. Single-crystal, X-ray diffraction data were collected at 150 K on a Nicolet $P2_1$ four-circle diffractometer using Mo K radiaiton. The solution of the structure by a combination of heavy atom Patterson, direct methods, and Fourier techniques and refinement by full-matrix least-squares methods was based on 2107 unique reflections. Anisotropic temperature factors were used for the non-carbon atoms in the anion and the carbon atoms in the cations, the phehnyl rings in the anion were refined isotropically as groups. At the current stage of refinement with all atoms present in the asymmetric unit R = 0.072.

(10) Koch, A. A.; Millar, M. *J. Am. Chem. Soc.* **1982**, *104*, 5255.

(11) Coucouvanis, D.; Salifoglou, A.; Kanatzidis, M. G.; Simopoulos, A.; Papaefthymiou, V. *J. Am. Chem. Soc.* **1984**, *106*, 6081.

(12) Kanatzidis, M. G.; Baenziger, N. C.; Coucouvanis, D.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1984**, *106*, 4500.

(13) Determined by the NMR method.

(14) The diamagnetic values for the chemical shifts of the *p*-CH_3 and phenyl protons in *p*-$CH_3C_6H_4OH$ are 2.25 and 6.80 ppm, respectively.

(15) Cyclic voltammetry in CH_3CN on a Pt electrode with Bu_4NClO_4 as supporting electrolyte. Potentials are reported with SCE as a reference electrode.

(16) Haselkorn, R.; Lammers, J.; Rice, D.; Robinson, S. J. In "Advances in Nitrogen Fixation Research"; Veeger, C., Newton, W. E., Eds.; Nljhoff-Junk Pudoc Wageningen: Holland, **1984**; p 653.

(17) Antonio, M. R.; Teo, B. K.; Orme-Johnson, W. H.; Nelson, M. J.; Groh, S. E.; Lindahl, P. A.; Kanzlarich, S. M.; Averill, B. A. *J. Am. Chem. Soc.* **1972**, *104*, 4703.

(18) The reaction of I with PhSH in acetonitrile solution is instantaneous and the characteristic electronic spectrum of the $[Fe_6S_6(SPh)_6]^{3-}$ appears.[5b] This spectrum rapidly changes to that of the $[Fe_4S_4(SPh)_4]^{2-}$ cluster.

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.

Acknowledgment. This research was supported by a grant from the National Institutes of Health (No. GM-26671). X-ray equipment used in this research was obtained in part by Grant CHE-8109065 from the National Science Foundation.

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.

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(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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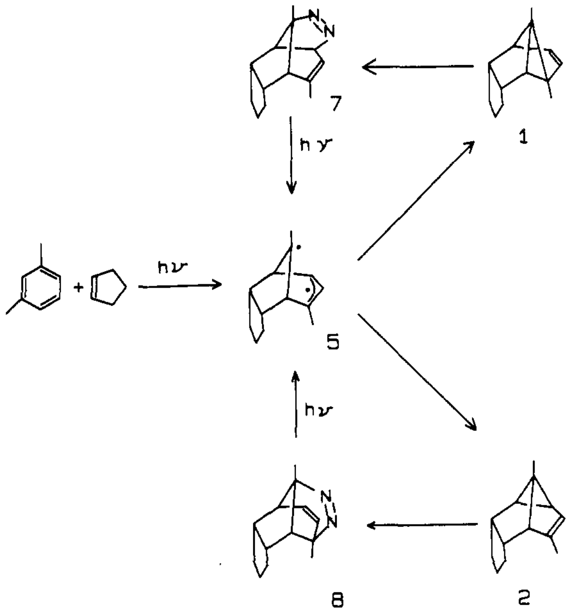
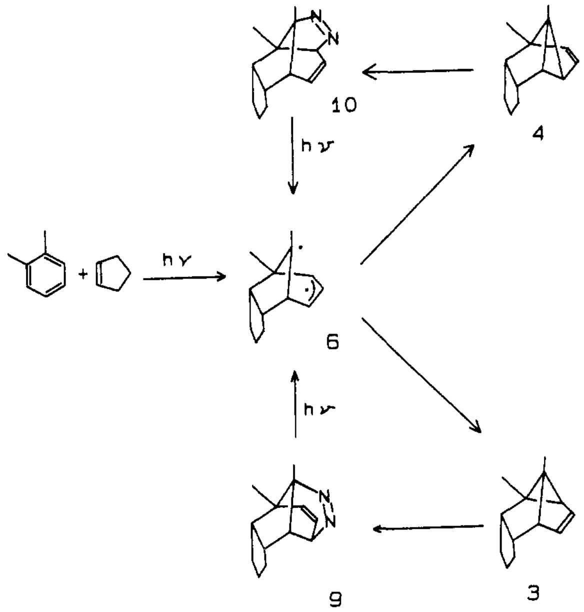
The meta photoaddition of aromatic compounds to olefins continues to fascinate mechanistic[1] and synthetic chemists.[2] Although the general regiochemistry of addition has been rationalized on the basis of frontier orbital overlap in exciplex intermediates,[3] subsequent mechanistic details are less 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 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 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-

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(1) Gilbert, A. *Pure Appl. Chem.* **1980**, *45*, 3139 and references therein.

(2) (a) Wender, P. A.; Howbert, J. J. *Tetrahedron Lett.* **1983**, *24*, 5325. (b) Wender, P. A.; Dreyer, G. B. *Tetrahedron Lett.* **1983**, *24*, 4543. (c) Wender, P. A.; Dreyer, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 5805. (d) Wender, P. A.; Howbert, J. J. *Tetrahedron Lett.* **1982**, *23*, 1983. (e) Wender, P. A.; Dreyer, G. B. *Tetrahedron* **1981**, *37*, 4445. (f) Wender, P. A.; Howbert, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 688. (g) Hoye, T. R. *Tetrahedron Lett.* **1981**, *22*, 2523.

(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.

(6) Cornelisse, J.; Merritt, V. Y.; Srinivasan, R. *J. Am. Chem. Soc.* **1973**, *95*, 6197.

(7) Structures were confirmed by ^{1}H 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.

0002-7863/85/1507-3360$01.50/0