

Table II. Temperature Effect on the Photooxidation of 1-Ethylthio-2-ethylhexene-1 in Acetone

Temp, °C	Relative yields, %	
	Dioxetane mode	Ene mode
56	55	45
20	78	22
-78	100	0

chloromethane (Table II). Under the reaction and analytical conditions, the products are neither isomerized nor destroyed. The surprising temperature dependency for singlet oxygen reaction probably fits a scheme in which the ene mode, which arises from the peroxide A of vinyl sulfide, stands at higher potential than the dioxetane mode—in contrast to vinyl ether in which dioxetane stands at higher potential than the ene mode by unfavorable stabilization of zwitterion B.

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Matrix Photolysis of 1,2,3-Thiadiazole. On the Possible Involvement of Thiirene

Sir:

The mechanism of the photolysis of 1,2,3-thiadiazole (1) and its derivatives is of considerable interest because of the seemingly unpredictable variation of product structure with changes in substituents^{1,2} and the possible involvement of thiirenes³ in these reactions. Based on chemical trapping experiments, Strausz³ has concluded that thiirenes are formed as intermediates in the photodecomposition of parent (1) and 5-methyl-1,2,3-thiadiazole. Other workers have proposed that thiadiazole photoproducts arise from reactions of diradicals^{1,2,4} and/or thioketenes. This communication describes direct evidence for the formation of thioketene (2) in the photolysis of 1 and implicates thiirene (3) as a precursor to the photoproduct ethynyl mercaptan (4).

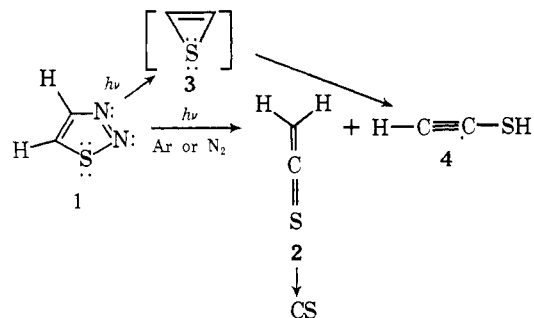


Table I lists the infrared bands observed upon irradiation with a medium-pressure mercury lamp of 50–80-mm samples of 1 (M/R ≡ host/guest ~500) in an argon or nitrogen matrix using Pyrex filtered light. The most intense band (1760 cm⁻¹) in the spectrum of

(1) W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **614**, 4 (1958).

(2) K.-P. Zeller, H. Meier, and E. Müller, *Tetrahedron Lett.*, 537 (1971); *Justus Liebigs Ann. Chem.*, **766**, 32 (1972).

(3) O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 4806 (1967).

(4) P. Krauss, K. P. Zeller, H. Meier, and E. Müller, *Tetrahedron*, **27**, 5953 (1971).

Table I. Infrared Bands Resulting from the Irradiation of 1,2,3-Thiadiazole- d_0 , d_1 , and d_2 ^k

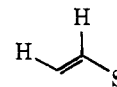
Photolyzed 1		Photolyzed 5 or 6		Photolyzed 1,2,3-thiadiazole- d_2	
(cm ⁻¹)	Assignment	(cm ⁻¹)	Assignment	(cm ⁻¹)	Assignment
3320 ^b (s)	≡C—H str	3320 ^a (m)	≡C—H str	2580 ⁱ (s)	≡C—D str
3010 ^a (w)	≡C< ^H _H str	3060 ^f (w)	≡C< ^H _D str	2240 ⁱ (s)	≡C< ^D _D str
2600 ^b (vw)		2638 ^h (vw)		1925 ⁱ (vw)	C≡C str
2060 ^b (vw)	C≡C str	2585 ^h (m)	≡C—D str	1835 ⁱ (vw)	S—D str
1840 ^d (m)		2270 ^f (s)	≡C< ^H _D str	1735 ⁱ (vs)	C=C str
1760 ^a (vs)	C=C str	2060 ^g (vw)	C≡C str	860 ⁱ (w)	CD ₂ def
1410 ^d (w)		1925 ^h (vw)	C≡C str	725 ^d (w)	
1320 ^a (m)	C=S str	1835 ^g (vw)	S—D str	560 ⁱ (s)	CD ₂ rock
1110 ^d (w)		1760 ^f (vs)	C=C str	430 ^f (m)	≡C—D bend ⊥ to plane
960 ^d (w)		1210 ^f (w)	C=S str		
850 ^a (w)	CH ₂ wag	1110 ^d (w)			
700 ^a (m)	CH ₂ rock	960 ^d (vw)			
690 ^{c,e} (s)		870 ^f (w)	C< ^H _D def		
660 ^b (w)	≡C—H bend to plane	770 ^d (w)			
560 ^b (m)	≡C—H bend ⊥ to plane	680 ^d (w)			
400 ^a (vw)	C=C=S bend	640 ^f (m)	C< ^H _D rock		
		630 ^e (s)			
		560 ^g (m)	≡C—H bend ⊥ to plane		
		430 ^h (w)	≡C—D bend ⊥ to plane		

^a Assigned to thioketene- d_0 2. ^b Assigned to ethynyl mercaptan 4. ^c Does not appear in nitrogen matrices. ^d Weakness of these bands precludes a definite assignment at this time. ^e Decreased upon warming to 50°K in argon. ^f Assigned to thioketene- d_1 . ^g Assigned to ethynyl mercaptan 7. ^h Assigned to ethynyl mercaptan 8. ⁱ Assigned to thioketene- d_2 . ^j Assigned to ethynyl mercaptan- d_2 . ^k Bands due to 4 are relatively weaker than those due to 2 in nitrogen and carbon monoxide matrices.

products is assigned to 2, based upon a previous report by Howard⁵ and the similar positions of the C=C stretch of known thioketene derivatives.⁶⁻⁹ Bands at 3010, 1320, 700, and 400 cm⁻¹ are also attributed to 2 because of the similarity of their intensity vs. time plots, to the 1760 cm⁻¹ absorption. The correctness of these assignments is most clearly evident upon photodecomposition ($\lambda > 220$ nm) of 2 which results in the formation of carbon monosulfide (1520 cm⁻¹)^{10,11} and loss of the thioketene spectra. Photolysis of either d_1 - or d_2 -thioketene (*vide infra*) yielded the same band at 1520 cm⁻¹, of similar intensity.

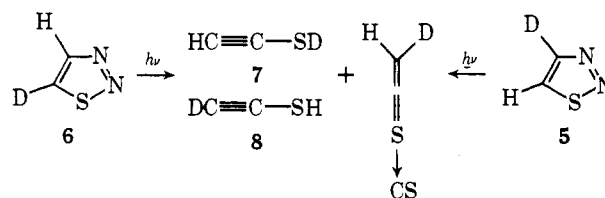
Another photoproduct, that can be differentiated from 2 because of its resistance to photodecomposition, possesses bands at 3320 (≡C—H str) and 2060 cm⁻¹ (C≡C str), which are suggestive of acetylenic functionality. This species is assigned the ethynyl mercaptan structure 4 because of the similarity of its bands to those of methyl ethynyl sulfide¹² (≡C—H str, 3329 cm⁻¹) and

(C≡C str, 2059 cm⁻¹). The possibility of thiirene 3 or an open form



giving rise to these observed bands seems unlikely¹³ because of the invariance of the position of the 3320-cm⁻¹ band in the product spectrum of 5 or 6. The appearance of a band at 2585 cm⁻¹ (≡C—D str)^{12a} in the product spectrum of 5 or 6, which is more intense in the photolysate of 1- d_2 , fortifies our assignment.

Measurement of the growth rates of bands of comparable intensity in the spectra of 2 and 4 indicate that these species are increasing at a similar rate.¹⁴ Photolysis of 4-deuteriothiadiazole¹⁵ (5) or its 5-isomer



(5) E. G. Howard, Jr. (U.S. Patent 3,035,030 (1962)), *Chem. Abstr.*, 57, 13617f (1962), reported the synthesis of thioketene, but cited only a band in the infrared (1755 cm⁻¹) as evidence of structure. Thioketene polymerizes above -80°.

(6) M. S. Raasch, *J. Chem. Soc., Chem. Commun.*, 577 (1966).

(7) E. U. Elam, F. H. Rash, J. T. Dougherty, V. W. Goodhett, and K. C. Brannock, *J. Org. Chem.*, 33, 2738 (1968).

(8) M. S. Raasch, *J. Org. Chem.*, 35, 3470 (1970); 37, 1347 (1972).

(9) G. Seybold, *Tetrahedron Lett.*, 555 (1974).

(10) (a) R. Steudel, *Naturforschung*, 21B, 1106 (1966). (b) No bands attributable to methylene were observed, but this species has proved to be difficult to detect in previous matrix experiments. (c) See C. B. Moore, G. C. Pimentel, and T. D. Goldfarb, *J. Chem. Phys.*, 43, 63 (1965). (d) H. E. Hallam, Ed., "Vibrational Spectroscopy of Trapped Species," Wiley, New York, N. Y., p 192.

(11) D. Little and R. J. Donovan, *J. Photochem.*, 1, 371 (1972/73), have observed CS formation in studies of the addition of sulfur atoms to acetylene but claim the molecule arises from the photoexcitation of acetylene.

(12) (a) A. G. Moritz, *Spectrochim. Acta, Part A.*, 23, 167 (1967), has observed a shift of the mode at 3329-2590 cm⁻¹ upon deuteration of methyl ethynyl sulfide; (b) D. H. Christensen and D. den Engelsens, *ibid.*, 26, 1747 (1970).

(13) (a) That the 3320-cm⁻¹ band corresponds to a C—H stretch is confirmed by the shift of this mode to 2585 cm⁻¹ in the spectrum of photolyzed 1,2,3-thiadiazole- d_2 . (b) For example, vinyl hydrogens in cyclopropene are coupled by 35 cm⁻¹, G. L. Closs, *Advan. Alicyclic Chem.*, 1, 72 (1966).

(14) Increase of the M/R ratio had no observable effect on the course of photolysis of the thiadiazole.

(15) This isomer was prepared by a modification of a procedure of C. D. Hurd and R. I. Mori, *J. Amer. Chem. Soc.*, 77, 5359 (1955).

(6)¹⁶ gives products whose spectra contain absorption characteristic of $\equiv\text{C}-\text{H}$ (3320 cm^{-1}) and $\equiv\text{C}-\text{D}$ (2585 cm^{-1}) stretches.^{12a} At even low photoconversions, the spectrum of products from the irradiation of **5** is virtually identical with the spectrum of products from **6**. A most significant point is that the isotopic species **7** and **8** are formed in the same ratio from the irradiation of either **5** or **6**.

Under the conditions of the photolysis, 4- and 5-deuteriothiadiazole are not interconvertible, and, hence, this potential isomerization is not responsible for the production of the mixture of ethynyl-*d*₁ mercaptans **7** and **8**.¹⁷ Photolysis of parent **1**, embedded in an acetylene-*d*₂ host, leads to thioketene-*d*₀ **2** ($\text{C}=\text{C}$ str, 1760 cm^{-1}), lacking detectable amounts of thioketene-*d*₂ ($\text{C}=\text{C}$ str, 1735 cm^{-1}). Thus, a hypothetical pathway involving trapping of sulfur atoms by acetylene to give products can be eliminated.¹⁸ The most economical tentative interpretation of our observations with parent and labeled **1** involves the intervention of a symmetrical species, most likely thiirene, from which **7** and **8** are derived.

Acknowledgment. We gratefully acknowledge support of this research from a grant made available by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(16) R. S. Olofson, J. M. Landesberg, K. N. Houk, and J. S. Michelman, *J. Amer. Chem. Soc.*, **88**, 4265 (1966).

(17) (a) Products **2** and **4** do not interconvert under our experimental conditions. (b) 1,3,4-Thiadiazole is stable to our photochemical conditions, but with $\lambda > 220\text{ nm}$ gives hydrogen cyanide as a major product.

(18) We have also established that photolysis of ethylene sulfide in carbon monoxide matrices leads to carbonyl sulfide, suggesting that solid carbon monoxide can act as a trap for sulfur atoms. Photodecomposition of **1** to **2** and **4** in a matrix of carbon monoxide ($M/R \sim 200$) is not accompanied by carbonyl sulfide.¹⁹ This result gives support to our contention that sulfur atoms are not being formed from **1**.

(19) Nor is the formyl radical [D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **51**, 277 (1969)] formed, which indicates that hydrogen atoms are not playing a detectable role in our system.

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Preparation of *B*- σ -Metallocarboranes by Oxidative Addition. Model Intermediates for Transition Metal Catalyzed Hydrogen-Deuterium Exchange in Boron-Hydrogen Containing Species

Sir:

The recent report of transition metal catalyzed exchange of deuterium gas with hydrogen at terminal B-H bonds in a wide variety of boron compounds¹ postulated intermediates formed by oxidative addition of the B-H bonds to a transition metal complex. Stable *B*- σ -metallocarboranes have now been prepared in this manner which presage the existence of a new area in metallocarborane chemistry.

Slow addition of hexane to a cooled solution prepared by heating $(\text{PPh}_3)_3\text{IrCl}$ with a threefold excess of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ in toluene at the reflux temperature produced a small quantity ($\sim 5\%$) of yellow crystals, **I**. Further addition of hexane precipitated the major

(1) E. L. Hoel and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 4676 (1974).

product, $\text{Ir}(\text{PPh}_3)_2[(o\text{-C}_6\text{H}_4)\text{PPh}_2]\text{HCl}$, the result of intramolecular ortho metalation in $(\text{PPh}_3)_3\text{IrCl}$.² The infrared spectrum (Nujol mull) of **I** exhibited a strong band at 2560 cm^{-1} assigned to ν_{BH} and a pair of sharp, medium intensity bands at 2209 and 2199 cm^{-1} assigned to ν_{IrH} . The 251-MHz ¹H nmr spectrum (in CD_2Cl_2) consisted of resonances in the τ 2.0–2.8 region assigned to coordinated PPh_3 , a typically broad carboranyl C-H singlet at τ 7.29, and a 1:2:1 triplet at τ 28.08 ($J_{\text{PIrH}} = 14.3\text{ Hz}$), assigned to the hydride. The 80.53-MHz ¹¹B nmr spectrum (Figure 1a) consisted of an unresolved set of broad, overlapping resonances between 0.0 and +20.0 ppm (from $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$) of relative area 9.1 and a broad singlet (width at half-height *ca.* 300 Hz) at +34.4 ppm of relative area 0.9.

On the basis of the spectral data, **I** was formulated as a five-coordinate complex of iridium(III) bonded to two triphenylphosphine ligands, a hydride, a chloride, and a carboranyl moiety σ -bonded through a boron atom. Chemical analysis confirmed the empirical formula. The stereochemistry about iridium was postulated to be a trigonal bipyramid with the bulky triphenylphosphine and carboranyl ligands in the trigonal plane. Support for this assignment is provided by both the ir and ¹H nmr spectra. The symmetrical hydride triplet is consistent with two equivalent phosphines cis to the hydride, and the chemical shift and position of ν_{IrH} are consistent with chloride trans to the hydride.³ Although a square pyramidal structure with an axial hydride would also have phosphines cis to the hydride, Shaw and coworkers have shown that such species exhibit ν_{IrH} at about 2000 cm^{-1} and the hydride resonance at about τ 60.⁴

The position of substitution on the carborane cage is not readily apparent from the ¹¹B nmr spectrum. The singlet at +34.4 ppm clearly represents the boron atom to which the metal is bonded, but the remainder of the spectrum cannot be readily assigned, except to note the general similarity to the spectrum of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ (Figure 1b), allowing for small shifts and extensive line broadening.⁵ However, the existence of only one carboranyl C-H resonance in the ¹H nmr spectrum requires the metal to be substituted on the plane of symmetry between the carbon atoms, *i.e.*, at either B(3,6) or B(8,10). On the basis of the results of transition metal catalyzed deuterium exchange on 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$, which indicated that the order of deuterium incorporation follows the nucleophilic substitution pattern $\text{B}(3,6) > \text{B}(4,5,7,11) > \text{B}(8,10) > \text{B}(9,12)$,¹ the position of substitution would be expected to be B(3,6). This was later confirmed (*vide infra*). The proposed structure of **I**, 3- $[(\text{PPh}_3)_2\text{IrHCl}]-1,2\text{-C}_2\text{B}_{10}\text{H}_{11}$ is shown in Figure 1.

It seemed probable that **I** was formed either by oxidative addition of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ to $(\text{PPh}_3)_3\text{IrCl}$ followed by loss of PPh_3 or by prior dissociation of PPh_3 followed by oxidative addition to $(\text{PPh}_3)_2\text{IrCl}$. In either case,

(2) M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

(3) E. L. Muetterties, "Transition Metal Hydrides," Marcel Dekker, New York, N. Y., 1971.

(4) C. Masters, B. L. Shaw, and R. E. Stainbank, *J. Chem. Soc., Dalton Trans.*, 664 (1972).

(5) The nature of the relaxation phenomena responsible for the broadening is not known but is probably not due to paramagnetic impurities since the spectra are reproducible and the ¹H nmr spectra are not affected. Similar broadening was observed for **II**, **III**, and triphenylarsine analogs.