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Characterization of Matrix-Isolated Antiaromatic Three-Membered Heterocycles. Preparation of the Elusive Thiirene Molecule

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Abstract: The preparation and characterization of thiirene (**4**), a heterocyclic analogue of cyclobutadiene (**1**), which is derived from the photolysis of 1,2,3-thiadiazole (**5**), is described. The methodology exploits the C_{2v} symmetry of the species **4** and utilizes isotopic labeling to aid in the characterization and narrow band-pass filters to protect thiirene from reaction with light of $\lambda > 2700$ Å, when it is generated photochemically. The evidence for **4** is based on (1) the fact that the same monolabeled species [^{13}C]X is formed from distinctly labeled [^{13}C]-1,2,3-thiadiazoles, (2) the photoisomerization of labeled X to ethynyl mercaptan and thioketene both with randomized label, and (3) the likelihood that the observed infrared bands attributed to **4** belong to a single species possessing cyclopropenoid character. In addition to thiirene, ethynyl mercaptan (**14**) and thioketene (**15**) are derived from **5**. There are thus two paths ($\lambda > 2900$ Å) originating from **5** which give rise to **14** and **15**. One stems from thiadiazole without the intervention of **4** and does not scramble hydrogens or carbons; the other is mediated by thiirene, which necessarily makes the C–H bonds equivalent. Irradiation ($\lambda \sim 3500$ Å) of doubly labeled [^{2}H,^{13}C] thiirene gives all four possible ethynyl mercaptans, indicating at least one exchange of hydrogens between carbon atoms must occur. The most reasonable explanation for this exchange presumes that both hydrogens reside on a single carbon atom at some point during the photoisomerization of thiirene to ethynyl mercaptan (**14**).

Introduction

The stabilization and characterization of cyclic 4π-electron systems has been a problem of long-standing interest, embodied in the quest for the prototype antiaromatic, cyclobutadiene (**1**), the object of a century-long search.[1] Until 1972, no direct physical evidence of structure had been obtained for cyclobutadiene or any closely related derivative or analogue. Subsequently, the matrix isolation technique[2-4] permitted the unambiguous detection of **1**, its characterization by isotopic labeling, a determination of its photochemical (formation of acetylene) and thermal products, and made credible its status as an experimental observable.[5,6]

A considerable challenge is to further extend this technique to the stabilization of molecules which are not only bimolecularly reactive but are also prone to structural rearrangement or fragmentation (unimolecularly reactive species).

The heterocyclic analogues of cyclobutadiene, oxirene (**2**), azirene (**3**), and thiirene (**4**) are of considerable theoretical interest as models of antiaromatic molecules.[7] Because they are systems under the combined stress of ring strain and electronic destabilization, they should exhibit exceptional reactivity and may be difficult to stabilize when generated photochemically.

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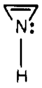

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The current work describes a methodology for the preparation and unambiguous characterization of such molecules. A preliminary report has been published by us[8] detailing the key findings which establish thiirene (**4**) as the first simple heterocyclic analogue of cyclobutadiene to be stabilized and characterized. Having defined the conditions that must be met in order to generate and preserve **4**, we have thus provided a procedure for the routine matrix isolation of thiirenes. Strausz has since confirmed our initial findings[9-11] and has reviewed the field.[12]

Prior to these reports, the prognoses for stabilizing molecules **2**–**4** were not optimistic.[13-17] New calculations bearing on the vibrational spectra and structure of thiirene have since appeared.[18,19]

Selection of Precursors

Argon matrix-isolated 1,2,3-thiadiazole (**5**), isothiazole (**6**), and thiazole (**7**) all release a C_2H_2S fragment upon photolysis. The

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(1) For reviews of the many important contributions preceding matrix isolation of **1**, see: (a) Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343; (b) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425; (c) Cava, M. P.; Mitchell, M. J. "Cyclobutadiene and Related Compounds"; Academic Press; New York, 1967.

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(6) (a) Masamune, S.; Sunto-Bachiller, F. A.; Machiguchi, T.; Bertie, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 4889. (b) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *Ibid.* **1973**, *95*, 614. (c) Chapman, O. L.; DeLa Cruz, D.; Roth, R.; Pacansky, J. *Ibid.* **1973**, 1337.

(7) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.

(8) (a) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1977**, *99*, 4842. (b) *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 16. (c) *J. Org. Chem.* **1979**, *44*, 2730. (d) *J. Labelled Compd. Radiopharm.* **1979**, *75*, 697. (e) Laureni, J.; Krantz, A.; Hajdu, R. A. *J. Am. Chem. Soc.* **1976**, *98*, 7872. (f) Krantz, A.; Laureni, J. *Ibid.* **1974**, *96*, 6768.

(9) Torres, M.; Clement, A.; Bertie, J. E.; Gunning, H. E.; Strausz, O. P. *J. Org. Chem.* **1978**, *43*, 2490.

(10) Torres, M.; Clement, A.; Gunning, H. E.; Strausz, O. P. *Nouv. J. Chim.* **1979**, *3*, 149.

(11) Torres, M.; Safarik, I.; Clement, A.; Bertie, J. E.; Strausz, O. P. *Nouv. J. Chim.* **1979**, *3*, 365.

(12) Torres, M.; Lown, E. M.; Strausz, O. P. *Heterocycles* **1978**, 11, 697.

(13) Zahradnik, R. *Adv. Heterocycl. Chem.* **1965**, *5*, 14.

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(15) Clark, D. T. *Int. J. Sulfur Chem., Part C* **1972**, *7*, 11; *Theor. Chim. Acta* **1969**, *15*, 225.

(16) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 3907.

(17) Although calculations by: Dewar, M. J. S.; Ramsden, C. A. *J. Chem. Soc., Chem. Commun. 1973*, 688 pointed toward more stable ground states **2**–**4** than others had predicted, more advanced calculations are in progress. Dewar, M. J. S., private communication, Mexico City, Mexico, Dec 1975.

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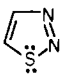

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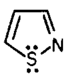

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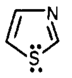

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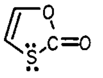

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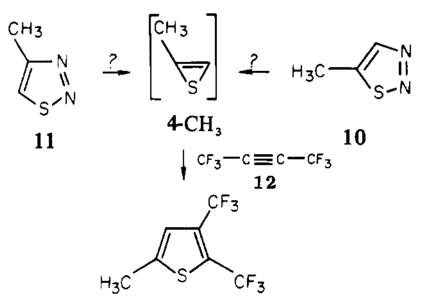
thiadiazole (**5**) is the most useful precursor because it is decomposed rapidly[20] and its absorption spectrum allows the photodecomposition to be studied over select regions of the ultraviolet spectrum (285–315 nm), thereby minimizing competition from secondary and higher order photoreactions. Heterocycles **8** and **9** split out fragments other than C_2H_2S species. 1,3,4-Thiadiazole (**8**) extrudes hydrogen cyanide,[8e] whereas **9** fissions to primarily carbon monoxide[21] rather than carbon dioxide.

1,2,3-Thiadiazole (**5**) and its 5-methyl derivative (**10**) have been previously explored photochemically by Strausz, Gunning, and co-workers[22] as a means of entry to the thiirene system. Only acetylene, polymer, carbon disulfide in the case of the parent, and corresponding products for **10** were observed. Meier, Müller, and Zeller,[23] however, were unable to confirm these findings, as they could not detect acetylenes in either gas-phase or in solution photolysis of **5** and **10**. Photolysis of either 5- or 4-methyl-1,2,3-thiadiazole, **10** or **11**, respectively, in the presence of perfluorobutyne-2 (**12**) yielded 2,3-bis(trifluoromethyl)-5-methylthiophene (**13**) as the sole thiophene product (eq 1).[22] This experiment confirms the intermediacy of a species common to both reactions, but a precise and unambiguous interpretation is clouded by our ignorance of the behavior of **12** with alternative C_2H_2S species. Neither the chemistry of ethynyl mercaptan (**14**) nor that of thioketene (**15**) with **12** has been investigated. Attempts at the preparation of **4** involving addition of sulfur atoms to acetylene suffer from similar ambiguities.

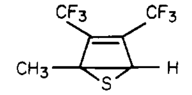


(1)

11 4-CH_3 10 12 13

$HC{\equiv}CSH$ **14** $H_2C{=}C{=}S$ **15**

A provocative aspect of the trapping experiments is the specificity of thiophene formation, which is formally derived by addition of **12** across the less substituted σ bond of the thiirene ring. This reaction is unprecedented for intact cyclopropenes, which react at the π bond in cycloadditions. Since the potential adduct **16** is unknown and the material balance for the photolysis of **10** has not been accounted for fully, it may be risky to speculate.



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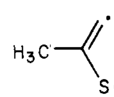
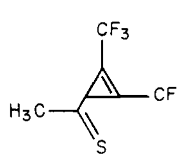
Regardless, the trapping experiments leave the matter of the *intermediacy* of thiirene open, because **4**-CH_3 could have been a relative maximum, with the product thiophene being derived from preferential capture of the diradical **17a** (or the corresponding dipolar form)[24a] or from isomerization of **17b**.

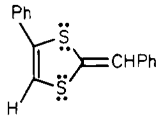


17a



17b

There are also precedents for photochemical reactions of more complex thiadiazoles. Kirmse and Horner[25] studied the photolysis of thiadiazoles with aromatic substituents. They reported the products to be the 1,4-dithiofulvene **18** from 5-phenyl-1,2,3-thiadiazole (**19**) and obtained more complicated mixtures which included 1,4-dithiins **20** and thiophenes from the disubstituted thiadiazoles. Their work was expanded by Zeller, Meier, and Müller[23] to cover a broader range of derivatives as well as the parent. Both Kirmse and Müller rationalized their results by a diradical formalism. Huisgen has emphasized the 1,3-dipolar character of such intermediates.[24a]



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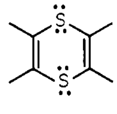

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Recent evidence has been presented bearing on the formation of thiirenes,[24] during the solution-phase photolysis of thiadiazoles,[24b] from attempts to trap metal complexes of **4**,[24c,d] and during the pyrolysis of thiadiazoles.[26,28] Derivatives of thiirene have also been invoked in a variety of circumstances.[24e–i] Carpino[24j] has prepared diphenyl thiirene sulfoxide and thiirenium salts have been found to be stable species.[24k] The relevance of these higher valent sulfur compounds to the parent thiirene or the question of antiaromatic character is yet uncertain.

Pyrex-Filtered Photolyses of 1,2,3-Thiadiazole (5). Preliminary studies[8f] indicated that two major products were formed (whose bands are listed in Table I) when **5** was irradiated with Pyrex-filtered light ($M/R \approx 500$). The most intense band of the spectrum, centered at 1755 cm^{-1}, is typical of thioketene (**15**), which has been identified in the thermal decomposition[27a] of **5**, since our original report. Unambiguous support for our assignment comes from microwave spectra which provide direct proof that the substance possessing bands at 3010, 1755, 1322, and 692 cm^{-1} is thioketene.[28] The product ethynyl mercaptan (**14**) exhibits absorption characteristic of an ethynyl group, 3315, 2065, and

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[20] For example, with a 2500-Å interference filter or a Pyrex filter ($\lambda >$ 2850 Å), using a 1000-W Hg-Xe lamp, 40–50-mm samples of **5** in argon ($M/R \approx 500$) are >90% decomposed in 40–60 min.

[21] Krantz, A.; Huang, B. S.; Laureni, J., unpublished results.

[22] (a) Strausz, O. P.; Font, J.; Dedio, E. L.; Kebarle, P.; Gunning, H. E. *J. Am. Chem. Soc.* **1967**, *89*, 4805. (b) Strausz, O. P. *IUPAC Suppl.* **1971**, *4*, 186; (c) See: Font, J.; Torres, M.; Gunning, H. E.; Strausz, O. P. *J. Org. Chem.* **1978**, *43*, 2487 for a recent account.

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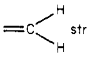
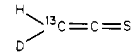
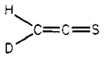
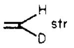
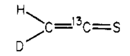
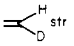
[26] Schaumann, E.; Ehlers, J.; Mrotzek, H. *Justus Liebigs Ann. Chem.* **1979**, 1734. Schaumann, E.; Ehlers, J.; Förster, W.-R.; Adiwidjaja, G. *Chem. Ber.* **1979**, *112*, 1769.

[27] (a) Seybold, G.; Heibl, C. *Chem. Ber.* **1977**, *110*, 1225; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 248. (b) Seybold, G. *Ibid.* **1977**, *16*, 365. (c) See also: Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1975**, *58*, 142. (d) Georgiou, K.; Kroto, H. W.; Landsberg, B. M. *J. Chem. Soc., Chem. Commun.* **1974**, 739 have detected thioketene by using microwave spectroscopy. (f) Bock, H.; Solouki, B.; Bert, G.; Rosmus, P. *J. Am. Chem. Soc.* **1977**, *99*, 1663 have recorded photoelectron spectra of **15** generated by pyrolysis of **5**.

[28] Børge, B.; Nielsen, O. J.; Svanholt, H.; Holm, A.; Toubro, N. H.; Krantz, A.; Laureni, J. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 161.

Table I. Infrared Bands of Argon Matrix-Isolated Thioketenes and Ethynyl Mercaptans (cm^{-1})[a]

$H_2C{=}C{=}S$ **15**	3010 (m)		$H_2C{=}^{13}C{=}S$ **34**	3042 (m)	 **66**	3050
	1840 (m)			1822 (m)		2259
	1755 (vs)	C=C str		1713 (vs)		1741
	1410 (w)			1418 (w)		686
	1322 (m)			1322 (m)		619
	692 (s)			695 (s)		
 **25**	3065		$H_2{}^{13}C{=}C{=}S$ **33**	3005 (m)	 **65**	3059
				1822 (m)		
	2273			1737 (vs)		2269
	1760	C=C str		1315 (m)		1730
	626			689 (s)		1696
						860
						680
						624
$HC{\equiv}C{-}SH$ **14**	3315	≡C–H str	$DC{\equiv}C{-}SH$ **27**	2589	$H^{13}C{\equiv}C{-}SH$ **31**	3300
	2575 (vw)	S–H str		2572		2575
	2065 (w)	C≡C str		436		2040
	1112 (m)					1105
	959 (w)					958
	558 (w)	≡C–H bend ⊥ to plane				555
$HC{\equiv}C{-}SD$ **26**	3315	≡CH str	$DC{\equiv}C{-}SD$	2585	$HC{\equiv}^{13}C{-}SH$ **32**	3315
	2065	C≡C str		2058		2575
	1110			436		1112
	555	≡CH bend ⊥ to plane				960
						560

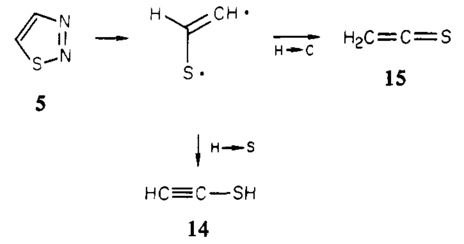
[a] The only bands listed in this table are those which can be followed kinetically using a Perkin-Elmer 180 spectrophotometer to monitor photolysate from samples with $M/R = 500\text{–}1000$. Initially 40–60 mm of sample was deposited at 20 K.

558 cm^{-1} having bands in common with ethynyl sulfides.[29] Intensity vs. time plots of bands of comparable intensity of **14** and **15** show that these species are increasing at a similar rate. After **5** is completely photodecomposed (8 K, $M/R = 500$, 40 mm, ~60 min, 100-W lamps) the spectrum of photolysate no longer changes with time, suggesting that both thioketene and ethynyl mercaptan are stable to Pyrex-filtered light. Compelling evidence for this conclusion are the facts that (1) thioketene (matrix isolated from the thermal decomposition of **5** in argon) is unchanged by Pyrex-filtered light and (2) Pyrex filtered irradiation of a mixture containing 90% randomized ^{13}C-ethynyl mercaptan and 80% unrandomized ^{13}C-thioketene does not lead to redistribution of the label (vide infra). Hence a photostationary state between **14** and **15** is not being established.

Thioketene can be selectively destroyed (bare lamp photolyses or 2200-Å interference filter) in the presence of ethynyl mercaptan. Thus, an isomer specific assignment of infrared bands can be made by observing spectral changes as the photodecomposition of **15** progresses. A product of the photolysis from thioketene (**15**) appears to be carbon disulfide (**21**) [based upon the effect of ^{13}C (shift to 1485 cm^{-1}) and the lack of an effect of deuterium substitution on the 1520-cm^{-1} band observed upon destruction of thioketenes]. Interestingly, Strausz and co-workers observed **21** during the gas-phase photodecomposition of **5**. We speculate carbon disulfide may be produced from small amounts of matrix-isolated thiadiazole dimers or perhaps by reaction of sulfur atoms or carbon monosulfide if short-range diffusion is promoted by local melting. Reducing the concentration of **5** lowers the yield of CS_2.

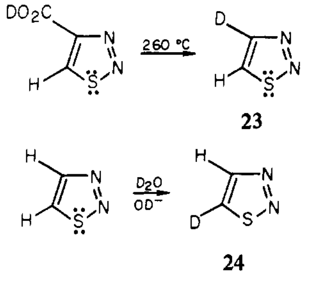
A simple picture which unites the products **14** and **15** through a common intermediate is drawn below[30] (Scheme I). To determine if thiadiazole and products are connected only by open forms of C_2H_2S and not by cyclic species like thiirene **4** and the

Scheme I

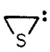


(2)

Scheme II



carbene **22** which possess only one type of hydrogen, we synthesized (Scheme II) and photolyzed the deuterated isomers **23** and **24**.



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Irradiation of either deuterated isomer by using Pyrex-filtered light produces monodeuteriothioketene (**25**), and both $HC{\equiv}C{-}SD$ (**26**) and $DC{\equiv}C{-}SH$ (**27**) in a constant ratio as judged by the relative intensities of bands (HC str/DC str ≈ 1.7). Clearly a more complex sequence of intermediates than that indicated in eq 2 is involved in the photodecomposition.

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(29) Moritz, A. G. *Spectrochim. Acta, Part A* **1967** *23A*, 167. Christensen, D. H.; den Engelsen, D. *Ibid.* **1970**, *26A*, 1747.

(30) The multiplicity and geometry of the intermediate is unspecified in this picture.

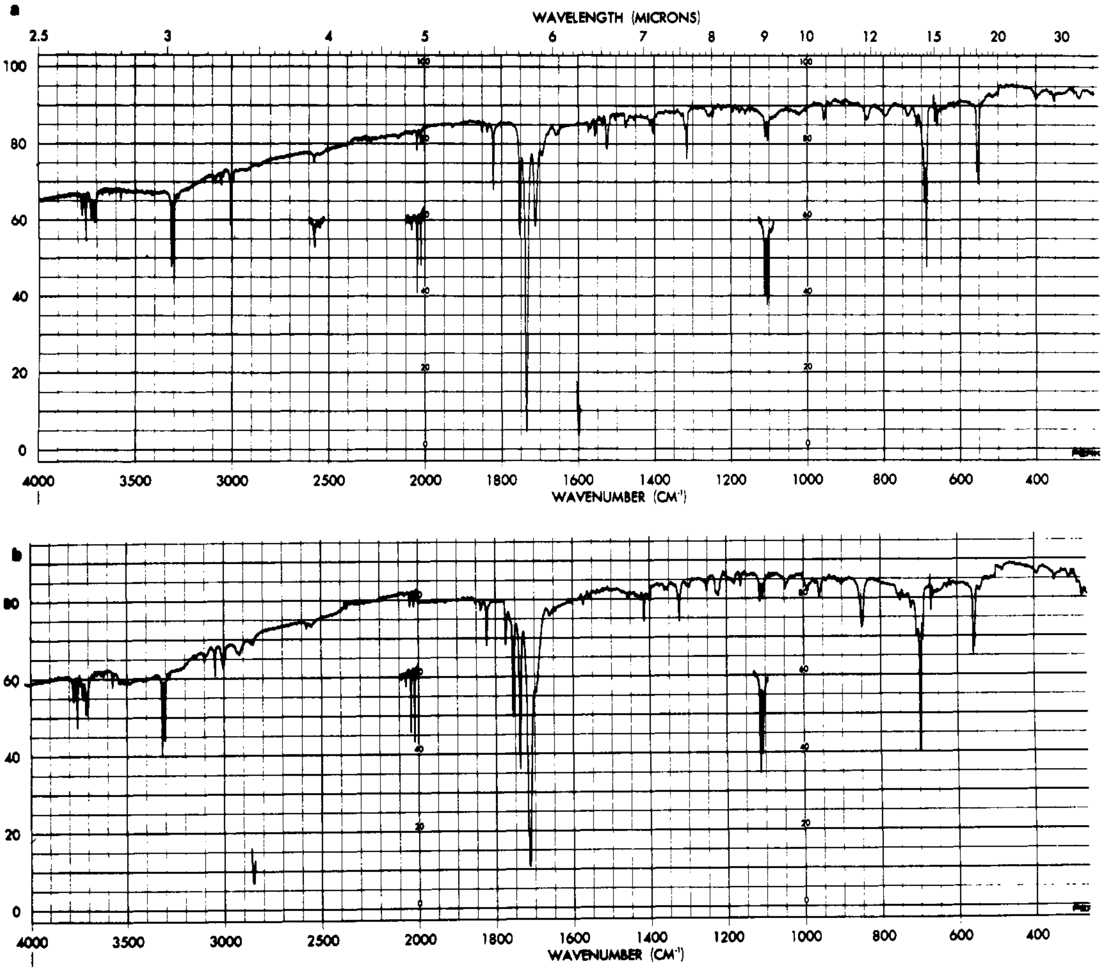
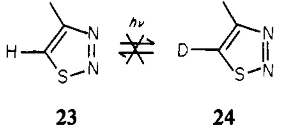


Figure 1. (a) Infrared spectrum of argon matrix-isolated [4-^{13}C]-1,2,3-thiadiazole (**29**, 90% ^{13}C) after irradiation with Pyrex-filtered mercury lamp light for 75 min. [2-^{13}C]-Thioketene (**33**), [1-^{13}C]thioketene (**34**), [2-^{13}C]ethynyl mercaptan (**31**), and [1-^{13}C]ethynyl mercaptan (**32**) are the observed products as well as their unlabeled variants (10%). See Table I for assignments. (b) Infrared spectrum of argon matrix-isolated [5-^{13}C]-1,2,3-thiadiazole (**30**, 90% ^{13}C) after irradiation with Pyrex-filtered mercury lamp light for 75 min.

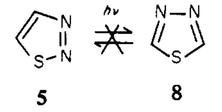
A number of controls are needed to ensure that the formation of two monodeuterated ethynyl mercaptans is a property of the pathway connecting thiadiazole to **14** and not a consequence of scrambling of the label in starting material or product. Phototranspositions of atoms in sulfur heterocycles are well-known reactions and have been observed for thiazoles and isothiazoles.[31]

The fact that **23** and **24** photodecompose at similar rates and possess mutually distinct intense bands (800 and 595 cm^{-1}, respectively) means that the formation of **23** in the presence of **24** can be easily ascertained from the IR spectrum. Since bands of **23** are not detected during the photolysis of **24**, and vice versa, we conclude that these isomers are not interconverting (eq 3 and 4).



23 **24**

(3)

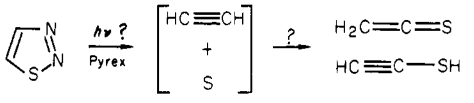


5 **8**

(4)

Whereas thiadiazole **5** is photodecomposed by Pyrex-filtered light, 1,3,4-thiadiazole (**8**) is stable and cannot be invoked as an intermediate to explain randomization of the label. Other thiadiazoles would be expected to exhibit similar stability under said conditions.[32,33] Hence, phototranspositions of the ring atoms are not responsible for the randomization.

The possibility that products arise from recombination of photochemically generated sulfur atoms with acetylene can be explored in two ways (eq 5).



5

(5)

If reactive sulfur atoms are formed from **5** and combine with acetylene to give products, the irradiation of **5** in a matrix of acetylene-d_2 (**28**) should produce S atoms in an environment dominated by **28**, leading to predominantly C_2D_2S products. The fact that only C_2H_2S products are formed from **5**, matrix isolated in dideuterioacetylene (23 mm, M/R = 500–1000, 20 K), is evidence against sulfur atom formation. Photolysis of **5**, matrix isolated in carbon monoxide, generates **14** and **15**, but no spectral evidence for carbonyl sulfide[34] or the formyl radical HCO[35] is obtained. These observations support the contention that neither free sulfur atoms nor hydrogen atoms play a major role in the Pyrex-filtered photodecomposition of **5**. (With light of shorter

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(31) Lablache-Combier, A. "Photochemistry of Heterocyclic Compounds"; Buchardt, O., Ed.; Wiley: 1976; Chapter 3.

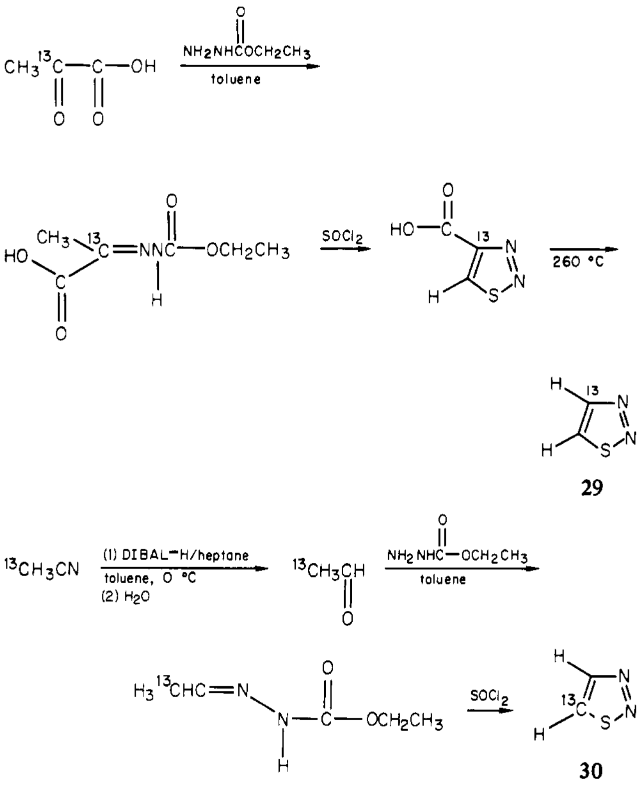
(32) Cantrell, T. S.; Haller, W. S. *J. Chem. Soc., Chem. Commun.* **1968**, 977.

(33) Goerdeler, J.; Ohm, J.; Tegtmeyer, O. *Chem. Ber.* **1956**, *89*, 1534.

(34) Herzberg, G. "Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand-Reinhold: New York, 1945; p 174.

(35) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1969**, *51*, 277.

Scheme III



wavelength, λ = 2200–2500 Å, the photolysis is considerably more complicated and bands characteristic of COS and HCO can be detected.) Finally, our failure upon warming of the matrix to observe the blue fluorescence characteristic of S_2 formation[36] is direct evidence against the formation of S atoms from **5**.

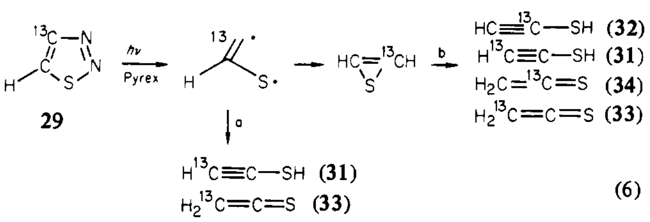
Studies with ^{13}C-Labeled Thiadiazoles with Pyrex-Filtered Light. The Odyssey of the C_2H_2S Fragment. For a sterner test of the involvement of **4** and a probe of the relationship between thioketene and ethynyl mercaptan, ^{13}C-labeled thiadiazoles **29** and **30** were synthesized[8d] as in Scheme III and photolyzed.

The results of irradiating [4-^{13}C]-1,2,3-thiadiazole (**29**) (90% isotopically pure) in solid argon are featured in Figure 1. The closely related sets of bands at 3300, 2040, and 555 cm^{-1} and 3315, 2020, and 560 cm^{-1} signal the formation of a pair of ^{13}C-labeled ethynyl mercaptans (**31** and **32**); the pair are formed in similar amounts but with a slight bias for **31**, as judged by the relative intensities of comparable infrared modes. Inspection of the bands due to thioketene indicates that one isotopic form dominates the spectrum. The latter point is most apparent from a comparison of the intensity of the band at 1737 cm^{-1} assigned to **33**, with the corresponding mode at 1713 cm^{-1} belonging to **34**. Specifically, the bands at 3005, 1737, and 689 cm^{-1} are approximately 9 times more intense than corresponding bands at 3040, 1713, and 695 cm^{-1}.

From [5-^{13}C]-1,2,3-thiadiazole (**30**), the ethynyl mercaptans are formed in approximately equal amounts but with a slight preference for **32**. The ratio of labeled thioketenes **33** and **34** is nearly the inverse of that obtained from **29** (compare spectra in parts a and b of Figure 1). Hence, to a good approximation, relative intensities reflect relative concentrations.

These labeling experiments establish unequivocally that the bulk of the thioketene product (nonrandomized label ~80%) cannot be derived from precursors whose symmetry leads to randomization of the label (~90%) in ethynyl mercaptan.

One way to rationalize these discrepancies in the labeling pattern is to assume (1) that one set of products stems from a single C_2H_2S species (path a) in which the integrity of the label is preserved and that (2) the other set (with randomized label) is descended from thiirene (path b) (eq 6).

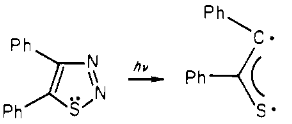


(6)

[33]/[34] ≈ 90/10; [31]/[32] ≈ 55/45

Although the relative amounts of ethynyl mercaptan and thioketene are unknown, the ratio $(14/15)_b$:$(14/15)_a$ calculated from band intensities for the above scheme is between 30 and 40. Clearly, product-determining intermediates in the respective paths cannot be identical; considerably more ethynyl mercaptan and less thioketene is formed via path b involving thiirene than via path a.

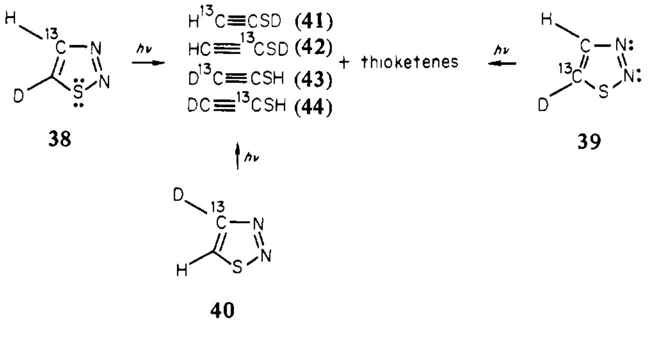
The situation is reminiscent of the C_3H_4 system[37] in which the multiplicity and geometry of the first formed intermediate ($C-H_2CHCH$) is a function of the precursor, cyclopropene (**35**), pyrazoline (**36**) or allyldiazomethane (**37**), and can be product determining. Although carbene and diradical intermediates have been detected in the C_3H_4 manifold, to date no information on the nature of intermediates from the thiadiazole photolysis has been forwarded. An electron spin resonance study of thiadiazole photolysis[38] did not uncover any relevant sulfur species, although recently Strausz[39] has claimed the formation of triplet thiobenzoylphenylmethylene from diphenyl-1,2,3-thiadiazole (eq 7).



(7)

Photolysis of Doubly Labeled [^{2}H,^{13}C]-1,2,3-Thiadiazoles. To probe more intimately the path leading to ethynyl mercaptan, we prepared and photolyzed [5-^{2}H,4-^{13}C]-1,2,3-thiadiazole [**38**], [5-^{2}H,5-^{13}C]-1,2,3-thiadiazole [**39**], and [4-^{2}H,4-^{13}C]-1,2,3-thiadiazole (**40**) (Scheme IV) with Pyrex-filtered light. A most dramatic consequence of the mechanistic pathway is revealed by comparing the infrared spectrum of photolyzed **38** with the photolysate of its isomers **39** or **40** (Figure 2). That part of each spectrum corresponding to ethynyl mercaptan products is very similar and indicates the formation of all four isomeric, monodeuterated ^{13}C-labeled ethynyl mercaptans **41–44**. Hence, the structural integrity of the C–H bond has been violated; the hydrogen on carbon in ethynyl mercaptan is not necessarily the one

Scheme IV



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[36] (a) Barnes, A. J.; Hallam, H. E.; Howells, J. D. R. *J. Mol. Struct.* **1974**, *23*, 463. (b) Pimentel, G. C. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 2.

[37] (a) Davis, J. H.; Goddard, W. A., III; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2427. Pincock, J. A.; Boyd, R. J. *Can. J. Chem.* **1977**, *55*, 2482.

[38] Krauss, P.; Zeller, K. P.; Meier, H.; Müller, E. *Tetrahedron* **1971**, *27*, 5953.

[39] Murai, H.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1979**, *101*, 3976.

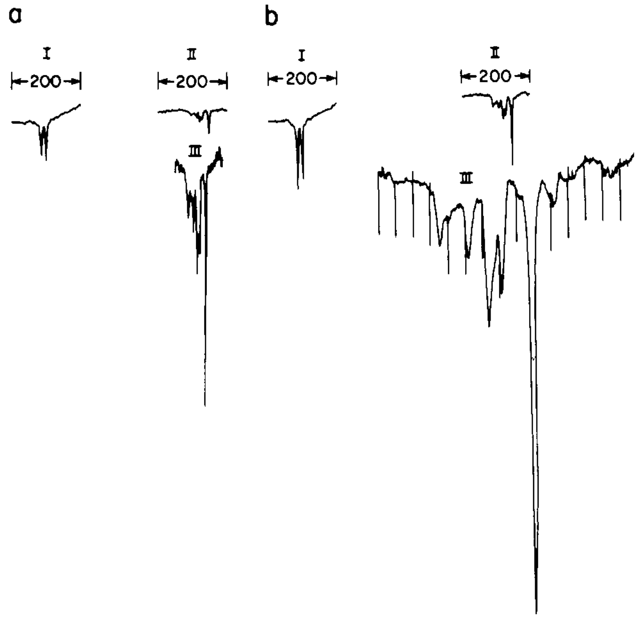


Figure 2. (a) Acetylenic carbon–hydrogen (I) and carbon–deuterium stretch (II) regions of the infrared spectrum of photolysate from Pyrex-filtered irradiation of [5-^{2}H,4-^{13}C]-1,2,3-thiadiazole (**38**). The region from 3400 to 3200 cm^{-1} (I) and 2700 to 2500 cm^{-1} (II) is shown. III is identical to II but with ordinate expanded 10×. Note that the S–H stretch also absorbs in this region II and Fermi resonances may contribute to the appearance of the spectrum. (b) Acetylenic carbon–hydrogen (I) and carbon–deuterium stretch (II) regions of the infrared spectrum of photolysate from Pyrex-filtered irradiation of [4-^{2}H,4-^{13}C]-1,2,3-thiadiazole (**40**). III is identical with II but with 10-cm^{-1} markers, and ordinate and abscissa are expanded 5×. Note that the S–H stretch also absorbs in this region (II) and Fermi resonances may contribute to the appearance of the spectrum.

linked to it in thiadiazole. At least one interchange, tantamount to hydrogen swapping between carbon atoms, must occur to satisfy the data.

Either a facile degenerate rearrangement of ethynyl mercaptan (**14**) mediated by hydrogen shifts takes place with no detectable intermediates under our conditions or the exchange is a property of the path leading from **5** to **14**. The former possibility appears remote in view of the apparent photochemical stability of both **14** and, the most obvious candidate for mediating the degenerate rearrangement, thioketene (**15**).

It must be emphasized that the four mercaptans (**41**–**44**) in the photolysate of doubly labeled thiadiazole can be generated under conditions (3000-Å interference filter or Pyrex-filtered light) in which thioketene (**15**) and ethynyl mercaptan (**14**) are photostable. At shorter wavelengths λ = 2200–2500 Å, thioketene is photoisomerized to ethynyl mercaptan (eq 8).

$$\underset{\mathbf{15}}{H_2C{=}C{=}S} \xrightarrow{\lambda\,=\,2200\text{–}2500\ \text{Å}} \underset{\mathbf{14}}{HC{\equiv}C{-}SH} \qquad (8)$$

$$\underset{\mathbf{34}}{H_2C{=}^{13}C{=}S} \xrightleftharpoons{\lambda\,=\,2200\ \text{Å}} \underset{\mathbf{33}}{H_2{}^{13}C{=}C{=}S} \qquad (9)$$

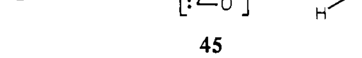
In fact, irradiation with λ = 2200 Å of an 80:20 mixture of [1-^{13}C]-**34** and [2-^{13}C]thioketene (**33**) (matrix isolated at 20 K by quenching a gaseous mixture of thiadiazole **30** in argon which was pyrolyzed at 610 °C) results not only in the formation of [^{13}C]ethynyl mercaptans but also in the interconversion of thioketene (**34**) with its isomer, **33**. The latter reaction is made manifest by an approach toward equalization of the intensities of the 1713- and 1737-cm^{-1} bands of **34** and **33**, respectively, during the irradiation. (This de facto degenerate rearrangement is also very much in evidence during the bare-lamp photolysis of the "Pyrex" photolysate of **29** or **30**. Interestingly, the label is only partially scrambled in ethynyl mercaptan product when thioketene **34** is irradiated with λ ≈ 2500 Å, suggesting that a reaction involving a 1,3 shift from thioketene to ethynyl mercaptan (**14**) may be induced in this region of the ultraviolet. However, these processes from **15** at shorter wavelength are definitely *not* contributing to the formation of ethynyl mercaptan nor to the scrambling of the label in this species during the photolysis of thiadiazoles **38**, **39**, and **40** with λ > 2900 Å.

Table II. Detectable Thiirene Infrared Bands (cm^{-1})[a]

precursor		
5 (Ar, 8 K)	5 (N_2, 8 K)	6 (Ar, 8 K)
3207	3202	3207
3169	3161	3167
3166		3166
1663	1660	1666
912	910	914
563	570	572

[a] See text for assignments and comment on band at 655 cm^{-1}.

Thus for an explanation of the formation of isomers **41**–**44** with Pyrex-filtered light, a hypothetical path involving the thiocarbene **22** is appealing. Note that the corresponding oxocarbene **45** presumably mediates the scrambling of labeled carbon from the reactions of singlet methylene ($^{14}CH_2$) with carbon monoxide[40a] (eq 10) and the formation of [^{14}C]carbon monoxide from [2-^{14}C]ketene (**46**).



(10)

45

Thiirene Formation from 1,2,3-Thiadiazole (5)

Randomization of the carbons and hydrogens of ethynyl mercaptan implies a thiirene precursor. To test whether thiirene had actually been trapped and stabilized but was unstable to Pyrex filtered light, we irradiated **5** by using narrow band-pass filters. Photolysis of argon matrix-isolated 1,2,3-thiadiazole with light from a 1000-W Hg-Xe lamp filtered through a 3000-Å interference filter produced **14**, **15**, and a new species (X), possessing bands (Table II, column 1; Figure 3) reminiscent of cyclopropene (**35**).[41] (The yield of X can be improved by irradiating **5** at even shorter wavelengths (λ = 2200–2500 Å).) The positions and relative intensities of X's bands do not vary significantly over a tenfold range in *M*/*R* values (250–2500), supporting an assignment to a monomeric species. The same species X is formed from **5** in nitrogen (Table II, column 2). X is also a photoproduct of matrix-isolated isothiazole (**6**), although its signals are slightly shifted according to its local environment (hydrogen cyanide is the coproduct). Light of λ = 3300–3700 Å converts X to **14** and **15**. These experiments establish unequivocally that X is a C_2H_2S species, and that the bands that we observe are not artifacts of the matrix-isolation method.

Irradiation (λ = 2350–2800 Å) of *either* [4-^{13}C]-1,2,3-thiadiazole (**29**) or [5-^{13}C]-1,2,3-thiadiazole (**30**) gives [^{13}C]X (**47**) with bands shifted to 3198, 3163, 3158, 1634, 910, and 558 cm^{-1}. [^{13}C]X (**47**) is transformed with light of λ = 3300–3700 Å to a pair of ethynyl mercaptans (each member is formed in essentially equal amounts) and a pair of thioketenes (each member is formed in essentially equal amounts) (eq 11). ([^{13}C]X is more slowly converted to products with 3000-Å light.) These experiments establish that the species X is responsible for scrambling of the label in thioketene and ethynyl mercaptan during the Pyrex filtered photolysis of **5**.

The observation that irradiation of [4-^{13}C]- or [5-^{13}C]thiadiazole gives the same C_2H_2S species (**47**), which is then photochemically converted to thioketene and ethynyl mercaptan with randomized

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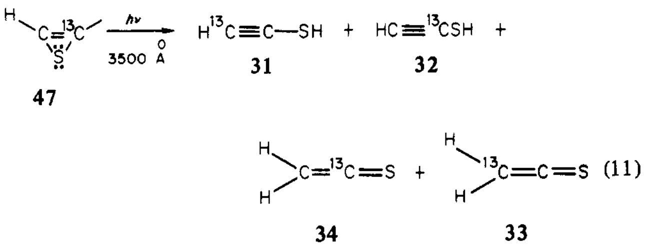
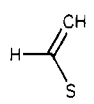
(40) (a) Russell, R. L.; Rowland, F. S. *J. Am. Chem. Soc.* **1970**, *92*, 7508. (b) Montague, D. C.; Rowland, F. S. *Ibid.* **1971**, *93*, 5381.

(41) (a) Wiberg, K. B.; Wendoloski, J. J. *J. Phys. Chem.* **1979**, *83*, 497. (b) Yam, T. Y.; Eggers, D. F., Jr. *Ibid.* **1979**, *83*, 501.



label, strongly suggests that X must be either thiirene or species derived from thiirene (**4**). The simplicity of the observed spectrum of X and the fact that isotopic labeling does not lead to "apparent splittings" of key bands, but to shifts in the frequencies, are in favor of a single species.

If X was an acyclic substance **48**, to satisfy symmetry requirements of the data each ^{13}C-labeled thiadiazole would have to give two species, **49** and **50**, and the double-bond stretch would appear to be split. The infrared spectrum of [^{13}C]X is also not compatible with a pair of three-membered ring carbenes **51** and **52**, which would not be expected to have an intense band at 1663 cm^{-1}. Furthermore, a spectrum containing the ^{13}C-labeled species, **51** and **52**, should have bands in common with that of unlabeled **22** (i.e., the frequencies of H–C modes of **22** and **51** should be virtually identical), but X and [^{13}C]X do not have common bands.



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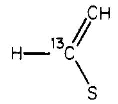

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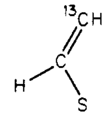

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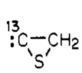

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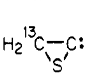
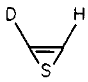


52

If X is a single species, it must be thiirene on the basis of the spectral properties which follow. Irradiation (λ = 2350–2800 Å) of *either* [4-^{2}H]-1,2,3-thiadiazole (**23**) or its 5-^{2}H isomer (**24**) produces [^{2}H]X (**53**) which exhibits bands at 3219, 3181, 3175, 2423, 2420, 2415, 1611, 892, and 467 cm^{-1}. Note that the three species X (**4**), [^{13}C]X (**47**), and [^{2}H]X (**53**) do not have bands in common. The methyl- and dimethyl-1,2,3-thiadiazoles, when photolyzed as above, also give intermediates, which possess spectra indicative of a thiirene and which are photoisomerizable to thioketenes. Hence, the production of thiirenes during the photodecomposition of 1,2,3-thiadiazoles is quite probably a general process. The bands that we have been able to observe for thiirenes **4**, **47**, and **53**–**56** are collected in Table III.



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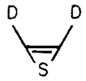

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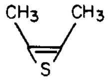

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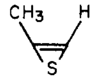

56

The behavior of the mode absorbing at 1663 cm^{-1} may be compared with the "double-bond stretching mode" of cyclopropene (**35**). Closs[42] has discussed the unique properties of the latter in terms of strong coupling between the double bond and the bonds to the substituents. As a consequence of the strong coupling, very marked shifts (~50 cm^{-1} per deuterium on the double bond) to low frequency of the "double-bond stretch" have been noted for cyclopropene (**35**) upon deuterium substitution. For example (Table IV), substitution of deuterium for an olefinic hydrogen of cyclopropene lowers the frequency 54 cm^{-1}; a second olefinic deuterium lowers this mode 50 cm^{-1}.[42] We have observed the same pattern for X with **4**, **53**, and **54** absorbing at 1663, 1611, and 1567 cm^{-1}, respectively. Much smaller shifts of the "double-bond stretch" have been observed for all other olefins in which the effect of deuterium and methyl substitution is known.[43]

Whereas methyl substitution on the double bond of 3,3-dimethylcyclopropene raises the frequency of the "double-bond" mode approximately 100–151 cm^{-1} per methyl group (Table IV), methyl substitution on an acyclic double bond raises its absorption frequency only 15 cm^{-1} per methyl group.[44] If the behavior of thiirene paralleled that of 3,3-dimethylcyclopropene, the "double-bond" mode of methylthiirene (**56**) would be expected to absorb around 1800 cm^{-1}. Unfortunately, this region of the spectrum is obscured by the intense bands of methyl thioketene. Dimethylthiirene (**55**), however, exhibits a band at 1923 cm^{-1} (a shift of 260 cm^{-1} compared to the double-bond mode of thiirene) in agreement with the shift predicted by the cyclopropene model.

Thus, our argument for the assignment of a thiirene structure to X rests on (1) the fact that the same monolabeled species [^{13}C]X is formed from distinctly labeled precursors **29** or **30**, (2) the convertibility of labeled X to ethynyl mercaptan and thioketene both with randomized label, and (3) the likelihood of the observed band positions and their behavior on isotopic and methyl substitution being due to a single species of cyclopropenoid character.

Our best attempts aimed at recording the UV spectrum of thiirene have resulted only in observing broad featureless absorption extending from 2200 to 3500 Å with no obvious maxima. It should be noted that the photolability of thiirene has implications for previous studies employing conventional unfiltered photolysis, in which the trapping of thiirenes has been claimed.[22]

The Infrared Spectrum of Thiirene. Assuming C_{2v} symmetry for **4**, a group-theoretical analysis indicates that the nine vibrational modes fall into four groups: four modes of A_1, one of A_2, one of B_1, and three of B_2 symmetry.[45]

The mode of A_2 symmetry is Raman active but infrared inactive. All other modes are both infrared and Raman active. Figure 4 depicts nine symmetry modes for thiirene. The bands that we have attributed to argon matrix-isolated thiirene (**4**) are located at 3207, 3169, 3166, 1663, 912, and 563 cm^{-1}.[46] Although the pair of bands absorbing at 3169 and 3166 cm^{-1} do not coalesce upon annealing of the argon matrix, only a single band at 3161 cm^{-1} is observed for the nitrogen matrix-isolated species. Hence the two bands at 3166 and 3169 cm^{-1} are likely to result from an environmental effect.[3,4,47] Possibly the splitting of the fundamental C–H stretch is related to the presence of the coproduct nitrogen molecule, which could form a host-separated pair and/or an intimate pair with **4**.[48] Thus only five bands corresponding to five fundamentals were explicitly attributed to thiirene by using continuous-wave infrared spectroscopy.

Detectable absorption of **4** is found in regions typical of C–H stretching modes (3207 cm^{-1}; 3169 and 3166 cm^{-1}), a C=C stretching mode (1663 cm^{-1}), and a C–H out-of-plane bending mode (563 cm^{-1} (ν_6)). A careful review of the behavior of the most intense band at 912 cm^{-1} indicates that it shifts very little upon monodeuteration of **4**, but upon dideuteration shifts to 718 cm^{-1} and is most probably a C–H in-plane bend. These assignments are tentative and must await detection of all the fundamentals of **4**.

Strausz had repeated our experiments[9] and had assigned two additional bands at 660 and 425 cm^{-1} to thiirene[9] but subsequently stated[11] that the 425-cm^{-1} band was an artifact in the Fourier transform (FT) computer subtraction.

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(42) Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53.

(43) (a) Dyer, J. R., "Applications of Absorption Spectroscopy of Organic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1965. (b) Pinchas, S.; Laulicht, I. "Infrared Spectra of Labelled Compounds"; Academic Press: New York, 1971.

(44) Bellamy, L. J., "The Infra-red Spectra of Complex Organic Molecules"; 3rd ed.; Wiley: New York, 1975.

(45) Cotton, F. A. "Chemical Applications of Group Theory", 2nd ed.; Wiley-Interscience: New York, 1971.

(46) The splitting (3169, 3166 cm^{-1}) of this C–H stretch is not an intrinsic property of thiirene but is matrix dependent (Table II).

(47) Chadwick, B. M. *Spec. Period. Rep.*: *Mol. Spectrosc.* **1975**, *3*, 281.

(48) Other bands of nitrogen matrix-isolated thiirene are split. Possibly this is the result of two distinct situations: one, in which the coproduct nitrogen molecule occupies the same cavity as thiirene; the other, in which thiirene is the sole occupant of the site, with the nitrogen coproduct being incorporated into the host structure.

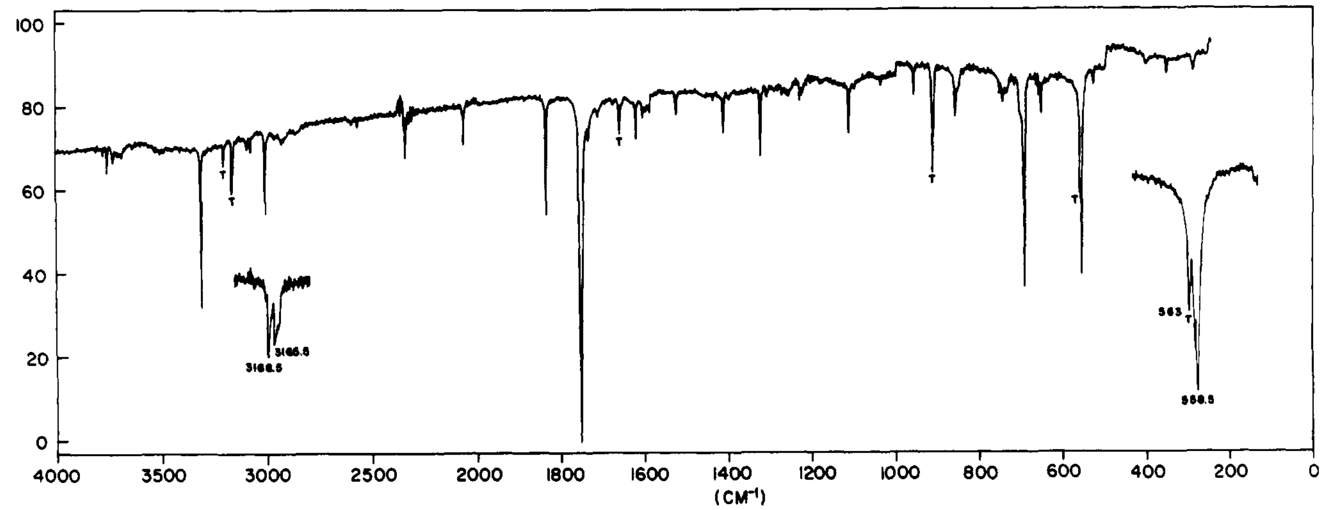
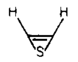
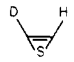
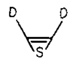
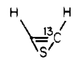
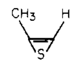
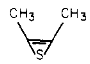


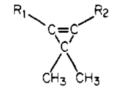
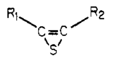
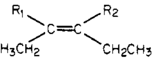
Figure 3. Infrared spectrum of argon matrix-isolated 1,2,3-thiadiazole (M/R = 500, 44 mm) after irradiation for 40 min with a 1000-W mercury-xenon lamp fitted with a 2500-Å interference filter. Observe bands assigned to thiirene at 3205, 3169, 3166, 1663, 912, and 563 cm^{-1} are indicated by the letter T. Note inset 1, of expansion of abscissa 10 times, which clearly shows resolution of bands at 3169 and 3166 cm^{-1}, and inset 2, showing bands at 563 and 558 cm^{-1}, more clearly resolved.

Table III. Infrared Bands for Thiirenes (cm^{-1})[a]

 **4**	 **53**	 **54**	 **47**	 **56**	 **55**
3207 (w)	3219 (vw)	2485 (w)	3198 (w)	3203 (w)	2970 (w)
3169 (m)	3181 (w)	1567 (w)	3163 (w)	2930 (vw)	2921 (m)
3166 (m)	3175 (w)	718 (m)	3158 (w)	1440 (m)	2865 (w)
1663 (w)	2423 (vw)	423 (m)	1634 (w)	1429 (m)	1923 (w)
912 (m)	2420 (w)		910 (m)	1036 (m)	1440 (m)
563 (m)	2415 (w)		558 (s)	897 (m)	1427 (m)
	1611 (w)			650 (w)	1041 (s)
	892 (w)				586 (w)
	467 (m)				471 (w)

[a] Relative intensities as observed in the spectrum of products: vw = very weak, w = weak, m = medium, s = strong (in argon). These values are reported as is; splittings may be due to matrix effects. The spectra are incomplete because of the limits of detection under the experimental conditions.

Table IV. The "Double-Bond" Stretching Vibrations of (cm^{-1}) Cyclopropenes,[a] Thiirenes,[b] and *cis*-3-Hexenes[c]

R_1, R_2			
H, H	1632	1663	1654
H, D	1578	1611	1643
D, D	1528	1566	1632
H, CH_3	1768		
CH_3, CH_3	1877	1923	

[a] Reference 42. [b] This work. [c] Shroetter, A. W.; Hoffman, E. G. *Justus Liebigs Ann. Chem.* 1964, *672*, 44.

The band, at 660 cm^{-1}, is problematical because it is difficult to measure its growth and decay accurately. Recently, we have reexamined the spectrum of d_0-, d_1-, d_2-, and ^{13}C-labeled thiirene. The 660-cm^{-1} band (our study 655 cm^{-1}) *qualitatively* grows and decays with a similar dependence as the bands we can confidently assign to **4**. Further there appears to be comparable bands in the spectra of the ^{13}C and d_1 species at 650 and 640 cm^{-1}, respectively. Presently, both the Stony Brook and Edmonton groups are in agreement regarding the bands attributed to thiirene-d_0, -d_1, and -d_2 in Table III.

The Ethynyl Mercaptan-Thiirene Connection. The unknown thioformyl methylene conformers **59** and **60** and diradicals **61** and **62** would appear to be eligible precursors to thioketene, thiirene, and ethynyl mercaptan as indicated in eq 12. However, an explanation of the labeling pattern in ethynyl mercaptans derived from [^2H,^{13}C]thiadiazoles **38**–**40** (vide supra) requires the con-

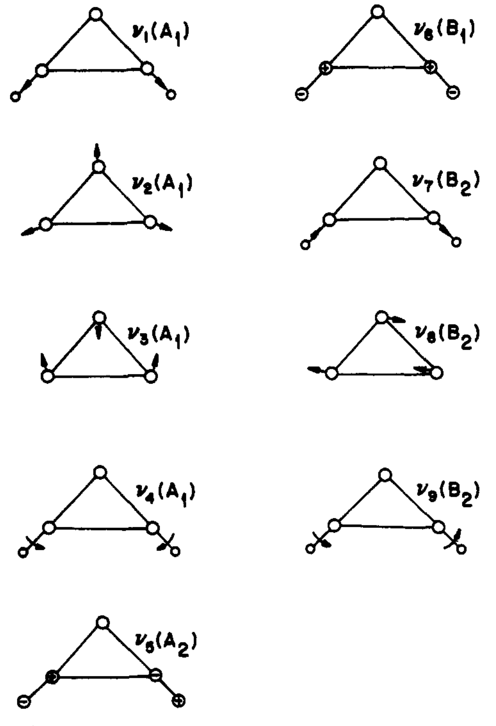
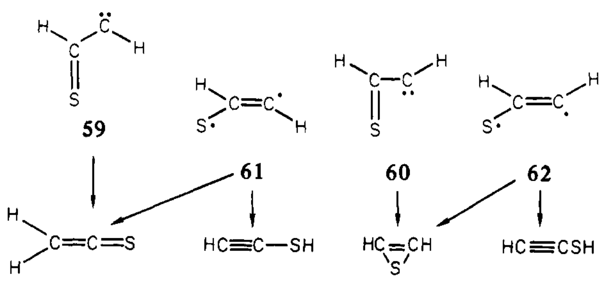


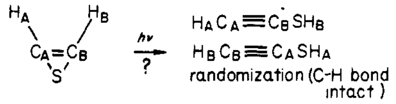
Figure 4. Symmetry modes of (C_{2v}) thiirene. In some cases, the compensating motions of hydrogens (or the carbon framework) are not shown for purposes of clarity.

sideration of at least one additional C_2H_2S species.

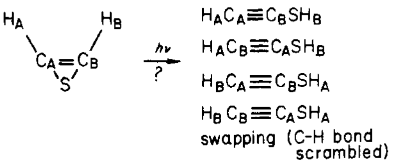


(12)

The intermediacy of thiirene implies randomization[49] of hydrogen and carbon atoms in **14** but, a priori, is neither a necessary nor a sufficient condition for the hydrogen-swapping reaction (eq 13 and 14).

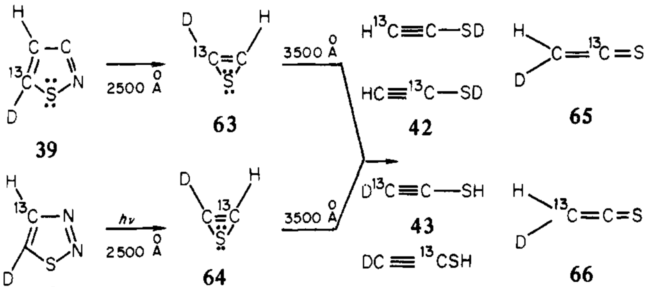


(13)



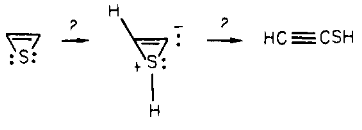
(14)

To determine whether the latter process occurs prior, or subsequent to, the production of thiirene (**4**), we irradiated the doubly labeled isomers **38** and **39** with light of λ = 2350–2800 Å (eq 15).



(15)

The thiirenes detected from **38** and **39** are distinct and can be most easily differentiated by their C–D stretching frequencies.[50] As expected, the thiirene (**63**) possesses a lower frequency C–D stretch (2394 cm^{-1}) than does **64** (2420 cm^{-1}). Each thiirene is converted to a similar collection of all four ethynyl mercaptans. To account for our results with doubly labeled [^{2}H,^{13}C]thiadiazoles, Strausz[12] has proposed the zwitterion **67** as an intermediate between ethynyl mercaptan and thiirene (eq 16). However this speculation is

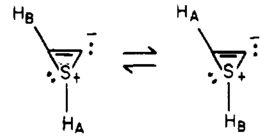


67

(16)

incorrect insofar as it fails to explain the formation of all four mercaptans (**41–44**) from **38**, **39**, or **40**. Further, Strausz[12] argues that his failure to detect mercaptans in the photolysis of methyl-substituted thiadiazoles is consistent with the notion that methyl substitution at carbon would be expected to destabilize zwitterion **67** by an unfavorable inductive effect. However, this explanation may not be tenable for chemistry in rare-gas matrices where the *intrinsic* ability[51,52] of a methyl group to stabilize both positive and negative charges may be a determinant.

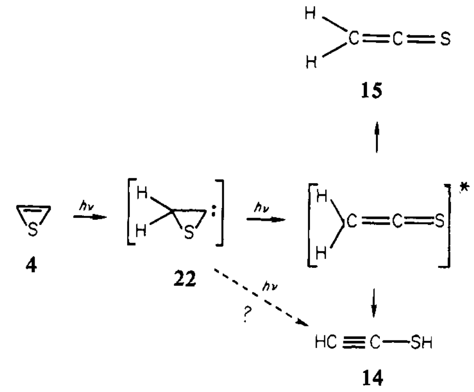
To rationalize the data by using Strausz's intermediate, one would have to invoke degenerate rearrangements of zwitterions (see eq 17).



(17)

A more plausible hypothesis would involve an intermediate in which hydrogens reside on the same atom. Of the choices, thiirenylidene **22** is the least problematical and, in fact, has been calculated to be very close in energy (0.3 kcal/mol difference) to thiirene.[12,18] Thiirenylidene **22** is thus an appealing candidate for mixing hydrogens between the carbon atoms. On the basis of the preservation of the integrity of C–H bonds in the thiadiazole–thiirene conversion, **22** cannot be a precursor to thiirene but, if it is involved, must be descended from **4** via a photochemical pathway.

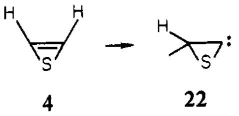
Conceivably thiirenylidene (**22**) may become matrix stabilized and be further photolyzed to products (see eq 18). Intuition would



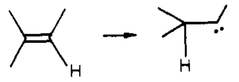
(18)

favor a direct correlation of **22** with thioketene (**15**) (principle of least motion)[53] rather than **14**, although constraints imposed upon **22** are probably dependent on its multiplicity.

The reaction of **4** to give **22** is formally the reverse of a carbene rearrangement involving a 1,2 shift of a vicinal hydrogen (eq 20).



(19)



(20)

This type of rearrangement has recently been the subject of theoretical analyses.[54] A very large barrier is suggested for the triplet carbene to triplet olefin rearrangement.[54a] Barriers to

$$H_2C{=}C{:} \rightarrow HC{\equiv}CH \qquad (21)$$

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[49] Randomization in this context means that the nonequivalent C–H bonds in the starting material **5** become equivalent during the conversion of **5** to **14**.

[50] However, owing to the weakness of these bands we cannot state that there is absolutely no crossover to give small amounts of a minor thiirene. A study of isotope effects on the photoreactions of **38**, **39**, and **40** is planned.

[51] (a) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986. (b) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *Ibid.* **1979**, *101*, 6046, 6056.

[52] Gebicki, J.; Krantz, A., unpublished results.

[53] Hine, J. *J. Am. Chem. Soc.* **1966**, *88*, 5525.

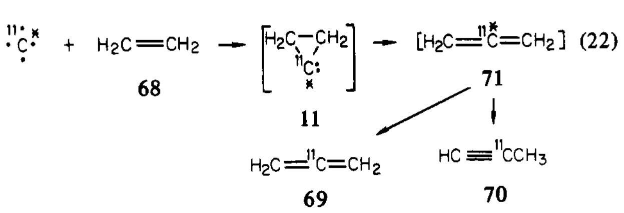
[54] (a) Altmann, J. A.; Csizmadia, I. G.; Yates, K. *J. Am. Chem. Soc.* **1974**, *96*, 4196. (b) Bodor, N.; Dewar, M. J. S. *Ibid.* **1972**, *94*, 9103.

rearrangement for the singlet have been reported to be 0[54b] and 21 kcal/mol.[54a] For the vinylidene rearrangement, a barrier of no more than 8 kcal/mol is predicted (eq 21). Schaefer,[55a] to rationalize enigmatic experimental results in the laser photodissociation of formaldehyde,[55b,c] has considered the intermediacy of the hydroxycarbene (CH(OH)). The formation of such oxocarbenes from ketones is a well-known photoreaction.[55d-f]

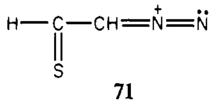
Srinivasan[56] has recently proposed carbon skeletal rearrangements formally analogous to eq 20, to rationalize reactions of cyclic olefinic hydrocarbons, which are induced by high-energy (6.7-eV) photons. Suffice it to say that multiple bond-carbene rearrangements have been rarely documented but are receiving increased attention. The thiirene–thiirenylidene (**4**–**22**) isomerization may be a case in which the similar stabilities[18] of the two forms permit conversion in the direction of the carbene, most likely through singlet excited states.

It is also conceivable if thiocarbene **22** is converted to an electronically excited or highly vibrationally excited ground state thioketene that the latter may possess enough energy to shift a hydrogen to give ethynyl mercaptan. An observation that may be relevant to this point is the matrix dependence of the ratio **14**/**15**, which decreases through the series argon, nitrogen, carbon monoxide, and acetylene. Although other explanations may be tenable, this trend jibes with the notion that as the matrix host becomes more "guestlike" (i.e., as the vibrational modes of the host more closely match the vibrational modes of the guest) energy transfer (to host) from the vibrationally excited organic guest (thioketene) becomes more efficient. Thus the speculation that an excited form of thioketene may rearrange to **14** in nitrogen and rare gas matrices, before it can transfer excess energy and stabilize.

The reaction of **15** to give **14** has precedent in the analogous hydrocarbon case.[57,58] Hot or thermal ^{11}C atoms when added to ethylene (**68**) produce allene (**69**) and methylacetylene (**70**) (eq 22). The data indicate that most of the allene and a significant fraction of methylacetylene are center labeled and are likely formed by carbon atom addition to the ethylene bond. A transient allene (**71**) has been invoked as a precursor to center-labeled **70** to account for this result.



Although vibrational energy transfer in condensed phases is generally believed to be rapid compared to structural reorganization,[59] there may be limiting cases, especially in molecules containing only a few atoms, in which structural reorganization is competitive with energy transfer, the vibrationally excited species being exquisitely sensitive to the matrix environment. Presently we regard the direct transfer of a hydrogen from **15** to give **14** as probably occurring from an electronically excited state of **15**, rather than from **15** in a vibrationally excited ground state. However, a decision about the mechanism of formation of products must await an unequivocal determination of the energy surfaces connecting various C_2H_2S species in ground and excited states and a possible role for the unknown thioformyldiazomethane **71**.



$H{-}C(=S){-}CH{=}\overset{+}{N}{=}\ddot{N}{:}$

71

Summary

This work represents the first direct evidence for a stable heterocyclic analogue of cyclobutadiene. Thiirene (**4**) can be detected by using infrared spectroscopy after (**5**) has been photodecomposed with light of λ = 2150–3000 Å. The yield of **4** is higher at shorter wavelengths because thiirene is less photolabile. With λ = 3300–3700 Å **4** is rapidly photoisomerized to ethynyl mercaptan (**14**) and thioketene (**15**), which are not photoreactive at λ > 2800 Å. With λ ≈ 2150–2600 Å thioketene undergoes photodecomposition and conversion to ethynyl mercaptan. At least a portion of the latter reaction occurs via a direct 1,3 shift of hydrogen.

The present study provides a methodology for the preparation and characterization of three-membered molecules of especial interest because of their potential antiaromatic character.[7] The methodology exploits the symmetry of the C_{2v} species and utilizes band-pass filters for their detection and preservation. Both thiirene and selenirene[60] exhibit the character of a cyclopropene from analysis of the infrared spectra of their isotopically labeled variants. Other members in the heterocyclopropene series, oxirene and azirene, are likely to ape thiirene in their infrared characteristics and display a common cyclopropenoid signature.[60]

Experimental Section

Proton NMR spectra were recorded on a Varian Associates EM 360 or HFT-80 spectrometer. Carbon-13 NMR spectra were recorded on a Varian Associates CFT-20 spectrometer. Infrared spectra of matrix-isolated species were obtained by using a Perkin-Elmer 180 spectrophotometer in the constant I_0 mode or with a Perkin-Elmer Model 521 spectrophotometer. All other infrared spectra were recorded on a Perkin-Elmer Model 727 spectrophotometer. Ultraviolet spectra were measured with a Varian Associates Techtron spectrometer.

Vapor-phase chromatography (VPC) was performed with a Varian Aerograph Model 90-P instrument, using the following columns for final purification of the 1,2,3-thiadiazoles: 15% SE-30 on 80/100 mesh Chromosorb W (5 ft × $^1/_4$ in.) maintained at 90 °C, 30% UCON nonpolar on 80/100 mesh Chromosorb W (5 × $^1/_4$ in.) at 90 °C, and 15% Carbowax 20M on 80/100 mesh Chromosorb W (5 ft × $^1/_4$ in.) at 100 °C.

A Displex, closed-cycle, two-stage refrigerator, Model CS 202, manufactured by Air Products and Chemicals Inc. was utilized in these studies. Commercial grade helium (Grade 6) was employed as the refrigerant.

A cesium iodide plate in contact with a copper block with indium O rings supported the matrix deposit for infrared spectral studies. The infrared transmitting outer windows were also cesium iodide. Suprasil quartz plates served as windows for photolysis. For dual IR and UV experiments, BaF_2 plates were employed. The temperature of the sample window was monitored with a chromel–gold–0.07 atom % iron thermocouple.

Photochemical Reactions. Photochemical reactions were carried out with either General Electric H100A 38-4/T medium-pressure mercury lamps (with the outer Pyrex envelope removed) or a 1000-W mercury–xenon lamp (Hanovia no. B977B0010) as the light source. Interference filters (Oriel Corp. of America, no. G-572-09, Stamford, CT) were used as indicated.

Sample Preparation. General Procedure. The organic compound (matrix guest) was cooled externally with liquid nitrogen and degassed several times, under vacuum, by the usual freeze-thawing technique. The degassed sample was allowed to expand into an evacuated 3-L bulb until the pressure of the system reached 0.1 torr, as measured with a Data Systems Model 1174 Barocell Electronic Manometer fitted to a type 570A-1000T-0A1-V1 pressure sensor (1000 torr range). The M/R value (mole ratio of host gas (M) to guest (R)) was adjusted by adding the requisite amount of host gas, purified as below, to the 3-L bulb.

Argon (Matheson, prepurified, 99.998% min) and nitrogen (Linde, high-purity dry grade, 99.99% min), the most commonly used host gases, were prepurified by passage through a spiral trap cooled with liquid oxygen and then stored in 5-L bulbs. Final purification of the host gas

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(55) (a) Schaeffer, H. F., III *Acc. Chem. Res.* **1979**, *12*, 288. Lucchese, R. R.; Schaeffer, H. F., III *J. Am. Chem. Soc.* **1978**, *100*, 298. (b) Houston, P. L.; Moore, C. B. *J. Chem. Phys.* **1976**, *65*, 757. (c) Lewis, R. S.; Tang, K. Y.; Lee, E. K. C. *Chem. Phys. Lett.* **1976**, *43*, 232. (d) Yates, P.; Kilmurry, L. *Tetrahedron Lett.* **1964**, 1739. (e) Turro, N. J.; Morton, D. R. *Adv. Photochem.* **1974**, *9*, 197. (f) Yates, P.; Loutfy, R. O. *Acc. Chem. Res.* **1975**, *8*, 209.

(56) Srinivasan, R.; Brown, K. H. *J. Am. Chem. Soc.* **1978**, *100*, 4602.

(57) Marshall, M.; MacKay, C.; Wolfgang, R. *J. Am. Chem. Soc.* **1964**, *86*, 4741. But see also Hops, H.; Priebe, H.; Walsh, R. *Ibid.* **1980**, *102*, 1210.

(58) Chapman, O. L. *Pure Appl. Chem.* **1975**, 511.

(59) Dubost, H. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 112.

(60) This paper was abstracted in part from a dissertation by J.L. submitted to the Graduate School of SUNY at Stony Brook, Jan 1977, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

was achieved during preparation of the sample by passing the host through a column heated to 150 °C packed with R-311 catalyst (Chemical Dynamics, Inc., South Plainfield, NJ).

The sample was deposited at the rate of 0.4 torr/min. All photochemical experiments unless otherwise indicated were carried out at 8 K. Gaseous samples ranged in *M*/*R* from 50 to 5000. The unlabeled thiadiazoles were prepared by standard methods.[60,61] The labeled thiadiazoles were prepared and characterized as previously described.[8d]

Photoirradiation of 1,2,3-Thiadiazole (5) in Solid Argon or Nitrogen. Initial experiments involved approximately a 5-min irradiation through a water filter, with the bare 100-W Hg lamp, which resulted in 70–90% destruction of the starting material (20–30 mm). The original infrared spectrum was replaced by a new spectrum with bands assigned to thioketene (**15**) at 3010 (w), 1755 (vs), and 692 cm^{-1} (m), and additional absorption including bands at 3315 (s), 2065 (vw), and 558 cm^{-1} that were assigned to ethynyl mercaptan **14**. The bands of **14** and **15** grew at the same rate. Continued irradiation resulted in destruction of thioketene (**15**). Concurrent with the destruction of thioketene, a band appeared at 1520 cm^{-1} belonging to carbon disulfide. Photolysis of 1,2,3-thiadiazole **1a** in a nitrogen matrix also gave **14** and **15** as products, but in a different ratio as judged by the relative intensities of bands. Preliminary experiments with deuterium-labeled species were carried out in a similar manner.

Photoirradiation of 1,2,3-Thiadiazole (5) in a Carbon Monoxide Matrix. 1,2,3-Thiadiazole (**5**) was mixed with carbon monoxide ($M/R \simeq$ 110, 16–38 mm) and deposited on the cesium iodide window at 20 K. Irradiation of matrix-isolated **5** to decomposition with Pyrex-filtered light also gave **14** and **15** as the major products. Within the limits of detectability of the Perkin-Elmer 521 spectrophotometer, neither bands due to carbonyl sulfide (ν = 2063 cm^{-1}) nor the formyl radical (ν_3 = 1863 cm^{-1}) were detected.

Photoirradiation of 1,2,3-Thiadiazole (5) in Acetylene-*d*$_2$ (28). 1,2,3-Thiadiazole **5** was mixed with acetylene-*d*$_2$ (**28**) ($M/R \simeq$ 200, 20 mm) and deposited at 50 K. Photolysis of **5** to decomposition with Pyrex-filtered light resulted in the formation of thioketene **15**. There was no evidence for thioketene-*d*$_2$ (ν_{max} = 1735 cm^{-1}, C=C str).

Photoirradiation of 1,3,4-Thiadiazole (8) in an Argon Matrix. 1,3,4-Thiadiazole (**8**) was mixed with argon ($M/R \simeq$ 250 mm) and deposited on the CsI sample window which had been precooled to 20 K. Upon irradiation with a water-filtered mercury lamp light hydrogen cyanide dimer [ν_{max} = 3302, 2090 cm^{-1} (w)] was observed as the major product.

General Procedure for Photolysis of ^{13}C-Labeled Thiadiazoles. Photolysis for 40 to 60 min of a matrix-isolated sample (40–50 mm) of isotopically labeled 1,2,3-thiadiazole in argon or nitrogen ($M/R \approx$ 500–1000) at 8 K with a 1000-W mercury–xenon lamp fitted with a 2500-Å interference filter resulted in loss of starting material and growth of bands belonging to thioketene, ethynyl mercaptan, and thiirene.

Initially ethynyl mercaptan and thioketene were formed directly from ^{13}C-labeled 1,2,3-thiadiazoles and maintained the integrity of the label (i.e., **31** was formed from **29**). If photolysis was carried out with Pyrex-filtered light, thiirene was not observed in the photolysate owing to its photoconversion to ethynyl mercaptans (**31** and **32**) and thioketenes (**33** and **34**). With 2500-Å light, thiirene is only slightly labile. Irradiation of thiirene using a 3500-Å interference filter resulted in its conversion to ethynyl mercaptan and thioketene. It was possible to selectively photolyze thiirene ($\lambda \sim$ 3500 Å) in the presence of small quantities of **5**. The bands, assigned to labeled ethynyl mercaptans, thioketenes, and thiirenes that have been observed during the irradiation of labeled thiadiazoles, are listed in the tables.

Irradiation of Argon Matrix-Isolated Isothiazole (6) at 8 K. Photolysis of isothiazole (**6**) ($M/R \approx$ 400) with light from a 1000-W mercury–xenon lamp fitted with a 2500-Å interference filter for 330-min led to destruction of the starting material and replacement of the starting infrared spectrum by bands assigned to thioketene (**15**) at ν_{max} = 3010 (w), 1755 (vs), and 692 (s) cm^{-1}, ethynyl mercaptan (**14**) at ν_{max} = 3315 (m) and 570 (m) cm^{-1}, thiirene (**4**) at ν_{max} = 3207, 3167, 3166, 1666, 914, and 572 cm^{-1}, and hydrogen cyanide at ν_{max} = 3303 and 720 cm^{-1}. Further irradiation using a 3500-Å filter led to loss of bands due to **4**.

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Kinetics and Thermodynamics for Ion-Molecule Association Reactions

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Abstract: Rate constants for ion-molecule association reactions have been calculated according to a simple model. The model, which mimics RRKM results, is constrained to reach limiting values corresponding to ADO (or Langevin) collision frequencies at the high-pressure limit and the strong-collison energy-transfer rate constant at the low-pressure limit. For those reactions at the low-pressure limit, the required information is the density of states (entropy) of the association complex. Low-pressure-limit rate constants and those in the "fall-off" regime are compared with data.

Introduction

Ion–molecule clustering or association reactions are of interest in physical, organic, and atmospheric chemistry. The overall process, typically written

$$A^+ + B + M \underset{k_r}{\overset{k_f}{\rightleftarrows}} AB^+ + M \tag{1}$$

can more descriptively be illustrated as

$$A^+ + B \underset{k_b}{\overset{k_c}{\rightleftarrows}} (AB^+)^* \xrightarrow{k_s[M]} AB^+ \tag{2}$$

The collision rate constants, k_c and k_s, are given by Langevin[1] and ADO theory[2-4] as appropriate.

It has already been pointed out[5,6] that this type of reaction is totally analogous to neutral radical-combination reactions. Thus, since it is really the microscopic reverse of a unimolecular bond-scission process, all the considerations associated with the

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