

decreases with decreasing distance of the dihalide inlet from the cold window, indicating that the bulk of the reaction occurs in the gas phase. If the alkali metal vapor is omitted in the experiment, no **1** is formed, and the IR spectrum reveals only **2** and a generally increased background, presumably due to partial indiscriminate destruction of **2** by metastable argon atoms (these appear to be completely quenched in the presence of metal atoms).

In a large number of spectra obtained under various conditions and with varying degrees of conversion, we have observed little if any evidence for the monoradical **3**. However, when the dihalide inlet is placed very near the microwave cavity, a product different from **1** is formed. Its structure has not been elucidated so far (radical anion of **1**?).

The identification of **1** is based on comparison with its known UV, fluorescence, and excitation spectra (Figure 4).²⁻⁴ The calculations shown were performed using selected⁸ singly and doubly excited configurations and appropriate⁹ parameter values. They account for the observed spectra and support the previous belief³ that an unobserved transition to a doubly excited state, presumably involved in the known photochemical conversion of **1** to benzocyclobutene, is buried under the intense first transition.

The IR (Figure 2) and Raman (Figure 3) spectra also fit the structure well. IR bands occur at 436 (w, shoulder), 442 (m), 638 (m), 675 (m), 737 (m), 742 (m), 776 (s), 779 (w, sh), 866 (w, sh), 870 (s), 953 (w), 1000 (w), 1158 (w), 1303 (w), 1333 (w), 1427 (w), 1465 (w), 1471 (w), 1490 (w), 1542 (w), 1552 (m), 1576 (w), 1741 (w), 2950 (w), 3045 (w), 3070 (w), and 3105 (w) cm^{-1} . Raman bands occur at 779 (w), 866 (w), 870 (w, 0.6), 1293 (m, 0.5), 1529 (m, 0.48), 1552 (s, 0.45), 1576 (w, 0.3) and 3045 (w) cm^{-1} (depolarization ratios in parentheses, frequencies common to the two spectra are italicized). The fluorescence spectrum can be analyzed in terms of two vibrational spacings, ~ 450 and ~ 1550 cm^{-1} , and we identify these with the 442- and 1552- cm^{-1} frequencies observed in the vibrational spectra. The spectra are independent of whether sodium or potassium was used in the reaction.

As numerous organic dihalides are easily available, the present approach to organic biradicaloid and similar reactive species promises to be widely applicable. Preliminary experiments with α, α' -dibromo-*p*-xylene (**4**) and 1,2-dibromobenzocyclobutene (**5**) produced argon-matrix isolated *p*-xylylene¹⁰ (**6**) and benzocyclobutadiene¹¹ (**7**), identified by comparison of UV and IR spectra with those published previously. The use of α, α' -dibromo-*m*-xylene (**8**) produced only small amounts of organic material in the matrix using the apparatus of Figure 1, and it appears that shorter lived biradicals will have to be prepared closer to the matrix surface.

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Karl L. Tseng, Josef Michl*

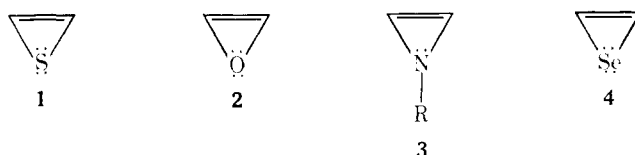
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received April 19, 1977

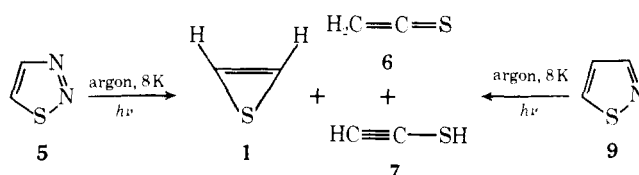
A Methodology for the Preparation and Characterization of Three-Membered, Potentially Antiaromatic Molecules. Preparation of Matrix-Isolated Thiirene and Selenirene

Sir:

Because of their strain and putative electronic destabilization, three-membered heterocycles¹ possessing a cyclic array of 4π electrons offer a considerable challenge to synthesis. Such molecules are expected to be both unimolecularly and bimolecularly reactive, if they exist at all as energy minima.² Thiirene (**1**) and its kindred systems, oxirene (**2**), azirene (**3**), and selenirene (**4**) are of interest because of their theoretical significance as prototypes of antiaromatic species.³ To date, neither the parent nor a single derivative of these heterocyclic molecules has been prepared and characterized.⁴



We wish to report the preparation and characterization of thiirene (**1**). Strausz and co-workers⁵ implicated thiirene as a transient in the gas-phase photodecomposition of 1,2,3-thiadiazole (**5**). We have previously noted that irradiation of matrix-isolated 1,2,3-thiadiazole (**5**) at 8 K produces thioketene (**6**) and ethynyl mercaptan (**7**).⁶ Studies with isotopically labeled **5** show that the hydrogens and carbon atoms are extensively randomized in ethynyl mercaptan (**7**). Preliminary evidence for thiirene (**1**) in the form of infrared data has been presented by us.⁷



Irradiation of argon matrix-isolated 1,2,3-thiadiazole (**5**) with light of $\lambda = 2350$ – 2800 Å produces ethynyl mercaptan (**7**) and thioketene (**6**) along with a substance "X" which

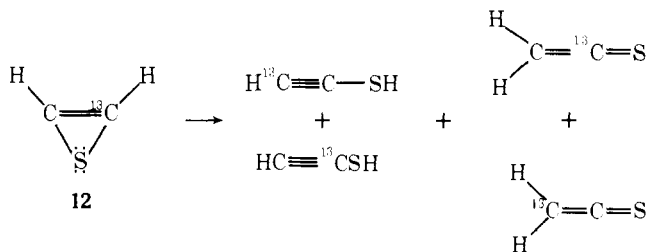
Table I. Infrared Bands for Thiirenes (in cm^{-1})^a

1	15	16	12	18 ^b	17
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)	873 (w)	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 Reference 10. Relative band intensities as observed in the spectrum of the mixture: vw, very weak; w, weak; m, medium; s, strong. ^b The "C=C stretch" of **18** is apparently obscured by absorption from methylthioetene.

possesses bands at 3207, 3169, 3166, 1663, 912, and 563 cm^{-1} . The positions of these bands are reminiscent of bands in the spectrum of cyclopropene^{8,9} (**8**). X is converted by light of 3300–3700-Å wavelength to **6** and **7**, the latter being the major product from X. Isothiazole (**9**) is an independent precursor to the species X, albeit a poor one.

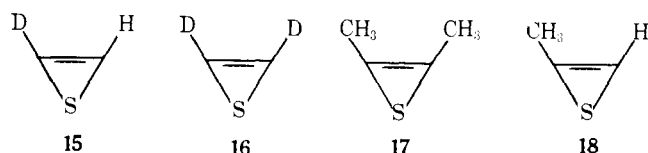
Irradiation¹⁰ ($\lambda = 2350\text{--}2800$ Å) of either [4-¹³C]-1,2,3-thiadiazole (**10**) or [5-¹³C]-1,2,3-thiadiazole (**11**) gives [¹³C]-X (**12**) with bands shifted to 3198, 3163, 3158, 1634, 910, and 558 cm^{-1} . [¹³C]-X (**12**) is transformed with light of $\lambda = 3300\text{--}3700$ Å to ethynyl mercaptan and thioketene, with the C-13 label scrambled in both products.



The observation that irradiation of [4- or 5-¹³C]thiadiazole gives the same $\text{C}_2\text{H}_2\text{S}$ species (**12**), which is then photochemically converted to thioketene and ethynyl mercaptan with randomized label, strongly suggests that X must be thiirene or species derived from thiirene (**1**). 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 is a single species it must be thiirene based on the spectral properties which follow.

Irradiation ($\lambda = 2350\text{--}2800$ Å) of either [4-²H]-1,2,3-thiadiazole (**13**) or its 5-²H isomer (**14**) produces [²H]-X (**15**) which exhibits bands at 3219, 3181, 3175, 2423, 2420, 2415, 1611, 892, and 467 cm^{-1} . Note that the three species, X (**1**), [¹³C]-X (**12**), and [²H]-X (**15**), do not have bands in common.

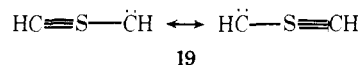
The methyl and dimethyl derivatives of **5**, when photolyzed as above, also give intermediates, which possess spectra indicative of a thiirene and which are photoisomerizable to thioketenes. Hence, the production of thiirenes during the photodecomposition of 1,2,3-thiadiazoles is quite probably a general process. The bands that we have been able to observe for thiirenes **1**, **12**, and **15–18** are collected in Table I.



Very marked shifts (~ 50 cm^{-1}) to low frequency of the "double bond stretch" have been noted for cyclopropene⁹ upon deuterium substitution. We have observed the same pattern for X with **1**, **15**, and **16**, absorbing at 1663, 1611, and 1567 cm^{-1} , respectively.

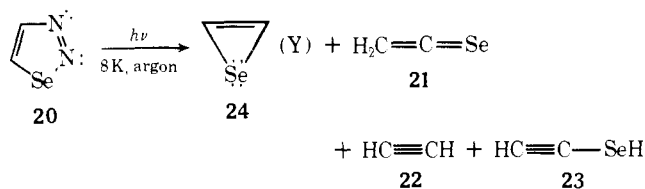
The cyclopropenoid character of the ring is further supported by the fact that dimethylthiirene (**17**) (Table I) shows absorption at 1923 cm^{-1} , paralleling the very marked high frequency shift of the "double bond stretching frequency" from 1641 (parent) to 1885 cm^{-1} (1,2-dimethyl derivative) in the case of cyclopropene.

Thus, our argument for the assignment of a thiirene structure to X rests on (1) the fact that the same monolabeled species [¹³C]-X is derived from distinctly labeled precursors **10** or **11**, (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 substitution being due to a single species of cyclopropenoid character. The latter point rules out structure **19** whose sole qualification for consideration is its symmetry.

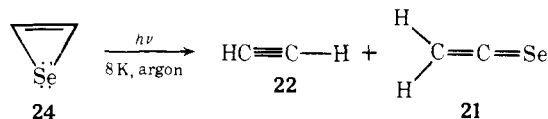


Thus, thiirene (**1**) represents the first example of a heterocyclic 4π -electron system to be stabilized and characterized.

Irradiation ($\lambda = 2350\text{--}2800$ Å) of 1,2,3-selenadiazole (**20**) produces selenoketene (**21**), acetylene (**22**), and ethynyl selenol (**23**), as well as a species Y absorbing at 3197, 3161, 3155, 1681,¹¹ 1637,¹¹ and 868 cm^{-1} . The positions and shapes of



these bands are strikingly similar to those of thiirene (**1**) and are reasonable for the analogous selenirene molecule (**24**). Irradiation ($\lambda = 2750\text{--}3250$ Å) of the mixture leads to the destruction of Y (which we tentatively regard as selenirene (**24**)) and to the growth of bands due to acetylene (**22**) and selenoketene (**21**). If irradiation is then continued using light of $\lambda = 2350\text{--}2800$ Å, selenoketene (**21**) and acetylene (**22**) bands are reduced in intensity, whereas the bands assigned to



selenirene (**24**) reappear and those belonging to ethynyl selenol (**23**) are enhanced.

Further efforts using the above approach to prepare other members in this series and to determine how the "antiaromatic quartet" influences their chemical and physical properties are underway.

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A. Krantz,* J. Laureni

Department of Chemistry, State University of New York
Stony Brook, New York 11794

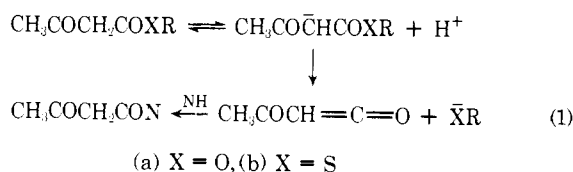
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A Ketene Intermediate in S-Acetoacetyl Coenzyme A Hydrolysis. Direct Comparison of Relative Leaving Abilities of Anionic Oxygen and Sulfur(II) Groups from an Acyl Center

Sir:

It has long been accepted that thiol esters have pronounced acidic properties with respect to the hydrogen atoms on the α -carbon site and many of the cozymic functions of S-acetyl coenzyme A have been rationalized on this basis.¹⁻³

Aryl acetoacetates with powerful leaving groups and acidic α -hydrogen atoms undergo hydrolysis and acyl transfer by means of an elimination-addition (E1cB) mechanism (eq 1a)



involving a ketenoid transition state.⁴ More recently, general reviews of the area of elimination-addition acyl transfer have

appeared^{5,6} and established its centrality in the transfers of many biologically important compounds.⁶ However, little attention has been paid to the possibility, either in enzymic or nonenzymic reaction, of such a route for thiolacetoacetates (eq 1b), of which S-acetoacetyl coenzyme A is an important example. Accordingly, we have studied the basic hydrolysis of a series of leaving-group-substituted thiolacetoacetates bearing directly on this question⁵ of a ketenoid transition state for S-acetoacetyl coenzyme A reactions.

The most useful criterion⁴⁻⁶ for distinction of such E1cB reactions from associative, bimolecular mechanisms, involving tetracoordinate intermediates,⁷ is the value of β_{LG} , the Brønsted exponent for correlation of the logarithms of the rate constants with the $\text{p}K_{\text{a}}$ of the conjugate acid of the leaving group. The magnitudes of β_{LG} found for E1cB reactions are commonly very much higher than in corresponding bimolecular solvolyses.⁴⁻⁶

Thiolacetoacetates were synthesized either by literature procedures⁸ (alkyl) or by amine-catalyzed reaction of diketene with the thiol (aryl); details will be reported subsequently. In degassed, 0.01 to 0.10 M sodium hydroxide solutions (ionic strength = 0.1, 25 °C) in the presence of 10^{-5} M ethylenediaminetetraacetic acid, the observed pseudo-first-order rate constants for thiolacetoacetate hydrolyses were found to be independent of hydroxide ion concentration. Kinetics were followed spectrophotometrically using the UV absorption band (~ 300 nm) of the ester enolate ions; in some cases a pH-stat method was used, yielding consistent results. Under these conditions (high pH) we are able to measure directly the reaction of the conjugate base form of the substrate. Values of $k^{\text{S}}_{\text{plateau}}$ (the pH independent value of k_{obsd} (s^{-1}) for thiolacetoacetates in strongly basic media) for seven esters yielded a Brønsted relationship (eq 2) with β_{LG} (-1.13) close to that observed by Pratt and Bruce⁴ (-1.28) for the E1 collapse of aryl acetoacetate anions (eq 3, calculated by least-squares analysis of some of their data⁴). This large, negative value of β_{LG} provides strong evidence^{3,5,6} of an E1cB route for thiolacetoacetates.

$$\log k^{\text{S}}_{\text{plateau}} = 7.60 - 1.13 \text{ p}K_{\text{LG}} \quad (r = 0.997) \quad (2)$$

$$\log k^{\text{O}}_{\text{plateau}} = 11.50 - 1.28 \text{ p}K_{\text{LG}} \quad (r = 0.999) \quad (3)$$

The $\text{p}K_{\text{LG}}$ range studied was 6–10.6, the faster, aryl thiolacetoacetates being studied by means of stopped-flow spectrophotometry. Other parameters (e.g., deuterium kinetic solvent isotope effects, activation parameters) have been used to differentiate between uni- and bimolecular hydrolytic mechanisms for esters but are often equivocal.^{5,6} We have found that, at 40.0 °C, $k_{\text{H}}/k_{\text{D}} = 1.5$ for the plateau term for S-acetoacetyl-N-acetylcysteamine, comparable with previous values for E1 collapse of ester anions.^{4,6} For this ester, $\Delta S^{\ddagger}_{25^\circ\text{C}}$ for the k_{plateau} term is +11.3 eu, again consistent with a markedly unimolecular transition state. The apparent second-order rate constant ($k_{\text{HO}^-} = k_{\text{plateau}} \times K_{\text{a}}/K_{\text{w}}$) for S-acetoacetyl-N-acetylcysteamine, hydrolyzing by the E1cB route, is some 600-fold greater than the observed⁹ value of the k_{HO^-} for N,S-diacetylcysteamine. The magnitude of the "rate enhancement" is markedly leaving group dependent (because of the difference in β_{LG} values) and we estimate a rate difference of 10^5 – 10^6 -fold for the 4-chlorothiophenyl esters,¹⁰ taking the $\text{p}K_{\text{a}}$ of 4-chlorophenyl thioacetoacetate as 8. At the thioethyl ester level, little difference is seen.

As the k_{plateau} term refers to the unimolecular fragmentation of the ester conjugate base, it reflects largely the bond-breaking process ($-\text{CO}-\text{XR}$ cleavage in eq 1) and the first, direct comparison of the relative leaving tendencies of oxygen and sulfur anionic leaving groups becomes possible for an acyl center. Such an approach to leaving group comparison was first suggested by Pratt and Bruce for malonate esters.⁴ In the case