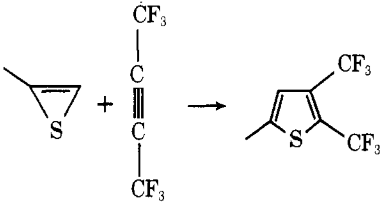
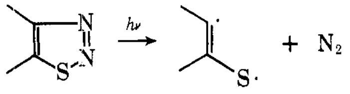
pointed out that the IR spectra of the matrix isolated photolyzate of 1,2,3-thiadiazole and its 4-methyl, 5-methyl, 4-*tert*-butyl, 5-*tert*-butyl, 4-methyl-5-carboethoxy, 5-methyl-4-carboethoxy, and 4-trifluoromethyl derivatives did not indicate the presence of the cyclic carbene, V.[13]

Thus, the most likely precursor left for thiophene formation is the thiirene structure, and the formation of only the 5-methyl isomer appears to be a consequence of the combined electronic and steric effects of the methyl substituent and can be rationalized by addition of the alkyne to thiirene across the less hindered C-S side:



The enthalpy change of the reaction



VI I

can be estimated to be about 50–60 kcal/mol; photolysis at $\lambda > 220$ nm would therefore provide sufficient excess energy to form the singlet excited state of thioketocarbene which, according to recent MO calculations,[19] lies only 8.8 kcal/mol above its ground triplet state and also to form singlet thiirene which lies 15.5 kcal above the singlet state thioketocarbene. Thiirene would thus be formed on a singlet surface by analogy with the oxirene–ketocarbene rearrangement[20] which in the case of the sulfur system lies above the ground state triplet surface.

These results are in line with those obtained from the photolysis of matrix-isolated 1,2,3-thiadiazoles.[11-13] They provide chemical evidence for thiirene formation and do not contradict previous results on the solution photolysis of 1,2,3-thiadiazoles. On the contrary, matrix isolation photolysis studies have shown that thiirene rearranges to thioketene on photolysis.[13]

Acknowledgments. The authors thank the National Research Council of Canada for financial support and Dr. E. M. Lown for helpful assistance.

Registry No.—II ($R_1 = R_2$ H), 157-20-0; II ($R_1 = CH_3$; $R_2 = H$), 45345-86-6; hexafluoro-2-butyne, 692-50-2.

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Low-Temperature Matrix Isolation of Thiirenes

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Several thiirene molecules have been prepared by the argon matrix photolysis of 1,2,3-thiadiazoles at 8 K and identified by IR spectroscopy. Of the expected eight IR absorption bands of the parent thiirene molecule, seven have been located and a tentative assignment of them made. Thiirene, trifluoromethylthiirene, and benzothiirene are highly unstable, but electron-withdrawing substituents exert a marked stabilizing effect on the 4π-electron ring system: carboethoxymethylthiirene is stable up to at least 73 K.

The synthesis of thiirene, like that of the analogous three-membered heterocycles, oxirene and 2-azirene, presents a formidable challenge to the synthetic chemist since they belong to the $4n$ π-electron ring systems which defy Hückel's aromaticity rule. According to Breslow's postulate[1] these systems possess an antiaromatic character as manifested by their low thermodynamic stability. Indeed, detailed molecular orbital computations confirm this prediction and oxirene,[2] 2-azirene,[3] and thiirene[4] are all computed to be thermodynamically less stable than their acyclic isomers, the ketocarbenes, or 1-azirene. Coupled with their thermodynamic instability is the apparent kinetic instability of the ring system since the ab initio MO computed activation energy of the ring-opening reaction of oxirene is only 7 kcal/mol.[2] Although none of these species could be isolated until quite recently, there are several reports in the literature[5] providing indirect although compelling evidence for their transient existence as short-lived intermediates. The possibility of chemical trapping of thiirenes, from the gas-phase photolysis of 1,2,3-thiadiazoles, with hexafluoro-2-butyne to give the corresponding thiophene has also been demonstrated.[6] Photolysis of 1,2,3-thiadiazole in the presence of hexafluoro-2-butyne yields

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2,3-bis(trifluoromethyl)thiophene and the photolyses of 4-methyl- and 5-methyl-1,2,3-thiadiazoles both yield only one and the same thiophene, namely the 5-methylbis(trifluoromethyl) derivative. This suggests addition of the acetylene across the less hindered C–S side of the methylthiirene molecule.

In recent developments the low-temperature matrix isolation of thiirene, methylthiirene, and dimethylthiirene has been reported. Krantz et al.[7] in the argon matrix isolated photolyzate of 1,2,3-thiadiazole (1) (λ >290 nm) at ~8 K have detected thioketene and ethynylthiol by IR spectroscopy. The 268-nm photolysis of 1 under otherwise identical conditions afforded an IR spectrum consisting of six bands (3207 (w), 3169 (m), 3166 (m), 1663 (w), 912 (m), and 563 (m) cm^{-1}) which have been attributed to thiirene. No assignment of the individual bands was attempted. The appearance of three absorptions in the C–H stretching region around 3100 cm^{-1} is inconsistent with the thiirene structure. The thiirene molecule should have nine normal modes of which the A_2 out-of-plane C–H bending should be IR inactive and consequently the spectrum should consist of eight absorptions, only two of which, the symmetric and asymmetric C–H stretchings, should lie in the 3100–3200-cm^{-1} region. The IR spectrum of the photolysis product of monodeuterio-1,2,3-thiadiazole reportedly shows three absorptions in the C–H stretching region and three in the C–D region, contrary to the expected single C–H and C–D stretchings.

Probably, the low intensity of the spectrum attributed to thiirene and its contamination with the intense spectra of thioketene, ethynylthiol, and possibly of unphotolyzed 1 made the analysis of the thiirene spectrum difficult and somewhat uncertain.

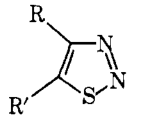
In the present article we wish to report the results of our studies on the matrix isolation photolysis of 1 and several of its derivatives which are relevant to the chemistry of thiirene.

Experimental Section

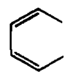
Apparatus. A cryostatic system Model LT-3-110 liquid helium transfer refrigerator with a WMX-1A shroud from Air Products and Chemicals Inc. was employed throughout the investigation. The shroud was equipped with two cesium iodide windows and two spectrosil windows. The cryostatic system was connected to a standard high-vacuum apparatus. The light source was a medium-pressure mercury arc, Hanovia Model 30620, equipped with either a 7910 Vycor filter or a 265 nm (or 215 nm) interference filter. Alternatively a 254-nm Hanovia low-pressure mercury resonance lamp was used.

A Varian Aerograph (90P) GC was employed for preparative purposes and a Hewlett Packard 5750 instrument for analysis. UV spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer; preliminary IR spectra of matrix isolated species were recorded on a Beckman Acculab I spectrophotometer and final IR spectra on a Nicolet 7199 FT infrared spectrophotometer. Argon and xenon from Union Carbide (Linde Division) research grade were dried only before use. Commercial reagent grade chemicals were used without further purification.

1,2,3-Thiadiazole (1), benzothiadiazole (2), 4-trifluoromethyl-1,2,3-thiadiazole (3), and 4 methyl-5-carboethoxy- and 5 methyl-4-carboethoxy-1,2,3-thiadiazole (4 and 5, respectively) were prepared according to known procedures.[8-10]



1, R = H; R' = H

2, R + R' = 

3, R = CF_3; R' = H

4, R = CH_3; R' = COOEt

5, R = COOEt; R' = CH_3

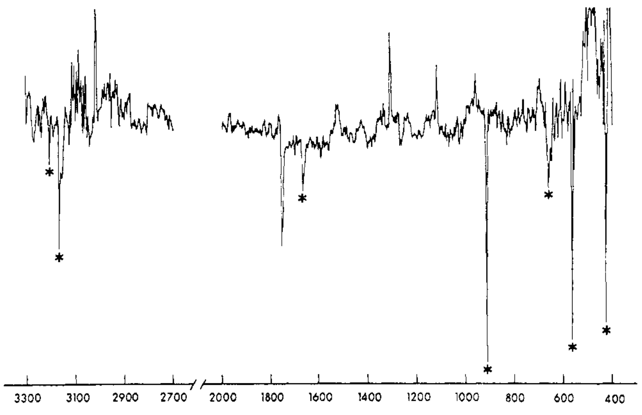


Figure 1. IR spectrum of the argon-matrix-isolated photolyzate of 1,2,3-thiadiazole at 8 K and with λ 215 nm as obtained after computed substraction of the thioketene, ethynylthiol, and remaining 1,2,3-thiadiazole spectra by a Nicolet 7199 FT-spectrophotometer. The asterisk indicates an assignment to thiirene.

Procedure. Samples with sufficient vapor pressure at room temperature (1 and 3) were introduced together with the host (argon or xenon) in a mixing reservoir and stirred constantly. The mixture was then directed to the cell and deposited on the plate (cesium iodide for IR studies and spectrosil for UV studies) that had been previously cooled at 8 K; guest to host ratios were less than 1:700. Alternatively, samples with low vapor pressure were placed in a finger trap close to the cell and warmed to 40–50 °C; they were then swept into the cell by a flow of argon. The irradiation was followed by IR or UV spectroscopy and was continued until the disappearance of the IR spectrum of the starting material.

Results and Discussion

The photolysis of 1, isolated in an argon matrix at 8 K, at 265 nm yielded a product with an IR spectrum composed of intense absorptions due to thioketene and ethynylthiol and exhibiting certain weak absorption bands attributed by Krantz et al.[7] to thiirene. The 254-nm photolysis of 1 resulted in a similar IR spectrum as above; however, attempts to carry out the photolysis to completion resulted in the partial disappearance of the thioketene and thiirene spectra and in the appearance of the characteristic 1528-cm^{-1} absorption of CS_2.

The UV spectrum of the matrix-isolated photolyzate obtained from 1 upon photolysis at λ >210 nm at 8 K featured a window at 215 nm where 1 also absorbs weakly. Irradiation of 1 was then carried out using a 215-nm interference filter under the same conditions used earlier. This resulted in a decrease in the rate of photolysis and, more significantly, in an appreciable increase in the IR absorption of the bands attributable to thiirene and ethynylthiol as compared to the absorption of thioketene. This enhancement in the spectral intensity made it possible to identify the bands which could be assigned to the thiirene molecule. On this basis, seven of the eight bands (3208 (w), 3170 (m), 1660, 912 (s), 660 (m), 563 (m), and 425 (m) cm^{-1}, Figure 1) expected for thiirene could be located and only two of these lie in the C–H stretching region. Based on the similarity between the fully optimized ab initio molecular orbital geometry of thiirene[4] and that of cyclopropene[11] and thiirane,[12] Table I, it is possible to make the following tentative assignments of the observed bands.

From the parallelism between the IR spectrum of cyclopropene and the one observed for thiirene, the missing band should be assigned to a C–H in-plane bending and would be expected to lie at ~1000 cm^{-1}. In fact, some weak absorption is present at 1010–1020 cm^{-1}, but its assignment at the moment is uncertain. IR studies of isotopic substituted thiirene, now in progress, will allow a more definitive assignment.

It was also observed that prolonged photolysis of the pri-

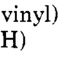
Table I. Tentative Assignment of the Observed Bands of Thiirene (cm^{-1})

	Thiirene	Reference compd
C—H stretch	3208	3124[a]
	3170	3158[a]
C═C stretch	1660	1656[a]
C—H in-plane bend		1010[a]
	912	905[a]
C—H out-of-plane bend	425	570[a]
Ring deformation	660	633[b]
	563	646[b]
	Geometry	
R(C═C)	1.270 Å[c]	1.300 Å[d]
R(CH)(vinyl)	1.074 Å[c]	1.070 Å[d]
α(C═CH)	149° 55′[c]	149 ° 18′[d]
R(CS)	1.810 Å[c]	1.819 Å[e]

[a] Cyclopropene, ref 13. [b] Thiirane, ref 14. [c] Calculated for thiirene, ref 4. [d] Cyclopropene, ref 11. [e] Thiirane, ref 12.

mary photolyzate resulted in a slow decrease in the intensity of the thioketene spectrum, accompanied by a slow increase in the spectrum of ethynylthiol, indicating that at this wavelength thioketene is converted to ethynylthiol without the formation of CS_2.

The effect of substituents was also investigated. The photolysis of benzothiadiazole (**2**) with 265-nm radiation resulted in the formation of the 1,3-butadienylenethioketene (**6**) and another species in low yield which exhibited IR absorptions at 1670 (w) (tentative), 1440 (m), 970 (w), 950 (m), 720 (s), 680 (m), and 670 (w) cm^{-1}, and which was converted to the thioketene on further irradiation with λ >210 nm radiation, in a manner similar to that reported for the photolysis of **1** at 300 nm.[7] Thus, the spectrum is due either to benzothiirene or to the isomeric species **7** and/or **8**. On the other hand, photolysis of **2** in liquid benzene solution has been reported[15] to yield thianthrene (**9**) as the sole product, which is a clear indication of the stability of the intermediate diradical **7** or benzothiirene toward rearrangement. Moreover, thermolysis of sodium *o*-bromobenzenethiolate (**10a**) also yields thianthrene (**9**) and the 4-methyl derivative **10b** gives a 1:1 mixture of the thianthrenes **11a** and **12a**[16] which can only arise from a benzothiirene intermediate. Similarly, a mixture of thianthrenes **11b** and **12b** has recently been reported in the thermolysis of 6-carbomethoxy-1,2,3-thiadiazole[17] and this provides additional evidence for the benzothiirene intermediate. Thus, the combined evidence would strongly suggest that the observed spectrum is that of benzothiirene.



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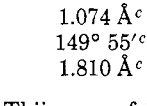

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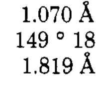

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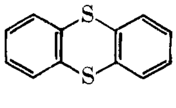

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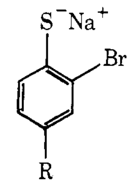
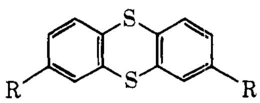
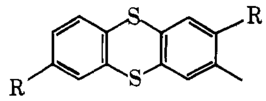


10a, R = H
b, R = CH_3



11a, R = CH_3
b, R = COOMe



12a, R = CH_3
b, R = COOMe

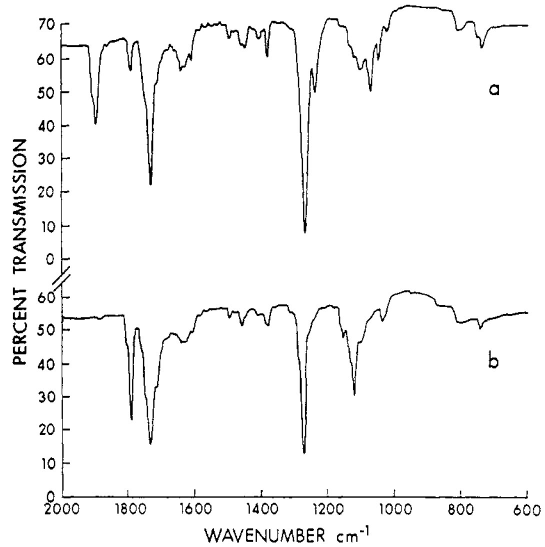
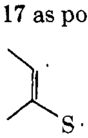


Figure 2. (a) IR spectrum of the argon-matrix-isolated photolyzate of 4-methyl-5-ethoxycarbonyl-1,2,3-thiadiazole at 8 K and with λ 265 nm. (b) IR spectrum of the above sample after irradiation with a Vycor filtered mercury arc.

The photolysis of 4-trifluoromethyl-1,2,3-thiadiazole (**3**) at 265 nm affords an intermediate in much higher yield than from any previously described thiadiazole to which we have assigned the absorptions 3210 (w), 1240 (s), 1190 (s), 1180 (s), and 720 (w) cm^{-1} and which is again converted to trifluoromethylthioketene upon further irradiation using a Vycor filter. In addition to this intermediate, trifluoromethylthioketene, 3,3,3-trifluoropropyne, and possibly $CF_3C{\equiv}CSH$ were observed.

A much clearer indication of the presence of thiirene was obtained in the photolysis of 4-methyl-5-carboethoxy and 5-methyl-4-carboethoxy-1,2,3-thiadiazole (**4** and **5**, respectively). Irradiation of either **4** or **5** using a 265-nm interference filter resulted in the appearance of a spectrum (Figure 2a) with significant absorptions at 3205 (vw), 3000 (w), 1875 (m), 1715 (s), 1440 (w), 1400 (w), 1370 (m), 1270 (s), 1070 (m), 1040 (m), 1020 (w), 760 (w), 730 (w), and 490 (w) cm^{-1}. Replacement of the 265-nm interference filter by a Vycor filter and continuation of the photolysis resulted in the disappearance of the intermediate spectrum and the appearance of the spectrum of thioketene (Figure 2b). This excludes diradical thioketocarbene intermediate, **13**, **14**, and **15**, leaving structures **16** and **17** as possible carriers.



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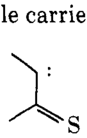

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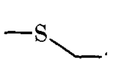

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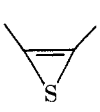

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17

Photolysis, in this case, could also be carried out with the 265-nm source and complete disappearance of the IR spectrum of the starting material occurs without appreciable decomposition of the intermediate. No acetylene absorption was observed, indicating that substitution quenches the thiirene → acetylene rearrangement, and the low intensity of the characteristic 1785-cm^{-1} absorption of thioketene indicated the virtual absence of this species.

The presence of an absorption of 1875 cm^{-1} for a C═C stretching indicates an unusually large shift from the value of 1660 cm^{-1} for the parent compound; however, this again parallels the behavior of cyclopropenes, since similarly substituted cyclopropenes exhibit an absorption at 1840 cm^{-1} which was assigned to the C═C stretching.[18] Therefore, the spectrum obtained and reproduced in Figure 2a can be attributed only to the thiirene structure **16**.

The species responsible for the spectrum exhibits remarkable stability. Experiments carried out using a xenon matrix have shown that the spectrum persists up to at least 73 K, the softening point of the xenon matrix. This is a manifestation of the stabilizing effect of the electron-withdrawing substituents on the thiirene molecule which parallels the behavior of cyclobutadiene; similarly substituted cyclobutadiene has been reported[19] to be stable at room temperature.

In conclusion it may be stated that the IR spectrum consisting of seven bands that has been obtained in the argon matrix isolated photolyzate of **1** is consistent with the carrier being the thiirene molecule. The tentative assignment of the bands is based on analogous data reported for cyclopropene and thiirane.

The IR spectra of the matrix-isolated photolyzate of **4** and **5** are identical and bear close resemblance to the spectrum of the parent thiirene. The shifts in the C=C stretching frequencies of the photolyzates of **4** and **5** with respect to the parent thiirene are similar to those observed for cyclopropene and similarly substituted cyclopropenes. The spectrum is undoubtedly due to methylcarboethoxythiirene. The parallelism in the behavior of thiirene and cyclopropene also extends to their ring-opening reaction, leading respectively to methylacetylene[20] and ethynylthiol. The presence of alkyl substituents apparently hinders the rearrangement of thiirene. Substituents in general, and electron-withdrawing substituents in particular, endow the thiirene ring with an increased stability which manifests itself in an enhanced yield and persistence to higher temperatures on warming of the matrix.

Additional work in the area of thiirene formation and chemistry is presented in the accompanying paper.

Acknowledgments. The authors thank the National Research Council of Canada for financial aid and Drs. E. M. Lown and I. Safarik for helpful discussions.

Registry No.—**1**, 288-48-2; **2**, 273-77-8; **3**, 65702-19-4; **4**, 18212-20-9; **5**, 29682-53-9; **6**, 54191-78-5; thiirene, 157-20-0; benzothiirene, 65330-66-7; trifluoromethylthiirene, 65702-20-7; carboethoxymethylthiirene, 65702-21-8.

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Intra- and Intermolecular Photocycloadditions of Acetylenic Esters to Benzo[*b*]thiophenes

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Direct and sensitized irradiation of 2-(3-benzo[*b*]thienyl)ethyl but-2-ynoate (**1**) leads to an unrearranged intramolecular cycloaddition product, **2**, as primary photoproduct, which can rearrange to **3** on extended photolysis. An intramolecular cycloaddition product, **6**, has been obtained on sensitized irradiation of 2-(2-benzo[*b*]thienyl)ethyl but-2-ynoate (**5**), although a desulfurized naphthopyranone has been isolated as a major product. Reinvestigation of the photochemical cycloaddition of methyl phenylpropiolate to 2-methylbenzo[*b*]thiophene also shows the presence of small quantities of unrearranged photoproducts **14** and **15**. On sensitized and direct irradiation of (2-benzo[*b*]thienyl)alkyl phenylpropiolates **18** and **19**, only cycloadducts of the solvent benzene with the triple bond are observed. In the latter case, an intramolecular cycloaddition product, **23**, has been shown to be present. The mechanism of formation of the unrearranged products is discussed.

The photochemical addition of acetylenic esters to fused heteroaromatic compounds like benzo[*b*]thiophene,[1,2] benzo[*b*]furan,[3] and *N*-methylindole[4] has been investigated extensively in our laboratories. In general, these compounds give cyclobutenes, formed via [$_\pi 2_s + {}_\pi 2_s$] addition of the acetylene to the 2,3 position of the heteroaromatic compound.[1-5] These cyclobutenes, however, are often not stable and undergo further photochemical[1-6] and/or thermal changes.[4,7] Thus, only rearranged cyclobutenes are found in the photoaddition of dimethyl acetylenedicarboxylate, methyl propiolate, and methyl phenylpropiolate to benzo[*b*]thiophene.[2]

Several important mechanistic questions present themselves in the relatively simple photoaddition of an alkyne ester to benzo[*b*]thiophene. Among these are which excited state

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