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THE DETECTION AND PROPERTIES OF THIIRENES

by

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Thiirenes, the 4 π-electron antiaromatic sulfur heterocycles, have been implicated as intermediates in a variety of chemical reactions but were only recently detected by ir spectroscopy in the low temperature argon matrix photolysis of 1,2,3-thiadiazoles. Structural identification and vibrational assignments of the parent thiirene are based on the nature of the band shifts observed upon substitution and isotopic labelling of the source compound. Thiirene is unstable and undergoes rearrangement to thioketene and ethynylthiol as well as decomposition to acetylene, carbon disulfide and polymer. Electron-withdrawing substituents exert a marked stabilizing effect. Theoretical calculations on thiirene and its isomers predict the experimentally observed order of stability and are helpful in the formulation of an overall mechanism for the photochemical decomposition of 1,2,3-thiadiazoles.

This review is comprised of the following sections:

I. Introduction.

II. Chemical evidence for the transient existence of thiirenes.

III. Low temperature photolysis of matrix isolated 1,2,3-thiadiazoles: isolation of thiirenes.

IV. Theoretical studies and mechanistic considerations.

V. Properties of thiirenes.

I. INTRODUCTION

One of the first applications of molecular orbital theory to organic chemistry was what is known today as Hückel's aromaticity rule,[1] according to which those monocyclic coplanar systems of trigonally hybridized carbon atoms which contain 4n+2 π-electrons will possess electronic stability.[2] The concept of aromaticity, initially developed for hydrocarbon systems, was soon extended to heterocyclic conjugated systems such as pyridine and further to those heterocyclic compounds such as furan, thiophene and pyrrole in which the lone pair of electrons on the heteroatom participate in the π-electron network. Although there are as yet no accepted criteria according to which the extent of aromatic stabilization can be evaluated quantitatively, the Hückel rule has proven to be one of the most fruitful concepts in organic chemistry.[3]

In contrast to the 4n+2 π-electron systems, planar cyclic conjugated systems with 4n π-electrons are not stabilized and therefore are non-aromatic. Moreover, according to Breslow;[4] some of these compounds may actually be destabilized relative to their acyclic isomers and have been called "antiaromatic". Obviously, quantitative evaluation of the antiaromatic destabilization is as problematic as that of aromatic stabilization. In fact, 4n π-electron systems either deviate from planarity and thus have localized π bonds, e.g. *cyclo*octatetraene, or are planar and exist only as highly elusive intermediates, e.g. *cyclo*butadiene. The simplest examples of aromatic (a), antiaromatic (b), and non-aromatic (c) compounds are listed in Table 1.

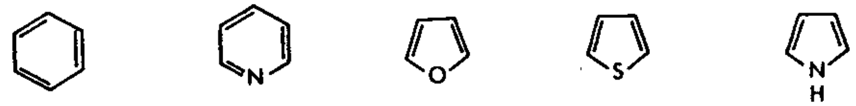
*Cyclo*butadiene was the first 4 π-electron species to be isolated[5] and its ground state geometry, either the antiaromatic square, or the non-aromatic rectangle with localized double bonds, is still the object of controversy.[6,7] The argon matrix isolation of a derivative of the heterocyclic

4 π-electron azete (aza*cyclo*butadiene) has also been reported.[6] The synthesis of aza*cyclo*octatetraene has not yet been reported, but by comparison with *cyclo*octatetraene it is expected to be non-planar and hence not antiaromatic.

Table 1. Non ionic conjugated π-electron systems

4n+2 (n=1):

a)



benzene pyridine furan thiophene pyrrole

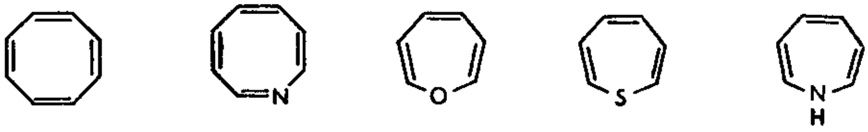
4n (n=1):

b)

*cyclo*butadiene azete oxirene thiirene 2-azirene

4n (n=2):

c)



*cyclo*octatetraene aza*cyclo*octatetraene oxepin thiepin azepine

Those 4n π-electron heterocycles which are the counterparts of furan, thiophene and pyrrole, are oxepin, thiepin and 1-H azepine for n=2 and oxirene, thiirene and 2-azirene for n=1. Although substituted oxepins,[8,9] thiepins[8,10] and azepines[8] are known, oxepin remains the only parent compound that has been isolated to date.[11] As expected, all the data point to a non-planar geometry and thus to the non-antiaromaticity of these systems, in spite of the low ring strain energies involved. For 4 π-electron heterocyclic systems, however, planarity is enforced and only small distortions in the C-H bond angles are possible. As a consequence, oxirene, thiirene and 2-azirene are expected to be antiaromatic and therefore highly unstable.

Since Berthelot's attempted synthesis of oxirenes nearly a century ago,[12] continuous efforts have been made to isolate these theoretically interesting compounds. Compelling evidence has been presented for the transient formation of oxirenes in the photochemical Wolff rearrangement of α-diazo ketones[13] and, more recently, 2-azirenes have been implicated in a variety of reactions[14] but neither of these compounds nor their substituted derivatives have so far been synthesized.

Interest in the chemistry of thiirene has evolved only in the past decade and the first reaction in which thiirenes were postulated as reactive intermediates, in 1967, was the addition of $S(^1D_2)$ atoms to acetylenes.[15] The matrix isolation of thiirene and several of its derivatives, the first antiaromatic three membered heterocycles to be synthesized, has been achieved recently.

II. CHEMICAL EVIDENCE FOR THE TRANSIENT EXISTENCE OF THIIRENE

1. The $S(^1D_2)$ + acetylene reaction

Electronically excited ($^1D_2$) sulfur atoms, produced by the gas phase photolysis of COS, react with acetylene to form CS_2, benzene and thiophene in low (5-10%) and pressure dependent yields.[16] Analogous products were obtained with methyl and dimethylacetylene. However, the reaction with hexafluoro-2-butyne led to the formation of perfluorotetramethylthiophene as the only product, in high yield.

Since $S(^1D_2)$ atoms have been shown[17,18] to add across unsaturated bonds and insert into C-H (but not C-C) bonds, the structure of the primary C_2H_2S adduct could be a diradical 1 (equivalent to thioketocarbene 2), thiirene 3 or ethynylthiol 4:

1 2

3

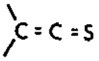
-C≡C-SH

4

Addition of C_2H_2S to another molecule of acetylene then leads to the formation of thiophene:

$C_2H_2S + C_2H_2 \rightarrow$  (1)

Other possible isomeric structures which could be formed upon rearrangement of the primary adduct prior to reaction with acetylene include thioketene 5, thiirenylidene 6 and thiolvinylidene carbene 7:



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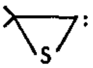

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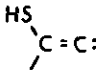

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The thiophene-forming reaction (1) is conceptually difficult to visualize if either of structures 4-7 is involved since two or more rearrangements would be required; the following observations clearly militate against their intermediacy.

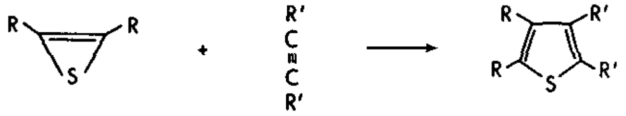
Ethynylthiol 4 can only be formed in the cases of C_2H_2 and monosubstituted acetylenes yet the thiophene yields are the highest for disubstituted acetylenes. Hence its intermediacy can be discounted.

Flash photolysis-kinetic mass spectroscopic studies[16,19] on various COS-acetylene mixtures clearly showed the formation of S + acetylene adducts having extraordinarily long decay half lives, ranging from a few tenths of a second to several seconds, Table 2. These results clearly are not compatible with excited state or radical species 1, 2, 6 or 7 as the transient detected. There is, however, a distinct possibility of isomerization in the mass spectrometer which may not occur in the static system prior to reaction. It should also be noted that bis(trifluoromethyl)thioketene is stable at room temperature[20] yet it is seen from Table 2 that this adduct has the shortest half-life of all those examined. This indicates that at least in this case thioketene is not the transient.

Table 2. Half lives of the transients formed in the reactions of $S(^1D_2)$ atoms with acetylenes.[16,19]

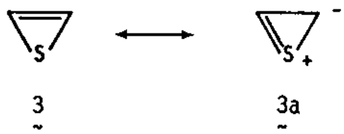
Alkyne	Decay half life (sec)
Acetylene	2
Propyne	5
Butyne-2	7
Hexafluorobutyne-2	> 0.1

For thioketene 5 to be formed, an intramolecular hydrogen or methyl shift in the primary adduct would be required: the former being more facile, the product yields should decrease with substitution, in contrast to experiment. Moreover, if thioketene is the precursor of thiophene then a reversal of this shift would be required in reaction (1), yet the product yield for the case of perfluoro-2-butyne was the highest obtained in spite of the low migratory aptitude of the trifluoromethyl group. It is therefore unlikely that 5 is the reaction intermediate and the only possible alternative remaining is thiirene 3. The reactions of $S(^1D_2)$ atoms with an equimolar mixture of acetylene and hexafluoro-2-butyne afforded the asymmetrical 2,3-bis(trifluoromethyl)thiophene as the only cross product.[19] It would therefore appear that thiophene is formed by addition of the acetylene across the C-S bond of thiirene:



(2)

The absence of unsubstituted thiophene among the products points to the nucleophilic character of the intermediate. This is only compatible with a thiirene structure, especially if the resonance contribution from 3a is significant.



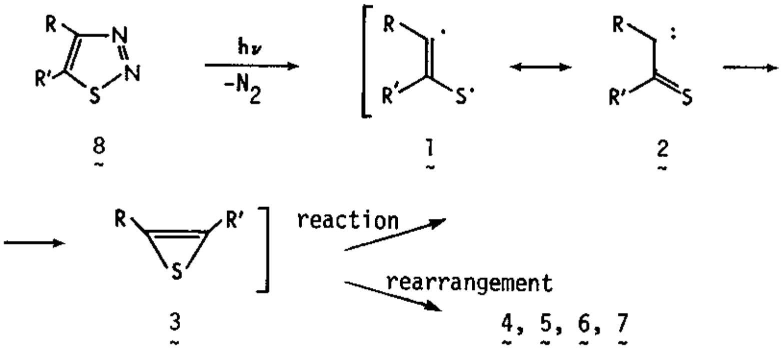
(3)

All these observations strongly point to the intermediacy of thiirene in the $S(^1D_2)$ + acetylene reaction.

2. The decomposition of 1,2,3-thiadiazoles

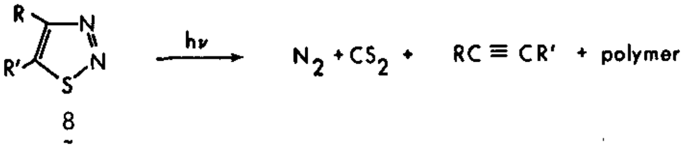
a) Gas phase photolysis

1,2,3-Thiadiazoles containing an azo linkage are potential sources of thiirenes or their isomers upon photolysis. The intermediates produced by nitrogen extrusion could undergo bimolecular reactions with scavengers present in the system or unimolecular isomerizations.



(4)

Conventional gas phase photolysis of 1,2,3-thiadiazole 8a, 4-methyl-, 8b, and 5-methyl-1,2,3-thiadiazole 8c[16,21] leads to the formation of N_2, CS_2, the corresponding acetylene, and a polymeric material:



(5)

The results are summarized in Table 3.

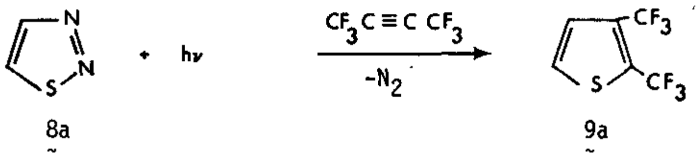
Table 3. Product yields from the gas phase photolysis of 1,2,3-thiadiazoles[a,b]

	%		
Thiadiazole	Alkyne	Methane	CS_2
8a	12.6	-	1.8
8b	14.4	5.0	3.6
8c	16.1	4.8	4.8

[a] Percentages are given in terms of N_2.

[b] Reproduced with permission by the American Chemical Society from J. Font, M. Torres, H.E. Gunning and O.P. Strausz, "Gas-Phase Photolysis of 1,2,3-Thiadiazoles: Evidence for Thiirene Intermediates", *J. Org. Chem.* 43, 2487 (1978). Copyright by the American Chemical Society.

When the photolysis of 1,2,3-thiadiazole 8a was carried out in the presence of hexafluoro-2-butyne, the principal product was 2,3-bis(trifluoromethyl)thiophene 9a:



(6)

The reaction parallels that described for the $S(^1D_2)$ + acetylene system and suggests the intervention of thiirene. More definitive evidence for the formation of thiirene was obtained from the gas phase photolysis of 4-methyl-, 8b, and 5-methyl-1,2,3-thiadiazole, 8c, in the presence of hexafluoro-2-butyne. In both cases only one thiophene was formed, in very similar and pressure dependent yields, and was identified as 5-methyl-2,3-bis(trifluoromethyl)thiophene 9b. The results are summarized in Table 4.

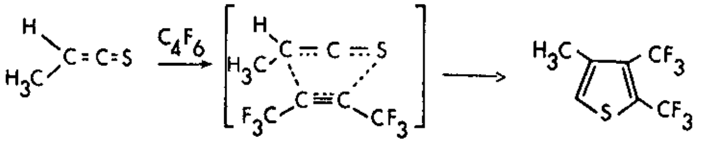
Table 4. Yield of 5-methyl-2,3-bis(trifluoromethyl)thiophene 9b as a function of the pressure of hexafluoro-2-butyne[a,b]

P (C_4F_6), Torr	Yield of 9b From 8b	 From 8c
270	12.3	12.5
600	20.8	30.5
900	23.1	34.0
1200	33.3	37.5

[a] In terms of N_2 produced.

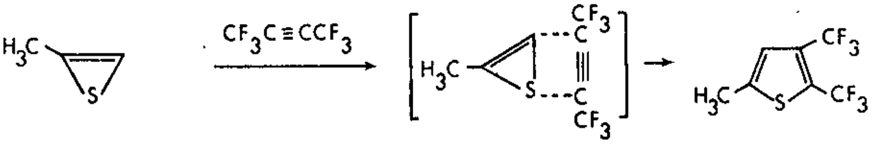
[b] Reproduced with permission by the American Chemical Society from J. Font, M. Torres, H.E. Gunning and O.P. Strausz, "Gas-Phase Photolysis of 1,2,3-Thiadiazoles: Evidence for Thiirene Intermediates", *J. Org. Chem.* 43, 2487 (1978). Copyright by the American Chemical Society.

The completely analogous behaviour of 4-methyl- and 5-methyl-1,2,3-thiadiazole 8b and 8c can only be rationalized in terms of a common intermediate which makes methyl substitution in either isomer indistinguishable. Consequently, this rules out diradical 1 and thioketocarbene 2, leaving thioketene 5 and thiirene 3 as the only possible intermediates. The intervention of the other possible isomers 4, 6, 7 can also be discounted.[21] Methylthioketene has been detected only in matrix isolation experiments[22] and is unlikely to be the common intermediate since, on the basis of the relative rates of hydrogen and methyl migration, the expected product of 1,3 cycloaddition of methylthioketene with C_4F_6 is 4-methyl-2,3-bis(trifluoromethyl)thiophene 9c:



9c (7)

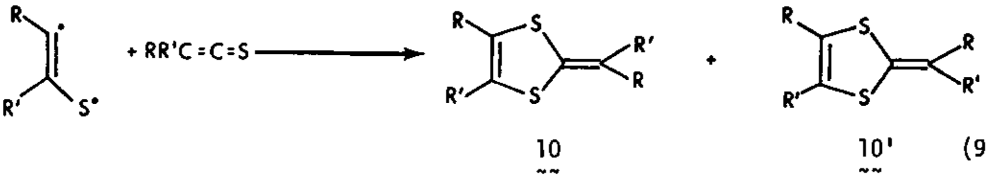
On the other hand, no rearrangements are required in the methyl thiirene + C_4F_6 complex and the formation of the single thiophene isomer is a consequence of combined electronic and steric effects of the methyl substituents, forcing addition of the alkyne across the unhindered C-S side:



9b (8)

b) Solution phase photolysis

The formation of thiofulvenes 10 upon photolysis of 1,2,3-thiadiazoles in a benzene solution was originally reported by Kirmse and Hörner.[23] These earlier studies have since been re-examined for a wider range of substituted thiadiazoles.[24,25] The yields of thiophenes 9, thiofulvenes 10, 1,4-dithiins 11 and 1,2,5-trithiepins 12 obtained from the photolysis of a variety of thiadiazoles in benzene solution are summarized in Table 5. These products were assumed to have been formed *via* self and cross combination reactions of diradicals 1 and thioketene 5



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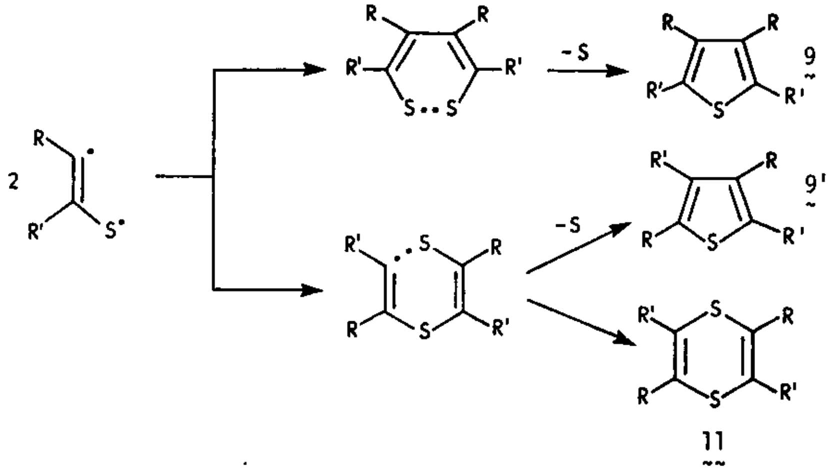

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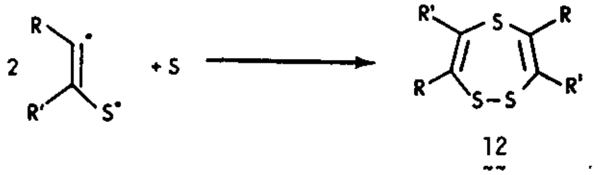
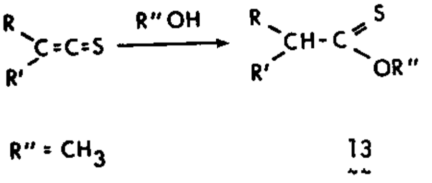
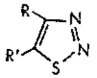


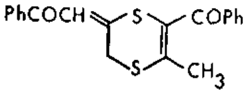
(11)

Photolysis of 4-methyl-5-carboethoxy-1,2,3-thiadiazole (8d R = CH_3, R' = COOEt) in methanol solution also led to the formation of 10 as the major product; however, small amounts of the intermediate thioketene could be trapped as the thionoesther 13:[26]



(12)

Table 5. Product distribution (%) in the photolysis of  in benzene solution[a]

R	R'	**9**	**9'**	**10**	**11**	Other	Reference
Ph	H			100			24
benzo					100		24
Ph	Ph			80	20		24
COOMe	Ph	91		9			24
COOEt	H	8		92			25
CH_3CO	H	71	29				25
CH_3CO	CH_3	100					25
COOEt	CH_3	6		94			25
PhCO	CH_3	49	34				25

[a]Absolute yields are 40-50%.

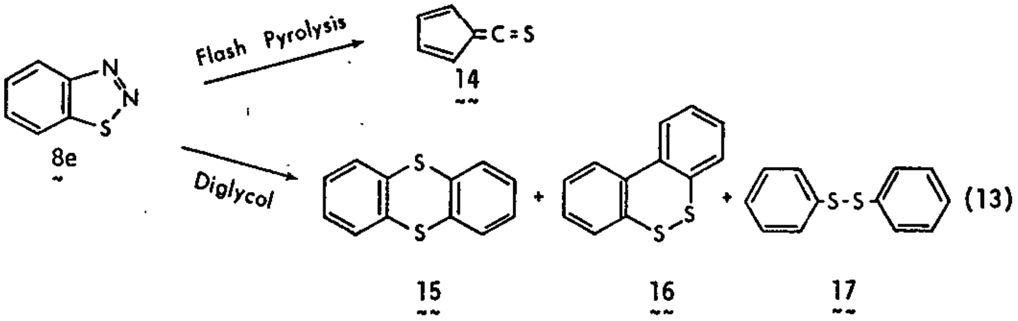
Although the intervention of thiirene intermediates is not explicitly required in order to explain the various products obtained in the solution photolysis of 1,2,3-thiadiazoles and thioketene has been positively identified as an intermediate, on the other hand there is no evidence that would militate against the transient formation of thiirenes and subsequent rearrangement to thioketene. In this connection it is interesting to note that the photolysis of 4-*tert*-butyl-1,2,3-thiadiazole in methanol solution produces *tert*-butylacetylene in 12% yield as the only product.[26] The expected product from the reaction of the corresponding thioketene with methanol was not detected in spite of the relatively long lifetime reported for *tert*-butylthioketene.[27] It is our opinion that thiirenes are probably formed in the solution phase photolysis of 1,2,3-thiadiazoles but perhaps to a lesser extent than in the gas phase. Definitive conclusions await the results of proper isotopic labelling studies.

c) Pyrolysis

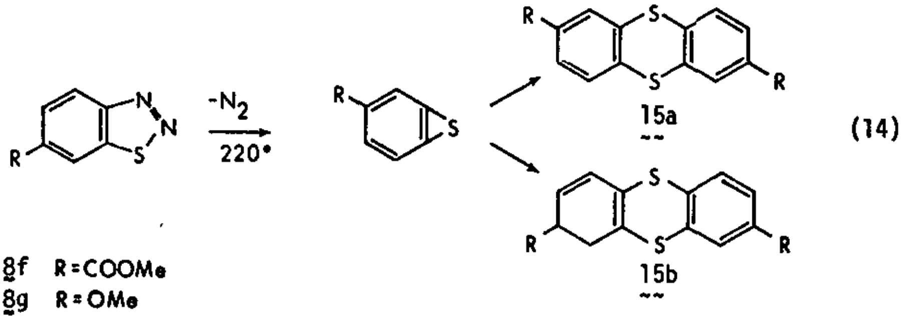
Flash pyrolysis of 1,2,3-thiadiazoles at 500-600°C has been carried out by Seybold and Heilb[27] in connection with the synthesis of thioketenes, but no attempts were made to elucidate the mechanism of the rearrangement. Pyrolysis of several substituted 1,2,3-thiadiazoles in diglycol solution at 250°C has been studied by Bühl and co-workers;[28] under these conditions radical dimerizations and cross combinations are suppressed and only the thionoesthers **13** (Eq. 12) (R'' = CH_2-CH_2-O-CH_2-CH_2OH) of the corresponding thioketenes were isolated. However, some interesting observations were reported which, in our opinion, at least in one case clearly indicate the intermediacy of thiirene. Thus, pyrolysis of either 4-phenyl or 5-phenyl-1,2,3-thiadiazole yields the same amount of thioketene, in spite of the widely differing migration energy requirements of hydrogen atoms and phenyl groups should thiirene not be a precursor. Under the same conditions 4,5-diphenyl-1,2,3-thiadiazole does not yield thioketene, which would also be formed *via* phenyl migration, and instead the dimerization product tetraphenylthiophene is obtained. The identical behaviour of 4- and 5-monosubstituted-1,2,3-thiadiazoles has also been observed in the flow pyrolysis of methyl and *tert*-butyl-1,2,3-thiadiazoles followed by matrix isolation of the products and is only consistent with a common thiirene intermediate.[26]

One of the secondary products of the photolysis of argon matrix isolated 4-trifluoromethyl-1,2,3-thiadiazole is 1-thiol-3,3,3-trifluoropropyne,[29] probably produced from fragmentation of the initially formed trifluoromethylthiirene. The same acetylene was detected in the matrix isolated products formed in the flow pyrolysis of the parent compound[30] and it would appear that in this case as well, thiirene is the precursor.

Although some evidence for the formation of 1,3-butadienylenethioketene 14 was obtained in the flash thermolysis of 1,2,3-benzothiadiazole 8e,[27] no thionoesther derived therefrom could be detected in the diglycol solution pyrolysis of 8e; instead, dimers 15-17 were obtained,[28] the formation of which point to the long lifetime of the benzothiirene intermediate:



Recently, the intermediacy of thiirene in the pyrolysis of benzo-1,2,3-thiadiazole has been the object of controversial reports.[31,32] Thus, thermolysis of 6-carbomethoxy-1,2,3-thiadiazole 8f (R = COOMe) leads to the formation of 2,7- and 2,8-dicarbomethoxythianthrene 15a and 15b (R = COOMe) which can only arise *via* dimerization of the thiirene intermediate,[31]

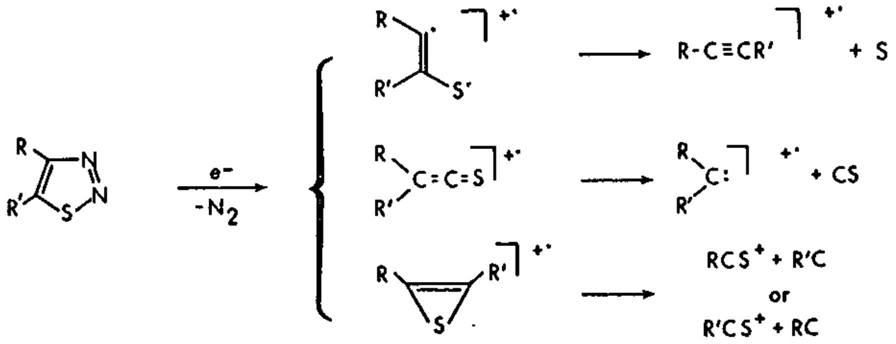


whereas pyrolysis of 6-methoxy-1,2,3-thiadiazole 8g (R = OCH_3) has been reported to yield only 2,7-dimethoxythianthrene 15a (R = OCH_3) which does not necessarily implicate a thiirene intermediate. The different nature of the substituents possibly may accommodate both results which, however, cannot be extrapolated to parent benzo-1,2,3-thiadiazole.

Although thiirene was not identified in the thermolysis of parent 1,2,3-thiadiazole 8a[33] and its intermediacy has been disproven in the pyrolysis of ^{13}C labelled 4,5,6,7-tetrahydro*cyclo*hexa-1,2,3-thiadiazole,[34] for some substituted 1,2,3-thiadiazoles it would appear that thiirene intermediates are formed. It is likely that, as observed for the case of α-diazoketones, in which the extent of oxirene participation in the decomposition strongly depends on substitution and temperature,[13] the formation of thiirene in the decomposition of 1,2,3-thiadiazoles follows a similar trend.

d) Electron impact fragmentation

The mass spectra of various 1,2,3-thiadiazoles have been reported by Zeller et al.[35] and by Millard and Pain.[36] All the thiadiazoles studied undergo N_2 elimination to give rise to the $M-N_2$ radical ion. The two groups differ, however, in the assignment of the structure of this fragment. Whereas Millard and Pain assign the thiirenium radical-ion structure to the $M-N_2^{+\cdot}$ fragment, in line with traditional mass spectrometric assignments for cyclic sulfur compounds,[37] Zeller's group on the other hand prefers the thioketene structure in order to account for the successive fragmentations of this ion. Since isotopic labelling experiments have not been done, the assignments are rather speculative although Zeller et al. report more convincing evidence for the formation of thioketenes in the cases of phenyl and diphenyl substituted 1,2,3-thiadiazoles. Three main structures for the $M-N_2^{+\cdot}$ fragment were considered: the diradical, the thioketene and the thiirene radical ion. Zeller et al. propose that the subsequent fragmentations for each species would involve the loss of an S atom from the diradical, loss of CS from the thioketene and loss of RCS from the thiirene radical ion:



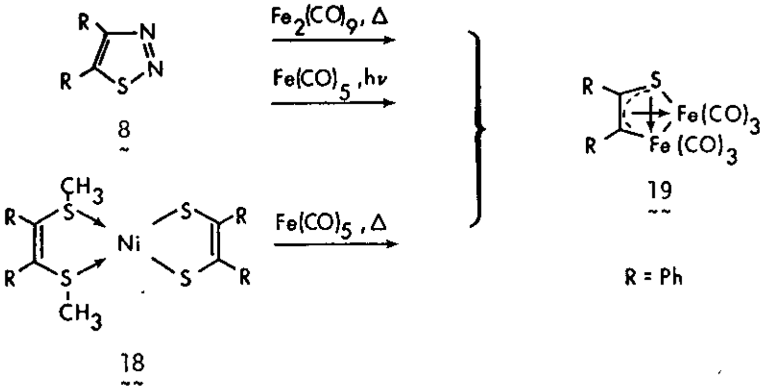
(15)

This generalization should be viewed with caution, however, since recent mass spectrometric studies on alkylthiazoles,[38] which have fragmentation patterns somewhat similar to those of 1,2,3-thiadiazoles, point to the initial formation of thiirenium ions which do not fragment by loss of RCS.

3. From metal complex stabilization

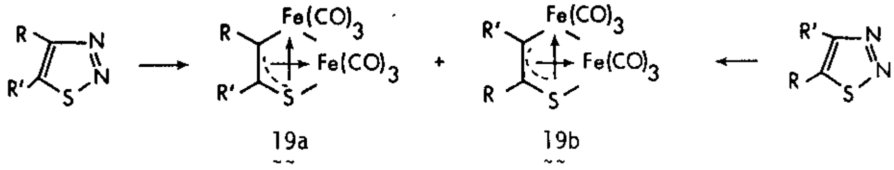
In 1956, Longuett-Higgins and Orgel predicted that *cyclo*butadiene could be stabilized by means of metal complexes.[39] This prediction has met with great success, first for substituted *cyclo*butadienes[40] and later for the parent compound,[41] and as a consequence the novel chemistry of metal complexes of *cyclo*butadiene[42] has attracted a great deal of attention. The fact that thiirene is also a 4 π-electron system, therefore isoelectronic with *cyclo*butadiene, suggests that thiirene may also be stabilized as a metal complex in spite of the fact that Orgel predicted that the degree of stabilization would be less than for the case of *cyclo*butadiene.[43]

Attempts to trap metal complexes of thiirene to date include the thermal decomposition of 1,2,3-thiadiazoles **8** in the presence of diironnonacarbonyl,[44] their photolysis in the presence of iron pentacarbonyl[45] and the thermal decomposition of metal dithienes of the type **18**[45] in the presence of iron pentacarbonyl. In neither case was the expected thiirene-metal complex observed but instead a thioketocarbene metal complex 19 was trapped:



(16)

However, when the two substituents on the 1,2,3-thiadiazole were different, both possible isomeric thioketocarbene-complexes were obtained from either thiadiazole:



(17)

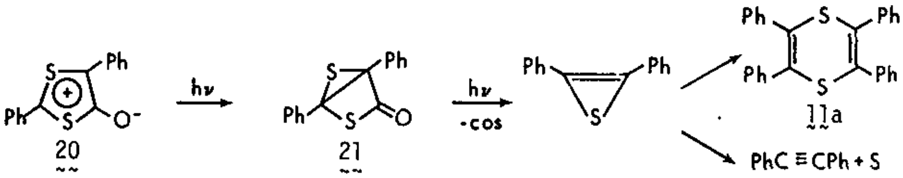
$R = Bu^t$ $R' = Ph$

$R = p\text{-}Bu^tC_6H_4$ $R' = Ph$

Although the yields of both complexes depended on the starting material, the component retaining the C-C-S skeleton was the major one in each case. It would therefore appear that these originate from a common precursor and equilibration must have taken place to some extent. Since thioketocarbene-complexes do not isomerize under the reaction conditions employed, the intermediacy of thiirene or its metal complex prior to the formation of the thioketocarbene-metal complex is the most likely explanation.

4. Other precursors

Thiirene has also been claimed to be an intermediate in a few other systems, such as the photolysis of the mesoionic 2,5-diphenyl-1,3-dithiol-4-one **20**. Photolysis of **20** in benzene solution resulted in the formation of tetraphenyl-1,4-dithiin **11a**, diphenylacetylene and sulfur,[46] the latter two being produced by decomposition of the intermediate diphenylthiirene:

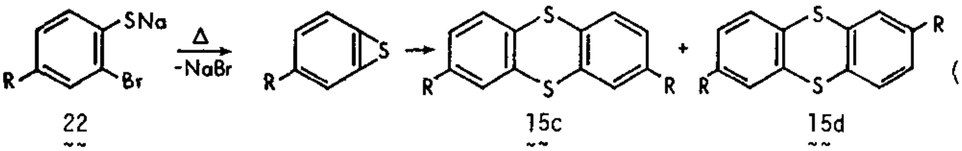


(18)

it is interesting that in this case the formation of thiirene requires bonding between carbon atoms which were non-bonded in the source compound. The bicyclic thiolactone intermediate proposed, **21**, is the analog of Corey's lactone[47] used in the synthesis of *cyclo*butadiene.[5]

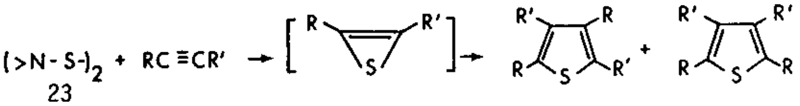
The intermediacy of bis(trifluoromethyl)thiirene has also been claimed[48] in the photolysis of tetrakis(trifluoromethyl)thiophene; however, no supporting evidence was presented.

Compelling evidence has been reported[49] for the formation of a substituted benzothiirene. Thermolysis of sodium 2-bromobenzenethiolate **22a** (R = H) yielded thianthrene **15** (R = H) in 41% yield; however, thermolysis of sodium 2-bromo-4-methylbenzenethiolate **22b** (R = CH_3) produced the two isomeric thianthrenes **15c** and **15d** (R = CH_3) in similar yields, *via* dimerization of the methylbenzothiirene intermediate:



(19)

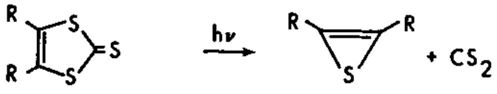
More recently, the intermediacy of thiirenes has been postulated in the reaction of acetylenes with bis-amine disulfides **23**[50] in order to account for the formation of the two isomeric thiophenes:



23

(20)

Finally, it has been shown by matrix isolation techniques that photolysis of trithiocarbonates 24 produces thiirene and CS_2 in high yields:[51]



24

(21)

III. LOW TEMPERATURE PHOTOLYSIS OF MATRIX ISOLATED 1,2,3-THIADIAZOLES. ISOLATION OF THIIRENES

The low temperature matrix isolation technique was developed concurrently by Porter[52] and Pimentel[53] and has been successfully applied to the generation and observation of a wide variety of unstable and free radical species. Three main spectroscopic techniques are used for the observation of an intermediate isolated in a rigid medium at low temperatures, ir, uv and esr. The most important of these, for general identification purposes in organic chemistry, is infrared spectroscopy which provides information on the functional character of the molecule and moreover is very sensitive to impurities. Originally, the nature of the hydrocarbons used to make rigid glasses imposed severe limitations on the ir range which could be employed and this was probably the cause of the delay in the successful application of matrix isolation techniques to organic chemistry. However, it has recently met with great success, especially since the closed cycle helium refrigerator has become commercially available. Close to liquid helium temperatures, nitrogen and noble gases such as neon, krypton, argon and xenon can be used as inert hosts and all share the advantage of being transparent from the far infrared to the vacuum ultraviolet.

Although there are several methods for generating reactive species in a matrix[54,55] the most commonly used one for organic species is by photolysis of a suitable precursor already matrix isolated at low temperatures, bearing in mind the following requirements:

1. the precursor should generate the reactive species by extrusion of a stable fragment which would not undergo a cage reaction and be as transparent as possible in the ir region;
2. the fragment should also be transparent at the wavelength of irradiation;
3. the reactive species should not photodecompose at the wavelength of irradiation.

Since low temperature matrix isolation is generally used for the study of species for which the spectral characteristics are unknown, identification of the species responsible for the observed spectrum is occasionally difficult. In these cases, the use of reactive matrices such as CO, C_2H_2 etc. or the inclusion of reagents in the matrix has proven to be extremely useful.[56,57] Fractional distillation of the photolyzed matrix followed by mass spectrometric analysis of the volatile products can also provide additional information. However, definite vibrational assignments can only be achieved by measuring the band frequency shifts upon isotopic labelling of the source compound and by carrying out normal coordinate analyses. It is also helpful if alternative precursors are available.

Thiirene, as a member of the 4 π-electron heterocyclic system, is expected to be unstable with respect to dimerization and polymerization as well as to rearrangement. Therefore, its synthesis and observation are only possible if low temperature matrix isolation techniques are used. 1,2,3-Thiadiazoles, for which there was already convincing evidence for the transient formation of thiirenes, are almost ideal precursors since they generate nitrogen as a photoagment.

The first argon matrix photolysis of 1,2,3-thiadiazole at 8°K was carried out by Krantz and Laureni in 1974.[58] Attempts to detect thiirene, however, were unsuccessful and ethynylthiol and thioketene were the only identifiable products:

8

(22)

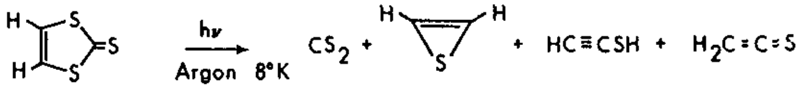
They were able to observe, however, that either 4-deutero- or 5-deutero-1,2,3-thiadiazole produces monodeuterothioketene and comparable yields of the two isomeric monodeuteroethynylthiols:

(23)

This is a significant result since, by analogy with the gas phase photolysis of 4-methyl and 5-methyl-1,2,3-thiadiazole, it would appear that a symmetrical intermediate with equivalent hydrogens, most likely thiirene, is formed. The obvious question is, if thiirene is indeed an intermediate, why could it not be isolated? If it is thermally unstable even at 8°K then clearly further attempts to detect it, at least for the case of the parent compound, are doomed to failure. However, it is possible that the wide wavelength range used in the photolysis ($\lambda>290$ nm) may have induced secondary photofragmentation of thiirene. Indeed, photolysis of matrix isolated 1,2,3-thiadiazole using filtered radiation in the range 235-280 nm led to the appearance of a new transient spectrum.[22,59] Thioketene and ethynylthiol were also formed under these conditions. It was also reported that the low temperature matrix photolysis of either 4-deutero- or 5-deutero-1,2,3-thiadiazole as well as of either 4-^{13}C or 5-^{13}C-1,2,3-thiadiazole produces the same intermediate spectrum and moreover, the observed shifts in the C=C st band upon substitution are consistent with a *cyclo*propanoid type of transient.

These results strongly point to the intervention of thiirene in the photolysis of matrix isolated 1,2,3-thiadiazoles; more definite support comes from the effects of substituents on the intensities and positions of the ir bands, and vibrational analyses of the ir spectra of the parent and labelled compounds, as will be described later.

We have also shown [51] that vinylene trithiocarbonate **24a** is a very good alternative precursor of thiirene. Photolysis using λ=230 nm radiation of matrix isolated **24a** produces CS_2 and very good yields of thiirene **3** and ethynylthiol **4**; only very small amounts of thioketene **5** were detected.

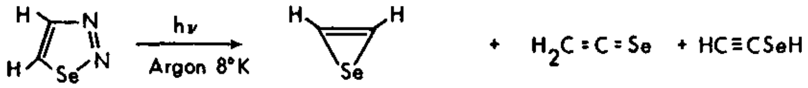


(24)

24a **3** **4** **5**

Isothiazole also produces thiirene upon low temperature matrix photolysis but the yields are very low.[59]

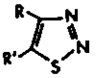
Parallel to this work, the selenium analog, 1,2,3-selenadiazole **25**, has also been matrix isolated and photolyzed. By analogy to the case of 1,2,3-thiadiazole, the authors claim the synthesis of selenirene **26**, thioselenoketene **27** and ethynylselenol **28**.[58,59]



(25)

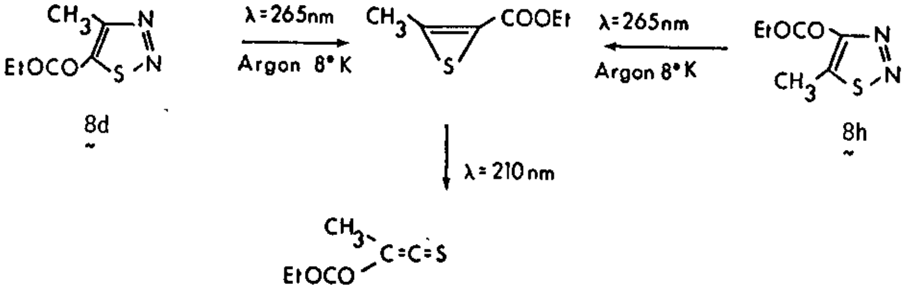
25 **26** **27** **28**

With the expectation that substituents may enhance the stability of thiirene and that in fact properly substituted thiirene, like *cyclo*butadiene,[60] could even be stable at room temperature, we have succeeded in isolating, in good yields, several substituted thiirenes from photolysis of the appropriate matrix isolated 1,2,3-thiadiazoles. From the results, summarized in Table 6, it can be concluded that indeed substituents in general, and electron withdrawing substituents in particular, exert a marked stabilizing effect. The most dramatic enhancement in the absorption intensities and the most convincing evidence for the intermediacy of thiirene in these systems was observed in the cases of 4-methyl-5-carboethoxy and 5-methyl-4-carboethoxy-1,2,3-thiadiazole 8d and 8h respectively. Photolysis of either substrate with λ=265 nm radiation led to the appearance of an identical spectrum and very little, if any, thioketene was observed under these conditions.[29]

Table 6. Matrix isolated thiirenes from the photolysis of 

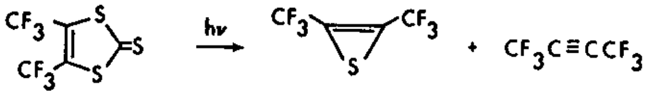
1,2,3-Thiadiazole		λ (nm)	ir frequencies observed (cm^{-1})	Reference	Thiirene Yield
R	R'				
H	H	265 or 215	3208, 3170, 1660, 912, 660, 563.	22, 29, 59	fair
CH_3	H	265	3203, 2930, 1440, 1429, 1036, 897, 650.	22	fair
CH_3	CH_3	265	2970, 2921, 2865, 1923, 1440, 1427, 1041, 586, 471.	22	fair
		265	1670, 1440, 490, 950, 729, 680, 670.	29	poor
CF_3	H		3210, 1240, 1190, 1180, 720.	29	moderate
CH_3	COOEt	265	3205, 3000, 1875, 1715, 1440, 1400, 1370, 1270, 1070, 1040, 1020, 760, 730, 490.	29	high
COOEt	CH_3				

However, subsequent photolysis with λ>210 nm resulted in the disappearance of the intermediate spectrum and the appearance of the thioketene spectrum:



8d **8h** (26)

The most stable thiirene derivatives should be the di-*tert*-butyl- and the bis(trifluoromethyl) substituted ones, the former because of the known stabilizing effect of *tert*-butyl groups on small ring compounds[60,61] whereby bimolecular reactions and intramolecular rearrangements are suppressed, and the latter because of the strong electron-withdrawing effect of the trifluoromethyl group and the resistance of the trifluoromethyl groups to migration. In fact, tetrakis(trifluoromethyl)*cyclo*butadiene has been prepared and indeed possesses noticeable stability.[62] The syntheses of 4,5-di-*tert*-butyl and 4,5-bis(trifluoromethyl)-1,2,3-thiadiazoles present some difficulties but we have succeeded in isolating bis(trifluoromethyl)thiirene from the argon matrix photolysis of 1,3-bis(trifluoromethyl)-1,3-dithiol-2-thione **24b**.[51] As expected, no bis(trifluoromethyl)thioketene was formed. Instead, hexafluorobutyne-2 was detected as a secondary photolysis product:



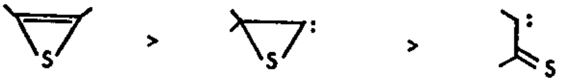
24b (27)

Bis(trifluoromethyl)thiirene appears to be the most stable of all the derivatives synthesized to date, and its thermal stability is currently being examined.

IV. THEORETICAL STUDIES AND MECHANISTIC CONSIDERATIONS

Both semiempirical[63,64] and *ab initio*[63,65] molecular orbital computations have been used to predict the relative stability of thiirene since the first semiempirical Hückel molecular orbital calculation was published by Zahradnik in 1965.[66]

In complex systems such as C_2H_2S, where limited experimental data are available and thus unambiguous reaction paths cannot be established, the results of detailed molecular orbital calculations can be a valuable tool in both the predictive and experimental sense. Although the available calculations were done at different levels of sophistication and only in one case[65] were carried out for fully optimized geometry, the agreement between the predicted geometries is reasonably good, cf. Table 7. Not unexpectedly, however, the relative energies of some of the C_2H_2S isomers calculated by semiempirical and *ab initio* methods differ widely. Thus, MINDO/3 predicts the order of stability



(28)

with a difference in energy between thiirene and thioformylmethylene of 27.6 kcal/mol^{-1} in favour of the former;[64] in contrast, *ab initio* calculations at the STO-4G level, illustrated in Figure 1, predict the reverse order of stabilities and an energy difference between thiirene and thioketocarbene of 15.5 kcal mol^{-1} in favour of the latter.[65]

As Figure 1 indicates, calculations were performed for the lowest singlet and triplet states of six C_2H_2S isomers: thioketocarbene 2, thiirene 3, ethynylthiol 4, thioketene 5, thiirenylidene 6, and thiolvinylidene 7. Ground singlet state thiirene 3 is only marginally less stable than thiirenylidene 6, the calculated energy separation being only 0.3 kcal mol^{-1} and thioketene 5 is 15.5 kcal mol^{-1} more stable than thiirene but only slightly less stable than

Table 7. Computed geometry of ground state thiirene

	Method			
	CNDO/2	MINDO/3	*Ab Initio*	*Ab Initio* optimized
r_{C-C} (Å)	1.304	1.270	1.290	1.270
r_{C-S} (Å)	1.767	1.800[a]	1.803	1.810
r_{C-H} (Å)	1.100	1.083[a]	1.106	1.074
∢HCC(°)		154.5		149.3
Reference	63	64	63	65

[a] average value

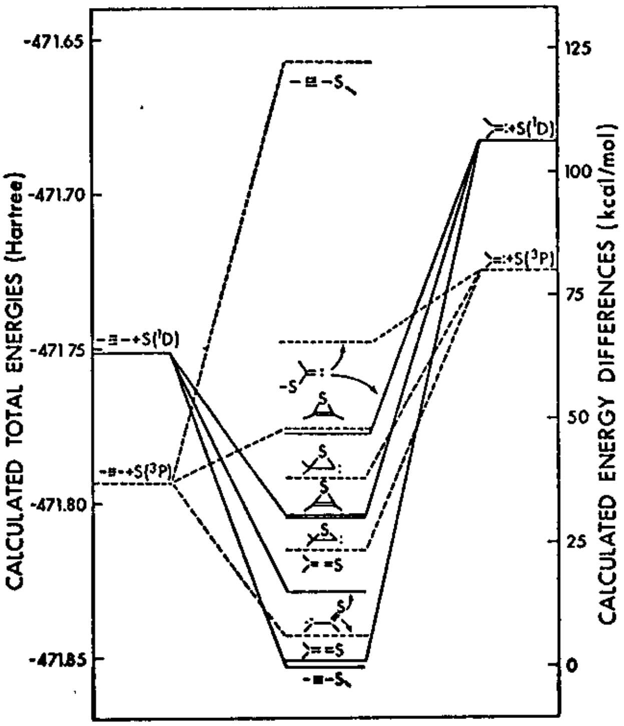


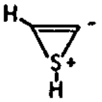
Figure 1. Calculated Energy Differences ($kcal/mol^{-1}$). Solid lines singlet, dotted, triplet.

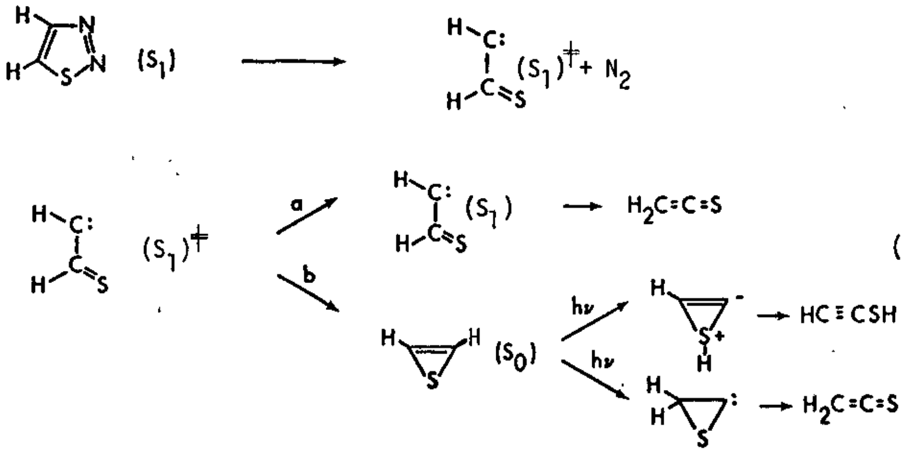
ethynylthiol **4** by 0.9 kcal mol^{-1}.

These relative energy levels are in excellent agreement with experimental results. Thus, it has been shown that matrix isolated thiirenes undergo secondary photolysis to thioketenes and ethynylthiols (the latter, only in the cases of C_2H_2S and CF_3CHS), clearly pointing to the order of stability thiirene < thioketene ≈ ethynylthiol. The very small predicted energy separation between thiirene and thiirenylidene is also in agreement with the suggestion[59] that an additional, though minor, photodecomposition path leading to the formation of thiirenylidene might be operative.

Theoretical calculations have also confirmed the predicted basicity of thiirenes and suggested that the antiaromaticity may be removed *via* the formation of thiirenium ions. Thus, Clark[63] has calculated a proton affinity of 8.76 eV for unsubstituted thiirene. Substituted thiirenium ions have been isolated[67] as relatively stable species.

Although the kinetic stabilities of the C_2H_2S isomers are not known, some of the reaction channels involved in the photochemical decomposition of 1,2,3-thiadiazoles can be elucidated on the basis of experimental observations, the calculated relative energies of the intermediates and the parallelism between the Wolff rearrangement of diazoketones[13,68,69] and the decomposition of 1,2,3-thiadiazoles.

It is proposed that decomposition of electronically excited 1,2,3-thiadiazole gives rise to the formation of vibrationally excited S_1 state thioketocarbene which either undergoes unimolecular isomerization to the higher lying thiirene S_0 state or vibrational relaxation. Thiirene then may be stabilized as such, and the vibrationally relaxed thioketocarbene (the correct specific name for this species is thioformyl methylene) will probably collapse without significant activation energy[64] to the more stable thioketene structure (and perhaps small amounts of ethynylthiol). Thiirene (which has a broad absorption in the uv above 200 nm) can undergo secondary photolysis to form mostly ethynylthiol *via* the zwitterion  and, but to a much lesser extent, thioketene *via* thiirenylidene. The proposed photodecomposition sequence is summarized below:



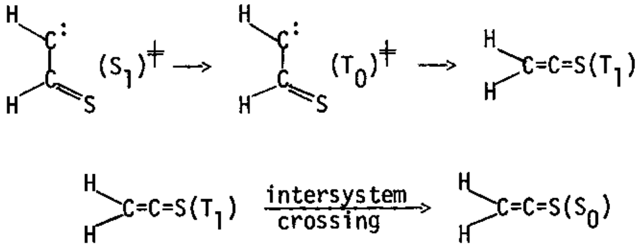
(29)

The existence of the two parallel, competing decay processes (a) and (b) for $(S_1)^{\dagger}$ thioketocarbene is supported by the following observations:

1) photolysis of either 4- or 5-^{13}C-1,2,3-thiadiazole leads to the formation of randomly labelled ethynylthiol but in the case of thioketene, the isotopic form retaining the original skeleton predominates.[59] Moreover, photolysis of 4-*d*-4-^{13}C-1,2,3-thiadiazole produces all four possible isomeric ethynylthiols. Therefore, the major portion of the thioketene product must be formed from an unsymmetrical intermediate, likely thioketocarbene (path a), whereas most of the ethynylthiol must originate from a symmetrical precursor, *i.e.* thiirene (path b).
2) photolysis of 1,2,3-thiadiazole at λ=215 nm, where the photolyzate features a window and the thiadiazole still absorbs, results in a marked

enhancement of the ethynylthiol and thiirene bands, as compared to those of thioketene.

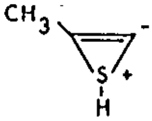
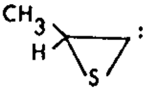
The intervention of T_0 ground state thioketocarbene in the mechanism cannot be excluded, but it is unlikely to play a major role.



(30)

The latter observation suggests the existence of a substantial activation energy for the thioketocarbene → thiirene isomerization. Indeed, we have observed that the thioketene/ethynylthiol ratio depends on the nature of the matrix and increases in the order neon < argon < xenon. The more polarizable xenon matrix should be a much more effective quencher, thereby increasing the contribution of path a. Similar observations have been reported[59] for the series argon, N_2, CO and C_2H_2, probably for the same reason.

The computed activation energies for the ketocarbene → oxirene and ketocarbene → ketene isomerizations are 19.1 and 5.7 kcal mol^{-1} respectively[69] and thus provide a rationale for the experimental observation that the extent of oxirene participation in the Wolff rearrangement of α-diazoketones and α-diazoesters requires excess internal energy. It would appear that the formation of thiirene in the photochemical decomposition of 1,2,3-thiadiazoles is also dependent on the internal energy content of the initially formed thioketocarbene.

On the basis of substituent effects and isotopic labelling studies, it is postulated here that thiirene can isomerize either to the zwitterion structure, leading to the formation of ethynylthiol, or to thiirenylidene, to form thioketene. Thus, methyl substitution would be expected to increase the energy of  relative to  and in fact methylethynylthiol was not detected in the photolysis of 4-methyl-1,2,3-thiadiazole; on the other hand, trifluoromethyl substitution should exert a stabilizing effect and indeed $CF_3C{\equiv}C$-SH is a photolysis product of 4-trifluoromethyl-1,2,3-thiadiazole. The intervention of the zwitterion is suggested by the fact that all four possible ethynylthiol isomers are formed from the photolysis of 4-*d*-4-^{13}C-1,2,3-thiadiazole, thus requiring intramolecular hydrogen transfer* and at the same time, equivalence of the carbon atoms in the intermediate; the intervention of thiirenylidene would explain the small degree of scrambling observed in the thioketene product. Note that the m.o. calculations[65] predict an energy difference of only 0.3 kcal mol^{-1} between thiirene and thiirenylidene.

It must be stressed that although the proposed mechanism is in agreement with experimental results reported thus far, it should be regarded only as a reasonable hypothesis; obviously, much more work is needed before the individual mechanistic pathways and intermediates can be fully elucidated.

V. PROPERTIES OF THIIRENE

1. The Ir Spectrum

As mentioned above, the identification of thiirene as the structure responsible for the intermediate ir spectrum observed in the low temperature photolysis of matrix isolated 1,2,3-thiadiazole was originally made on the basis of substituent and isotopic labelling effects. For example, the effect of substituents on the band assigned to the C=C st frequency is similar to

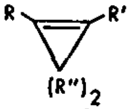
---

*(Note. The hydrogen must be equivalent and the hydrogen transfer must take place while prescreening the carbon equivalence.)

that observed in the case of *cyclo*propene[70] and indicates a distinct *cyclo*propanoid character in the intermediate. These are summarized in Table 8.

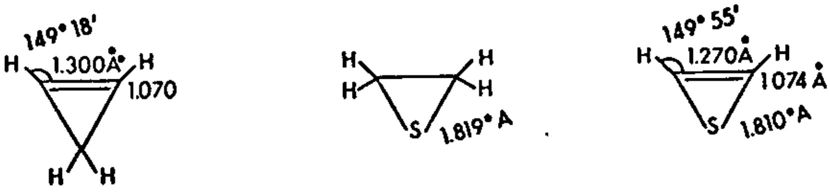
Table 8. Observed C=S st frequencies for some thiirenes

and *cyclo*propenes



Substituent		Thiirene		*Cyclo*propene		
R	R'	$\nu_{C=C}$ cm^{-1}	Reference	R"	$\nu_{C=C}$ cm^{-1}	Reference
H	D	1660	22, 29	H	1656	70
H	D	1610	22, 71	CH$_3$	1578	72
D	D	1565	22, 71	H	1572	70
CH$_3$	CH$_3$	1923	22	H	1885	72
				CH$_3$	1870	72
CH$_3$	COOEt	1875	29	CH$_3$	1840	72
CF$_3$	CF$_3$	1800	51	F	1820	73

Also, comparison between the known geometries of *cyclo*propene[74] and thiirane[75] with that calculated for thiirene[65] indicates close similarities between the



(31)

*Cyclo*propene Thiirane Thiirene

C-S bond lengths of thiirane and thiirene, the C=C and C-H bond lengths, and the C=C-H angles of *cyclo*propene and thiirene. The band assignments,[29] together with the corresponding ones for *cyclo*propene[76] and thiirane[77] are listed in Table 9.

Table 9. Assignment of the observed bands (cm^{-1}) of thiirene and thiirene-d_2.

	Thiirene		Thiirene-d_2		Reference Compound
	a	b	a	b	
C-H Stretch	3208	3237	2495	2496	3158 [c]
C=C Stretch	1660	1668	1565	1540	1656 [c]
C-H bend in-plane	912	922	715	705	1010 [c]
Ring def. sym.	660	655	610	613	646 [d]
C-H bend out-of-plane	-	647	-	529	-
C-H bend out-of-plane	563	566	423	426	570 [c]
C-H Stretch	3170	3172	2355	2334	3124 [c]
C-H bend in-plane	-	888	-	735	905 [c]
Ring def. asym.	(510)[e]	547	-	491	633 [d]

[a] observed frequencies

[b] calculated frequencies

[c] *cyclo*propene[76]

[d] thiirane[77]

[e] tentative

In order to obtain a more reliable assignment of the vibrational structure of thiirene a normal coordinate analysis of the spectra of C_2H_2S and C_2D_2S was carried out.[71] In spite of the fact that the experimental geometry of thiirene is not known, it was felt that sufficient confidence could be placed in the calculated optimized *ab initio* geometry (Table 7) to make a vibrational analysis worthwhile. The calculation of the force field and potential energy distribution would lead to a better understanding of the thiirene molecule and allow meaningful comparisons with other 4 π-electron systems in general.

Thiirene is a planar molecule which belongs to the C_{2v} symmetry group with its nine normal vibrations distributed among the different symmetry species as follows: $4a_1 + 1a_2 + 1b_1 + 3b_2$. One normal vibration which belongs to the b_1 species is ir inactive and the same symmetry considerations apply to thiirane-d_2. Although the presence of thioketene, ethynylthiol and traces of starting material made the observation of all the bands difficult and somewhat uncertain, the results obtained, Table 9, are very encouraging.

The two characteristic C-H and C=C stretching frequencies can be easily correlated with those of similar compounds. The behaviour of C=C st upon substitution follows the same general trend observed for endocyclic C=C st frequencies, which are very sensitive to changes in the ring angle.[78] Thus, as seen in Table 8, substitution causes a large shift to higher frequencies regardless of the nature of the substituent, in very close analogy to the case of *cyclo*propene. However, the nature of the substituents exerts a greater effect on the extent of the shift in the case of thiirene. This is not unexpected since electronic effects will probably exert a greater influence in 4 π-electronic thiirene than in *cyclo*propene.

The C-H st frequencies fall within the expected region; the corresponding values are 3048, 3126 cm^{-1} for *cyclo*butene,[79] 3100, 3069 for *cyclo*propenone[80] and 3157, 3124 cm^{-1} for *cyclo*propene.[71,76] Higher values are generally associated with shorter bond distances but this does not appear to be the case for thiirene (cf. (31)).

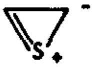
2. Electronic spectrum

The uv spectrum of matrix isolated thiirene has been recorded in our laboratories and features a very weak broad absorption from 200 nm to 350 nm with no apparent maximum. No fine structure could be discerned. That of bis(trifluoromethyl)thiirene is similar except for a distinctive maximum at 310 nm. The absence of vibrational structure indicates that the excited state is repulsive, in agreement with the observed bleaching of the thiirene spectrum upon photolysis with unfiltered radiation.

In the case of *cyclo*butadiene some weak uv bands have been reported in the region 300-305 nm but there is no agreement on the band locations and it has been questioned whether in fact these bands correspond to "free" *cyclo*butadiene.[6] Molecular orbital calculations[81] predict a dipole forbidden $'A_g \rightarrow 'B_{1g}$ transition in this region.

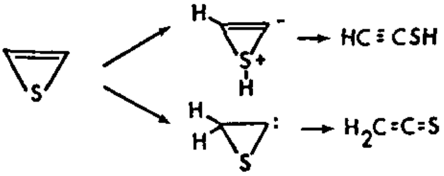
3. Chemical reactivity

Although thiirene is an inherently unstable species, the results described above have shed some light on its structure and chemical reactivity, which will now be briefly summarized.

Thiirene was first trapped in the $S(^1D)$ + acetylene system, in particularly high yields for the case of hexafluoro-2-butyne. More definitive evidence for the transient existence of thiirene was subsequently reported from the gas phase photolysis of 4-methyl- and 5-methyl-1,2,3-thiadiazole in the presence of hexafluoro-2-butyne where the single isomer, 5-methyl-2,3-bis(trifluoromethyl)thiophene was formed in each case.[16,21] The latter observation indicates that the thiirene ring can react as an entity, across the less hindered C-S side. The nucleophilic character of thiirene is evidenced by the fact that in the $S(^1D_2)$ + acetylene + hexafluoro-2-butyne system, only the asymmetrical 2,3-bis(trifluoromethyl)thiophene was formed.[19] Thus, resonance contribution from  may be important. It is also possible that reactions involving the double bond, such as a Diels Alder addition, could take place under very mild conditions since the antiaromaticity would thereby be released.

The C=C bond distance in thiirene[65] is shorter than the corresponding one in ethylene or *cyclo*propene, indicating a more efficient C=C overlap and therefore chemical properties intermediate between double and triple bonds.

At the same time the weaker C-S bond becomes more reactive and thus most of the *reactions of thiirene, i.e. rearrangement, self and cross dimerization,* proceed *via* opening of the ring. It has been shown, for example, that ethynylthiol and a small part of the thioketene product from the 8°K photolysis of 1,2,3-thiadiazole arise from secondary photolysis of thiirene.[22,29,58,59] We tentatively propose that the former arises from a zwitterion intermediate and the latter from thiirenylidene:



Substitution markedly alters the relative stabilities of these intermediates as well as those of the products, and very likely influences the activation energies for the rearrangements. For example, methyl substitution should increase the energy of the zwitterion intermediate while the reverse would be expected for the trifluoromethyl derivative and in fact $CH_3C{\equiv}C\text{-}SH$ is not observed from 4- or 5-methyl-1,2,3-thiadiazole.[30,59] There is no evidence that disubstituted thiirenes undergo rearrangement to ethynyl sulfides and it is expected that the thiirene → thiirenylidene and, but to a lesser extent, the thioketocarbene → thioketene rearrangements should also be less favoured. Hence, for the case of thiirenes containing bulky substituents such as phenyl groups, one would expect the dominant reactions to be of the 1,3 diradical type - which are actually observed in those systems where thiirene may be involved.[23-26,28,31,46.]

The major products of the gas phase photolysis of 1,2,3-thiadiazoles are N_2, the corresponding acetylenes and CS_2[16,21] and, in the presence of *cis*-2-butene, we detected 2-butene-1-thiol among the products. The latter observation seems to point to the involvement of $S(^1D_2)$ atoms. Moreover, the methanol solution phase photolysis of 4-*tert*-butyl-1,2,3-thiadiazole[26] and the benzene solution phase photolysis of 2,5-diphenyl-1,3-dithiol-4-one[46] produced *tert*-butylacetylene and diphenylacetylene, respectively. Thus, in addition to rearrangement and C-S bond cleavage, thiirene can undergo decomposition to acetylene + $S(^1D_2)$ which, according to m.o. calculations, is an orbital symmetry and spin allowed reaction having an enthalpy change of 33 kcal mol^{-1}:

$$\rightarrow \quad HC{\equiv}CH + S(^1D_2)$$

This reaction was not observed in low temperature matrix photolysis experiments of thiadiazoles with the exception of trifluoromethyl substituted thiadiazoles[29] but appears to be a major photodecomposition pathway for the case of 1,2,3-selenadiazole[59] and bis(trifluoromethyl)vinylene trithiocarbonate.[51]

In conclusion, the detection and isolation of thiirene has opened up a novel and exciting new field for both the experimentalist and the theoretician. More detailed studies on the effects of substitution, isotopic labelling, temperature and photolysis wavelength, along with molecular orbital calculations on the activation energies associated with the rearrangements and decomposition of thiirene are underway and should help to further elucidate not only the physicochemical properties of thiirene but also the detailed photodecomposition pathways of 1,2,3-thiadiazoles. The syntheses of thiirenes from other precursors will also be useful in this regard.

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