

## 4n- $\pi$ ELECTRON ANTIAROMATIC HETEROCYCLES

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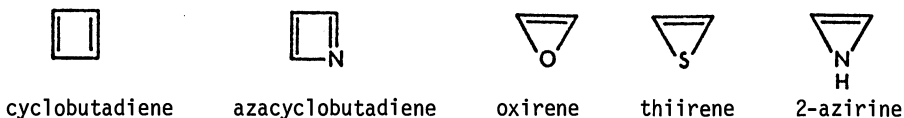
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**Abstract** - The 4n- $\pi$  electron heterocycles oxirene, thiirene and 2-azirine are expected to be antiaromatic and therefore inherently unstable. In the past decade isotopic labelling and chemical scavenging experiments have provided compelling, although indirect evidence for the transient existence of these molecules in a variety of reactions but to date only thiirene has been isolated and characterized, using low temperature matrix isolation techniques. Vibrational assignments for thiirene and its deuterated analogs were made possible by means of a normal coordinate analysis based on computed *ab initio* optimized geometries. Mono- and dimethyl-, trifluoromethyl-, bis(trifluoromethyl)-, benzo- and methylcarboethoxythiirene have also been synthesized. Recent *ab initio* molecular orbital calculations on the thermodynamic stabilities of the C<sub>2</sub>H<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub>S isomers provide a useful framework for the elucidation of the various interconversions observed in the photolysis of the source compounds  $\alpha$ -diazoketones and 1,2,3-thiadiazoles. The extent of oxirene participation in the Wolff rearrangement (WR) is primarily governed by the relative rates of the keto-carbene-oxirene and ketocarbene-ketene interconversions which, in turn, depend on the nature of the substituents. Other important factors include the phase, nature of the solvent, and the wavelength of irradiation. In addition to isomerization, oxirene and thiirene can depose to acetylene + O (or S). The available data on 2-azirine are not very extensive but evidence for its transient existence as an intermediate, e.g. in the decomposition of benzotriazoles, is very compelling. *Ab initio* MO calculations have been carried out on the singlet and triplet energy manifolds of some of the C<sub>2</sub>H<sub>3</sub>N isomers.

## INTRODUCTION

One of the earliest and most outstanding achievements of molecular orbital theory was Hückel's prediction that monocyclic ring systems having (4n+2)- $\pi$  electrons are aromatic, i.e. are conjugatively stabilized. Those systems containing 4n- $\pi$  electrons were denoted as being "pseudoaromatic" until 1965 when Breslow (1) and, independently, Dewar (2) observed that some of these molecules were actually destabilized relative to suitable reference compounds and Breslow coined the term "antiaromatic" for these species. Subsequently, theoretical calculations of resonance energies of some of these antiaromatic species (3) led to the predictions of negative absolute conjugation energies, in agreement with Breslow's experimental observations (1). Quantitative estimation of the extent of destabilization, however, is still a contentious issue (4).

The highest  $\pi$  electron energies, i.e. the greatest amounts of destabilization, obtain for monocyclic compounds where n=1 because planarity is enforced and only small distortions in the C-H bond angles are possible. The simplest molecular species are:

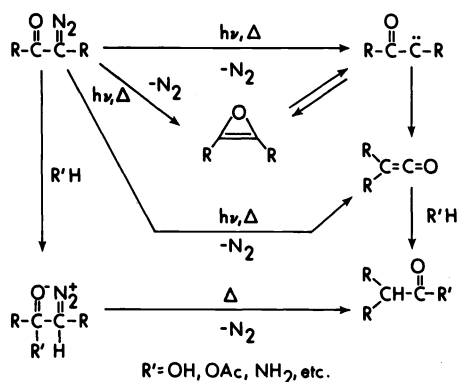


A few substituted cyclobutadienes (5) have been synthesized but because these molecules are inherently unstable, much of the information on their chemistry and indeed on their transient existence has to be deduced from product analysis and scavenging studies. In the past few years, however, the technique of low temperature matrix photolysis coupled with *ir* spectroscopy has led to the successful isolation and characterization of cyclobutadiene (6), and thiirene (*vide infra*).

In this paper we shall confine ourselves to a discussion of the detection and chemical properties of the three-membered heterocycles oxirene, thiirene and 2-azirine. Where possible, the experimental results related to their relative stabilities, rates of interconversion to other isomers, *etc.*, will be compared with theoretical predictions derived from molecular orbital calculations.

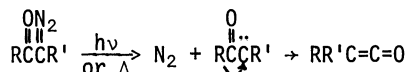
### OXIRENE

Oxirene has had a long and controversial history ever since Betherlot's first attempted synthesis in 1870 (7). Its substituted analogs have been proposed as intermediates in a variety of reactions, in particular the Wolff rearrangement (WR) of  $\alpha$ -diazoketones and esters which can be brought about by direct photolysis, thermolysis and catalysis. Several different mechanistic pathways have been suggested for the WR (8) and are summarized in Scheme 1.



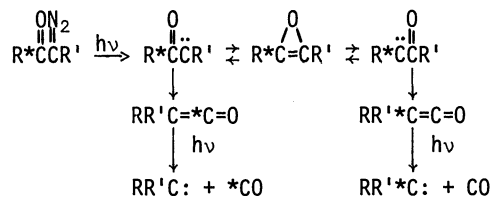
Scheme 1.

The possible intervention of oxirene, possessing equivalent ring carbon atoms, can in principle readily be established by isotopic carbon labelling in the source compound. This technique was exploited in the early work of Huggett *et al.* (9) and Franzen (10) who examined the thermal and photochemical WR of diazoacetophenone and azibenzil, respectively, labelled in the carbonyl position, and reported that no scrambling had taken place during the rearrangement. Therefore, for many years the commonly accepted mechanism (8) was



in spite of the lack of direct evidence at that time for the intermediacy of ketocarbenes. Later, however, the *esr* spectra of triplet phenylbenzoylmethylene, carboethoxy and carbo-methoxymethylene were observed upon low temperature photolysis of the corresponding diazo compounds (11) and Chapman's trapping experiments with matrix isolated diazoaceneaphthenone clearly point to the ketocarbene as a precursor of ketene (12).

A decade ago it was observed that the gas phase photochemical WR of  $^{13}\text{C}$  labelled 3-diazo-2-butanone, diazoacetone, ethyldiazoacetate and methyldiazoacetate led to scrambling in the products, from which it was concluded that the extents of oxirene participation were 100,  $\geq 16$ ,  $\geq 32$  and  $\geq 28\%$ , respectively (13,14):

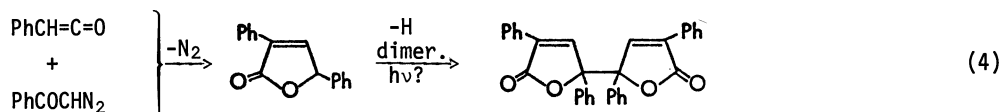


Subsequently, Franzen's experiments on azibenzil were carefully repeated (15,16) under experimental conditions similar to those employed by Franzen and again scrambling was observed, leading to a value of 46% for the extent of oxirene involvement. Shortly after these observations were published, the transient existence of oxirene was verified by other workers as well. Thus, Rowland and coworkers (17,18) reported evidence to the effect that chemically activated ketene formed from the  $\text{CH}_2(^1\text{A}_1) + \text{CO}$  reaction rearranges to oxirene, and Matlin and Sammes reported oxirene formation in the WR of a number of  $\alpha$ -diazoketones (19).

In the photochemical WR the ketene is seldom isolated. Thus, in the gas phase ketene undergoes secondary decomposition to CO and a carbene, whereas in reactive solvents is trapped as the ketene + solvent adduct. In less reactive solvents ketene can either react with unphotolyzed diazoketone or can undergo secondary photolysis to CO and a carbene. For example, the photolysis of diazoacetophenone in alcohol solution (20) afforded the corresponding esters,



whereas in cyclohexene the major product is a dilactone:



The major products from the triplet sensitization of diazoketones, however, have been rationalized in terms of abstraction and non-stereospecific addition reactions of triplet state ketocarbenes (21):



The product yields from the direct and triplet sensitized (Michler's ketone) photolysis of  $\text{PhCOCHN}_2$  in cyclohexene, methanol and isopropanol are summarized in Table 1 (20). These

TABLE 1. Direct and sensitized photolysis of  $\alpha$ -Diazoacetophenone

Solvent	Yields (%) <sup>a</sup>			
	$\text{PhCOCH}_3$	$\text{PhCH}_2\text{COOR}$	Dilactone	7-Benzoylnorcaradiene
cyclohexene	3	-	28	2
	36 <sup>b</sup>	-	n.d. <sup>b</sup>	trace
MeOH	trace	85	-	-
	10 <sup>b</sup>	64 <sup>b</sup>	-	-
i-PrOH	2	72	-	-
	50 <sup>b</sup>	2 <sup>b</sup>	-	-

<sup>a</sup>In terms of  $\text{N}_2$  evolved. <sup>b</sup>Sensitized with Michler's ketone.

results, together with other observations (22) suggest that the WR takes place on a singlet surface\* and ab initio calculations at the STO-4G level on all five possible  $\text{C}_2\text{H}_2\text{O}$  isomers (23) predict that only the formylmethylene structure has a triplet ground state; the triplet-singlet energy gap has been calculated to be small, of the order of  $25 \text{ kcal mol}^{-1}$  (24).

Oxirene is also an intermediate in the thermal decomposition of diazoketones and its yield is strongly dependent on the temperature. Table 2 lists some representative data, along with results from photolysis for comparison. From these results it is clear that only those singlet state ketocarbenes having excess vibrational energy will be able to isomerize to oxirene; these can be readily formed in photoexcitation since even at  $\lambda \sim 290 \text{ nm}$  four different excited states of the diazoketone can be reached (26). Since the ground state of ketocarbenes is triplet ( $T_0$ ), photoexcitation of a diazoketone should lead to the formation of an electronically excited ( $S_2$ ) state ketocarbene,



\*The high yields of  $\text{PhCH}_2\text{COOR}$  in the methanol solution triplet sensitized experiment will be discussed later (vide infra).

TABLE 2. % Oxirene yields from the photolysis and thermolysis of benzoylmethyldiazomethane and 3-diazo-4-heptanone

Diazoketone	Reaction	Solvent	Temperature °C	% Oxirene	Reference
PhCOCN <sub>2</sub> CH <sub>3</sub>	photolysis	CH <sub>3</sub> OH	65	44	(25)
PhCOCN <sub>2</sub> CH <sub>3</sub>	thermolysis	CH <sub>3</sub> OH	65	4	(25)
PhCOCN <sub>2</sub> CH <sub>3</sub>	thermolysis	CH <sub>3</sub> OH	220	55	(25)
C <sub>3</sub> H <sub>7</sub> COCN <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	photolysis	CH <sub>3</sub> OCH	25	43	(19)
C <sub>3</sub> H <sub>7</sub> COCN <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	thermolysis	cyclohexane	81	17.5	(19)
C <sub>3</sub> H <sub>7</sub> COCN <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	thermolysis	-	225	32.5	(19)

from which rapid internal conversion to the vibrationally excited lowest singlet state takes place:



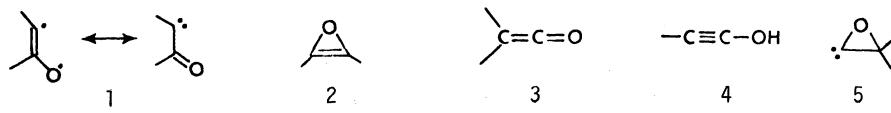
$(S_1)^\dagger$  ketocarbenes can isomerize to ketene or to oxirene, or be collisionally deactivated,



but this thermolyzed species, likely identical to the one formed in low temperature thermolysis, can only rearrange to ketene:



At this point it is necessary to take cognizance of molecular orbital predictions. Theoretical calculations have been performed on oxirene and some of its valence isomers at several levels of sophistication and, as expected, the results are widely disparate. We shall refer only to the more recent *ab initio* computations with full geometric optimization. The total energies of the lowest singlet states of the five C<sub>2</sub>H<sub>2</sub>O isomers,



have been calculated using the double zeta quality SCF method, together with the energy barriers for interconversion along the lowest energy paths (27). The results, illustrated in Figure 1, are consistent with experimental observations and are also in agreement with the

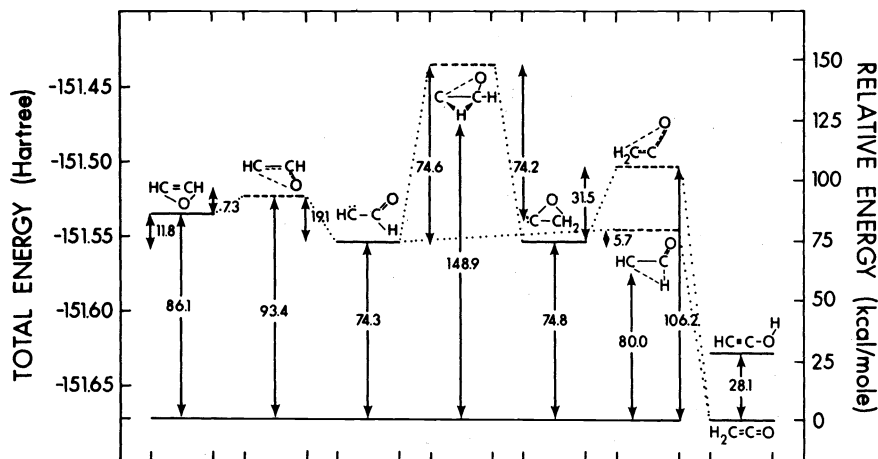


Figure 1. Relative energies of the C<sub>2</sub>H<sub>2</sub>O isomers and activated complexes.

results obtained from a similar calculation but which employed polarization functions and included configuration interaction (28).  $S_1$  formylmethylene, 1, as expected, is less stable than ketene 3 by 74-80 kcal mol<sup>-1</sup>. The formylmethylene-oxirene rearrangement features an activation energy of 19.1 kcal mol<sup>-1</sup> as compared to  $E_a = 5.7$  kcal mol<sup>-1</sup> for the ketocarbene-ketene isomerization, in agreement with the experimentally observed vibrational energy requirement for oxirene formation. Although oxirene is thermodynamically unstable, it is kinetically stable with respect to C-O cleavage, for which  $E_a = 7.3$  kcal mol<sup>-1</sup>.

The oxirene yields from the photolysis of some related <sup>13</sup>C O labelled diazoketones are summarized in Table 3. As we shall soon see, the extent of oxirene participation in a given

TABLE 3. % Oxirene formation from the photolysis of some diazoketones

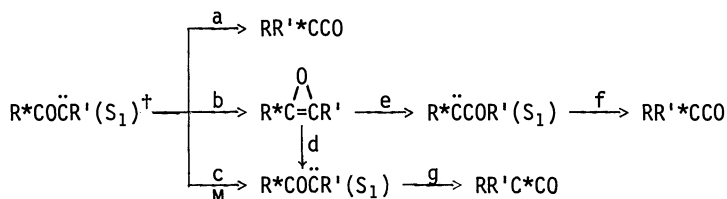
Diazoketone	Phase	$\lambda$ , nm	% Oxirene	Reference
HCOCHN <sub>2</sub>	PhCH <sub>2</sub> OH	>220	13-16 <sup>a</sup>	(30)
CH <sub>3</sub> COCHN <sub>2</sub>	gas	>220	≥19.2 <sup>b</sup>	(20)
	MeOH	>220	≥ 5 <sup>c</sup>	(20)
HCOCN <sub>2</sub> CH <sub>3</sub>	gas	>220	≥20.5 <sup>b</sup>	(20)
	MeOH	>220	≥ 6.7 <sup>c</sup>	(20)
CH <sub>3</sub> COCN <sub>2</sub> CH <sub>3</sub>	gas	>220	100 <sup>b</sup>	(13)
	<u>c</u> -C <sub>5</sub> H <sub>10</sub>	>220	70 <sup>b</sup>	(29)
	dioxane-water (2:1)	>220	~61 <sup>c</sup>	(29)
PhCOCN <sub>2</sub> CH <sub>3</sub>	<u>c</u> -C <sub>5</sub> H <sub>10</sub>	>220	≥83.6 <sup>b</sup>	(25)
	MeOH	>220	≥43.8 <sup>c</sup>	(25)
	dioxane-water (1:1)	>220	≥45.8 <sup>c</sup>	(25)
	dioxane-water (13:2)	254	≥68.3 <sup>a</sup>	(31)
CH <sub>3</sub> COCN <sub>2</sub> Ph	<u>c</u> -C <sub>5</sub> H <sub>10</sub>	>220	≥12.3 <sup>b</sup>	(25)
	MeOH	>220	≥ 0 <sup>c</sup>	(25)
	dioxane-water (13:2)	254	≥ 4.4 <sup>a</sup>	(31)
PhCOCN <sub>2</sub> Ph	<u>c</u> -C <sub>5</sub> H <sub>10</sub>	>220	60-70 <sup>c</sup>	(29)
	dioxane-water (2:1)	>220	~50 <sup>c</sup>	(29)
PhCOCHN <sub>2</sub>	<u>c</u> -C <sub>5</sub> H <sub>10</sub>	>220	≥20-30 <sup>b</sup>	(29)
	MeOH	>220	≥15-19 <sup>c</sup>	(29)
<u>p</u> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COCN <sub>2</sub> Ph	dioxane-water (13:2)	>290	≥10 <sup>a,c</sup>	(32)
	dioxane-water (13:2)	254	≥17 <sup>a,c</sup>	(32)
<u>p</u> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COCN <sub>2</sub> CH <sub>3</sub>	dioxane-water (13:2)	>290	≥25.5 <sup>a,c</sup>	(32)
	dioxane-water (13:2)	254	≥45 <sup>a,c</sup>	(32)
CH <sub>3</sub> COCN <sub>2</sub> C <sub>6</sub> H <sub>4</sub> <u>p</u> -CH <sub>3</sub> O	dioxane-water (13:2)	>290	≥ 6 <sup>a,c</sup>	(32)
<u>p</u> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCN <sub>2</sub> CH <sub>3</sub>	dioxane-water (13:2)	254	≥69 <sup>a,c</sup>	(32)
CH <sub>3</sub> COCN <sub>2</sub> C <sub>6</sub> H <sub>4</sub> <u>p</u> -NO <sub>2</sub>	dioxane-water (13:2)	254	≥ 2 <sup>a,c</sup>	(32)

<sup>a</sup>determined from the <sup>13</sup>C NMR spectrum of the ester or acid.

<sup>b</sup>from the mass spectrum of the CO fraction.

<sup>c</sup>from the mass spectrum of the ester or acid.

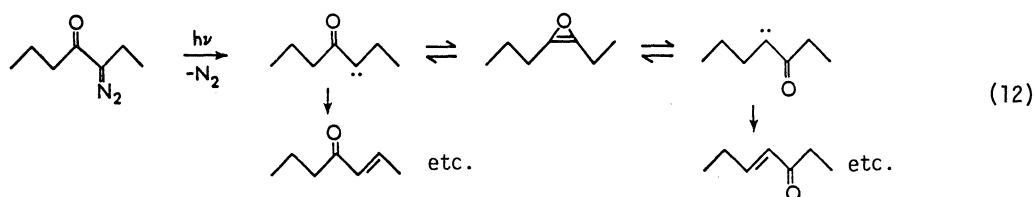
reaction is governed by many factors and there is no simple way to predict a priori the degree of oxirene formation. For convenience, the various ketocarbene-oxirene-ketene rearrangements are summarized in Scheme 2. The rate of vibrational deactivation, step c, should be strongly dependent on the phase and, as expected, the oxirene yields from the solution phase photolyses of CH<sub>3</sub>COCHN<sub>2</sub>, HCOCN<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>COCN<sub>2</sub>CH<sub>3</sub> are considerably smaller than those obtained in the gas phase. The rate of ring closure, step b, should depend only on the energy content of the ketocarbene but the rate of rearrangement to ketene, step a, depends on the migratory aptitudes of the substituents. Migratory aptitudes in the photochemical WR appear to be H > CH<sub>3</sub> > Ph > NR<sub>3</sub> > OR whereas in the thermal case CH<sub>3</sub> and Ph are reversed (8). Hence, the oxirene yield depends on the rate ratios  $k_a/k_b/k_c$ . The extent of scrambling, however, further depends on the mode of ring opening, *i.e.*  $k_d/k_e$  and inspection of the data in Table 2 reveals that substituents can play a major role. Thus, electron withdrawing substituents such as Ph, p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> seem to promote C-O cleavage on that side of the ring to which the substituent is attached, whereas electron releasing substituents such



Scheme 2.

as  $p\text{-CH}_3\text{OC}_6\text{H}_4$  will favour ring opening on the opposite side. Therefore, the extent of scrambling observed from unsymmetrically substituted diazoketones represents a minimum value for the extent of oxirene participation. For the  $\text{CH}_3\text{COCHN}_2/\text{HCOCN}_2\text{CH}_3$  pair, however, no such selectivity is apparent and the oxirene yields from the gas phase photolysis of these compounds are surprisingly low. Obviously, more systematic data will have to become available in order to fully understand the kinetic and structural parameters influencing these rearrangements.

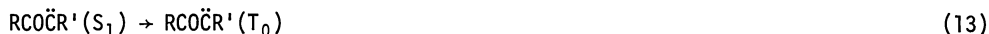
Polar solvents might be expected to lead to a further decrease in the yields as a result of complexation of the carbonyl group, or suppression of secondary oxirene formation in the photolysis of the ketene product, and indeed the results in Table 2 appear to substantiate these suggestions. It should be pointed out, however, that the opposite trend was reported (19) for the case of  $\alpha$ -diazo dialkyl ketones which, upon photolysis, do not undergo the WR but rearrange to unsaturated ketones via oxirene intermediates:



There is no obvious explanation for this discrepancy.

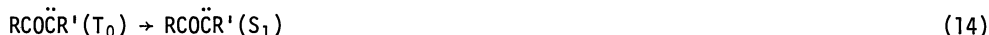
Increasing photonic energy leads to an increase in the oxirene yields, as expected. In this connection it is interesting to note that Franzen (10) employed a "sun lamp" in his experiments and therefore it is not at all surprising that he did not observe scrambling.

Thus far we have seen that oxirene is an intermediate in the photochemical and thermal WR of a number of simple  $\alpha$ -diazo ketones and esters, that the ketocarbene-oxirene interconversion takes place on a singlet surface and only when the ketocarbene is vibrationally excited. Earlier semiempirical Hückel calculations (26) had indicated that the ground state of ketocarbene was a singlet and therefore for many years it was believed that the initially formed electronically excited ( $\text{S}_1$ ) ketocarbene undergoes internal return to a vibrationally excited ( $\text{S}_0$ )<sup>†</sup> level, from which isomerization to oxirene takes place. However, as mentioned above, recent *ab initio* calculations (23,24) predict a triplet ground state for these species and the  $\text{T}_0\text{-S}_1$  separation for the case of  $\text{H}\ddot{\text{C}}\text{CHO}$  is predicted to be small, of the order of 25 kcal mol<sup>-1</sup>. Substituent effects,  $\text{H}\ddot{\text{C}}\text{X}$  and  $\text{X}\ddot{\text{C}}\text{X}$ , were also examined for a number of carbenes and it was concluded that most  $\pi$ -electron acceptor groups do not alter the  $\text{T}_0\text{-S}_1$  gap sufficiently to cause a  $\text{T}_0\text{-S}_1$  change in the ground state (24). Hence, in addition to rearrangement to ketene, reaction (11), there should be an additional mode of decay of ( $\text{S}_1$ ) ketocarbene, namely, intersystem crossing to the ground ( $\text{T}_0$ ) state:



In view of the predicted small energy gap, this step may effectively compete with ketene formation. In agreement with theoretical predictions we have obtained clear evidence for the occurrence of  $\text{S}_1\text{-T}_0$  intersystem crossing, step (13). Thus, the direct photolysis of  $\text{PhCOCN}_2\text{H}$  in cyclopentane affords small but persistent yields of  $\text{PhCOCH}_3$  (20), a typical triplet state abstraction product. Also, the 77°K photolysis of  $\alpha$ -diazoketones affords triplet state ketocarbenes (11). In general, the rate of  $\text{S}_1\text{-T}_0$  intersystem crossing should depend on the energy separation (which, in turn, is governed by the substituents) and, in our opinion, by the nature of the solvent (*vide infra*). The existence of this additional mode of decay of singlet state ketocarbenes introduces an ever greater degree of complexity to the mechanistic pathways involved in the WR.

There is also clear evidence for the occurrence of the reverse  $\text{T}_0\text{-S}_1$  intersystem crossing:

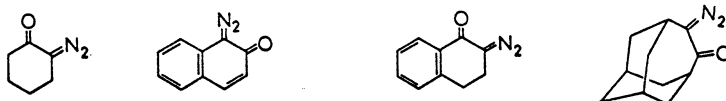


Thus, Roth and Manion (33) studied the solution phase triplet (benzophenone) sensitization of diazoacetone in  $\text{CHCl}_3$  and observed two different chemically induced dynamic nuclear polar-

ization (CIDNP) signals which were assigned to singlet and triplet state radical pairs. They concluded that, in competition with abstraction from the solvent, the triplet ketocarbene can undergo efficient intersystem crossing to the upper singlet state. Moreover, they were able to show that the relative rates of carbene-solvent reactions and of intersystem crossing can be radically altered by the appropriate use of solvents. For example, in cyclohexene/CHCl<sub>3</sub> only the triplet signal was observed: evidently the rate of addition of the triplet ketocarbene to cyclohexene is much faster than the rate of intersystem crossing. On the other hand, in CCl<sub>4</sub> only the singlet signal was detected since, owing to the inefficiency of Cl-abstraction by carbenes, the rate of intersystem crossing, step (14), is enhanced.

These results provide a rationale for some hitherto puzzling aspects of state multiplicity and of the extent of oxirene intervention in the WR. Thus, on going from isopropanol to methanol, where H abstraction is more difficult, triplet state PhCOCH: generated from the triplet benzophenone sensitization of PhCOCHN<sub>2</sub> undergoes efficient crossover to the S<sub>1</sub> state: this explains the high ester yields obtained in this solvent (Table 1). Similarly, the intervention of oxirene in the triplet (Michler's ketone) sensitization of PhCOCHN<sub>2</sub> (29) can be interpreted in terms of T<sub>0</sub>-S<sub>1</sub> intersystem crossing. This raises the question of vibrational excitation in the T<sub>0</sub> ketocarbene, since only vibrationally excited S<sub>1</sub> ketocarbene can isomerize to oxirene. Alternatively, the triplet ketocarbene generated upon sensitization (E<sub>T</sub> benzophenone = 69 kcal mol<sup>-1</sup>, E<sub>T</sub> Michler's ketone = 62 kcal mol<sup>-1</sup>) (34) may be the electronically excited T<sub>1</sub> state. It is not possible at present to decide between these possibilities.

To summarize, the extent of oxirene involvement in the WR of α-diazoketones depends on a number of factors, the major ones being the relative rates of substituent migration and ring closure, the nature of the substituents, which affect the rate of migration and the mode of ring opening, the phase, the solvent, and the rate of S<sub>1</sub>-T<sub>0</sub> intersystem crossing in the ketocarbene. For these reasons, the oxirene yields reported in the literature should be regarded only as those pertaining to the actual experimental conditions employed and not as an overall indication of the extent of oxirene formed from photolysis of a particular source compound. As an example, Zeller and coworkers have investigated the possible effects of ring strain on the WR of ketocarbenes (35). Photolysis (λ > 290 nm) of the <sup>13</sup>C labelled diazoketones



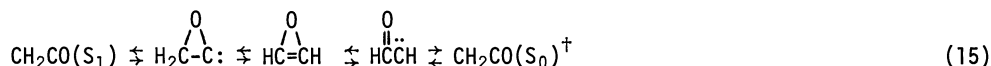
in dioxane-water (10:1) led to no appreciable scrambling in the products and it was concluded that cyclic or annelated oxirenes are not formed because of prohibitively high ring strain. However, oxirene yields are usually lower in this solvent and at the wavelength employed (Table 3). While ring strain may indeed inhibit cyclization in these systems, more definitive conclusions can only be reached upon conducting the experiments in an inert solvent and at higher photonic energies.

As noted above, oxirene formation is not limited to the WR, but also takes place in the gas phase direct photolysis of ketenes, although to a much lesser extent. Scrambling was not observed upon Hg(<sup>3</sup>P<sub>1</sub>) sensitization (17). The results are summarized in Table 4. Chemically

TABLE 4. % Oxirene participation in the photolysis of ketenes

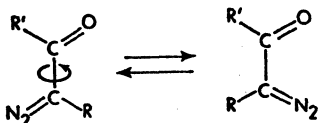
Ketene	Phase	% Oxirene	Reference
CH <sub>2</sub> C=C=O	gas	~4	(17)
(CH <sub>3</sub> ) <sub>2</sub> C=C=O	gas	20	(29)
(CH <sub>3</sub> ) <sub>2</sub> C=C=O	c-C <sub>5</sub> H <sub>10</sub>	16	(29)
Ph <sub>2</sub> C=C=O	c-C <sub>5</sub> H <sub>10</sub>	30	(29)
PhHC=C=O	c-C <sub>5</sub> H <sub>10</sub>	4	(29)
CH <sub>3</sub> (H)C=C=O	gas	16	(20)

activated ketenes produced from the CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) + CO reaction also isomerize to oxirene, but not the triplet state ketenes formed from CH<sub>2</sub>(<sup>3</sup>B<sub>2</sub>) (18). Thus, oxirene formation in the photochemical decomposition of ketenes, as in the WR, takes place on a singlet surface, and the parallelism is further evidenced for the case of CH<sub>2</sub>CO where a greater degree of scrambling was observed upon reducing the pressure of the scavenger gas C<sub>2</sub>H<sub>4</sub> (17). On the basis of the m.o. computational results, Figure 1, a plausible reaction sequence would be the one originally proposed by Russell and Rowland (17):



This rearrangement takes place in parallel and in competition with decomposition to CO + CH<sub>2</sub>.

In the past decade matrix isolation techniques have been used with great success for the isolation and characterization of highly reactive species. However, photolysis of argon matrix isolated diazoacetaldehyde and ethyl diazoacetate yielded only ketene and ethoxyketene, respectively, and no new transient spectrum was detected (36); either oxirenes are thermally unstable or photochemically labile under the conditions used. Proper substituents may be expected to exert a stabilizing effect on the oxirene ring and thus increase the activation energy for the oxirene-ketene rearrangement. However,  $\alpha$ -diazoketones, ideal precursors of oxirene, are known to exist in a conformational cis-trans equilibrium:



whereas the cis conformer is the most stable for the case of diazoacetaldehyde, increasing substitution will inevitably favour the trans form (37), and the activation energy for the ketocarbene-oxirene interconversion will thus be increased by the amount  $E_a$  (trans  $\rightarrow$  cis).

In an attempt to discover other precursors to oxirene we have photolyzed argon matrix isolated vinylene thioncarbonate (in which the cis conformation is fixed); however, only COS and ketene were detected.



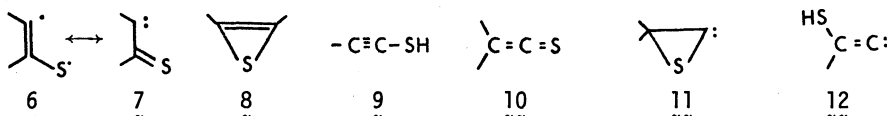
Photolysis of *o*-phenylenethioncarbonate also resulted in the formation of COS and cyclopentadienyldiideketene, and thus COS elimination and WR of the ketocarbene intermediate is probably a general photolytic pathway in the decomposition of cyclic thioncarbonates. This constitutes a new methodology for the generation of ketocarbenes and we intend to pursue this approach in our efforts to isolate oxirenes.

#### THIIRENE

In contrast to oxirene, thiirene has had a shorter and less controversial history. It was first proposed (38) as a theoretical possibility, then a few years later was invoked as the spin and symmetry allowed primary adduct in the  $S(^1D) + \text{acetylene}$  reaction (39). The only retrievable products are thiophene and CS<sub>2</sub>, formed in very small yields. With fluorinated acetylenes, however, the thiophene yields are enhanced and in direct proportion to the degree of fluorination. Thiophenes are presumably formed via condensation between the adduct and the acetylene:



Of the several possible C<sub>2</sub>H<sub>4</sub>S isomers,

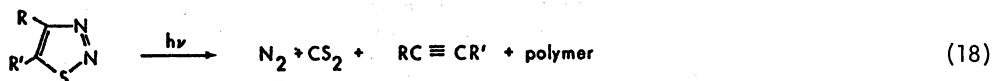


structures 9-12 are not likely to be involved in the thiophene-forming reaction since two or more rearrangements would be required. Moreover, CF<sub>3</sub> group migration has never been observed; yet, as mentioned above, the thiophene yield is the highest for the case of C<sub>4</sub>F<sub>6</sub>S + C<sub>4</sub>F<sub>6</sub>. Finally, flash photolysis-kinetic mass spectroscopic studies (39,40) on various COS + acetylene mixtures revealed the transient existence of R<sub>2</sub>C<sub>2</sub>S adducts having extremely long decay lifetimes, of the order of tenths to several seconds, clearly incompatible with excited state or radical carriers. For these reasons it was concluded that thiirene 8 is the initial adduct in reaction (17).

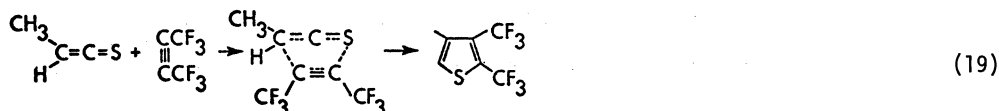
In the search for alternative precursors of C<sub>2</sub>H<sub>2</sub>S, the photochemistry of 1,2,3-thiadiazoles was examined. One would expect nitrogen extrusion and the formation of singlet state diradical species 6 (equivalent to the thioketocarbene 7). By analogy with the known reactions of ketocarbenes, WR to thioketene 10 could take place, possibly via thiirene 8. Other rearrangements to 9, 11 and 12 are also possible. As for the case of ketocarbene, the ground state of 6 is predicted to be a triplet whereas the ground states of 8-12 are singlet (vide infra). As expected, the 77°K powder crystal photolysis of 4-5-diphenyl-1,2,3-thiadiazole led to the appearance of an esr spectrum which was assigned to triplet thiobenzoylphenylmethylene (41).



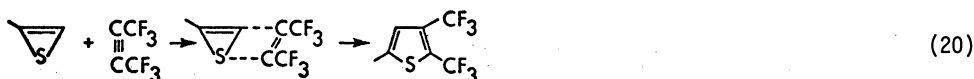
The gas phase photolysis of 1,2,3-thiadiazoles yields  $N_2$ , polymer, small amounts of  $CS_2$  and the corresponding alkyne (39,42):



However, in the presence of  $C_4F_6$ , 2,3-bis(trifluoromethyl)thiophene was the principal product, paralleling the  $S(1D) + C_4F_6$  case. Photolysis of either 4-methyl- or 5-methyl-1,2,3-thiadiazole in the presence of  $C_4F_6$  led to the formation of only one thiophene, 5-methyl-2,3-bis(trifluoromethyl)thiophene. This means that upon photolysis, both thiadiazoles give rise to the same intermediate, which makes the type of methyl substitution in the precursor indistinguishable. Of all the possible  $C_2H_2S$  isomers, only thiirene and thioketene can be considered as viable structures. If methylthioketene were the intermediate, however, two rearrangements would be required and the expected product would be the 4-methyl substituted isomer because of the different migratory aptitudes of H and  $CH_3$ :



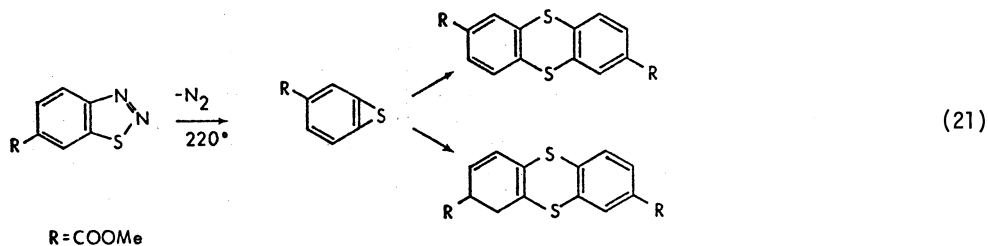
In the methylthiirene +  $C_4F_6$  complex, however, no rearrangements are required. Based on this and other considerations (43) we conclude that thiirene is the reactive intermediate and it would appear that electronic and steric effects exerted by  $CH_3$  force addition across the unhindered C-S side:



The solution phase photolysis of 1,2,3-thiadiazoles has been widely examined. The major products were assumed to have been formed via self and cross combination reactions of diradicals  $\begin{array}{c} R \\ | \\ \dot{C} \\ | \\ R \\ | \\ S \cdot \end{array}$  and thioketenes  $R_2C=C=S$  (44). Although small amounts of the intermediate

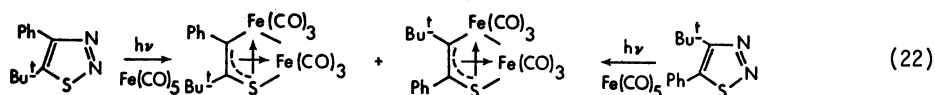
methylcarboethoxythioketene have been trapped in the methanol solution photolysis of 4-methyl-5-carboethoxy-1,2,3-thiadiazole (45) and could have been formed via rearrangement of the thiirene precursor, there is no evidence militating either against, or for, the involvement of thiirene in the solution phase photolysis of 1,2,3-thiadiazoles: isotopic labelling studies should be more definitive in this regard.

The gas phase thermolysis of 1,2,3-thiadiazoles has recently been used as a convenient approach to the synthesis of thioketenes (46) and a few cases can be cited as indirect, but strong evidence for the intermediacy of thiirenes. Thus, either 4-phenyl- or 5-phenyl-1,2,3-thiadiazole yield the same amount of thioketene, despite the fact that H migrates much faster than phenyl; under the same conditions the intermediate from the thermolysis of 4,5-diphenyl-1,2,3-thiadiazole does not rearrange to thioketene, but dimerizes to yield tetraphenylthiophene (47). Identical behavior has also been observed in the case of flow pyrolysis of 4- and 5-*tert*-butyl-1,2,3-thiadiazoles (45). Thermolysis of 6-carbomethoxy-1,2,3-thiadiazole leads to the formation of 2,7- and 2,8-dicarbomethoxythianthrene and the only plausible rationale for these is dimerization of the two isomeric thioketocarbene formed from the intermediate thiirene (48):



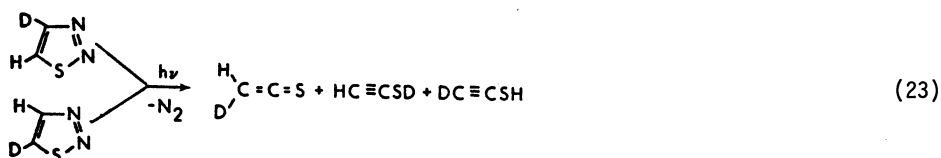
Some results, however, are inconclusive (49), and at least in one case (50), the intermediacy of thiirene has been disproven. Interestingly, the high temperature (1100°K) flow thermolysis of isotopically labelled 1,2,3-thiadiazole has been recently reported (51) to yield small amounts (~10%) of scrambled thioketene. It is our opinion that, as has been shown for the case of oxirene, the intervention of thiirene in the thermolysis of 1,2,3-thiadiazoles is strongly dependent on the temperature at which decomposition is carried out, and also on the nature of the substituents. Further studies are clearly warranted.

Some attempts have been made to trap thiirenes in the form of metal carbonyl complexes but in those few cases examined, only the thiokecarbonyl complex was isolated (52,53). However, photolysis of either 4-*tert*-butyl-5-phenyl or 4-phenyl-5-*tert*-butyl-1,2,3-thiadiazole in the presence of  $\text{Fe}(\text{CO})_5$  led to the formation of both isomeric complexes (53):

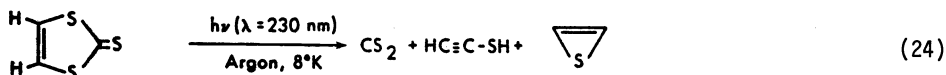


In each case, the product retaining the C-C-S skeleton was the major one, but because both are formed it would appear that they originate from a common precursor and that some equilibration must have taken place. Since the product complexes were shown not to isomerize under the conditions employed, it seems that they are formed via either thiirene or its metal complex.

Infrared analysis of the products formed upon the  $\lambda > 290$  nm photolysis of argon matrix isolated 1,2,3-thiadiazole indicated that only ethynylthiol and thiokecarbonyl had formed (54). However, photolysis of either 4-deutero- or 5-deutero-1,2,3-thiadiazole produced monodeutero-thiokecarbonyl and comparable yields of the two possible isomeric thiols,

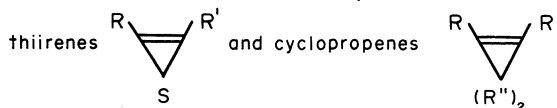


implying that they are formed from a symmetrical precursor, most likely thiirene. In order to ascertain whether thiirene was photolabile at  $\lambda > 290$  nm, the photolysis was carried out using filtered radiation (235-280 nm) (55). In addition to ethynylthiol and thiokecarbonyl, a new transient spectrum was observed. Moreover, photolysis of either 4-deutero- or 5-deutero-, as well as of either 4- $^{13}\text{C}$ - or 5- $^{13}\text{C}$ -1,2,3-thiadiazole led to the appearance of the same transient spectrum and it was concluded that the common carrier was thiirene. We have also examined the low temperature photolysis of a number of matrix isolated substituted 1,2,3-thiadiazoles (56) and have shown (57) that vinylene trithiocarbonate is an excellent source compound for the generation of thiirene:



(This precursor offers the advantage that only small amounts of thiokecarbonyl are formed at  $\lambda = 230$  nm). Krantz and coworkers noted that the observed isotopic shifts in the *ir* band assigned to C=C st are consistent with a cyclopropanoid type of transient. The same conclusion was reached upon comparing the effects of substituents on the C=C st frequencies of thiirenes and the analogous cyclopropenes (43). The data are summarized in Table 5.

TABLE 5. Observed C=C st frequencies for some



Substituent		Thiirene		Cyclopropene		
R	R'	$\nu_{\text{C=C}}$	Reference	R''	$\nu_{\text{C=C}}$	Reference
H	D	1660	(55) (56)	R	1656	(59)
H	D	1610	(55) (58)	$\text{CH}_3$	1578	(60)
D	D	1565	(55) (58)	H	1572	(59)
$\text{CH}_3$	$\text{CH}_3$	1923	(55)	H	1885	(60)
				$\text{CH}_3$	1870	(60)
$\text{CH}_3$	$\text{COOEt}$	1875	(56)	$\text{CH}_3$	1840	(60)
$\text{CF}_3$	$\text{CF}_3$	1800	(57)	F	1820	(61)

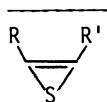
As a final proof for the spectral assignment to thiirene we carried out a normal coordinate analysis of the spectra of  $C_2H_2S$  and  $C_2D_2S$ , the bands of which were assigned partly on the basis of isotopic shifts, and partly by comparison with the vibrational assignments of the known spectra of cyclopropene and thiirane, molecules possessing geometries similar to that of thiirene (58). Geometrical parameters were taken from an *ab initio* molecular orbital calculation using an ST0-4G minimal basis set (62). Although good agreement was obtained between the observed and calculated frequencies, a recent reevaluation of the spectrum of cyclopropene (63,64) prompted us to reexamine our former band assignments (65). Normal coordinate analysis was again carried out but this time, the force field was constructed using to the fullest extent the analogous force constants derived from the cyclopropene spectrum (64) and then refined to fit the observed frequencies of thiirene and thiirene- $d_2$ . The results, summarized in Table 6, led to a reassignment of the 912  $cm^{-1}$  band (C-H in plane bend, formerly  $a_1$ ) to the  $b_2$  mode but none of the other assignments were affected.

TABLE 6. Observed and calculated vibrational frequencies ( $cm^{-1}$ )

	Thiirene- $d_0$		Thiirene- $d_2$	
	observed	calculated	observed	calculated
$a_1$ C-H stretch	3208(w)	3222	2487(m) 2484(m)	2468
C=C stretch	1660(w)	1683	1565(w)	1567
C-H bend, in plane	-	951	681(m)	697
Ring deform. sym.	657(m)	674	-	656
$a_2$ C-H bend, out of plane	-	647	-	529
$b_1$ C-H bend, out of plane	563(s)	566	422(s)	426
$b_2$ C-H stretch	3169(m) 3165(mw)	3183	2355(m) 2352(w)	2341
C-H bend, in plane	912(mw) 910(s)	882	716(s)	739
Ring deform. asym.	-	489	-	434

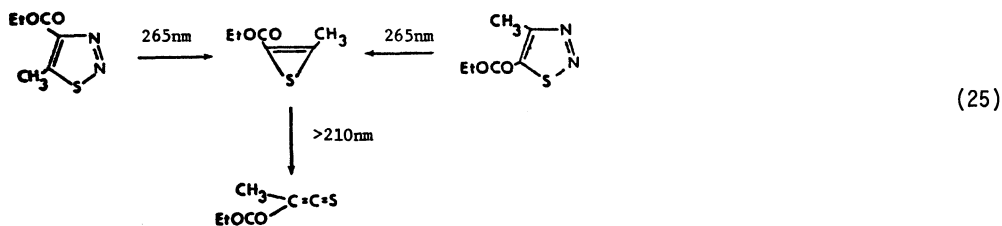
The *ir* frequencies observed for those thiirenes which have been isolated to date are summarized in Table 7, where it is seen that electron withdrawing substituents exert a high

TABLE 7. Infrared frequencies of thiirene and substituted thiirene

		ir frequencies observed ( $cm^{-1}$ )	Thiirene yield	Reference
R	R'			
H	H	3208, 3170, 1660, 912, 660, 563.	fair	(54) (55)
CH <sub>3</sub>	H	3203, 2930, 1440, 1429 1036, 897, 650.	fair	(54)
CH <sub>3</sub>	CH <sub>3</sub>	2970, 2921, 2865, 1923, 1440, 1427, 1041, 586, 471.	fair	(54)
		1670, 1440, 490, 950, 729, 680, 670.	poor	(55)
CF <sub>3</sub>	H	3210, 1240, 1190, 1180, 720.	moderate	(55)
CH <sub>3</sub>	COOEt	3205, 3000, 1875, 1715, 1440, 1400, 1370, 1270, 1070, 1040, 1020, 760, 730, 490.	high	(55)
COOEt	CH <sub>3</sub>			
CF <sub>3</sub>	CF <sub>3</sub>	1800, 1320, 1255, 1030, 975, 860, 760.	moderate	(56)

stabilizing influence on thiirene. The most dramatic effect was observed upon photolysis ( $\lambda = 265$  nm) of the 4-methyl-5-carboethoxy- and 4-carboethoxy-5-methylthiadiazoles: the resulting thiirene spectrum intensity was enhanced and very little thioketene was formed.

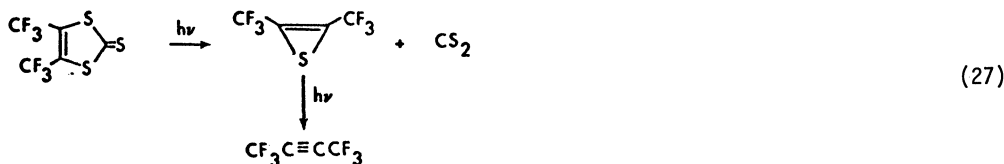
Subsequent photolysis at  $\lambda > 210$  nm, however, led to bleaching of the thiirene spectrum and to the appearance of the characteristic thioketene spectrum:



Like cyclobutadiene then, the transient existence of thiirene is now firmly established and some of its chemical properties have been brought to light. For example,  $S(^1D)$  atoms react with an equimolar mixture of  $C_2H_2$  and  $C_4F_6$  to yield the asymmetrical 2,3-bis(trifluoromethyl)-thiophene as the only cross product (40); the absence of unsubstituted thiophene points to the nucleophilic character of thiirene:

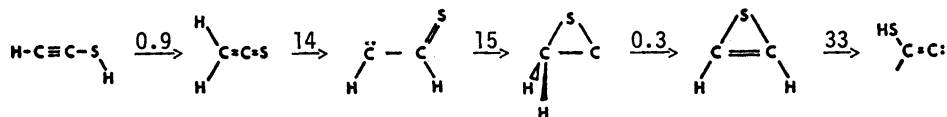


In agreement with this hypothesis we calculate the charge densities on sulfur and carbon to be + 0.1122 and - 0.1552, respectively (23). It has been shown that most of the thioketene (all of the ethynylthiol, for the case of parent 1,2,3-thiadiazole) arises from secondary photolysis of the intermediate thiirene (55,56). Therefore the thioketocarbene-thiirene-thioketene WR appears to be a general mechanistic pathway in the photodecomposition of 1,2,3-thiadiazoles. Bis(trifluoromethyl)thiirene, however, formed upon photolysis of argon matrix isolated bis(trifluoromethyl)-1,3-dithiol-2-thione, is the most photostable of all the derivatives synthesized to date, presumably because, owing to the low migratory aptitude of  $CF_3$ , the thiirene-thioketocarbene rearrangement cannot take place; instead,  $C_4F_6$  and S atoms are the photodecomposition products:



Alkynes are products of the gas phase photolysis of 1,2,3-thiadiazoles and probably are formed via this mechanism. This decomposition pathway for thiirenes parallels that for the oxirene case, *viz.* the small but persistent yields of  $C_4H_6$  produced in the gas phase photolysis of  $CH_3COCN_2CH_3$  (29). The presently available data are insufficient to allow any conclusions as to the effects of substituents on the mode of ring opening in thiirene but they probably play an important role.

Ab initio computations on the thermodynamic stabilities of all six  $C_2H_2S$  isomers have been made using an ST0-4G minimal basis set (62,66) and the results are shown in Figure 2. Only the thioformylmethylene isomer is predicted to have a triplet ground state, and the calculated  $T_0-S_1$  separation is very small, of the order of 9 kcal mol<sup>-1</sup>. For the singlet manifold, the order of stability and the energy separations (in kcal mol<sup>-1</sup>) are predicted to be:



As will now be shown, these results are in agreement with experimental observations. On the basis of the extensive results available for parent 1,2,3-thiadiazole, and by analogy with the formylmethylene-oxirene-ketene rearrangements, some of the reaction channels involved in the photochemical decomposition of 1,2,3-thiadiazoles can be elucidated.

Photolysis should initially produce  $S_2$  electronically excited thioketocarbenes, which then should undergo rapid internal conversion to the  $(S_1)^+$  state,



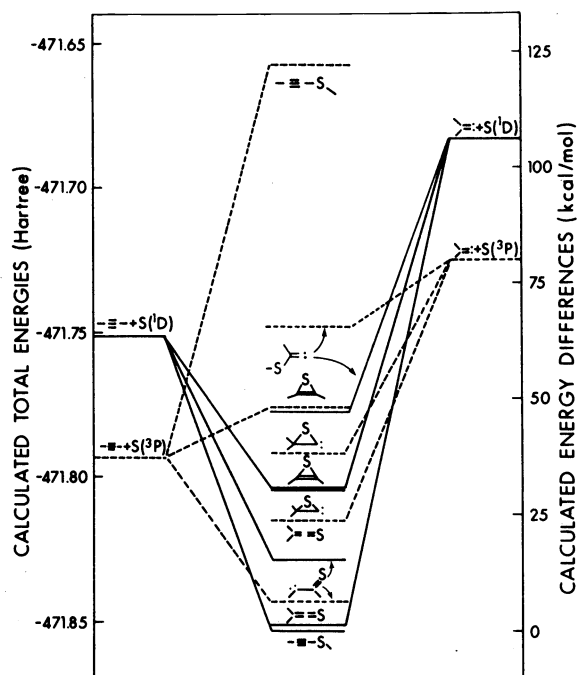


Figure 2. Calculated energy differences ( $\text{kcal mol}^{-1}$ ). Solid lines singlet, dotted, triplet.



where  $\dagger$  signifies vibrational excitation. Subsequently,  $(\text{S}_1)^\dagger$  thioketocarbene can undergo three parallel and competing reactions:



As in the oxirene case, it appears that excess vibrational energy is required for the thioketocarbene-thiirene rearrangement, step (30b). This conclusion is based on the following observations. Firstly, the  $\lambda = 215 \text{ nm}$  photolysis leads to a marked enhancement of the thiirene yield, compared to that obtained at  $\lambda = 265 \text{ nm}$  (56). Secondly, thiirene band intensities depend on the matrix used (43) and increase in the order  $\text{Xe} < \text{Ar} < \text{Ne}$ , i.e. in the reverse trend in polarizability, which would favour the deactivation step (30c).

As mentioned above, thiirene undergoes secondary photolysis to thioketene. With the exception of bis(trifluoromethyl)thiirene, this appears to be a general reaction of thiirenes and probably takes place via WR of  $\text{S}_1$  thioketocarbene formed as a result of C-S cleavage:



For thiirene and trifluoromethylthiirene a second, competing mode of decay is isomerization to the corresponding alkynylthiols and we propose a zwitter ion intermediate in this rearrangement:



Random labelling in ethynylthiol from the photolysis of labelled 1,2,3-thiadiazole requires the intervention of a symmetrical precursor in which the hydrogen atoms must be equivalent and intramolecular hydrogen transfer must take place while prescreening the carbon equivalence. Intervention of the zwitter ion in step (31b) provides a plausible rationale for this rearrangement and is conceptually more inviting than direct thiirene-ethynylthiol isomeriza-

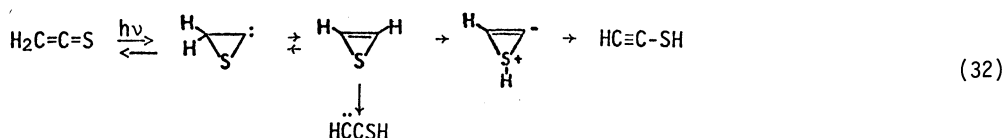
tion. Thus, formation of thiirenium ions which, under certain circumstances, can be isolated (67), removes the antiaromaticity of thiirene and indeed thiirenes are predicted to have a significantly basic character. Moreover, a  $\text{CH}_3$  substituent would be expected to destabilize the zwitter ion, whereas  $\text{CF}_3$  should exert an opposite effect: the fact that to date, only  $\text{HC}\equiv\text{C-SH}$  and  $\text{F}_3\text{CC}\equiv\text{C-SH}$  have been observed, is in agreement with these considerations. It is interesting to note that ethynol was not a product of the low temperature matrix photolysis of  $\alpha$ -diazoketone (36) or vinylene thioncarbonate (68) and in agreement with this observation

ab initio calculations on the thermodynamic stability of  $\text{H} \begin{array}{c} \diagup \\ | \\ \diagdown \end{array} \text{O}^+ - \text{H}$  did not predict an energy minimum for this species (23).

The possible intervention of thiirenylidene in the thiirene-thioketene rearrangement,



cannot be assessed at this time. On the other hand we have shown (56) that upon extended photolysis of 1,2,3-thiadiazole the intensities of the bands attributed to thioketene and ethynylthiol underwent a slow and parallel decrease and increase, respectively, indicating that at the wavelength employed (215 nm) thioketene is converted to ethynylthiol. We suggest that this interconversion takes place via thiirenylidene and thiirene which are computed (62) to be very close ( $\sim 0.3 \text{ kcal mol}^{-1}$ ) in energy:



The existence of these reversible rearrangements, analogous to the proposed ketene-oxirene pathway, equation (15), could also explain the yields of scrambled thioketene from the high temperature thermolysis of 1,2,3-thiadiazole (51). It has been noted that, for the case of isotopically labelled 1,2,3-thiadiazole, most of the thioketene is unscrambled and therefore steps (31a) and (31c) are not very important, at least for the unsubstituted example under matrix isolation conditions. It should be borne in mind, however, that changes in temperature and phase will have a drastic effect on the thermal stability of the intermediate thiirene. Thus, in the gas phase thermal decomposition will predominate. Fragmentation to the corresponding alkyne has been shown to take place but this is a minor process. The thermal equivalent of step (31a), expected to be the most important process, has not been observed but the thioketenes expected to have been formed from those thiadiazoles examined to date are unstable and readily polymerize under the experimental conditions employed.

Finally, intersystem crossing of  $S_1$  thioketocarbene to the ground  $T_0$  is possible,



and this is probably the state detected by esr (41). Interestingly, the triplet state adduct formed from the  $S(^3P) + \text{acetylene}$  reaction, very likely thioformylmethylene,



also adds to  $\text{C}_4\text{F}_6$  to yield 2,3-bis(trifluoro)thiophene: the yields are low (20-24%) at room temperature but increase to 100% (in terms of S atoms produced) around  $100^\circ\text{C}$  (69), pointing to a substantial activation energy requirement for this reaction. This is in contrast to formylmethylene, where the singlet and triplet states exhibit very markedly different reactivities.

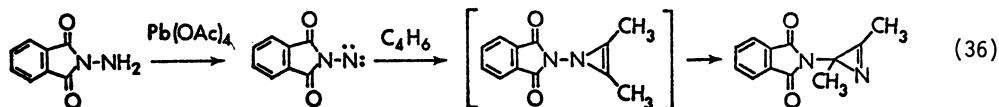
## 2-AZIRINE

Attempts to demonstrate the transient existence of 2-azirine took place more or less in parallel with studies on oxirene and thiirene. In principle, one might expect that 2-azirine would be the primary adduct in the nitrene + acetylene reaction



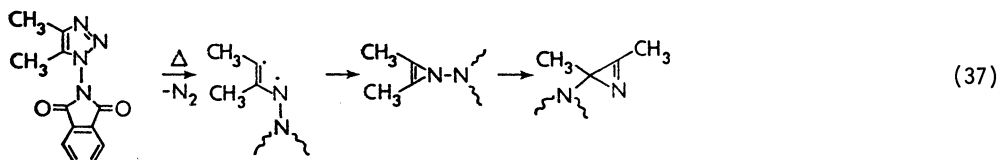
by analogy with the  $\text{R}\ddot{\text{N}}\text{:} + \text{R}'\text{C}=\text{CR}''$  reaction, which has been shown to yield aziridines as major products (70). Photochemically produced carboethoxynitrene reacted with 2-butyne, however, to produce an oxazole and larger amounts of another product corresponding to a ( $2\text{C}_4\text{H}_6 + \text{EtOCON}$ ) adduct (71). Shortly afterwards Rees and coworkers reported that upon oxidation of

N-aminophthalimide in the presence of acetylenes 1-azirines are produced, and speculated that these are formed *via* rapid rearrangement of the unstable 2-azirine primary adduct (72):



Both inter- and intramolecular rearrangement mechanisms could be visualized (73) but it was not possible to determine which was operative.

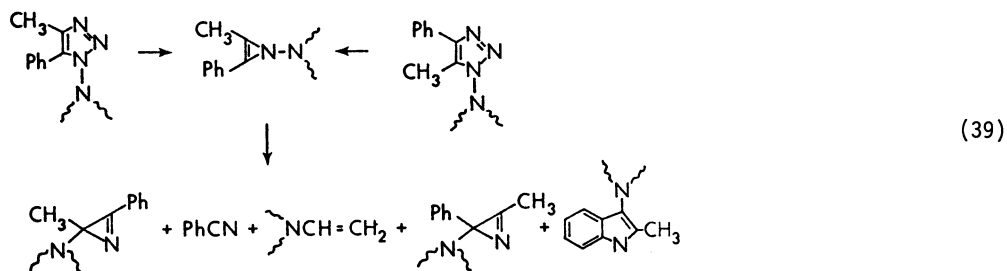
Benzotriazoles, which contain the thermally and photochemically unstable azo moiety, are likely to be more promising sources of 2-azirine. Flash pyrolysis of 1-phthalimido-4,5-dimethyl-1,2,3-triazole yielded 2,3-dimethyl-3-phthalimido-1-azirine and Rees and coworkers suggested the transient intervention of the 2-azirine analog in this case as well (73):



The 1-azirine product was shown to undergo a novel secondary fragmentation producing methyl-phthalimidocarbene, which rearranges to N-vinylphthalimide:

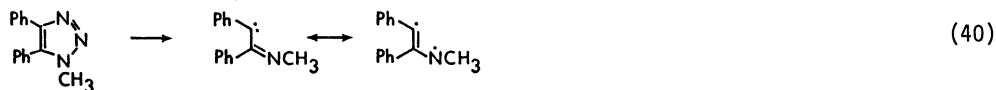


In order to obtain more convincing evidence for the transient existence of 2-azirine in the thermolysis of benzotriazoles, an asymmetrically substituted pair of triazoles was examined. Both yielded the same five products upon thermolysis, and in the same proportions, and since neither the starting materials nor the products were interconvertible under the experimental conditions used, it was concluded that a common, symmetrical intermediate was involved, namely, 2-azirine (73):

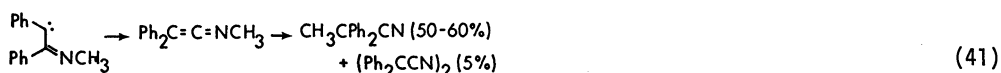


Subsequently, Rees and coworkers investigated the pyrolysis of a number of alkyl substituted isomeric pairs of benzotriazoles and concluded that the nature of the observed products was consistent with 2-azirine precursors (74). Moreover,  $^{13}\text{C}$  nmr analysis of the products derived from the thermolysis of 1,5-diphenyl-[5- $^{13}\text{C}$ ]-1,2,3-triazole showed that extensive scrambling had taken place, as would be expected from a symmetrical precursor (75).

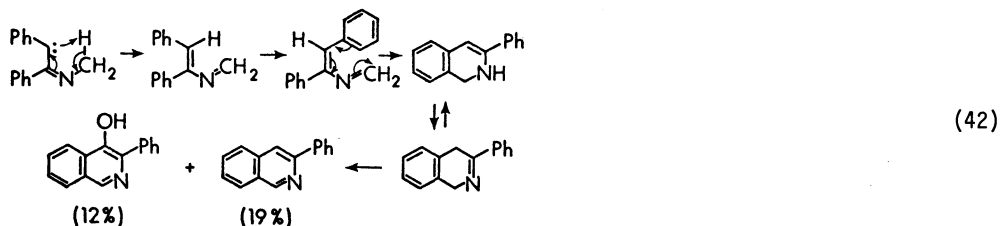
In parallel with these investigations, some interesting chemical interconversions have been brought to light. Intuitively, it was assumed (73) that the primary fragment of the decomposition sequence was an iminocarbene, *e.g.*



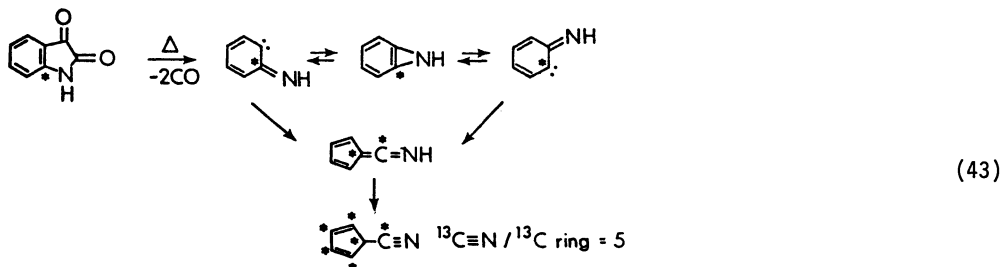
In fact, very recently we were able to detect the *esr* signals from triplet state iminocyclohexadienylidene, its N-methyl and N-phenyl derivatives, from the 77°K photolysis of the parent 1,2,3-benzotriazoles (76). The D values are consistent with a 1,3-diradical structure and for the N-phenyl isomer, the spectra of both rotameric conformers were resolved. Iminocarbene, as seen above (Eq. 37), can cyclize to 2-azirine; alternatively, they have been shown to undergo the Wolff rearrangement,



or a 1,4-hydrogen shift, offering a new synthetic route to isoquinolines (74,77):

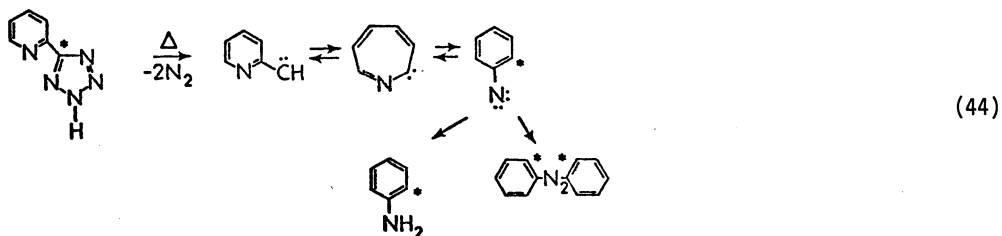


N-H triazoles undergo facile tautomerism and because it is impossible to locate the N-H moiety, the intermediacy of 2-azirine in the decomposition of these source compounds cannot be readily established. Isatin, however, contains two extrudable carbonyl groups and therefore should be a suitable precursor for the generation of iminocyclohexadienylidene and 2-azirine. The gas phase thermolysis of isatin yielded 1-cyanocyclopentadiene, formed via ring contraction of the iminocarbene and small amounts of aniline formed from abstraction by the iminocarbene (78). Thermolysis of methylisatins (78) afforded mixtures of toluidines consistent with ~10-12% interconversion of the iminocarbenes via the 2-azirine. Subsequently Thétaz and Wenstrup (79) carried out experiments on  $^{13}\text{C}$  labelled isatin and were able to show that the following rearrangements take place:



If the iminocarbene-azirine interconversion were complete, then the labelling ratio  $^*\text{C}\equiv\text{N} / ^*\text{C}_{\text{ring}}$  should be 1.0. However, owing to facile sigmatropic migrations of the  $\text{C}\equiv\text{N}$  group around the ring, the label at the  $\text{C}_1$  position is distributed over the entire ring and the observed labelling ratio is 5.

Interestingly, 2-azirines have also been shown to be intermediates in the characteristic ring contraction reaction of phenyl nitrenes (79). At  $400^\circ\text{C}$ , the gas phase thermolysis of  $^{13}\text{C}$  labelled 5-(2-pyridyl)tetrazole yields aniline and azobenzene, both exclusively labelled at the ortho positions:



However, at  $600^\circ$ , an additional product, cyanocyclopentadiene, is formed. Assuming complete nitrene-iminocarbene-azirine interconversions and allowing for sigmatropic  $\text{C}\equiv\text{N}$  migrations, the  $^*\text{C}\equiv\text{N} / ^*\text{C}_{\text{ring}}$  ratio should be 1.67. Experimentally, the ratio was 1.7 and thus ring contraction of phenyl nitrene is not a direct process, but takes place after isomerization to iminocyclohexadienylidene and 2-benzazirine:





The intermediacy of 2-azirine has also been verified in the ring contraction reaction of 2-naphthylnitrene but pyrazyl nitrenes and 2-pyrimidin nitrenes, on the other hand, undergo direct ring contraction to yield either C-nitriles or N-nitriles (80). It is significant that Wentrup (81) has clearly shown that only vibrationally excited phenyl nitrenes undergo the ring contraction reaction and has estimated, on the basis of thermochemical data, lower and upper limits of 30 and 51 kcal mol<sup>-1</sup>, respectively, for  $E_a$  (phenyl nitrene → cyanocyclopentadiene); also,  $E_a$  (phenyl nitrene → iminocyclohexadienylidene) > (iminocyclohexadienylidene → cyanocyclopentadiene).

In an attempt to isolate 2-benzazirine, we have carried out some preliminary studies on the argon matrix photolysis ( $\lambda = 270$  nm) of 1-methylbenzotriazole at 8°K. The spectrum of the photolyzate featured a strong absorption at 2070 cm<sup>-1</sup>, from which we tentatively identify the carrier as N-methyl-cyclopentadienylideneiminoketene (82) formed from the WR of N-methyl-iminocyclohexadienylidene. The failure to observe any transient spectrum does not necessarily mean that 2-benzazirine is not formed under these conditions. Indeed, the observed low photochemical conversion rate of 1-methylbenzotriazole suggests that even if N-methylbenzazirine is formed, it would undergo rapid secondary photolysis, thus preventing its observation. Flow pyrolysis of 1-methylbenzotriazole, on the other hand, resulted in the appearance of a different spectrum which we assign to 1-methyl-cyanocyclopentadiene, based on its strong absorption at 2220 cm<sup>-1</sup>.

*Ab initio* molecular orbital calculations confirm the predicted thermodynamic instability of 2-azirine. Thus, the singlet and triplet manifolds of eight C<sub>2</sub>H<sub>3</sub>N isomers have been calculated with an ST0-4G minimal basis set (83) and six of them are depicted in Figure 3.

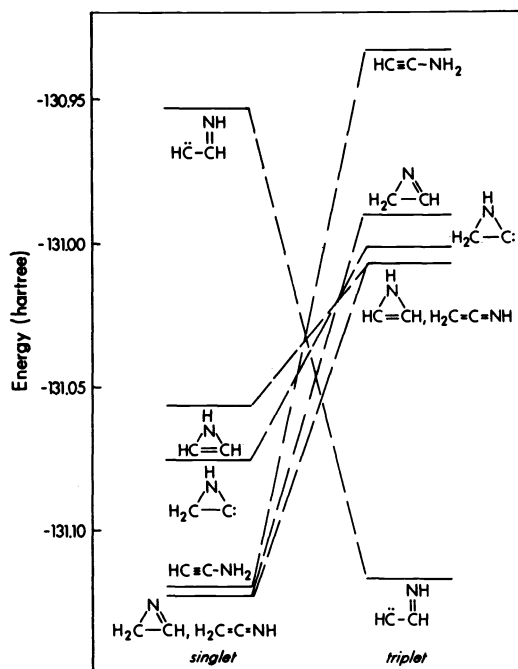


Figure 3. Computed energies of some C<sub>2</sub>H<sub>3</sub>N valence isomers using an ST0-4G minimal basis set.

Methyl cyanide, the most stable structure, is not shown. Next in order of stability are 1-azirine and ketenimine. 2-Azirine is predicted to lie 40 kcal mol<sup>-1</sup> above 1-azirine. Surprisingly, iminocarbene is predicted to be less stable than 2-azirine by 65 kcal mol<sup>-1</sup>, but its ground state is triplet, as expected. The calculated  $S_1-T_0$  energy separation, however, 102 kcal mol<sup>-1</sup>, is much too large. With the 6-31G extended basis set, however, a somewhat different scheme emerges, Figure 4 (84). Although the energy difference between 2-azirine and 1-azirine is relatively unchanged at 33 kcal mol<sup>-1</sup>, 1-azirine is predicted to be less stable than ketenimine by 36 kcal mol<sup>-1</sup>. Of more significance are the very small energy separations between 2-azirine, iminocarbene and vinyl nitrene, < 1 kcal mol<sup>-1</sup>. The reaction profiles for the iminocarbene → 2-azirine and vinyl nitrene → 1-azirine interconversions along the lowest energy paths have also been computed (84) and predict that energy barriers of 60 kcal mol<sup>-1</sup> and 10 kcal mol<sup>-1</sup>, respectively, are involved.

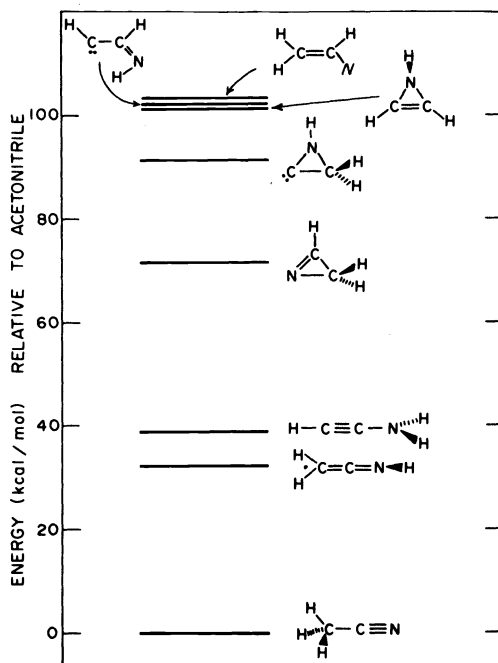
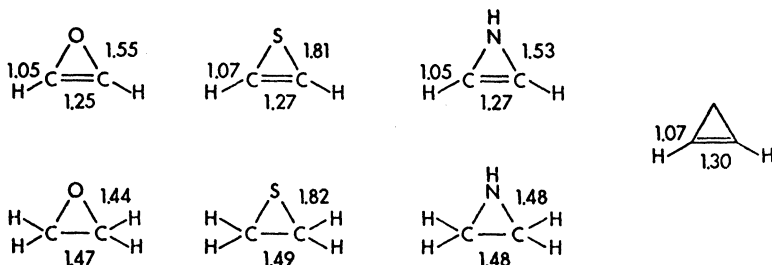


Figure 4. Computed energies of the  $C_2H_3N$  valence tautomers relative to acetonitrile using a 6-31G basis set.

#### CONCLUDING REMARKS

The transient existence of oxirene, thiirene and 2-azirine is now well established and they have been shown to be intermediates in the WR of the vibrationally excited lowest singlet states of ketocarbenes, thioketocarbenes, and iminocarbenes. The inherent instabilities of these species and the extreme conditions required for the isolation of thiirene point to their high energy contents and hence to their antiaromaticity. In this context it is interesting to compare the calculated C-X (X=O,S,NH) and C-H bond lengths of oxirene, thiirene and 2-azirine with those of their saturated counterparts oxirane (85), thiirane (86), aziridine (87), and the C=C and C-H bond lengths with those of cyclopropene (88). The basis sets used for the calculations were: double zeta (oxirene) (27), STO-4G (thiirene) (62), and 4-31G (2-azirine) (84). The results are summarized below:



Unsaturation leads to a predicted increase in the C-X bond lengths for the cases of oxirene and 2-azirine, while no change is predicted for thiirene. Associated with a lengthening of the C-X bond, a corresponding decrease in the C-H and C=C bond lengths would be expected and this is indeed the case for oxirene and 2-azirine. The predicted geometry of thiirene, however, does not follow this trend. On the other hand, the results of our normal coordinate analysis (58,65) point to a smaller C-S st force constant and a larger C-H st force constant than thiirane, implying that the C-S and C-H bond lengths in thiirene are larger and smaller, respectively, than those of thiirane and cyclopropene. Small basis sets, however, have been shown to predict less satisfactory geometries for cyclic molecules as compared to their acyclic isomers (89) and it is expected that the use of an extended basis set will lead to improved geometries. In this context, we have observed that on going from a minimal basis to an extended basis set, the calculated C-X and C-H bond lengths of oxirene and 2-azirine become larger and smaller, respectively, Table 8.

Very recently, Hess and Schaad (90) carried out *ab initio* calculations on thiirene using an extended 4-31G basis set. The resulting optimized geometry features a longer C-S (1.978 Å)

TABLE 8. Calculated bond lengths ( $\text{\AA}$ ) of oxirene and 2-azirine

Basis set	C-X	C=C	C-H	Reference
oxirene				
STO-4G	1.490	1.260	1.073	(23)
double zeta	1.550	1.254	1.050	(27)
2-azirine				
STO-4G	1.513	1.266	1.073	(83)
4-31G	1.531	1.265	1.057	(84)

and shorter C-H (1.056  $\text{\AA}$ ) bond length as compared to thiirane, and thus these trends now appear to be well established for 4n- $\pi$  antiaromatic heterocycles.

The longer C-X bonds in oxirene, thiirene and 2-azirine probably reflect the tendency of these molecules to minimize destabilizing conjugations, another manifestation of their antiaromatic character. They are also expected to be weaker than their saturated counterparts and in fact the reactions of thiirene and oxirene take place exclusively at this site. In the case of 2-azirine there is an additional competing reaction, 1,2-hydrogen shift to form 1-azirine, in which conjugation is no longer possible.

#### ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Research Council Canada for continuing financial support. We would also like to express our deep gratitude to all our former coworkers for their contributions to oxirene and thiirene chemistry. Finally, we thank Dr. R.K. Gosavi for helpful comments and suggestions during the preparation of this manuscript.

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90. We are indebted to B.A. Hess, Jr. and L.J. Schaad, for communicating their results to us prior to publication.