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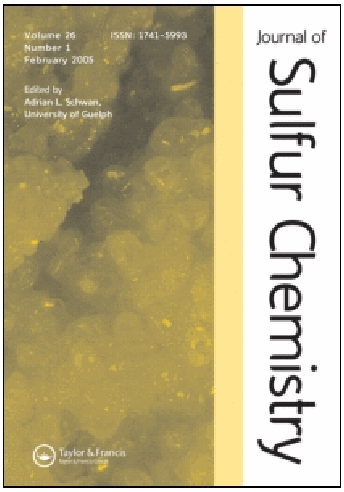

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$R^1R^2CSO_x$ Structures in the Conversion of Thiocarbonyl Compounds Into the Corresponding Oxo Derivatives

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$R^1R^2CSO_x$ STRUCTURES IN THE CONVERSION OF THIOCARBONYL COMPOUNDS INTO THE CORRESPONDING OXO DERIVATIVES

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The conversion of thiocarbonyl compounds into their corresponding oxo derivatives involves intermediary species of the general type $R^1R^2CSO_x$ in several cases. These structures may be generated either by direct oxidation of the thiocarbonyl compounds ($R^1R^2CS + x\,'O' \rightarrow R^1R^2CSO_x$) or by stepwise oxidation ($R^1R^2CSO_{x-y} + y\,'O' \rightarrow R^1R^2CSO_x$). Within the single series (R^1R^2CSO, $R^1R^2CSO_2$, and $R^1R^2CSO_3$) a variety of isomeric species may be obtained by thermally or photolytically induced intramolecular conversions. In some cases direct experimental evidence (*e.g.* oxathiiranes) or even isolation (*e.g.* sulfines, thiourea *S*-oxides) of $R^1R^2CSO_x$ compounds has been reported, but in several cases, based on experiments as well as on theoretical studies, only indirect evidence for their presence has been presented (*e.g.* sulfenes, oxathiirane oxides, dioxathietanes, trioxathiolanes). Investigations concerning the formation, thermal and photolytical decomposition, and physico-chemical properties of compounds with $R^1R^2CSO_x$ (x = 1, 2, 3, (4)) structures are reviewed, whereas chemical reactions involving these species are mentioned only briefly.

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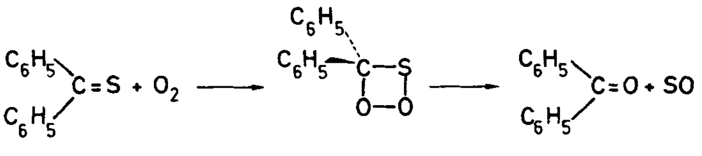
INTRODUCTION

In the course of time several authors have reported on the conversion of the thiocarbonyl function to the corresponding oxo derivatives. A wide variety of reagents has been applied, including *e.g.* nitric acid,[1] nitronium ions,[2] mercury acetate,[3] potassium permanganate,[4] manganese dioxide,[5] selenium dioxide,[6] benzeneseleninic anhydride,[7] alkyl nitrites,[8] nitrile *N*-oxides,[9] dimethyl sulfoxide/iodine,[10] alkyl/aryl selenoxides,[11] bis-(*p*-methoxyphenyl) telluroxide,[12] and halogen/alkoxides.[13] However, these reports deal only sparsely with mechanistic studies of the reactions involved, and no information concerning the actual identity of possible intermediary structures is given.

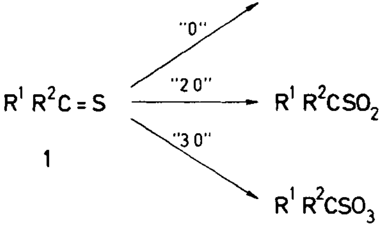
Oxidation of thiocarbonyl compounds can *a priori* give rise to reaction products of the general type $R^1R^2CSO_x$ ($x = 1$–3), which may further rearrange to the corresponding carbonyl compounds by extrusion of S, SO, or SO_2, respectively. During the past few decades several reports on $R^1R^2CSO_x$ structures have appeared in the literature, establishing their importance as intermediates, not necessarily thermally labile, in the conversion of thiocarbonyl compounds to the corresponding oxo derivatives.

As early as 1896 Gattermann investigated the reaction between thiobenzophenone and molecular oxygen, leading to benzophenone in high yield.[14] Mechanistically the reaction was formulated to proceed *via* the four-membered 4,4-diphenyl-1,2,3-dioxathietane.



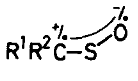
In 1928 Staudinger and Freudenberger[15] and Schönberg *et al.*[16] demonstrated that thiobenzophenone reacts with molecular oxygen in the dark as well as in sunlight to form benzophenone. However, recent investigations[17] reveal that the reaction between thiobenzophenone and oxygen in the dark apparently is more complex, since considerable amounts of the corresponding *S*-monoxide, thiobenzophenone *S*-monoxide (diphenyl sulfine), are formed (*vide infra*).

In the present report recent investigations of the formation, decomposition, and physicochemical properties of compounds with a $R^1R^2CSO_x$ structure are reviewed, whereas the possible participation of these compounds in different chemical reactions will be mentioned only briefly.



I R^1R^2CSO STRUCTURES

Oxidation of thiocarbonyl compounds (**1**) to the corresponding 'monoxide' derivatives may *a priori* lead to three possible products, which are sulfines (**2**), oxathiiranes (**3**), and the zwitterion/biradical (**4**), as a result of oxygen attack on sulfur, the carbon-sulfur double bond, and carbon, respectively.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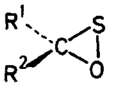
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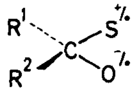
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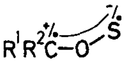
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The intermediacy of the fourth possible R^1R^2CSO structure, the carbonyl *O*-sulfide (**5**) in the photolysis of matrix isolated oxathiiranes is discussed separately.

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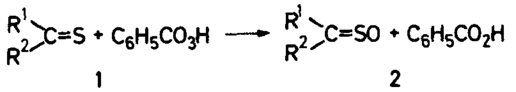
I.1 Sulfines (Thiocarbonyl S-monoxides)

In recent years it has been unequivocally established that oxidation of thiocarbonyl compounds with peroxycarboxylic acids leads to the corresponding *S*-monoxides, which in general can be isolated in high yields (R^1 =Ar/Alk, R^2 = Ar/Alk).[18]


1 2

In the cases of thioamides and thiourea derivatives, however, the peracid oxidation appears to be unsuccessful, whereas the reaction with hydrogen peroxide has been used advantageously.[19]

In the course of time a variety of sulfines has been prepared by application of several synthetic pathways, the peracid oxidation, however, being the more versatile. A selection of available thiocarbonyl *S*-monoxides is given in Table I.

S-Monoxides of cyclic thiocarbonyl compounds such as 1,2-dithiole-3-thiones[29] and 1,3-dithiole-2-thiones[27b] have been reported and recently representatives of the cumulated thioketene *S*-monoxides have been synthesized,[30,31] the latter, however, only achievable in the case of stabilization due to steric effects.

Finally, it is noted that a naturally occurring sulfine, propanethial *S*-monoxide (**2**: $R^1 = C_2H_5$, $R_2 = H$), has been isolated as the lachrymator in onions;[32] and very recently Baldwin *et al.* reported on a penicillin derived sulfine.[33]

For a more comprehensive account on sulfine chemistry a recent review by Zwanenburg[34] should be consulted.

A mechanistic study of the reaction between substituted thiobenzophenones and peracids revealed, in agreement with the electrophilic character of a peracid, a Hammett ρ-value of -0.88.[35] No other products with a R^1R^2CSO composition were observed.

The structure of sulfines has been elucidated by application of X-ray crystallorgraphy[36] as well as microwave spectroscopy.[20] Not surprisingly, the >CSO group being a

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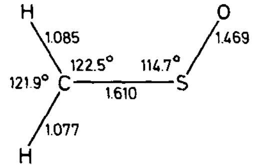
TABLE I

Thiocarbonyl *S*-Monoxides

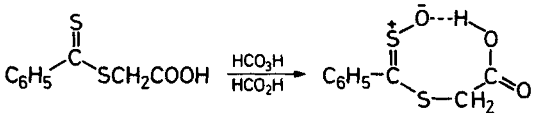
R^1	R^2	Ref.
H	H	20
Ar/Alk	Ar/Alk	18, 21
Ar	H	22
Ar/Alk	NR_2	19
NR_2	NR_2	19
Ar	Cl	23
Ar	N_3	24
Ar	SCN	25
Ar	SR	25
Ar	S(O)R	26
Ar	SO_2R	26
SR	SR	27
Cl	Cl	28

sulfur dioxide derivative, a bent structure was observed:

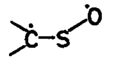


In the case of amino sulfines (**2**: $R^1 = NR_2$), a pronounced prolongation of the semipolar S—O bond is noted (rSO = 1.5–1.6 Å),[37] which is explained in terms of the electron-donating effect of the amino group, leading to a more polarized, *i.e.* longer and weaker, bond, an effect which is also reflected in the infrared spectra of compounds with a R^1R^2CSO structure (*vide infra*).

As a consequence of the bent nature of the CSO group, sulfines possessing two different substituents ($R^1 \neq R^2$) in general will exist in isomeric *E* and *Z* forms.[25,26,38] An exception appears to be dithiobenzoic acid carboxymethyl ester *S*-monoxide (**2**: $R^1 = C_6H_5$, $R^2 = SCH_2COOH$) where the *Z* isomer is preferred, apparently owing to stabilization by intramolecular hydrogen bonding.[39]



As indicated below several resonance structures are possible for the CSO group. However, based on the abovementioned experimental results for the CS and SO bond lengths[20,36] bond orders of 1.89 and 1.57 can be determined for the CS and the SO bonds, respectively.[40] The data apparently favor structure C; however, they may additionally suggest some biradical character. Since e.s.r. spectroscopic studies with sulfines reveal the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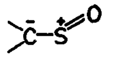
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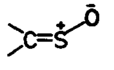
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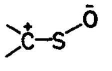
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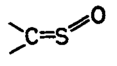
E

absence of unpaired electrons,[41] it is suggested that the sulfine structure is best described by contributions of C and A, the latter being a singlet biradical, in agreement with a recent *ab initio* molecular orbital study.[42]

The electronic absorption spectra of aliphatic thione *S*-monoxides exhibit a characteristic π,π^*-transition around 270 nm ($\epsilon \approx 10^4$ L mol^{-1} cm^{-1}),[18c,d] whereas aromatic sulfines (**2**:R^1 and/or R^2 = Aryl) display absorption bands around 330 nm ($\epsilon \approx$ 12.000 L mol^{-1} cm^{-1}),[18a,40] not surprisingly somewhat red-shifted relative to the parent thiones.

Infrared spectroscopically thione *S*-monoxides give rise to strong absorption bands around 850–905 cm^{-1} (thiourea *S*-monoxides),[19d] 900–1000 cm^{-1} (thioamide *S*-monoxides),[43] and 1100–1200 cm^{-1} (thioketone *S*-monoxides).[18a,20–22,44]. These absorptions are ascribed to the symmetric S—O stretching vibration. Thioketene *S*-monoxides are reported to exhibit S—O stretching vibrations around 1060 cm^{-1}.[36c] It is noted that the above mentioned effect on the S—O bond strength by amino substitution is clearly verified by the i.r. spectroscopic data.

In the course of time a variety of reactions involving thione *S*-monoxides has been reported. These include cycloaddition reactions,[18c,45] reactions with nucleophiles,[24,25b,46] electrophiles,[47] oxidation,[18b,48] and reduction.[47a,49] For a detailed review on sulfine reactions Ref. 34 is recommended. Thermal and photolytical decompositions of sulfines are reviewed in the following sections.

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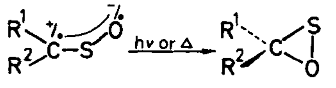
1.2 Oxathiiranes

As mentioned in the previous section, the exclusive product with a R^{1}R^{2}CSO structure to be isolated by direct oxidation of thiocarbonyl compounds are the corresponding *S*-monoxides, the sulfines (**2**). The possible intermediacy of other R^{1}R^{2}CSO structures in the oxidation reactions leading directly to the corresponding oxo derivatives cannot be excluded, however.

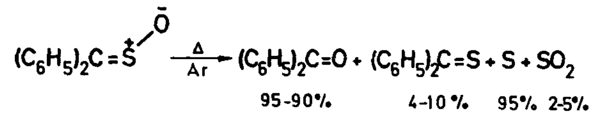
The thione *S*-monoxides constitute *a priori* an outstanding class of compounds as precursors for the cyclic R^{1}R^{2}CSO isomers, the oxathiiranes (**3**), the latter being obtained by an electrocyclic ring closure, a reaction which has been predicted to be achievable thermally as well as photochemically.[42,50] Experimentally, the feasibility of both types of reactions has been demonstrated.



2 **3**

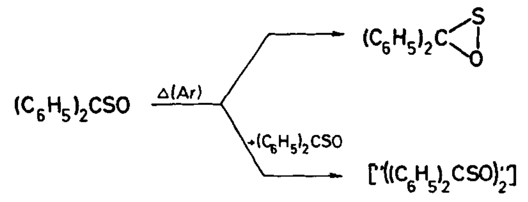
1.2.1 Thermolysis of thione S-monoxides. Thermally induced extrusion of elemental sulfur from sulfines, a reaction which *a priori* can be assumed to involve the intermediacy of oxathiiranes, has been reported by several authors.[19c,f,g,32a,51] As mentioned above, sulfines with aromatic or bulky aliphatic substituents are found to be thermally stable compounds at ambient temperature. However, at higher temperatures a decomposition to the corresponding ketones is observed. A detailed study of the thermal decomposition of thiobenzophenone *S*-monoxide (**2**:$R^1 = R^2 = C_6H_5$) in diphenylmethane solution has been reported.[52]

The decomposition of diphenylsulfine in an argon atmosphere around 403 K afforded benzophenone, thiobenzophenone, elemental sulfur, and sulfur dioxide. A pronounced variation in the single yields as a function of sulfine concentration was observed, *i.e.* by increasing sulfine concentration (0.15–0.5 M) an increasing yield of thiobenzophenone (4–10 %) and sulfur dioxide (2–5 %) was observed with a simultaneously decreasing yield of benzophenone (95–90 %). This strongly suggests the involvement of both

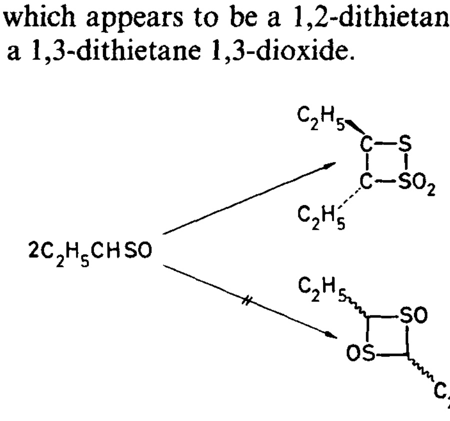


$$(C_6H_5)_2C{=}\overset{+}{S}{-}\bar{O} \xrightarrow[Ar]{\Delta} \underset{95\text{-}90\%}{(C_6H_5)_2C{=}O} + \underset{4\text{-}10\%}{(C_6H_5)_2C{=}S} + \underset{95\%}{S} + \underset{2\text{-}5\%}{SO_2}$$

monomolecular and bimolecular reactions as responsible for the formation of benzophenone/sulfur and thiobenzophenone/sulfur dioxide, respectively. Application of differential thermal analysis (dta)[53] clearly substantiated this suggestion. The analysis additionally revealed the presence of consecutive reactions, possibly involving reactions between starting sulfine and intermediary species. Exclusion of a reaction involving primary formation of diphenylcarbene and sulfur monoxide, consecutively leading to benzophenone and sulfur, led the authors[52] to conclude a ring closure to diphenyloxathiirane to be the initial monomolecular reaction in the thermal decomposition of diphenylsulfine. The bimolecular reaction, being responsible for the formation of thiobenzophenone, was tentatively suggested to proceed *via* a dimeric species, which,



however, could not be isolated. In this connection it is noteworthy that Block and coworkers recently isolated a dimeric species in the thermal decomposition of propanethial *S*-monoxide, which appears to be a 1,2-dithietane 1,1-dioxide,[54] and not, as suggested previously[32a] a 1,3-dithietane 1,3-dioxide.



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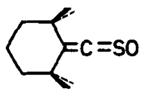
In contrast to the 'clean' thermal decomposition of thioketone *S*-monoxides discussed above, analogous studies of thioketene *S*-monoxides appear to be somewhat more complicated, and not explicable in terms of simple transformations.[55,56] However, a study of the gas-phase thermolysis of 1,1,3,3-tetramethyl cyclohexane-2-thione *S*-monoxide (**6**) displayed a more clear-out picture,[56,57] the reaction being carried out by application of the flash vacuum thermolysis/field ionization mass spectrometry technique,[58] *i.e.* only monomolecular reactions are observed.

Although a variety of products was observed, including the carbenes **7** and **8**, the ketone **9**, the ketene **10**, the thione **11**, and the thioketene **12**, the reaction scheme was rationalized in terms of rather simple primary reactions. The formation of the carbenes, found only in minor amounts, is the result of $C{=}C$ and $C{=}S$ bond ruptures, respectively.[59] The thioketene **12**, which was found to be the major product at high temperatures, was apparently generated by atomic oxygen extrusion.[60] The remaining three products (**9**, **10**, and **11**) were easily explained by a primary ring closure reaction leading to the methyleneoxathiirane **13**, the decomposition mechanisms for the latter being described in detail below.



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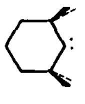

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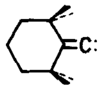

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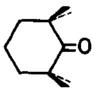

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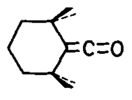

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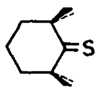

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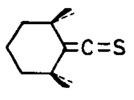

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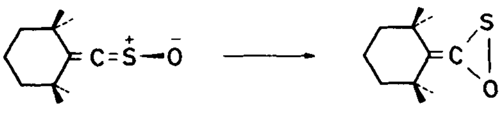
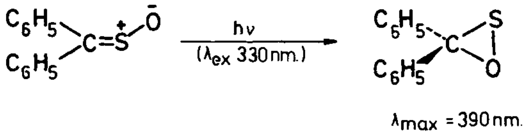


6 13

Finally, it is noted that thiobenzoyl azide *S*-monoxide ($\mathbf{2}: R^1 = C_6H_5$, $R^2 = N_3$) thermally decomposes around 240 K to give benzonitrile, nitrogen, sulfur, and sulfur dioxide, a reaction which does not involve the corresponding oxathiirane.[24,61]

1.2.2 Photolysis of thione S-monoxides A general characteristic of sulfines is photodesulfurization leading to the corresponding ketones in high yield.[22,23,38a,c,45a,62] Schlessinger and Schultz[62c] discuss the ketone formation in terms of two competing, concentration dependent reactions. At low sulfine concentrations the intermediacy of an oxathiirane is proposed, whereas a primary photodimerization, the dimer consecutively deomposing into the ketone, is suggested to be responsible for the ketone formation at high sulfine concentrations.

In 1976 Carlsen, Harrit, and Holm reported on the photolysis of matrix isolated diphenylsulfine, the reaction being followed by electronic absorption spectroscopy, at 85 K.[63] Irradiation into the long wave length absorption of diphenylsulfine (λ_{max} 329 nm, $\epsilon = 1.2 \times 10^4$ L mol^{-1} cm^{-1})[18b] produced monomolecularly a new weak absorption with a maximum at 390 nm. Assuming quantitative conversion the molar absorption coefficient was calculated to be *ca.* 200 L mol^{-1} cm^{-1}. On heating to ambient temperature benzophenone was produced quantitatively. Further photolysis of the intermediary species afforded benzophenone (75 %), thiobenzoic acid *S*-phenyl ester (14 %), and thiobenzoic acid *O*-phenyl ester (1 %), and a further intermediate species (10 %) giving rise to an intense absorption at 550 nm ($\epsilon \approx 11.000$ L mol^{-1} cm^{-1}).[41] Based on the thermal and photochemical behavior of the '390' intermediate, as well as the electronic absorption spectrum of the latter (*vide infra*), diphenyloxathiirane (**3**: $R^1 = R^2 = C_6H_5$) was regarded as responsible for the 390 nm absorption.



The intermediacy of diaryloxathiiranes (**3**: $R^1 = R^2$ = aryl) in the photolysis of diarylsulfines (**2**: $R^1 = R^2$ = aryl) at room temperature has been demonstrated by application of flash photolysis.[64]

In agreement with previous experiments,[38c,62a] a recent *ab initio* molecular orbital study on the H_2CSO system[42] revealed that thioformaldehyde *S*-monoxide (**2**: $R^1 = R^2$ = H) upon photolysis will most probably rearrange into the corresponding oxathiirane *via* an excited singlet state by nucleophilic attack of the negatively charged oxygen on the slightly positive carbon atom, a mechanism which gains support from a study of the relative quantum yields for the photolysis of a series of diarylsulfines, thiobenzophenone *S*-monoxide being chosen as reference. A slightly positive ρ-value of 0.8 is in good agreement with the proposed mechanism.[42]

In contrast to the above, photolysis of thioketene *S*-monoxide does not afford the corresponding ketenes, but, surprisingly, the thioketenes in almost quantitative yield.[65] The photodeoxygenation was rationalized as a reaction between the excited thioketene *S*-monoxide molecule and the solvent. Unfortunately, so far studies of the photolysis of thioketene *S*-monoxides in the gas phase have not been reported.

I.2.3 Electronic absorption spectra of oxathiiranes. The calculated first absorption band (CNDO/S-CI) in the electronic absorption spectrum of the parent oxathiirane (**3**: $R^1 = R^2$ = H) is predicted to exhibit a maximum at 396 nm,[66] which is remarkably close to that assigned to diphenyloxathiirane (**3**: $R^1 = R^2 = C_6H_5$) at 390 nm,[63,64]

The electronic absorption spectra of a series of matrix isolated diaryloxathiiranes, which in all cases displayed weak absorption bands around 390–400 nm, were compared to the theoretically generated spectra (CNDO/S-CI) of bisected (**3B**) and eclipsed (**3E**) monoaryloxathiiranes,[67] the maxima for the first absorption bands being given in

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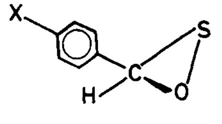
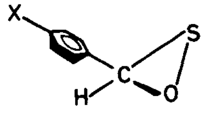
Table II. A good overall agreement between experimental and calculated λ_{max} values is noted, as the average value for the conformations **3B** and **3E** differs by a maximum of 9 nm from the experimental measurements only.



3B



3E

TABLE II

Observed First Absorption Band for Diaryl Oxathiiranes (3: $R^1 = R^2 = p$-X—C_6H_4) and the Corresponding Calculated Values for the Bisected (3B) and Eclipsed (3E) Monoaryl Oxathiirane Conformations (nm)

X	3	3B	3E
OCH_3	395	396	391
CH_3	392	398	392
H	390	399	394
Cl	385	396	392

Only sparse information is available on cyclic sulfenic acid esters, the class of compounds to which oxathiiranes belong. However, the recently reported value for the first absorption band for 1,2-oxathiolane (λ_{max} = 317 nm, ϵ = 53 L mol^{-1} cm^{-1})[68] is in good agreement with theoretical predictions for the sulfenate system,[66] and strongly supporting the assignment of the absorptions discussed above to the oxathiirane system.

The electronic structure of oxathiirane (3 : $R^1 = R^2 = H$) is characterized by doubly occupied valence π-orbitals, the lowest excited state being obtained by exciting one of the π-electrons to an antibonding σ-orbital.[42,66] The first absorption band for oxathiirane at 396 nm (CNDO/S-CI) originates from a pure (99 %) HOMO-LUMO transition,[66] the former being the antibonding S—O π-orbital, the latter the antibonding S—O σ-orbital.[42,66]

In the case of monoaryl substituted oxathiiranes (3 : R^1 = H, R^2 = p-X—C_6H_4) the picture is somewhat more complicated, since the transition appears to be a rich mixture of states, as the phenyl π-system mixes in to an extent of 15–35 %, the orbitals, however, largely being characterized by oxathiirane contributions.[67] Hence, it appears that the transition orbitals responsible for the '390 nm absorptions' contain less than a 4 % contribution from the X substituent, as reflected by the nearly constant λ_{max} values (cf. Table II).

1.2.4 Decomposition of oxathiiranes. As indicated above, oxathiiranes (**3**) appear to be thermally as well as photolytically rather labile species, the eventual formation of the corresponding oxo compound being the dominant reaction.

Photolysis of matrix isolated diphenyloxathiirane (3 : $R^1 = R^2 = C_6H_5$) at temperatures around 80 K lead to the formation of benzophenone, monothiobenzoic acid phenyl

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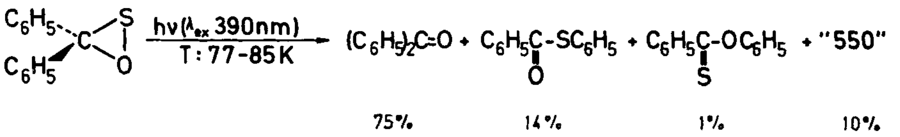
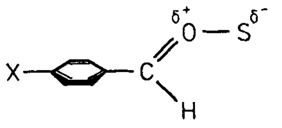
esters, and a strongly colored species, the latter exhibiting an absorption maximum at 550 nm (ϵ = 11.000 L mol^{-1} cm^{-1})[41,63]



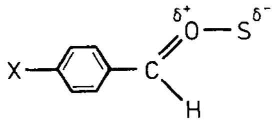
The compound responsible for the 550 nm absorption band appeared to be thermally as well as photolytically extremely labile, as heating to *ca.* 100–110 K or transitory irradiation (λ_{ex} 550 nm) afforded benzophenone in quantitative yield.[41,63] The formation of strongly colored, highly labile species by photolysis of matrix isolated diaryloxathiiranes (3: $R^1 = R^2 = p$-X—C_6H_4) appears to be a general feature[41] (cf. Table III).

Attempts to characterize the colored intermediate by means of ESR spectroscopy[63] and magnetic susceptibility measurements[41] have been reported unsuccessful. The latter type of experiments revealed that during the photolytical transformation (77 K) sulfine-oxathiirane-'550'-ketone less than 0.4 % of a ground-state triplet has been accumulated, leaving the zwitterionic and singlet-biradicaloid structures (**4**/**5**) as being responsible for the 550 nm absorption.

A theoretical study of the electronic absorption spectra of the '550' intermediates, comparing the experimentally observed λ_{max} values of **4**/**5** ($R^1 = R^2 = p$-X—C_6H_4) with those theoretically generated for **5′** and **5″** (R^1 = H, $R^2 = p$-X—C_6H_4) has been reported (Table III).[41]



5′



5″

In spite of the apparent discrepancy between the observed and calculated λ_{max} values, the authors concluded that the sum of available experimental and theoretical data is consistent with carbonyl *O*-sulfides (**5**) as intermediates in the photolysis of oxathiiranes,

TABLE III

Observed First Absorption Band for '550' Intermediates and the Calculated Values for the Carbonyl Sulfide Rotamers 5′ and 5″ (nm)

X	'550'	5′	5″
OCH_3	542	488	420
CH_3	549	487	429
H	550	488	438
Cl	567	492	448

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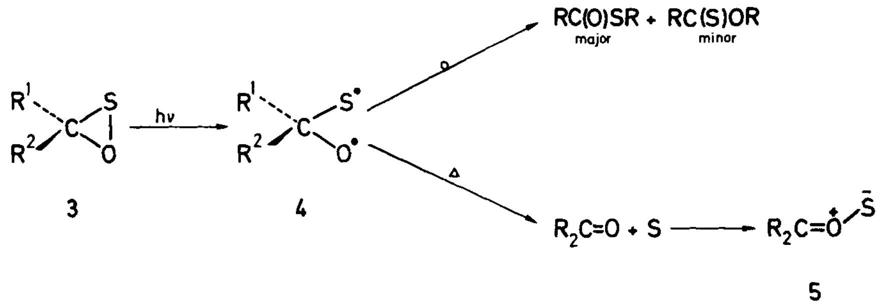
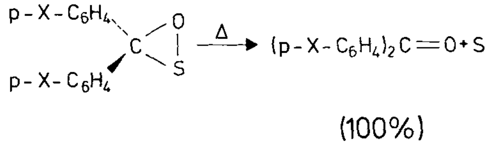
a conclusion which is supported by recent *ab initio* CASSCF calculations on the photolysis of oxathiirane ($3: R^1 = R^2 = H$).[42] However, the assumption that the carbonyl *O*-sulfides **5** are formed directly from the oxathiiranes by C—S bond cleavage appears to be erroneous. The *ab initio* study revealed that an important feature of the three lowest excited states of oxathiirane is the weakening of the S—O bond.[42] No weakening of the C—S bond was observed.

Most probably the photolytical decomposition of the oxathiiranes (**3**) is to be explained in terms of a primary S—O bond cleavage leading to a singlet biradical of type **4**, which extrudes elemental sulfur extremely easily either by vibrational relaxation (giving rise to $S(^1D)$) or as a consequence of a singlet-triplet transition, the latter state being dissociative (affording $S(^3P)$). It appears highly unlikely that matrix isolation at 77 K should be sufficient to prevent these reactions. However, the cold rigid matrix (EPA or PVC)[†] strongly reduces the possibility of moving the formed ketone and singlet sulfur atoms apart. The carbonyl *O*-sulfide (**5**), which is best described as a complex between a distorted sulfur atom and the ketone molecule, may consecutively be formed in a reaction between the ketone and the $S(^1D)$ atom, a reaction which, according to the *ab initio* study, proceeds without any reaction barrier.[42]

Since the theoretical considerations[42] additionally suggest the singlet biradical **4** to be responsible for the rearranged products, thiono- and thioloformic acid, the photolysis and consecutive thermal decomposition of oxathiiranes is rationalized in the following way:



Thermally, diaryloxathiiranes ($3: R^1 = R^2 = p\text{-}X\text{—}CH_6H_4$) eliminate sulfur quantitatively to form the corresponding ketones,[63,64] the reaction following pure first-order kinetics.[64] The half-life of diphenyloxathiirane is around 10^{-3} sec at room



temperature, but somewhat solvent dependent, however. The activation parameters for the thermal decomposition of diphenyloxathiirane in cyclohexane were determined as $E_a = 9.6 \pm 0.9$ kcal mol^{-1}, $\log A = 9.5 \pm 0.7$ sec^{-1}, and $\Delta S^\ddagger = -17.0 \pm 3.1$ gibbs mol^{-1}.[64] The values for log A and $\Delta S^\ddagger$ do not fit into a general picture of first-order

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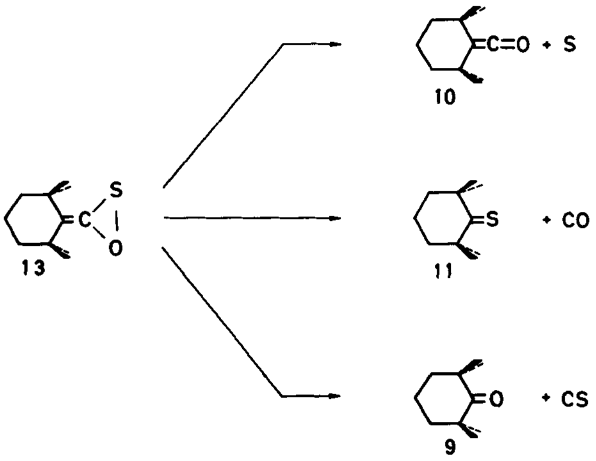
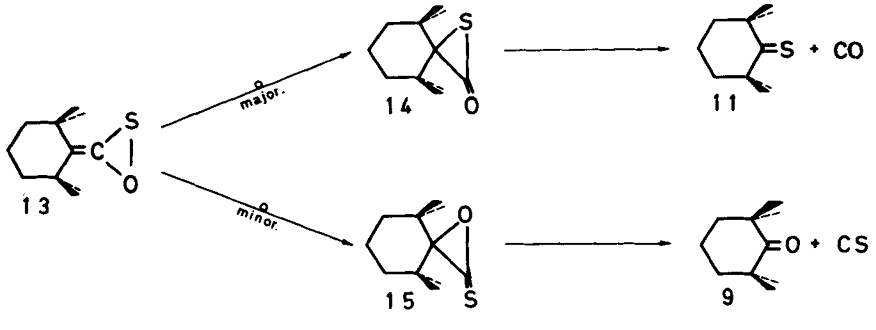
[†] EPA: ethanol:diethyl ether:2-methylbutane (2:5:5), PVC: polyvinyl chloride

kinetics and may suggest a more complicated decomposition reaction. Attempts towards a mechanistic study led to a rather confusing picture, as no straightforward rational substituent influence (X $= CH_3, H, Cl, Br, CF_3, NO_2$) was observed, nor was the solvent influence clear.[64] However, assuming a mechanism similar to the photodecomposition discussed above, involving a primary S—O bond cleavage followed by a solvent assisted singlet-triplet transition eventually leading to sulfur extrusion, the mutual contributions to the activation parameters by the different substituents and the solvents, respectively, may well be expected to superimpose, thereby causing the rather confusing data. The complexity of the 'simple monomolecular loss of elemental sulfur' has previously been discussed in connection with the thermal decomposition of benzonitrile *N*-sulfides.[69]

Methyleneoxathiiranes (*e.g.* **13**), thermolytically generated in the gas phase from thioketene *S*-monoxides, have been shown to decompose into the corresponding ketenes (**10**), thioketenes (**11**), and ketones (**9**).[57]



Whereas the ketene formation is recognized as the 'simple sulfur extrusion', the formations of the thioketone and the ketone has been rationalized as a result of primary rearrangement of the oxathiirane into the thiolo- (**14**) and the thionolactone (**15**), respectively. Thermolysis of authentic **14**,[70] under identical conditions,[57] afforded thioketone **11** in quantitative yield. The isomeric thionolactone **15** is not known; however, the analogy seems obvious.



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It is noteworthy that these rearrangements closely resemble those responsible for the thioester formations reported in the photolysis of matrix isolated diphenyloxathiirane[63] (*vide supra*), whereas no rearrangements are observed in the thermal decomposition of the latter. The reason for this apparent discrepancy is probably to be sought for in the creation of the gas-phase thermolytically generated methyleneoxathiirane **13** in a vibrationally excited state; here the vibrational energy is apparently sufficient to overcome the activation barrier for the generation of the lactones **14** and **15**. As in the case in the photoinduced rearrangement of diphenyloxathiirane, the rearrangement to sulfur (cf. **13** → **14**) is dominant, whereas the rearrangement to oxygen (cf. **13** → **15**) is observed to a minor extent only.[57]

These results strongly suggest a close resemblance between the thermal and photolytical decompositions of oxathiiranes, *e.g.* thermolysis of diaryloxathiiranes at higher temperatures is expected to lead to rearranged products as well, the primary reaction being an S—O bond cleavage. Hence, the biradical may consecutively eliminate elemental sulfur or rearrange the thermodynamically more stable monothioester.

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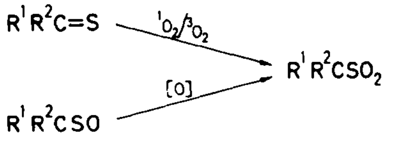
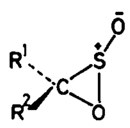
II $R^1R^2CSO_2$ STRUCTURES

Compounds with an $R^1R^2CSO_2$ structure may in principle be generated either by direct oxidation of thiocarbonyl compounds with singlet or triplet oxygen or by consecutive oxidation of primary formed monoxides.



A variety of structures are *a priori* conceivable, including cyclic (**16**–**18**) as well as acyclic (**19**–**21**) structures.



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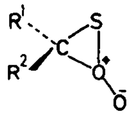

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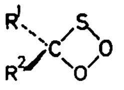

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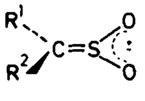

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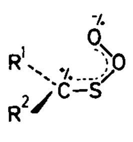

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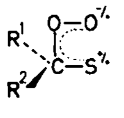

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The possible involvement of these structures in the conversion of thiones to the corresponding oxo derivatives, formally by loss of sulfur monoxide, is discussed below.

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II.1 Thione S,S-dioxides

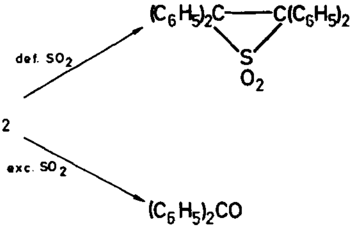
Analogous to the perception of sulfines as dioxide derivatives it seems reasonable to regard the corresponding dioxides, the sulfenes (**19**), as being derived from sulfur trioxide, *i.e.* the system is expected to exhibit a planar structure. Owing to the great thermal lability of sulfenes substituted with alkyl and/or aryl groups no experimentally obtained structural information is available. However, semi-empirical calculations (CNDO/B)[71,72] indicate a planar structure for the parent sulfene molecule (thioformaldehyde *S*-dioxide, **19**: $R^1 = R^2 = H$). On the other hand, analogous calculations for the diamino substituted system, *i.e.* thiourea *S,S*-dioxides (**19**: $R^1 = R^2 = NH_2$) suggest a non-planar structure, the angle between the NCN and the OSO planes being 68°, in excellent agreement with X-ray crystallographic studies on isolable thiourea *S,S*-dioxide derivatives.[73]

II.1.1 Sulfenes. Sulfenes, thione *S,S*-dioxides substituted with alkyl and/or aryl groups (**19**: $R^1 = R^2 = H/Alk/Ar$), are thermally highly labile compounds, which have been isolated indirectly at ambient temperatures as *e.g.* cycloaddition products with a variety of dipolarophiles. An important feature in the present context is that no reports on sulfene formation by direct oxidation of the corresponding thioketones or thioketone *S*-monoxides have appeared. An attempt to generate diarylsulfenes (**19**: $R^1 = R^2 = Ar$) by peracid oxidation of the corresponding sulfines quantitatively afforded the ketones, the reaction being formulated as involving the oxathiirane *S*-monoxide (**16**), whereas no evidence for the possible intermediacy of sulfenes was discovered[48a] (*vide infra*). It seems, however, reasonable to report briefly on the formation and properties of sulfenes.

A classical method to generate sulfenes is the reaction of diazo compounds with sulfur dioxide, as proposed by Staudinger and Pfenninger in 1916.[74] This reaction is most probably general, and typical sulfene products can be isolated.[75] A special variety of the

$$R^1X\,CN_2 + SO_2 \xrightarrow[-N_2]{} R^1X\,C{=}SO_2 + N_2$$

reaction is the formation of α-ketosulfenes (X = R—CO), compounds which undergo a series of reactions associated with the $O{=}C{-}C{=}SO_2$ structure.[76] However, although the reaction seems to be general, Staudinger[74] already observed in his early studies that excess as well as deficit of sulfur dioxide may lead to unwanted by-products.



A more versatile method for sulfene generation appears to be the reaction of sulfonic acid derivatives, possessing an α-hydrogen atom, with base,[23a,77] the leaving group X being typically Cl, nitrophenoxy, OSO_2CH_2Ph, $OSO_2CH_2CH_3$.

Sulfenes have been generated thermally by sulfo-Cope rearrangement[78] and retro-Diels-Alder reactions,[79] which, however, have limited synthetic applicability. Sulfene

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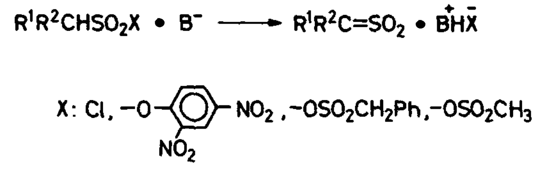
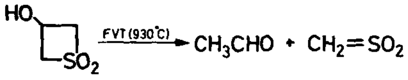


formation has been reported in flash-vacuum thermolysis of some thietane derivatives, *e.g.* 3-hydroxythietane 1,1-dioxide, which is cleaved (930 °C) to give sulfene and acetaldehyde.[80] Thiete 1,1-dioxide, on the other hand, undergoes ring opening to the

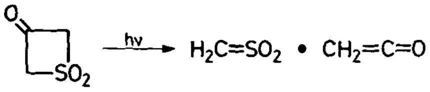


corresponding vinyl sulfene.[80,81] Sulfonic acid derivatives ($R^1R^2CHSO_2X$) appear to be sulfene precursors under flash-vacuum thermolytical conditions. King reports sulfene formation from chloro-sulfonylacetic acid and methanesulfonic acid anhydride, the reaction product being trapped at −196 °C and analyzed by infra-red spectroscopy.[82] Methanesulfonyl chloride and ethylenesulfonyl chloride have analogously been claimed to yield sulfenes.[83]

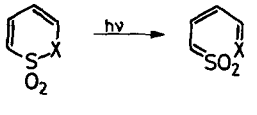
$$CH_3SO_2Cl \longrightarrow CH_2SO_2 \bullet HCl$$

$$CH_2{=}CH{-}SO_2Cl \longrightarrow ClCH_2CH{=}SO_2$$

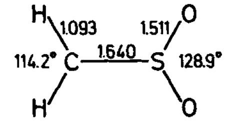
Photolysis of certain thietane derivatives, *e.g.* 3-thietanone 1,1-dioxide, gives rise to sulfene formation, the sulfene being trapped and identified spectroscopically (liquid nitrogen).[84]



Vinyl sulfenes are most probably intermediates in the photolytical conversion of thiete 1,1-dioxides to vinyl ketones, the latter formed by consecutive sulfur monoxide extrusion,[85] possibly involving oxathiirane *S*-monoxides (*vide infra*). Photolytical ring opening to sulfenes of cyclic sulfonic acid derivatives has also been reported.[86]



As mentioned above, the expected planarity of the sulfene molecule has been verified theoretically by semi-empirical CNDO/B studies;[71,72] however, as in the sulfine case[87] the SO bond is most probably overestimated by *ca.* 0.05Å, due to the application of an insufficient basis set, as well as the exclusion of 3*d*-orbitals.[72] Also the expanded OSO bond angle, relative to the calculated value of SO_2 (115°) shall be noted, probably associated with the localization of negative charge on oxygen ($\rho_H = +0.12$, $\rho_C = -0.21$, $\rho_S = +1.2$, $\rho_O = -0.62$).[71,72]



Spectroscopic data for sulfenes are sparse, owing to the thermal lability. However, the parent sulfene has successfully been isolated at low temperature[82b,84] and studied by infrared spectroscopy. The infrared sprectrum exhibits only five absorption bands at 3170, 3040, 1330, 1230, and 950 cm^{-1}, respectively, which are ascribed to sulfene. The former two absorptions are associated with the $=CH_2$ group, whereas the 1330 and 1230 cm^{-1} bands are assigned to the asymmetric and symmetric S—O stretching, respectively.[82b]

Owing to their thermal lability, sulfenes in general have been isolated only indirectly. Sulfenes have been reported to participate in a variety of reactions involving $2\pi + 2\pi$ and $2\pi + 4\pi$ cycloadditions, as 1,3-dipolarophiles, and as sulfonylating agents of H—X compounds, X being halogen, OH, or NR′R″. The chemistry of sulfenes has been treated comprehensively in a series of reviews,[88] which should be consulted for further information.

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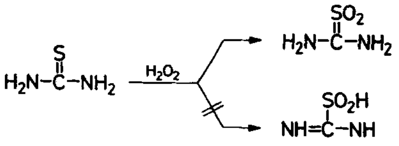
II.1.2 Thiourea S,S-dioxides, thioamide S,S-dioxides. Taking the high reactivity of sulfenes into account, it seems surprising at first sight that $R^1R^2CSO_2$ structures with R^1 and/or R^2 = NR′R″ are isolable compounds synthesized by hydrogen peroxide oxidation of the corresponding thioamides and thioureas.

As early as 1910 the first investigation of H_2O_2 oxidation of thiourea was reported,[89] the stable product being characterized as formamidine sulfinic acid ($NH{=}C(SO_2H)NH_2$). However, based on chemical studies.[90] and later X-ray crystallographic investigations[73] the oxidation product was unambiguously verified as the thiourea *S,S*-dioxide and not the sulfinic acid.



A comprehensive study of thiourea *S,S*-dioxides (spectroscopy, stability, etc. as function of substituents) has been reported by Walter.[91]

The structure of the CSO_2 group in the thioamide/thiourea *S,S*-dioxide system has been studied by X-ray crystallography,[73] the geometrical data being collected in Table IV.

Thiourea *S,S*-dioxide is found[73a] to be non-planar, the angle between the NCN and OSO planes being 68°. Of special interest to be noted is the very long CS bond, which is

TABLE IV

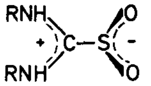
Geometric Data for the $>CSO_2$ Group

	rCS (Å)	rSO (Å)	∢OSO (degree)
Thiourea *S*,*S*-dioxide[73a]	1.851	1.490	111.7
4-Oxypyrimidine-2-sulfinate[73b]	1.835	1.516	108.4

approximately 0.03 Å longer than the generally accepted value for a CS single bond,[40a] a phenomenon which probably is to be ascribed to an interaction between the sulfur lone-pair and sulfur d-orbitals. However, the very long, and thus rather weak CS bond is in accord with the ease with which it cleaves.[91]

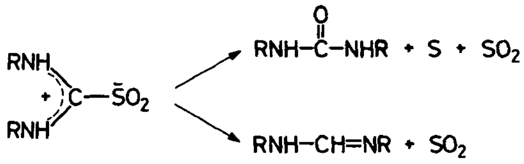
Thiourea *S*,*S*-dioxides are isolable and resonably stable compounds which are to be discussed partly in terms of a stabilizing effect by intramolecular NH . . . . O hydrogen bonding. In favor of the possible importance of intramolecular hydrogen bonding it can be mentioned that *N*,*N*,*N*′,*N*′-tetrasubstituted thiourea *S*,*S*-dioxides have not been reported.

Based on the above, it seems more reasonable to formulate thiourea *S*,*S*-dioxides as formamidinio sulfinates than as diaminosulfenes, as assumption which is supported by the observation of electrophilic attack, *e.g.* oxidation,[92] at sulfur is observed, in contrast to 'normal' sulfene reactivity where nucleophilic sulfur attack is observed.



Thiourea *S*,*S*-dioxides exhibit characteristic infrared absorption bands in the 1060–1100 cm^{-1} and 995–1025 cm^{-1} regions, ascribed to the asymmetric and symmetric SO valence vibrations, respectively.[91] The pronounced shift towards lower frequencies compared with the absorptions found for sulfene[82b] (*vide supra*) is in perfect agreement with the much more polar, and therefore weaker SO bonds as a result of the electron-donating effect of the NHR groups, which simultaneously is reflected in the rather long SO bonds (*ca.* 1.5 Å) (*cf.* Table IV). A similar trend was observed in the case of the thiourea *S*-monoxides (*vide supra*).

Although thiourea *S*,*S*-dioxides in certain cases are isolable compounds, they appear to have a somewhat limited thermal stability, especially in solution where decomposition generally is observed at room temperature, leading either to carbonyl compounds or to formamidines, depending on the substituents.[91]



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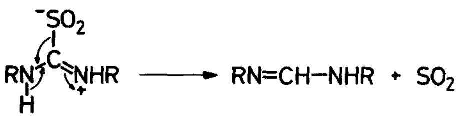
In the case of R = cyclohexyl the activation energy for formamidine formation (EtOH) was found to be 20.2 kcal mol^{-1} and the activation entropy -10.4 gibbs mol^{-1} [93] in agreement with loss of SO_2 and simultaneous hydrogen shift.



The formation of the carbonyl compounds, possibly involving an oxathiirane *S*-oxide, is described below.

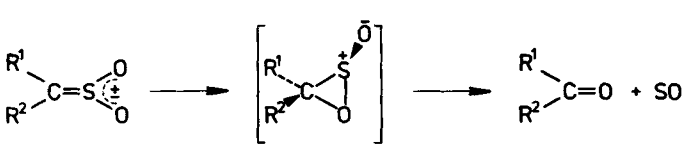
The acid- and base-catalyzed decomposition of thiourea *S,S*-dioxides leading to formamidine salts and ureas, respectively, has been studied.[91]

Finally, it should be noted that thioamide *S,S*-dioxides have not been isolated, their intermediary existence, however, has been postulated.[94]

II.2 Oxathiirane S-monoxides

In contrast to oxathiiranes (*vide supra*) no direct experimental verification, *e.g.* spectroscopical, of the existence of the corresponding *S*-oxides has been presented. However, a series of investigations strongly suggest the intermediacy of oxathiirane *S*-monoxides.

Several studies on sulfenes report the formation of carbonyl compounds, a reaction which has been rationalized as involving intermediary oxathiirane *S*-monoxides.[80,81a,82a,85,95]



A theoretical study predicts the electrocyclic ring closure of sulfene to oxathiirane *S*-monoxide to be a symmetrically allowed reaction path,[72] the transformation, however, requiring *ca.* 10 kcal mol^{-1} more than the corresponding sulfine–oxathiirane ring closure reaction. One possible explanation for this may be the changes in the highest occupied molecular orbitals (HOMO) (Fig. 1). In the sulfine-to-oxathiirane transformation the π_{HOMO} of the sulfine molecule correlates to the sulfur p_π lone pair in the oxathiirane ring,[50] whereas the sulfene π_{HOMO} converts into a lone-pair orbital on the *exo*-

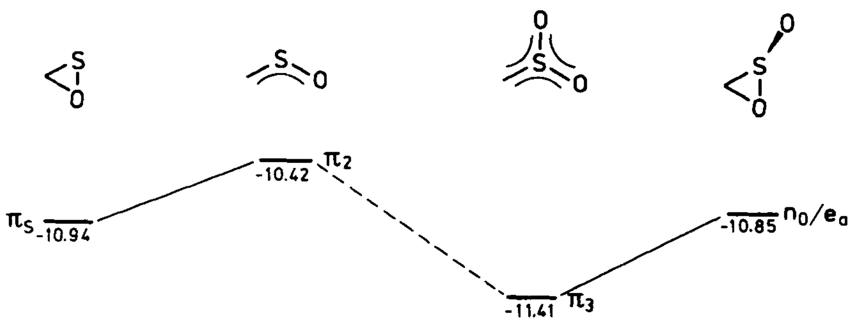


FIGURE 1 Variation in E_{HOMO} by the ring closure reactions: sulfine → oxathiirane and sulfene → oxathiirane *S*-monoxide.

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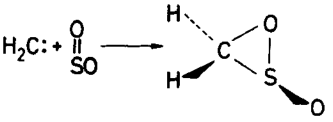
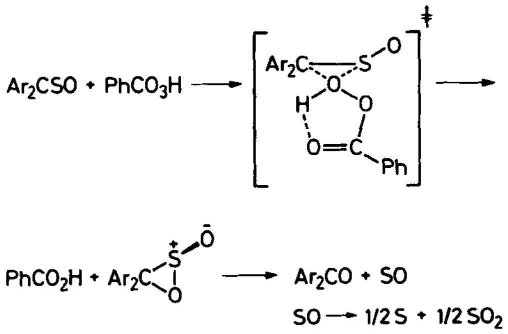
oxygen atom in the oxathiirane *S*-monoxide,[72] the latter being energetically relatively high compared to the sulfur lone pair, *i.e.* the sulfine–oxathiirane ring closure results in a decrease in E_{HOMO}, whereas an increase is observed in the sulfene–oxathiirane *S*-monoxide case.

Hiraoka proposed oxathiirane *S*-monoxides as the primary product in the reaction between methylene and sulfur dioxide,[96] a reaction which theoretically[72] has been predicted to be a symmetry allowed process. However, an alternative symmetry-allowed reaction has to be considered in this connection, since an attack of $:CH_2$ on one of the oxygen atoms in sulfur dioxide, at least from a theoretical point of view,[72] seems feasible. The study predicts a hypothetical *O*-sulfinyl-formaldehyde ($H_2C{=}O^+{-}SO^-$) as highly labile, leading to formaldehyde and sulfur monoxide without any barrier of activation, *i.e.* the attack of methylene on one of the oxygen atoms is assumed to afford formaldehyde and sulfur monoxide in a concerted reaction.



$$H_2C: + O{=}SO \longrightarrow \left[H_2C{\equiv}\overset{\delta+}{O}{\cdots}\overset{\delta-}{S}O\right]^{\ddagger} \longrightarrow H_2C{=}O + SO$$

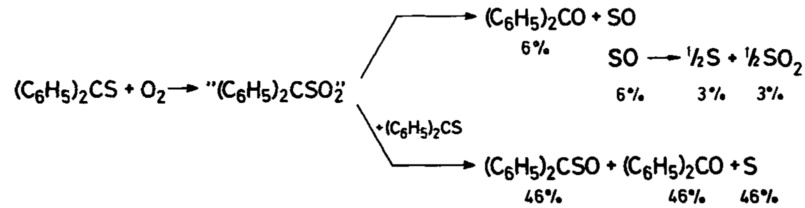
Finally, it can be mentioned that diaryloxathiirane *S*-monoxides have been formulated as intermediates in the peracid oxidation of diarylsulfines, a reaction leading to the corresponding benzophenones in high yields.[48a]



As the oxathiiranes are to be regarded as the simplest cyclic sulfenic acid esters, the corresponding *S*-monoxides can be described as the first members of the cyclic sulfinic acid ester series. On this background it seems reasonable to expect the oxathiirane *S* monoxides to be somewhat more stable that the corresponding oxathiiranes, although a direct isolation most probably is not achievable.

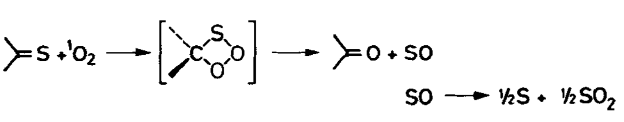
II.3 The Reaction Between Thiones and Oxygen

The reaction between a thiocarbonyl compound and molecular oxygen was first studied by Gatterman in 1896.[14] The reaction between thiobenzophenone and oxygen was reported to give benzophenone in high yield, the proposed mechanism involving the four-membered 1,2,3-dioxathietane ring system. Investigations by Staudinger and Freudenberger[15] and Schönberg *et al.*[16] confirmed this proposal and demonstrated that the reaction took place in the absence as well as in the presence of light. A reinvestigation of the reaction between thiobenzophenone and oxygen in the dark,[17] however, revealed the complexity of the reaction. Besides benzophenone considerable amounts of thiobenzophenone *S*-monoxide were formed together with sulfur and sulfur dioxide. The reaction was shown to involve a bimolecular step as responsible for the sulfine formation, and successful cross-over experiments provided support for an intermediary $(C_6H_5)_2CSO_2$ species. The percentages given below correspond to the reaction of a 0.05 molar methanolic solution of thiobenzophenone.

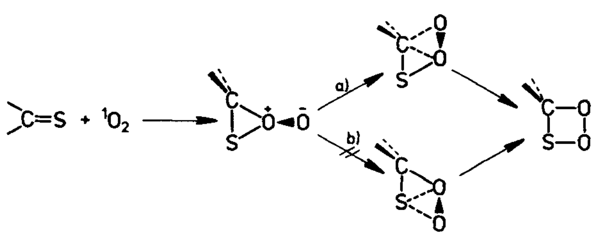


An interesting aspect in the present context is that thiobenzophenone apparently differs from other thioketones, *e.g.* substituted thiobenzophenones do not react with molecular oxygen in the dark, or at least only very slowly compared to the parent compound. On this background it is not surprising that only the limited number of reports on the 'dark reaction' mentioned above appeared.

In contrast to this the reaction between thiones and singlet oxygen, the latter being photochemically or thermally generated, has been quite intensively investigated during the past decade. In the early seventies the reaction between thioketones and singlet oxygen was reported to give the corresponding ketones, sulfur, and sulfur dioxide as the sole products,[97] the reaction being formulated to proceed *via* an intermediary 1,2,3-dioxathietane. More recently a similar observation was made by Ramamurthy[98a] and Suzuki.[98b]



A theoretical study of the reaction between thioformaldehyde and singlet oxygen[99] predicts, based on potential-energy surface calculations, a multi-step mechanism involving primary formation of an oxathiirane *O*-oxide (**17**), which rearranges to a 1,2,3-dioxathietane. The latter was tentatively suggested to decompose *via* a biradicaloid mechanism.



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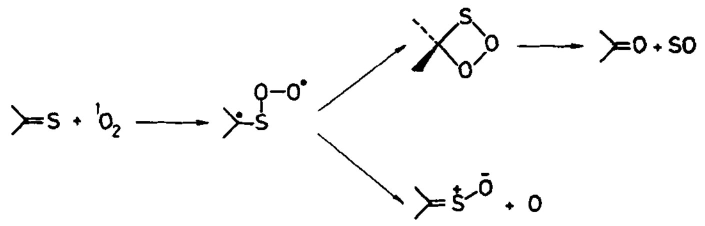
The most recent progress in this area of organic sulfur chemistry is probably the experimental verification of a 'sulfine mechanism' in the reaction between selected thiocarbonyls and singlet oxygen.[100,101]

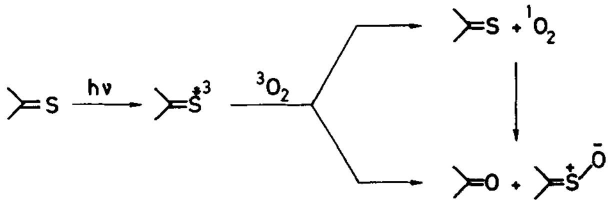
The formation of sulfines in the single-oxygen oxidation of thiones was explained by Tamagaki in terms of a bimolecular reaction between a primarily generated $R^1R^2CSO_2$ intermediate of zwitterionic or biradicaloid nature (*e.g.* **20**) and a second thione molecule.[100] However, based on a more thorough analysis of the reaction between di-*t*-butyl thioketone and singlet oxygen, reported by Ramamurthy,[101d] it appears more reasonable to describe the formation of sulfines as a monomolecular reaction. Ramamurthy concludes that 1,2,3-dioxathietanes (**18**) are intermediates in the ketone formation, whereas a zwitterionic/biradicaloid structure (**20**) seems to be responsible for the appearance of both the sulfine and the ketone. No evidence for the involvement of bimolecular reactions was found. The relative importance of the two pathways is most probably closely related to steric factors introduced by the substituents of the thione,[101e] but also electronic effects may play a dominant role.[101b]



The apparent discrepancy between the experimental results[101d] and the theoretically suggested mechanism[99] may well reflect the fact that the experiments were carried out in solution while the calculated reaction path corresponds to the behavior of the isolated molecule in the gas phase.

Finally the suggested monomolecular sulfine formation from a biradicaloid intermediate of type **20** shall be mentioned. Ramamurthy states[101d] that the fate of the oxygen atom is unknown. However, on taking the observed variations in reaction rate and sulfine/ketone yield into account[101d] it seems most reasonable that the reaction should be regarded as pseudo first-order, the intermediate **20** oxidizing the solvent, leaving the sulfine. A similar reaction has previously been suggested in the photolysis of thioketene *S*-monoxides.[65]

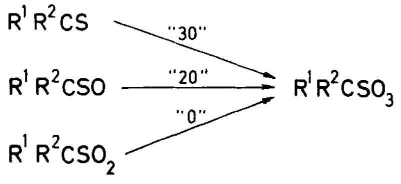
The reaction described above can be achieved either by chemically or photolytically (dye sensitized) generated singlet oxygen.[100,101] However, also direct irradiation of the thiones in the presence of oxygen apparently gives rise to analogous reactions,[100b,101d] in which case the thiocarbonyl compounds may act as sensitizers in the singlet oxygen production. It appears, on the other hand, that a second pathway may operate in this case, *i.e.* a reaction between the excited thione molecule and ground-state oxygen, leading, however, to identical products.



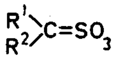
Attempts to study possible intermediates in the direct irradiation of thiones in the presence of oxygen at low temperature in a matrix have so far been unsuccessful[102] most probably owing to the strongly decreased mobility of the involved species under these conditions.

III $R^1R^2CSO_3$ STRUCTURES

Only little information on $R^1R^2CSO_3$ structures as intermediates in the thiocarbonyl–carbonyl conversion reactions is available, and it is almost limited to a series of studies on thiourea *S,S,S*-trioxides reported by Walter.[92,103] *A priori* $R^1R^2CSO_3$ may be obtained by direct oxidation of the thiocarbonyl compound, as well as by consecutive oxidation of $R^1R^2CSO_x$ ($x = 1,2$) precursors.



Apart from the thione *S,S,S*-trioxide structure (**22**) and the ring-closed isomer oxathiirane *S,S*-dioxide (**23**) a variety of open as well as ring-closed structures (**24–29**) obviously are conceivable, a series of which has been treated theoretically in a study devoted to the reaction between thioformaldehyde and ozone.[104]



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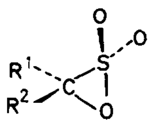

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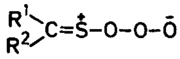

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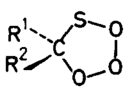

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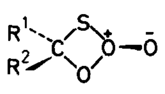

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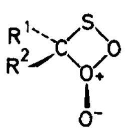

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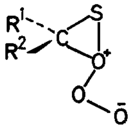

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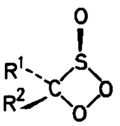

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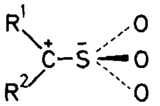
In the following account on the thione *S,S,S*-trioxides, the reaction betweeen thiones and ozone, and the singlet-oxygen oxidation of sulfines are given.

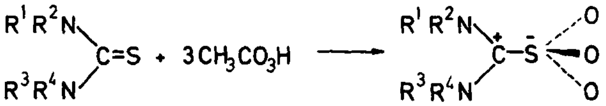
III.1 Thione S,S,S-trioxides

The first report about thiourea *S,S,S*-trioxides appeared in 1936, where Böeseken described the formation of the trioxide of the parent thiourea by peracetic acid oxidation of the corresponding dioxide.[105] As it will appear from the following, it seems incorrect to describe these compounds as thiocarbonyl derivatives, due to the presence of a sulfonato group (—SO_3^-), *i.e.* the thiourea *S,S,S*-trioxides are correctly named as formamidinio sulfonates, and consequently the parent 'thioformaldehyde *S,S,S*-trioxide', if it exists, as carbenio sulfonate. Since the sulfur in these compounds appears in the oxidation state +6, which means localization of a positive charge at the carbon atom, it seems highly unlikely that *S,S,S*-trioxides of simple thioketones can be prepared.

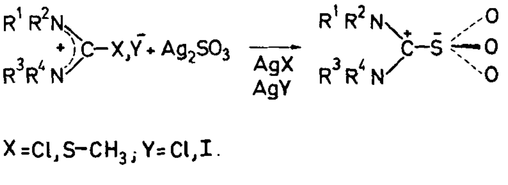


Nevertheless it seems reasonable, in order to draw some parallels to the corresponding mono- and dioxides, to treat this class of compounds as thione *S,S,S*-trioxides at least to some extent.

The most versatile procedure for the preparation of thiourea *S,S,S*-trioxides, thiosemicarbazide *S,S,S*-trioxides, and thiosemicarbazone *S,S,S*-trioxides is a direct peracid oxidation of the corresponding thiocarbonyl compound,[92,103a,106] or of the mono- or dioxides.[92,105]



In general *N*-mono-, *N,N*-di-, *N,N'*-di-, and in some cases *N*-aryl-*N,N'*-dialkyl thiourea *S,S,S*-trioxides can be prepared by this method.[106a,b] Likewise, the thiosemicarbazide and thiosemicarbazone derivatives can be prepared by direct oxidation if at least one N—H group is present.[106c] Tetrasubstituted and often also trisubstituted compounds are oxidized to formamidinium salts.[106b] Alternatively, the latter type of trioxides may be prepared by reaction between *N,N,N',N'*-tetraalkyl chloro formamidinium chloride, or *S*-methyl *N,N,N',N'*-tetraalkylisothiouronium iodides and silver sulfite.[103b,107]



X = Cl, S–CH_3; Y = Cl, I.

N,N,N',N'-Tetrasubstituted thiourea *S,S,S*-trioxides may be obtained from the corresponding trisubstituted compounds by alkylation with diazomethane.[106b]

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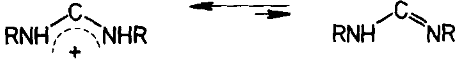
Preparation of thioketone S,S,S-trioxides (carbenio sulfonates) by direct oxidation will not be possible, since a primarily formed monoxide (sulfine) will be oxidized to the corresponding ketone (*vide supra*).[48a] The alternative approach, *i.e.* the reaction between diphenyldichloromethane and silver sulfite, appeared to be unsuccessful, since benzophenone was isolated in more than 90% yield.[108]

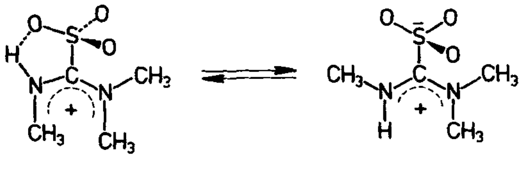
^{1}H-NMR spectroscopic investigations of N,N'-disubstituted thiourea S,S,S-trioxides in D_2O revealed equivalence between the substituents at the two nitrogen atoms, which can be taken as a proof for the 'trioxide structure', *i.e.* the compounds do not exist as undissociated sulfonic acids,[92] in agreement with molecular weight determinations, which gave the value of the undissociated species, as well as with the neutral reactions of the solutions of the trioxide.[92] A detailed study on the conformation of a series of trioxides has been reported by Walter.[103,106,107]



A verification of the formamidinio sulfonate character of the thiourea S,S,S-trioxides was obtained by an X-ray crystallographic analysis of N,N'-dimethylthiourea S,S,S-trioxide.[109] Not unexpectedly, a tetrahedral structure around the sulfur atom was found (rSO = 1.44 Å, rCS = 1.827 Å). Similarly to the dioxides (*vide supra*), the trioxide possesses a rather long carbon-sulfur bond which may be caused by the electron donating groups attached to the carbon atom.

I.r. spectroscopically thiourea S,S,S-trioxides exhibit characteristic absorptions in the regions 1220–1290 cm^{-1} and 1048–1065 cm^{-1} ascribed to asymmetric and symmetric SO streching vibrations, respectively,[92] in good agreement with absorptions found for heterosubstituted sulfonates and sulfonic acid betaines (1200–1250 cm^{-1} (asymm) and 1037–1052 cm^{-1} (symm)).[110] Additionally the spectra exhibit characteristic absorption bands in the 1540–1690 cm^{-1} region, ascribed to partial C—N double bonds.[106b] The actual position of these absorptions depends, not unexpectedly, on the substitution at the nitrogen atoms. The characteristic absorption regions are reported to be 1680–1690 cm^{-1}, 1650–1670 cm^{-1}, 1610–1645 cm^{-1}, and 1540–1600 cm^{-1} for mono-, di-, tri-, and tetrasubstituted thiourea S,S,S-trioxides, respectively.

Finally, it should be mentioned that trisubstituted thiourea S,S,S-trioxides exhibit NH absorption bands in the region 3265–3305 cm^{-1},[92,103b] suggesting the presence of NH....O hydrogen bonds. This is supported by the relatively high ΔG-value (13–16 kcal mol^{-1}) determined for the rotation around the C—NHR bond.[103b]



$\Delta G^{\ddagger}$ = 13 kcal / mole

A predominant feature of thiourea S,S,S-trioxides is their reactivity towards

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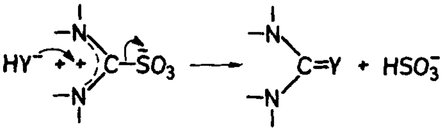
nucleophiles (such as H_2O, ^-OH, ^-SH)[106b]



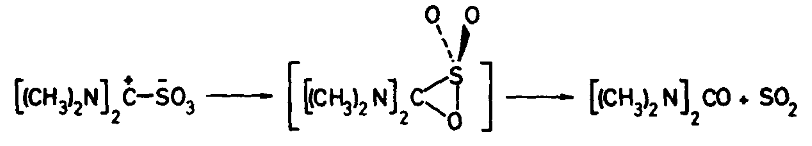
Y = S,O

In contrast to this, the compounds appear rather stable towards electrophilic attack.[92]

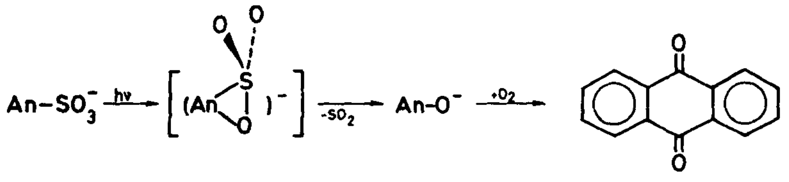
III.2 Oxathiirane S,S-dioxides

In analogy with the thione *S*-monoxides and *S*,*S*-dioxides it can be expected that thione *S*,*S*,*S*-trioxides may form oxathiirane *S*,*S*-dioxides by intramolecular ring closure. However, as stated in the previous section, the thiourea *S*,*S*,*S*-trioxides (formamidinio sulfonates) are the only known members of this class of compounds, and it seems reasonable to expect a somewhat atypical behavior, *e.g.* due to the strongly electron-donating groups attached to the carbon atom. In this connection it is worthwhile to remember the pronounced decrease in relative quantum yield for oxathiirane formation upon photolysis of diarylsulfines *para*-substituted with electron donating substituents (*vide supra*).[42]

Photolysis of tetramethylthiourea *S*,*S*,*S*-trioxide revealed a total lack of reaction,[111] tentatively regarded as a result of self-quenching. On the other hand, tetramethylthiourea *S*,*S*,*S*-trioxide was thermally converted to the corresponding urea and sulfur dioxide in 80 % yield.[111] For obvious reasons the conversion may be formulated as involving the intermediacy of bis(dimethylamino)oxathiirane *S*,*S*-dioxide; however, detailed mechanistic investigations, *e.g.* by differential thermal analysis (*cf.* ref. 52) are lacking.



An oxathiirane *S*,*S*-dioxide structure has been formulated by Izawa in the photolytical conversion of antracene-9-sulfonate (**30**) to 9,10-anthraquinone.[112] The reaction is postulated to involve a negatively charged oxathiirane *S*,*S*-dioxide (**31**), leading to the 9-anthrol anion (**32**), the latter subsequently reacting with oxygen.



30 **31** **32**

An = Antracen-9-yl.

Anthraquinone was found in *ca.* 40 % yield together with *ca.* 55 % anthracene, the latter being formed by desulfonation of **30**.

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III.3 The Reaction Between Thiones and Ozone

The reaction between thiones and ozone may *a priori* lead to species possessing an $R^1R^2CSO_3$ structure. As a first approach five structures (**24–28**) have to be considered as possible candidates.

In the course of time a numbers of reports on the ozonolysis of thiocarbonyl compounds have appeared;[48c,101b,c,113] however, in no case have species with $R^1R^2CSO_3$ composition been isolated or even detected. The general feature appears to be formation of mixtures of the corresponding ketones and sulfines, the mutual ratio unequivocally depending on the possible presence of sterical hindrance in the thiocarbonyl compound.[101c,48c] Zwanenburg reported formation of benzophenone in quantitative yield upon ozonolysis of thiobenzophenone,[48c] however, increased steric hindrance resulted in an increased yield of the corresponding sulfines in the reaction mixture. In the case of di-*t*-butyl thioketone the corresponding sulfine has been reported to be formed in 95 % yield.[101b] Similarly ozonolysis of di-*t*-butyl thioketene afforded the *S*-oxide in more than 90 % yield.[101c] It is, however, clear that also electronic effects do play an important role in directing the reaction towards ketones and sulfines.[101b]

A theoretical study of the possible intermediates in the ozonolysis of thiocarbonyl compounds has been conducted,[104] taking thioformaldehyde as the thiocarbonyl model. Based on potential-energy surface calculations as well as on the calculated relative energies of the intermediates **24–28**, it was concluded that the ozonolysis of sterically unhindered thiocarbonyl compounds most probably takes place *via* 1,2,3,4-trioxathiolane intermediates (**25**), a reaction which is analogous to the well investigated ozonolysis of alkenes.[114]

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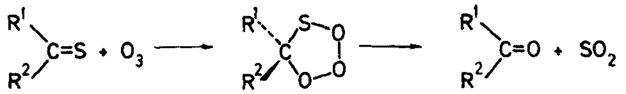

Experimental support for the proposed mechanism was obtained by treating thiobenzophenone with ozone at 130 K, the reaction being monitored by electronic absorption spectroscopy.[104] Immediate formation of *ca.* 68 % benzophenone was observed together with a new absorption band located at λ_{max} 321 nm; the latter decayed slowly with first-order kinetics upon standing ($t_{\frac{1}{2}} \approx 5$ min), forming quantitatively benzophenone. By comparison with the calculated electronic absorption spectrum of 1,2,3,4-trioxathiolane ($\lambda_{max}^{calc.} = 327$ nm), the 321 nm absorption band was assigned to 5,5-diphenyl-1,2,3,4-trioxathiolane.

In the case of sterically hindered thiones, which form mixtures of ketones and sulfines, Zwanenburg suggested the presence of an open chain intermediate **24**.[48c] However, the calculated lability of this species,[104] leading back to thioformaldehyde and ozone, suggests that an intermediate **25** may be present in the case of sterically hindered thiones as well, the course of decomposition being determined by steric and/or electronic effects. Unfortunately, no low-temperature studies of the ozonolysis of sterically hindered thiones have been conducted.

It should finally be mentioned that sulfines also react with ozone, which leads *e.g.* in the case of diphenylsulfine, quantitatively to benzophenone.[48c] By analogy, the reaction is formulated to proceed *via* an intermediary 1,2,3,4-trioxathiolane-4-oxide, the latter in

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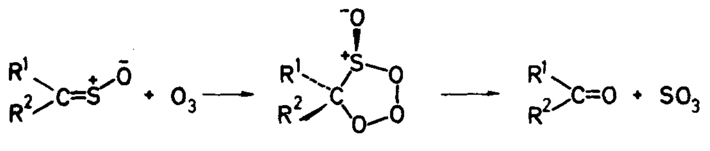
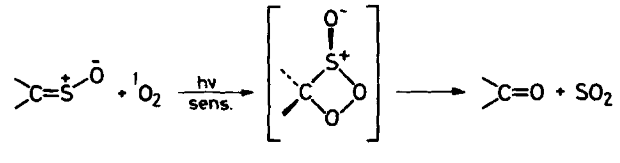
fact being the only reported member of the $R^1R^2CSO_4$ class, which, however, shall not be treated further.



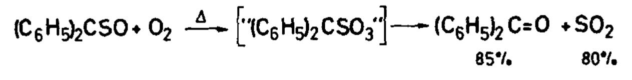
III.4 The Reaction Between Sulfines and Singlet Oxygen

Sulfines react with singlet oxygen to form exclusively the corresponding ketones,[48b] a reaction which can be conducted by dye sensitizing. By analogy to the thiocarbonyl-singlet oxygen reaction (*vide supra*) the conversion has been formulated to proceed *via* an intermediary 1,2,3-dioxathietane 3-oxide.



Apparently aryl-arylsulfinyl- and aryl-arylsulfonylsulfines do not react with singlet oxygen.

Finally, the decomposition of thiobenzophenone *S*-monoxide in an oxygen atmosphere shall be mentioned, the reaction affording benzophenone and sulfur dioxide in high yield.[52] In agreement with a differential thermal analysis this reaction was formulated as an oxidation of the sulfine by molecular oxygen, analogous to the oxidation of thiobenzophenone,[17] although the former reaction takes place at higher temperatures only.[52]



$$(C_6H_5)_2CSO + O_2 \xrightarrow{\Delta} [\text{"}(C_6H_5)_2CSO_3\text{"}] \longrightarrow \underset{85\%}{(C_6H_5)_2C{=}O} + \underset{80\%}{SO_2}$$

IV CONCLUDING REMARKS

The present report is an attempt to review available literature on intermediary species, of the general type $R^1R^2CSO_x$ (x = 1,2,3,(4)), in the conversion of thiocarbonyl compounds to their corresponding oxo derivatives. In some cases direct experimental evidence, even isolation, of $R^1R^2CSO_x$ compounds has been reported; however, in several cases their presence is suggested indirectly. This report is by no means an attempt to 'close the case'; on the contrary it may serve as an introduction to some of the large variety of exciting experiments which undeniable still are missing.

REFERENCES

1. A. Husemann, *Justus Liebigs Ann. Chem.*, **126**, 269 (1863).
2. M. P. Doyle and D. M. Hedstrand, *J. Chem. Soc. Chem. Comm.*, 643 (1977).
3. F. Challenger, E. A. Mason, E. C. Holdsworth, and R. Emmott, *J. Chem. Soc.*, 292 (1953).

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4. R. N. Hurd and G. DeLaMater, *Chem. Rev.*, **61**, 45 (1961).
5. T. C. Sharma, N. S. Sahni, and A. Lal, *Bull. Chem. Soc. Jpn.*, **51**, 1245 (1978).
6. R. Boudet, *Bull. Soc. Chim. Fr.*, 846 (1951).
7. (a) D. H. R. Barton, N. J. Cussans, and S. V. Ley, *J. Chem. Soc. Chem. Comm.*, 393 (1978); (b) N. J. Cussans, S. V. Ley, and D. H. R. Barton, *J. Chem. Soc. Perkin Trans. 1*, 1650 (1980).
8. K. A. Petrov and L. N. Andreev, *Russ. Chem. Rev.*, **40**, 505 (1971).
9. R. Grasley, G. Schroll, and M. Weidner, *Chem. -Ztg*, **100**, 496 (1976).
10. M. Mikolajczyk and J. Luzak, *Chem. Ind. (London)*, 76 (1972); *Synthesis*, 491 (1974); 114 (1975).
11. (a) M. Mikolajczyk and J. Luzak, *J. Org. Chem.*, **43**, 2132 (1978); (b) S. Tamagaki, I. Hatanaka, and S. Kozuka, *Bull. Chem. Soc. Jpn.*, **50**, 3421 (1977).
12. (a) D. H. R. Barton, S. V. Ley, and C. A. Meerholz, *J. Chem. Soc. Chem. Comm.*, 755 (1979); (b) S. V. Ley, C. A. Merholz, and D. H. R. Barton, *Tetrahedron Lett.*, **21**, 1785 (1980).
13. H. Singh, P. Singh, and N. Malhotra, *J. Chem. Soc. Perkin Trans. 1*, 2647 (1981).
14. L. Gattermann and H. Schulze, *Ber.*, **29**, 2944 (1896).
15. H. Staudinger and H. Freudenberger, *Ber.*, **61**, 1836 (1928).
16. A. Schönberg, O. Schütz, and S. Nickel, *Ber.*, **61**, 2175 (1928).
17. L. Carlsen, *J. Org. Chem.*, **41**, 2971 (1976).
18. (a) J. Strating, L. Thijs, and B. Zwanenburg, *Tetrahedron Lett.*, 65 (1966); (b) B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. Chim.*, **86**, 577 (1967); (c) B. Zwanenburg, A. Wagenaar, L. Thijs, and J. Strating, *J. Chem. Soc. Perkin Trans. 1*, 73 (1973); (d) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziee, Jr., *J. Chem. Soc. Chem. Comm.*, 539 (1975).
19. (a) R. Kitamura, *J. Pharmac. Soc. Jpn.*, **58** 246 (1938); (b) W. Walter, *Justus Liebigs Ann. Chem.*, **633**, 35 (1960); (c) W. Walter, J. Curts, and H. Pawelzik, *ibid.*, **643**, 29 (1961); (d) W. Walter and G. Randau, *ibid.* **722**, 52 (1969); (e) W. Walter and O. H. Bauer, *ibid.*, 248 (1979); (f) W. Walter and J. Curts, *Chem. Ber.*, **93**, 1511 (1960); (g) W. Walter and O. H. Bauer, *Justus Liebigs Ann. Chem.*, 1584 (1976).
20. E. Block, R. E. Penn, R. J. Olsen, and P. F. Sherwin, *J. Amer. Chem. Soc.*, **98**, 1264 (1976).
21. W. A. Sheppard and J. Diekmann, *J. Amer. Chem. Soc.*, **86**, 1891 (1964).
22. J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav. Chim.*, **83**, 631 (1964).
23. (a) J. F. King and T. Durst, *Tetrahedron Lett.*, 585 (1963); (b) *J. Amer. Chem. Soc.*, **85**, 2676 (1963).
24. A. Holm and L. Carlsen, *Tetrahedron Lett.*, 3203 (1973).
25. (a) B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. Chim.*, **89**, 687 (1970); (b) G. E. Veenstra and B. Zwanenburg, *ibid.*, **95**, 28, 195 (1976).
26. B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Lett.*, 2871 (1968).
27. (a) W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *J. Org. Chem.*, **30**, 3071 (1965); (b) T. J. Adley, A. K. M. Anisuzzaman, and L. N. Owen, *J. Chem. Soc. C*, 807 (1967).
28. B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Lett.*, 4461 (1969).
29. M. A. Pérez and G. Kresze, *Justus Liebigs Ann. Chem.*, 1510 (1980).
30. E. U. Elam, F. H. Rash, J. T. Dougherty, V. W. Goodlett, and K. C. Brannock, *J. Org. Chem.*, **33**, 2738 (1968).
31. E. Schaumann and W.-R. Klein, *Tetrahedron Lett.*, 3457 (1977).
32. (a) W. F. Wilkens, Ph.D. Thesis, Cornell Univ., Ithaca, NY 1961; (b) H. H. Brodnitz and J. V. Pascale, *J. Agr. Food Chem.*, **19**, 269 (1971); (c) E. Block, R. E. Penn, and L. K. Revelle, *J. Amer. Chem. Soc.*, **101**, 2200 (1979).
33. J. E. Baldwin, S. R. Herchen, G. Schulz, C. P. Falshaw, and T. J. King, *J. Amer. Chem. Soc.*, **102**, 7815 (1980).
34. B. Zwanenburg, *Rec. Trav. Chim.*, **101**, 1 (1982).
35. A. Battaglia, A. Dondoni, P. Giorgianni, G. Maccagnani, and G. Mazzanti, *J. Chem. Soc. B*, 1547 (1971).
36. (a) Th. W. Hummelink, *J. Cryst. Mol. Struct.*, **4**, 87, 373 (1974); *Cryst. Struct. Comm.*, **4**, 441 (1975), **5**, 169 (1976); (b) G. Rindorf and L. Carlsen, *Acta Cryst.*, **B35**, 1179 (1979); (c) E. Schaumann, S. Harto, and G. Adiwidjaja, *Chem. Ber.*, **112**, 2698 (1979); (d) R. B. Bates and G. A. Wolfe, *J. Amer. Chem. Soc.*, **90**, 6854 (1968).
37. (a) O.H. Jarchow, *Acta Cryst.*, **B25**, 267 (1969); (b) W. Walter, J. Holst, and J. Eck, *J. Mol. Struct.*, **9**, 151 (1971); (c) K. Kato, *Acta Cryst.*, **B28**, 2653 (1973).
38. (a) J. F. King and T. Durst, *Can J. Chem.*, **44**, 819 (1966); (b) S. Ghersetti, L. Lunazzi, G. Maccagnani, and G. Mangini, *Chem. Comm.*, 834 (1969); (c) B. Zwanenburg. L. Thijs, and J. Strating, *Tetrahedron Lett.*, 3453 (1967).
39. L. Carlsen, unpublished results.
40. (a) S. C. Abrahams, *Quart. Rev.*, **10**, 407 (1956); (b) Y. A. Kolesnik and V. V. Kozlov, *Russ. Chem. Rev.*, **37**, 519 (1968); (c) D. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

41. L. Carlsen, J. P. Snyder, A. Holm, and E. Pedersen, *Tetrahedron*, **37**, 1257 (1981).
42. G. Karlström, B. O. Roos, and L. Carlsen, submitted for publication.
43. W. Walter and H. P. Kubersky, *Justus Liebigs Ann. Chem.*, **694**, 70 (1966), and references cited therein.
44. (a) B. F. Bonini, S. Ghersetti, G. Maccagnani, and G. Mazzanti, *Boll. Sci. Fac. Ind. Bologna*, **27**, 419 (1969); (b) D. E. Powers, C. A. Arrington, W. C. Harris, E. Block, and V. F. Kalasinsky, *J. Phys. Chem.*, **83**, 1890 (1979).
45. (a) A. M. Hamid and S. Trippett, *J. Chem. Soc. C*, 1612 (1968); (b) B. Zwanenburg, L. Thijs, J. B. Broens, and J. Strating, *Rec. Trav. Chim.*, **91**, 443 (1972); (c) L. Thijs, J. Strating, and B. Zwanenburg, *ibid.*, **91**, 1345 (1972); (d) B. F. Bonini, G. Maccagnani, L. Thijs, aand B. Zwanenburg, *Tetrahedron Lett.*, 3569 (1973); (e) B. F. Bonini, G. Maccagnani, A. Wagenaar, L. Thijs, and B. Zwanenburg, *J. Chem. Soc. Perkin Trans. 1*, 2490 (1972); (f) L. Thijs, A. Wagenaar, E. M. M. van Rens, and B. Zwanenburg, *Tetrahedron Lett.*, 3589 (1973); (g) B. F. Bonini, G. Maccagnani, G. Mazzanti, L. Thijs, H. P. M. M. Ambrosius, and B. Zwanenburg, *J. Chem. Soc. Perkin Trans. 1*, 1468 (1977): (h) B. F. Bonini, G. Maccagnani, G. Mazzanti, and B. Zwanenburg, *Gazz. Chim. Ital.*, **107**, 289 (1977); (i) B. F. Bonini, G. Maccagnani, G. Mazzanti, P. Pedrini, and B. Zwanenburg, *ibid.*, **107**, 283 (1977); (j) B. F. Bonini, G. Maccagnani, G. Mazzanti, L. Thijs, G. E. Veenstra, and B. Zwanenburg, *J. Chem. Soc. Perkin Trans. 1*, 1218 (1978); (k) E. Schaumann, H. Behr, G. Adiwidjaja, A. Tangerman, B. H. M. Lammerink, and B. Zwanenburg, *Tetrahedron*, **37**, 219 (1981).
46. (a) A. G. Schultz and R. H. Schlessinger, *Chem. Comm.*, 747, 748 (1970); (b) C. G. Venier, C. G. Gibbs, and P. T. Crane, *J. Org. Chem.*, **39**, 501 (1974); (c) L. Carlsen and A. Holm, *Acta Chem. Scand.*, **B30**, 997 (1976); (d) J. A. Loontzes, M. van der Leij, and B. Zwanenburg, *Rec. Trav. Chim.*, **99**, 39 (1980); (e) M. van der Leij, H. J. M. Strijtveen, and B. Zwanenburg, *ibid.*, **99**, 45 (1980).
47. (a) J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav. Chim.*, **86**, 641 (1967); (b) L. Carlsen and A. Holm, *Acta Chem. Scand.*, **B30** 277 (1976); (c) G. E. Veenstra and B. Zwanenburg, *Rec. Trav. Chim.*, **95**, 37, 202 (1976).
48. (a) A. Battaglia, A. Dondoni, G. Maccagnani, and G. Mazzanti, *J. Chem. Soc. Perkin Trans. 2*, 609 (1974); (b) B. Zwanenburg, A. Wagenaar, and J. Strating, *Tetrahedron Lett.*, 4683 (1970); (c) B. Zwanenburg and W. A. J. Jassen, *Synthesis*, 617 (1973).
49. J. A. M. Kuipers, B. H. M. Lammerink, I. W. J. Still, and B. Zwanenburg, *Synthesis*, 295 (1981).
50. J. P. Snyder, *J. Amer. Chem. Soc.*, **96**, 5005 (1974).
51. J. Silhanek and M. Zbirovsky, *Chem. Comm.*, 878 (1969).
52. L. Carlsen, A. Holm, E. Koch, and B. Stilkerieg, *Acta Chem. Scand.*, **B31**, 679 (1977).
53. E. Koch, 'Non-Isothermal Reaction Analysis', Academic Press, London, 1977, and references cited therein.
54. E. Block, A. A. Bazzi, and L. K. Revelle, *J. Amer. Chem. Soc.*, **102**, 2490 (1980).
55. J. Ehlers, Thesis, University of Hamburg, 1978.
56. L. Carlsen, H. Egsgaard, E. Schaumann, and J. Ehlers, *Chem. Ind. (London)*, 851 (1979).
57. L. Carlsen, H. Egsgaard, and E. Schaumann, *J. Chem. Soc. Perkin Trans. 2*, 1206 (1980).
58. L. Carlsen and H. Egsgaard, *Thermochim. Acta*, **38**, 47 (1980).
59. At higher temperature (1043 K) a relatively large amount of the carbene **8** is observed, however, most probably due to rethermolysis of primarily generated thioketene **12**.[57,60]
60. The atomic oxygen extrusion is ascribed to a surface catalylic reaction: H. Egsgaard and L. Carlsen, *J. Anal. Appl. Pyrol.*, **5**, 1 (1983).
61. L. Carlsen, A. Holm, J. P. Snyder, E. Koch, and B. Stilkerieg, *Tetrahedron*, **33**, 2231 (1977).
62. (a) A. G. Schultz and R. H. Schlessinger, *J. Chem. Soc. Chem. Comm.*, 1483 (1969); 1051 (1970); (b) A. G. Schultz, C. D. DeBoer, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **90**, 5314 (1968); (c) R. H. Schlessinger and A. G. Schultz *Tetrahedron Lett.*, 4513 (1969).
63. L. Carlsen, N. Harrit, and A. Holm, *J. Chem. Soc. Perkin Trans. 1*, 1404 (1976).
64. L. Carlsen, A. Holm, and C. Lohse, to be published.
65. L. Carlsen and E. Schaumann, *J. Chem. Soc. Faraday Trans. 1*, 2624 (1979).
66. J. P. Snyder and L. Carlsen, *J. Amer. Chem. Soc.*, **99**, 2931 (1977).
67. L. Carlsen and J. P. Snyder, to be published.
68. A. P. Davis and G. H. Whitham, *J. Chem. Soc. Chem. Comm.*, 741 (1981).
69. A. Holm, J. J. Christiansen, and C. Lohse, *J. Chem. Soc. Perkin Trans. 1*, 960 (1979).
70. E. Schaumann and U. Behrens, *Angew. Chem.*, **89**, 750 (1977).
71. J. P. Snyder, *J. Org. Chem.*, **38**, 3965 (1973).
72. L. Carlsen and J. P. Snyder, *J. Org. Chem.*, **43**, 2216 (1978).
73. (a) R. A. L. Sullivan and A. Hargreaves, *Acta Cryst.*, **15**, 675 (1962); (b) J. Sletten, *J. Amer. Chem. Soc.*, **91**, 4545 (1969).
74. H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).

Downloaded At: 13:19 25 January 2011

75. (a) H. Kloosterziel, H. H. Deinema, and H. J. Backer, *Rec. Trav. Chim.*, **71**, 1228 (1952); (b) H. Kloosterziel and H. J. Backer, *ibid.*, **71**, 1235 (1952); (c) H. Kloosterziel, J. S. Boerema, and H. J. Backer, *ibid.*, **72**, 612 (1953); (d) G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957).
76. (a) J. B. Stothers, L. J. Danks, and J. F. King, *Tetrahedron Lett.*, 2251 (1971); (b) O. Tsuge, and S. Iwanami, *Bull. Chem. Soc. Jpn.*, **44**, 2750 (1971); (c) O. Tsuge and S. Iwanami, *Nippon Kagaku Zasshi*, **92**, 448 (1971) *Chem. Abstr.*, **77**, 005432 (1972); (d) M. Tanaka, T. Nagai, and N. Tokura, *J. Org. Chem.*, **37**, 4106 (1972).
77. (a) R. Fusco, S. Rossi, and S. Maiorana, *Chim. Ind.* (*Milano*), **44**, 873 (1962) *Chem Abstr.*, **60**, 13240b (1964), **45**, 564 (1963) *Chem. Abstr.*, **60**, 13133a (1964); (b) R. Fusco, S. Rossi, S. Maiorana, and G. Pagini, *Gazz. Chim. Ital.*, **95**, 774 (1965); (c) W. E. Truce, R. W. Campbell, and J. R. Norell, *J. Amer. Chem. Soc.*, **86**, 288 (1964); (d) W. E. Truce and R. W. Campbell, *ibid.*, **88**, 3599 (1966); (e) J. F. King and T. Durst, *ibid.*, **86**, 287 (1964); (f) J. F. King, E. G. Lewars, and L. J. Danks, *Can. J. Chem.*, **50**, 866 (1972); (g) J. F. King and B. P. Beatson, VIth Int. Symp. Org. Sulfur Chem., Bangor, 1974, Abstr. B20; (h) L. W. Christensen, *Synthesis*, 534 (1973); (i) A. leBerre, A. Ethienne, and B. Dumaitre, *Bull. Soc. Chim. Fr.*, 954 (1970); (j) J. F. King and S. M. Loosmore, *Chem. Comm.*, 1011 (1976).
78. J. F. King and D. R. K. Harding, *Chem. Comm.*, 959 (1971); *J. Amer. Chem. Soc.*, **98**, 3312 (1976).
79. J. F. King and E. G. Lewars, *Chem. Comm.*, 700 (1972); *Can. J. Chem.*, **51**, 3044 (1973).
80. C. L. McIntosh and P. deMayo, *Chem. Comm.*, 32 (1969).
81. (a) J. F. King, P. deMayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, **48**, 3704 (1970); (b) D. C. Dittmer, J. E. McCaskie, J. E. Babiarz, and M. V. Ruggeri, *J. Org. Chem.*, **42**, 1910 (1977).
82. (a) J. F. King, P. deMayo, and D. L. Verdun, *Can. J. Chem.*, **47**, 4509 (1969); (b) J. F. King, R. A. Marty, P. deMayo, and D. L. Verdun, *J. Amer. Chem. Soc.*, **93**, 6304 (1971).
83. W. J. Mijs, J. B. Reesink, and U. E. Wiersum, *Chem. Comm.*, 412 (1972).
84. R. Langendries, F. C. DeSchryver, P. deMayo, R. A. Marty, and J. Schutyser, *J. Amer. Chem. Soc.*, **96**, 2964 (1974).
85. R. F. J. Langendries and F. C. DeSchryver, *Tetrahedron Lett.*, 4781 (1972).
86. (a) T. Durst and J. F. King, *Can. J. Chem.*, **44**, 1869 (1966); (b) J. F. King, P. deMayo, E. Morkved, A. B. M. A. Sattar, and A. Stroessl, *ibid.*, **41**, 100 (1963); (c) J. L. Charlton and P. deMayo, *ibid.*, **46**, 55 (1968); (d) S. T. Weintraub and B. F. Plummer, *J. Org. Chem.*, **36**, 361 (1971); (e) B. Gorewit and M. Rosenblum, *ibid.*, **38**, 2257 (1973); (f) J. F. King, E. G. Lewars, D. R. K. Harding, and R. M. Enanoza, *Can. J. Chem.*, **53**, 3653 (1975).
87. J. P. Snyder and D. N. Harpp, *Chem. Comm.*, 1305 (1972).
88. (a) J. F. King, *Acc. Chem. Res.*, **8**, 10 (1975); (b) D. R. Hogg in 'Organic Compounds of Sulphur, Selenium and Tellurium' Chemical Society, Vol. 5, London, 1979, p. 136; (c) D. R. Hogg in 'Organic Compounds of Sulphur, Selenium and Tellurium' Vol. 6, Royal Society of Chemistry, London, 1981, p. 163.
89. E. de Barry Barnett, *J. Chem. Soc.*, **97**, 63 (1910).
90. J. Böeseken, *Rec. Trav. Chim.*, **55**, 1040 (1936).
91. W. Walter and G. Randau, *Justus Liebigs Ann. Chem.*, **722**, 80 (1969).
92. W. Walter and G. Randau, *Justus Liebigs Ann. Chem.*, **722**, 98 (1969).
93. L. Carlsen, unpublished results.
94. W. Walter and O. H. Bauer, *Justus Liebigs Ann. Chem.*, 305 (1975).
95. W. Walter and O. H. Bauer, *Justus Liebigs Ann. Chem.*, 1584 (1976).
96. H. Hiraoka, *Chem. Comm.*, 1014 (1974).
97. (a) N. Ishibe, M. Odani, and M. Sunami, *Chem. Comm.*, 118 (1971); (b) J. J. Worman, N. Shen, and P. C. Nichols, *Can. J. Chem.*, **50**, 3923 (1972).
98. (a) R. Rajee and V. Ramamurthy, *Tetrahedron Lett.*, 5127 (1978); (b) N. Suzuki, K. Sano, N. Tani, and Y. Izawa, *Heterocycles*, **16**, 1133 (1981).
99. L. Carlsen, *J. Chem. Soc. Perkin Trans. 2*, 188 (1980).
100. (a) S. Tamagaki, R. Akatsuka, and S. Kozuka, *Mem. Fac. Eng. Osaka City Univ.*, **20**, 97 (1979) *Chem. Abstr.*, **94**, 029839 (1981); (b) S. Tamagaki, R. Akatsuka, M. Nakamura, and S. Kozuka, *Tetrahedron Lett.*, 3665 (1979); (c) S. Tamagaki and K. Hotta, *J. Chem. Soc. Chem. Comm.*, 598 (1980); (d) S. Tamagaki, K. Hotta, and S. Kozuka, *Chem. Lett.*, 619 (1980).
101. (a) V. J. Rao and V. Ramamurthy, *Ind. J. Chem.*, **19B**, 143 (1980); (b) N. Ramnath, V. Ramesh, and V. Ramamurthy, *J. Chem. Soc. Chem. Comm.*, 112 (1981); (c) V. J. Rao and V. Ramamurthy, *ibid.*, 638 (1981); (d) V. J. Rao, K. Muthurama, and V. Ramamurthy, *J. Org. Chem.*, **47**, 127 (1982); (e) N. Ramnath, V. J. Rao, V. Ramesh, and V. Ramamurthy, *Chem. Lett.*, 89 (1982).
102. L. Carlsen, unpublished results.
103. (a) W. Walter and K.-P. Reuss, *Chem. Ber.*, **102**, 2640 (1969); (b) W. Walter and C. Rohloff, *Justus Liebigs Ann. Chem.*, 295 (1975).

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104. L. Carlsen, *Tetrahedron Lett.*, 4103 (1977).
105. J. Böeseken, *Rec. Trav. Chim.*, **55**, 1044 (1936).
106. (a) W. Walter and K.-P. Reuss, *Justus Liebigs Ann. Chem.*, 225, 243 (1974); (b) W. Walter and K.-P. Reuss, *ibid.*, 253 (1974); (c) W. Walter and C. Rohloff, *ibid.*, 1563 (1975); 447, 463 (1977).
107. W. Walter and C. Rohloff, *Justus Liebigs Ann. Chem.*, 491 (1977).
108. L. Carlsen, unpublished results.
109. W. Walter and J. Holst, *J. Mol. Struct.*, **9**, 413 (1971).
110. J. Voss, Thesis, University of Hamburg, 1965.
111. W. Walter and L. Carlsen, unpublished results.
112. Y. Izawa, N. Suzuki, A. Inoue, and T. Ito, *Chem. Comm.*, 1048 (1976).
113. (a) N. H. Nilsson and A. Senning, *Angew. Chem.*, **84**, 293 (1972); (b) N. H. Nilsson, C. Jacobsen, O. N. Sørensen, N. K. Haunsøe, and A. Senning, *Chem. Ber.*, **105**, 2854 (1972).
114. R. Criegee, *Angew. Chem.*, **87**, 765 (1975).

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