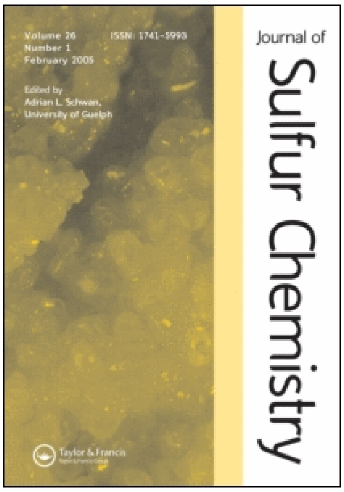

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SULFUR EXTRUSION REACTIONS - SCOPE AND MECHANISTIC ASPECTS

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This review details a significant and representative set of examples in the literature where one of the products in a chemical reaction is elemental sulfur. While the mechanism of such extrusions is not clearly understood, several mechanistic possibilities have been considered including the likelihood of thiosulfoxide intermediates, the concatenation of sulfur atoms and the elimination of singlet diatomic sulfur as a discrete species. Details of the mechanistic efforts that have been uncovered in the literature are included as well as our own work in this area. In order to help avoid confusion for the reader, the nomenclature (although sometimes inconsistent) is in most cases that which appeared in the original articles.

Key words: Desulfurization, diatomic sulfur, elemental sulfur, sulfur extrusion, sulfur loss, singlet sulfur.

CONTENTS

I. INTRODUCTION

There are innumerable examples in the literature where one of the products in a chemical reaction is sulfur. The sulfur that is lost is often inappropriately represented as S, [S], S^0 or S_1 and the implication is often that atomic sulfur is produced in the process. The mechanism by which the sulfur is produced in these reactions is not well understood. In several instances, the sulfur loss has been specifically proposed to proceed through a cheletropic loss of a singlet sulfur atom which could then combine to form elemental sulfur (S_8).

Under most conditions, formation of a singlet sulfur atom is not a reasonable pathway for the loss of sulfur to occur; the energy of formation of a sulfur atom $S(^1D_2)$ has been determined to be 66.3 kcal/mol.[1,2] Due to this high energy, single sulfur atom decomposition pathways certainly cannot account for many of the observed sulfur extrusions that occur under mild conditions; the sulfur loss must proceed through a lower energy transient species such as diatomic sulfur (S_2) or longer chain fragments.[2] These transient species could then combine to form elemental sulfur; this would result in an overall lower energy pathway for the extrusion. These possibilities have been further detailed[3] and will be considered in the context of some of the sulfur extrusions presented here.

There have been four previous reviews in the chemical literature that have dealt with sulfur extrusion. Two reviews which appeared in the 1960s dealt exclusively with extrusions from ring systems which resulted in the formation of stable aromatic molecules. The gain of aromaticity was considered to be the driving force for these reactions. Loudon[4] considered both the extrusion of bivalent sulfur and oxidized forms of sulfur. Dean and Stark[5] reviewed all types of extrusions; the reactions were first divided by the expelled species and then subdivided as to the form of the "residua" or intermediates formed during the process. All the examples were proposed to proceed through an intermediate in which there was a separation of charges. A recent review by Radl[6] in 1987 was titled "The Preparation of Five-Membered Heterocyclic Compounds by Extrusion of Sulfur". It gave examples where sulfur extrusion has been used as a synthetic method in the preparation of five-membered heterocycles. More recently, Guziec and Sanfilippo[6a] published a review dealing with extrusion reactions of organic sulfur, selenium and tellurium compounds. This review, like that of Dean and Stark, dealt with all varieties of extrusion processes. There is very limited overlap between the previous paper and this review, and those references have been included. The examples cited in the review by Radl have not been included here; those summarized by Loudon and by Dean and Stark are noted here for completeness.

The scope of this review includes essentially all organic reaction types which produce elemental sulfur as one of the reaction products. The review therefore does not contain loss of sulfur in other oxidation states or extrusions of molecules containing sulfur. Oxidized forms of sulfur not considered include sulfur monoxide and sulfur dioxide. Metal promoted extrusions produce the metal sulfide and are, therefore, not considered; copper assisted extrusion was the main reaction described in the reviews by Loudon and by Dean and Stark. Those extrusions which result from a direct nucleophilic attack on the sulfur atom are also not in this review; these include use of phosphines and alkyllithiums.

Extrusion reactions can be catalogued into five broad classes including thermal, base-induced, photolytic, and solvent-dependent processes, as well as certain reactions of sulfur compounds. This review has been catalogued by structural type; this was done to avoid many overlapping situations where a compound extruded sulfur and could be placed under several reaction types. The main division creates two separate classes (rings and chains) although some overlap may occur. The section on rings includes compounds that extrude sulfur or molecules that are formed as a result of a sulfur extrusion reaction. This section is then further subdivided by structural types as to ring size and the ring type such as; thiiranes, thiepins, dithiins, thiophenes and other heterocyclic ring systems.

The section on chains covers a broader base dealing with all those extrusions that cannot be placed in the ring section; thus the subdivisions are not as well defined. It has been divided into four sections: chain extrusions, thiocarbonyl compounds, reactions that produce sulfur and miscellaneous extrusions. Chain extrusion had a large number of structural types, but has been subdivided into three distinct species: carbon sulfides ($C-S_x-C$), carbon heterocyclic sulfides ($C-S_x-Y$), and diheterocyclic sulfides ($Y-S_x-Y$). Further subdivision is difficult, so compounds of similar structure or reaction type are grouped together in the same section. The section on thiocarbonyl compounds is subdivided roughly as to the second bond on the sulfur atom; for example thioketones, *S*-oxides and *S*-imides.

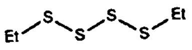
We attempted to make the review as comprehensive as possible, but there was great difficulty in identifying and locating the examples of a sulfur extrusion. This difficulty can be characterized by looking at the results of one Chemical Abstracts Service (CAS) search of sulfur extrusions using all three of the proximity operators; this results in different answers. A search of sulfur (with) extrusion (the two words are consecutive) results in 88 answers of which more than one third do not involve the formation of elemental sulfur. Sulfur (A) extrusion (the two words are consecutive in any order) gives 101 answers; again more than one third do not involve the production of elemental sulfur. Sulfur (2A) extrusion (the two words are within two words of each other in any order, and therefore includes "extrusion of sulfur" and "extrusion of elemental sulfur") results in 166 organic answers, again more than one third involve the loss of sulfur in some form other than elemental sulfur. A search of sulfur (L) extrusion (the two words are in the same information unit) gives three new answers all of which do not show elemental sulfur. Sulfur (and) extrusion (two words are in the same listing) gives only ten answers that have not previously been obtained, nine of which do not indicate sulfur formation, while the tenth involves the formation of diatomic sulfur. Other terms related to sulfur extrusion give similar results. Sulfur (2A) loss (includes "sulfur loss" and "loss of sulfur") resulted in 110 answers only eight of which were organic papers. Of the eight papers, five involved the loss of oxidized sulfur and the other three papers were previously obtained. A search of sulfur (2A) elimination (therefore includes "elimination of sulfur") gave 64 new answers of which more than 75% do not involve elemental sulfur.

In this review there are over 210 papers from the post-1967 literature, but the CAS searches can only account for about 130 of those. A 1984 paper by Pastor (ref. 60) entitled "Observation of a Sterically Hindered Hydroxyarenesulfenyl Chloride: Novel Base-Catalyzed Dimerization to a Diphenoquinone", is illustrative of this difficulty. A CAS search of many terms related to sulfur extrusion did not identify this paper as one of the answers because in the title or abstract there is no mention of the sulfur extrusion that occurs. Although there certainly will be some examples missing here, we feel that the review is representative. The nomenclature for all the structures is that which was used in the original literature to avoid any confusion from the original paper.

II. LOSS IN CHAINS

2.1. C–S$_x$–C

Diethyl tetrasulfide **1** and trisulfide **2** are unstable and extrude sulfur on attempted distillation. The tetrasulfide forms the trisulfide on attempted distillation at reduced pressure. At atmospheric pressure disulfide **3** was formed from the trisulfide. Diphenyl trisulfide **4** extruded one atom of sulfur to form the disulfide **5** on attempted purification by distillation.[7]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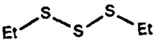
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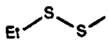
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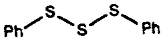
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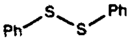
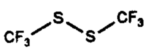

(5)

Bis(trifluoromethyl) disulfide **6** on irradiation in a silica vessel produced bis(trifluoromethyl) sulfide **7** and sulfur.[8] Bis(trifluoromethyl) trisulfide **8** on irradiation[9] also produces bis(trifluoromethyl) sulfide **7** and sulfur. The disulfide was found to be an intermediate in the conversion of the trisulfide to the sulfide. The bis(trifluoromethyl) sulfides **6**, **7** and **8** are decomposed by aqueous alkali into fluoride, sulfide and carbonate anions and sulfur. Trifluoromethanesulfenyl chloride **9** on photolysis gave sulfur and liquid products which were not identified.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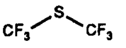
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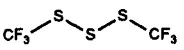
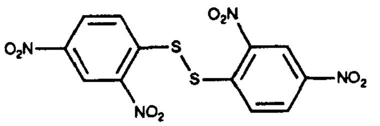

(8)

CF_3—SCl
(9)

When heated[10] in alcohol, bis(2,4-dinitrophenyl) disulfide **10** extrudes an atom of sulfur to form bis(2,4-dinitrophenyl) sulfide **11**. No extrusion was observed when the disulfide was heated in non-polar solvents. The authors proposed a mechanism where the conversion from disulfide to sulfide involved a thiosulfoxide intermediate.



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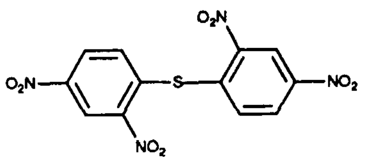
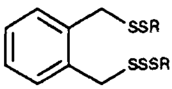


(11)

The trisulfide **12** ($R = p\text{-}CH_3C_6H_4$) was readily desulfurized to disulfide **13** when dissolved in methanol for 5 h at ambient temperature or on treatment with triphenylphosphine. When $R = CH_2\text{-}CH(OH)\text{-}CH_2OH$ the trisulfide was also unstable and underwent a facile loss of sulfur followed by disproportionation to the symmetrical disulfides.[11]



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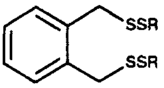

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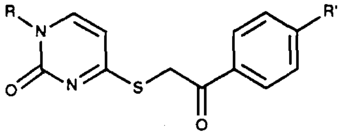
Roth[12] discovered that on attempted recrystallization, from 2-methoxyethanol at 125 °C, 4-(phenacylthio)-2(1*H*)-pyrimidinones **14** extruded an atom of sulfur to yield 4(3*H*)-(benzoylmethenyl)-2(1*H*)-pyrimidinones **15**. Attempts were made to study the reaction rate for the extrusion of sulfur from **14** ($R = H$, $R' = Br$) but erratic results were obtained.



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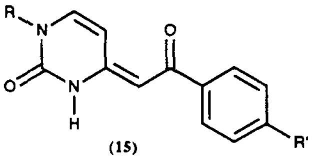
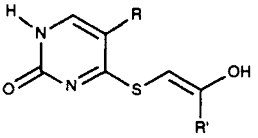


(15)

To determine the effect of the neighboring group on the extrusion, 5-methyl-4-(acetonylthio)-2(1*H*)-pyrimidinone **16** was prepared. This compound could be recrystallized from ethanol but extruded sulfur in 2-methoxyethanol forming **17** in 50% yield along with a 50% yield of elemental sulfur. 3-Methyl-4-thiouracil **18** did not give the pyrimidinone but rather the sulfur extrusion product upon warming in ethanol. Adjacent 3- or 5-methyl substituents in the pyrimidine ring therefore, assisted the sulfur extrusion.



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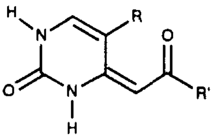

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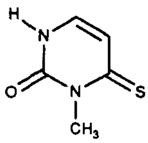
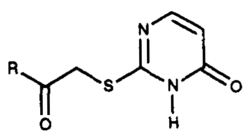


(18)

Phenacylthio derivatives of 2-thiouracil **19** were found to extrude sulfur to form **20** but at a rate about one seventh that of **14**.



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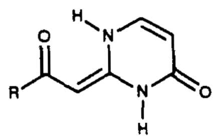
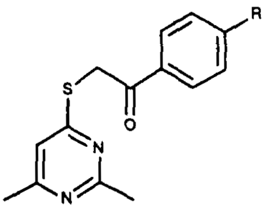


(20)

No reaction was observed in the absence of the 2-oxo group. No extrusion occurs with the introduction of a 2-amino group or an electron withdrawing *p*-nitrobenzyl group in place of the 2-oxo functionality. The effect of the α-oxo functionality on sulfur extrusion was also observed in the work of Singh as shown below. On heating in anhydrous *N*,*N*-dimethylformamide ω-[4-(2,6-dimethylpyrimidinyl)thio]acetophenones **21** underwent thermal sulfur extrusion to form ω-(2,6-dimethyl-3*H*-pyrimidinylene)acetophenones **22**.[13] α-[4-(2,6-Dimethylpyrimidinyl)thio]propiophenone **23** undergoes a similar sulfur extrusion to form α-[4-(2,6-dimethylpyrimidinyl)]propiophenone **24**.[13]



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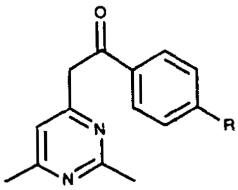

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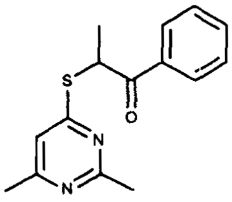

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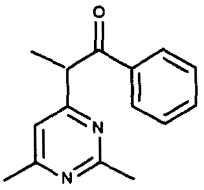
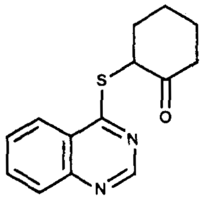


(24)

1-[(α-Oxocyclohexyl)thio]isoquinoline **25** extruded sulfur in refluxing DMF to form 1-(α-oxocyclohexyl)isoquinoline **26**. A similar extrusion was also observed for 4-[(α-oxocyclohexyl)thio]quinazoline **27** to form 4-[α-oxocyclohexyl]quinazoline **28**.[14] Similar compounds lacking the 2-oxo functionality did not lose sulfur under similar thermal conditions.



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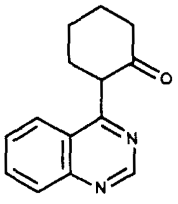

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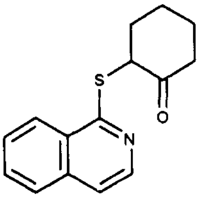

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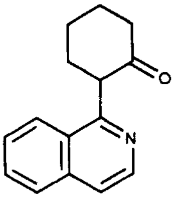
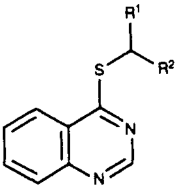


(28)

Singh, Narula and Gandhi[15] observed that treatment of 4-(1-acyl- and -acyloxy) alkylthioquinazolines **29** (R^1 = COR′, R^2 = H) with sodium ethoxide in *N*,*N*-dimethylformamide resulted in clean formation of 4-(1-acyl- and -acyloxy)alkylidene-3,4-dihydroquinones **30**. This was expanded to include thiocarboxamide derivatives of [α-(quinazolin-4-ylthio] ketones **29** (R^1 = COR′), esters **29** (R^1 = COOR′) and a nitrile **29** (R^1 = CN). they are conveniently desulfurized to the corresponding α-[quinazoline-4(3*H*)-ylidene] ketones **30**, esters **30** and nitrile **31** by sodium ethoxide in *N*,*N*-dimethylformamide.[16]



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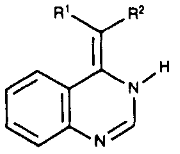

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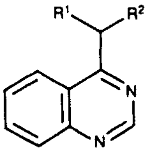
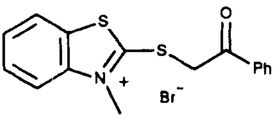


(31)

Singh, Gandhi and Bal found[17] that in the attempted cyclodehydration of 2-(4-quinazolinylthio)acetophenone **29** (R = COR′) with concentrated sulfuric acid, the major mode of reaction was sulfur extrusion. Work-up with perchloric acid results in the isolation of 2-(4(3*H*)-quinazolinylidene)acetophenone **30** (R = COR′). When heated under the same conditions **25** loses sulfur to form **26**.

Knott in his studies[18] on sulfur-containing chromophores investigated the action of bases on heterocyclic sulfide quaternary salts. Treatment of 3-methyl-2-phenacylthiobenzothiazolium bromide **32** with triethylamine in alcoholic solution gives 3-methyl-2-phenacylidenebenzothiazoline **33**, an unidentified product and sulfur. Treatment of the unidentified product with hydrogen bromide in acetic anhydride gives the acetate and elemental sulfur.



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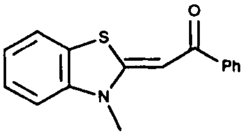
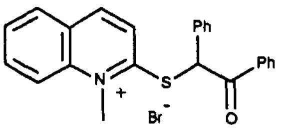


(33)

1-Methyl-2-α-phenylphenacylthioquinolium bromide **34** reacts[18] in the presence of base to form sulfur and 1,2-dihydro-1-methyl-2-α-phenylphenacylquinoline **35**.



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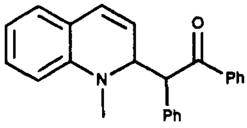

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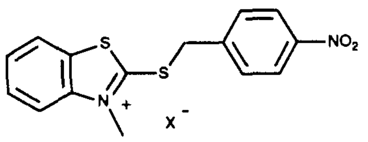
Base treatment[18] of the 2-*p*-nitrobenzylthiobenzothiazole quaternary salt **36** gave the desulfurized 3-methyl-2-*p*-nitrobenzylidenebenzothiazoline **37** as one of the products.



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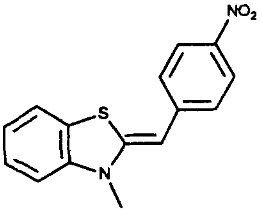
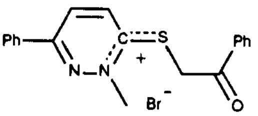


(37)

Sulfur extrusion[19] from the bromide of 2-methyl-3-phenylacylthio-6-phenylpyridazone **38** with potassium carbonate in DMF formed acyl-3-alkylidenedihydropyridazine **39**. The same procedure resulted in sulfur extrusion from the pyridazinium bromides **40** to form the 2-alkyl- and 2,6-dialkyl-3-*p*-bromophenylidenedihydropyridazines **41**.



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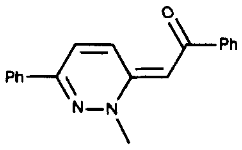

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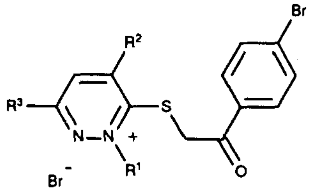

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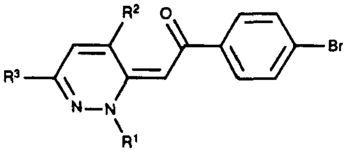
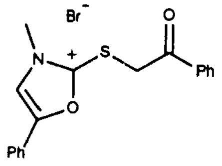


(41)

The salt of 2-phenacylthio-1,3-oxazolium **42** when treated[20] with sodium hydride in DMSO affords 2-phenacylidene-3-methyl-5-phenyl-1,3-oxazoline **43**. The sulfur ylide **44** was likely originally formed and then rearranged with the loss of sulfur to form **43**. A similar result is observed when the ylide **44** is treated with *p*-nitrobenzaldehyde. The resulting products are *p*-nitrochalcone **45** and elemental sulfur.



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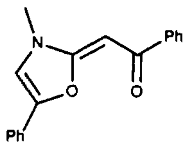

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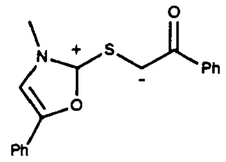

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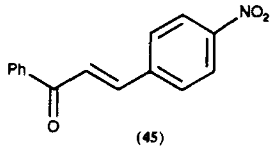
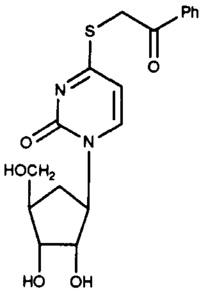


(45)

Heating of the 2-phenacylthio derivative of 4-thiouridine **46** in pyridine at reflux formed a product, **47**, which had lost one atom of sulfur.[21]



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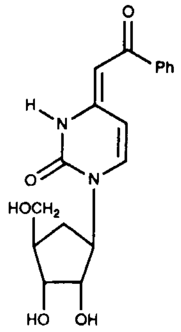
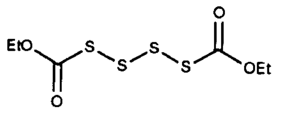


(47)

The initial example of a solvent-dependent sulfur extrusion was observed by Twiss[22] in 1927. The tetrasulfide **48** and trisulfide **49** of ethyl formate, when dissolved in ethanol, slowly deposited sulfur which resulted in the formation of disulfide **50**. The sulfides of ethyl formate decompose on heating to diethyl carbonate, carbon oxysulfide and sulfur. The action of alcoholic ammonia on the sulfides of ethyl formate results in the formation of ammonium *O*-ethylthiocarbonate **51**, ethyl urethane **52** and sulfur.



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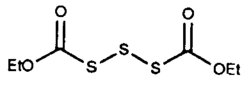

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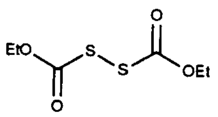

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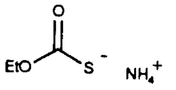

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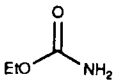
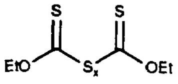


(52)

The sulfides of ethyl thioformate **53** (X = 1–3) and ethyl dithioformate **54** (X = 1–3) decomposed by heat in a similar fashion forming diethyl thiocarbonate **55** and diethyl trithiocarbonate **56**, respectively. This decomposition is only a side reaction for the sulfides of ethyl dithioformate. The sulfides of ethyl thioformate react with alcoholic ammonia to form ammonium xanthogenate **57**, xanthogen amide **58** and sulfur. A side reaction in the decomposition of the sulfides of ethyl dithioformate with ammonia formed ethanethiol, hydrogen sulfide, ammonium thiocyanate and elemental sulfur.



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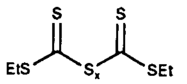

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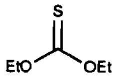

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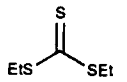

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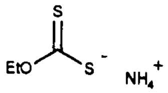

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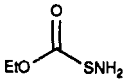
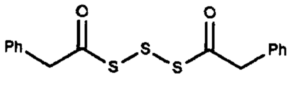


(58)

It has been reported that phenyl acetyl trisulfide **59** readily loses one third of its sulfur to produce the disulfide **60**.[23]



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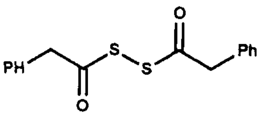
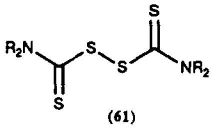


(60)

Dialkylthiuram disulfides **61** decompose in two ways on heating, thioureas **62** or mustard oils **63** are formed;[24] in both reactions one of the products was elemental sulfur. The sodium derivatives of isothiuram disulfides react with iodine to form a mustard oil and sulfur.[25,26] Tetramethylthiuram disulfide **61** (R = Me) when heated to its melting point irreversibly dissociates into *N,N,N′,N′*-tetramethylthiourea **63** (R = Me), carbon disulfide and elemental sulfur.[27] When **61** (R = Me) was treated[28] with a limited amount of chlorine in the form of sulfuryl chloride it gave as products *N,N*-dimethylthiocarbamoyl chloride **64**, sulfur dioxide and sulfur.



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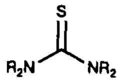
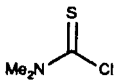


(62)

R_2—NCS

(63)

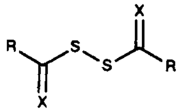


(64)

Disulfides containing α-carbonyls or thiocarbonyls **65** are decomposed by hydroxide anion into (if X = O) thioacids and acids or (if X = S) dithioacids and thioacids (depending on the starting material) and sulfur.[29]

Dixanthogens **65** (X = S and R = OR′) are hydrolysed by potassium hydroxide to form potassium xanthate, carbonate and sulfur. Reaction with potassium hydrosulfide produces potassium thiolate, hydrogen sulfide and sulfur.[30,31] Dixanthogen reacted with anhydrous chlorine to form a sulfenyl chloride **66**.[32]

Benzoyl disulfide **67** was reported to decompose on heating to form benzoic acid, hydrogen sulfide, sulfur and tetraphenylthiophene **68**.[33,34] When the disulfide was treated with ammonia the products were observed to be benzamide, ammonium thiobenzoate and sulfur.



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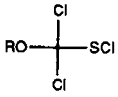

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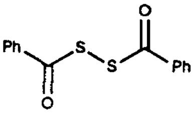

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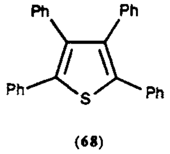
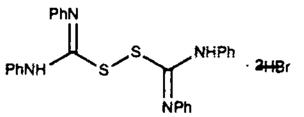


(68)

In 1968, Srivastava and Saleem noted that bis(diphenylformamidino) disulfide dihydrobromide **69** when treated with absolute ethanol extruded sulfur to give bis(diphenylformamidine) sulfide hydrobromide **70**.[35]



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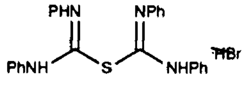


(70)

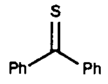
Bis-(diphenylmethyl) disulfide **71** on attempted distillation decomposes[36] into diphenylmethane **72**, thiobenzophenone **73** and sulfur. Trisulfide **74** on distillation decomposes into thiocamphor **75**, thioborneol **76** and sulfur. The primary decomposition products of dibenzyl disulfide **77** were reported to be stilbene, hydrogen sulfide and sulfur.[37]

$Ph_2CH—S—S—CHPh_2$

(71)

$Ph—CH_2—Ph$

(72)



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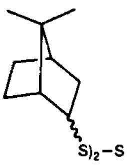

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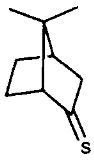
(75)



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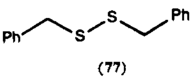
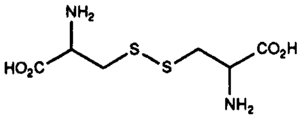


(77)

Cystine **78** reacts[38] with calcium hydroxide in water at room temperature to yield as two of the products 2-methylthiazolidine-2,4-dicarboxylic acid **79** and elemental sulfur; other inorganic compounds are also formed.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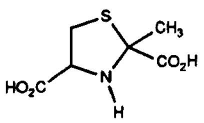
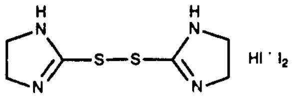

(79)

4,5-Dihydroimidazolyl disulfide periodide **80** on boiling in water evolves iodine and forms three products; 4,5-dihydroimidazolyl sulfide, sulfuric acid and sulfur.[39]

Bis(*N*-phenylbenzimidoyl) disulfide **81** (R = Ph) on refluxing in ligroin for 24 h at 95 °C decomposed[40] by sulfur elimination to bis(*N*-phenylbenzimidoyl) sulfide (R = Ph). The conversion was previously observed[41] at 110°C in the presence of benzoyl peroxide. Treatment of bis(*N*-phenylacetylacetimidoyl) disulfide **81** (R = CH_3) with thiobenzanilide resulted in the formation of *N*-(*N*′-phenylacetimidoyl)thioacetanilide **82** *via* a sulfur elimination.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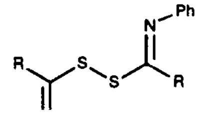
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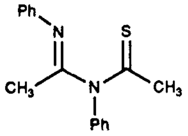
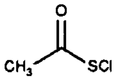

(82)

Addition of acetyl chloro sulfide **83** to unsaturated esters or amides gives mixtures of disulfides, **84** and its isomer. Removal of the acetyl group with alcoholic hydrogen chloride gave the thiol **85** and sulfur.[42]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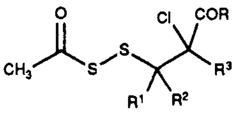
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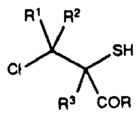
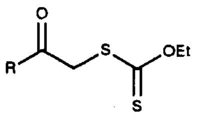

(85)

Bridges and Whitman[43] discovered that oxodithiocarbonates **86** react with sodium hydride with the evolution of hydrogen to give, most likely, the sodium salt **87**. When the reaction mixture was allowed to warm above 0 °C, a rearrangement occurred to form the *β*-oxothionoesters **88** where R = Ph or H. Treatment of *α*-acylthio esters **89** with lithium amide resulted in the formation of the *β*-keto ester **90** *via* a sulfur extrusion.[44]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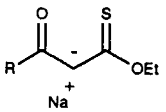
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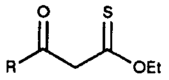
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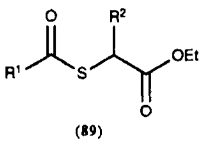
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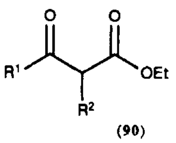
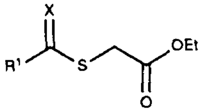

(90)

Reaction of the carbanion, obtained by the treatment of *O*-ethyl 5-ethoxycarbonyl methyldithiocarbonate **91** with LDA at −78 °C, with a carbonyl compound results in the formation of the corresponding α,β-unsaturated ester **92**, the formation of alcohol, sulfur and either carbon disulfide or carbon oxysulfide depending on the starting material.[45,46]

Kambe and Hayashi[47] observed that treatment of diethyl thiocyanatomalonate **93** with base resulted in the formation of diethyl cyanatomalonate **94** *via* a sulfur extrusion.

α-Halo sulfides on pyrolysis at reduced pressure undergo an elimination of hydrogen halide and sulfur to form the olefinic derivatives.[48]



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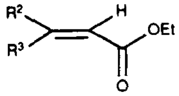

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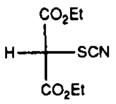
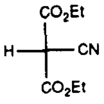


$\mathrm{H{-}C(CO_2Et)_2{-}SCN}$

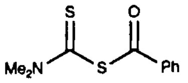
(93)



$\mathrm{H{-}C(CO_2Et)_2{-}CN}$

(94)

The photolysis[49] of benzoic acid *N*,*N*-dimethyl dithiocarbamic anhydride **95** was found to yield a mixture of benzoic acid, sulfur, benzoyl-*N*,*N*-dimethylthiocarbamyl disulfide **96**, tetramethylthiuram disulfide **61** and *N*,*N*-dimethylbenzamide. Under similar conditions, photolysis of benzoic acid *N*-methyldithiocarbamic anhydride **97** gave benzoic acid, sulfur, benzoyl *N*-methylthiocarbamyl disulfide **98**, dibenzoyl disulfide **67**, and *N*-methylbenzamide. The yield of each product depended on the photolysis conditions.



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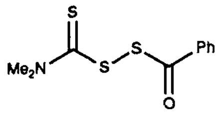

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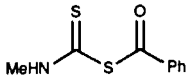

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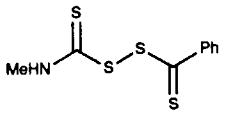
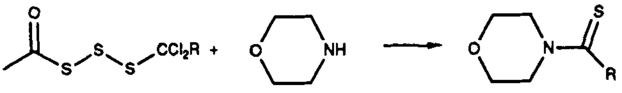
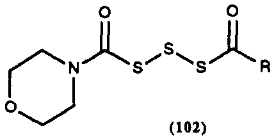


(98)

When studying acetyl α,α-dichloroalkyl trisulfides **99**, it was discovered that, on reaction with morpholine **100**, the only isolated products were the corresponding thioamides **101**. This occurred when R = trichloromethyl and R = *O*-pentachlorophenyl.[50] When the substituent was chlorine, the trisulfide **102** was originally isolated, after treatment with water, but quickly decomposed with loss of sulfur to the thioamide **101**.[51]



(99) **(100)** **(101)**



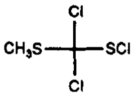
(102)

2.2 C-S_x-Y

Mott and Barany[52] observed that heating (methylthio)dichloromethanesulfenyl chloride **103** at 100 °C resulted mainly in the formation of methyl trichloromethyl sulfide **104** and sulfur.

In 1962 Gösl[53] succeeded in the synthesis of thiohydroxylamine-*S*-monothiocarboxylates **105**. These compounds are unstable and were slowly converted into *O*-alkylthiocarbamates **106** and sulfur at room temperature. The mechanism and rate of the extrusion was extensively studied and was found to be a monomolecular decomposition.[54]

Harpp and co-workers studied[55] the solvent dependent extrusion of sulfur from sulfenic sulfonic thioanhydrides **107**. It was observed that the thioanhydrides in polar solvents extruded *one atom of sulfur (the central sulfur) to give the corresponding* thiosulfonate **108**. The extrusion occurred in the following solvent mixtures; 1:1 acetone-water, methanol, ethanol, glacial acetic acid, 2-propanol, DMF and acetonitrile. Loss of sulfur did not take place under heating in non-polar aprotic solvents. The synthesis of other thioanhydrides of this type was attempted, (e.g. with electron donating groups etc.) but extrusion occurred immediately and only the thiosulfonates and sulfur could be isolated. In contrast, when sulfenyl thiosulfonates were prepared with nitro or chloro groups in the para position of the benzene ring, sulfur could *not* be induced to leave. A mechanism involving a sulfenium ion as intermediate was suggested but it is likely not correct.[3]

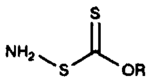


$CH_3S{-}CCl_2{-}SCl$

(103)

$CH_3S—CCl_3$

(104)



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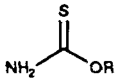


(106)

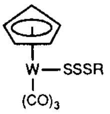
$R^1—SO_2SS—R^2$

(107)

$R^1—SO_2S—R^2$

(108)

The polysulfanotungsten complexes **109**, **110** and **111** were found to spontaneously lose sulfur[56] in solution at room temperature, to form the tungsten thiol **112**; the loss of sulfur was observed to be more rapid in benzene than in acetone. The disulfanes **110** on attempted purification by column chromatography form the sulfane **109** and sulfur.



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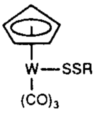

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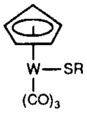

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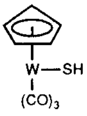
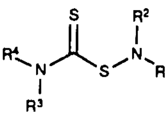


(112)

Thiocarbamylsulfenamides **113** are decomposed readily by heating or on long standing with the formation of a thiourea with loss of sulfur.[57] Alkoxythiocarbonylimino disulfides **114** decomposed with the loss of two atoms of sulfur to form the thionocarbamate **115** on standing at room temperature.[58] When the imino disulfides were prepared in the presence of catalytic amounts of sodium hydroxide or potassium *O*-alkyl xanthate the thionocarbamate was formed directly.



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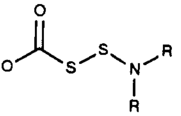

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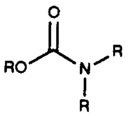
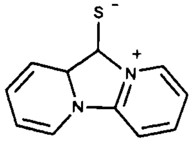


(115)

Dipyrido[1,2-*a*:1′,2′-*c*]imidazolium-11-thiolate **116** when refluxed with hydrobromic acid decomposed to elemental sulfur and dipyrido[1,2-*a*:1′,2′-*c*]imidazolium ion **117**, which could be isolated as the hexafluorophosphate or perchlorate.[59] Edward and Sheffler propose that the mechanism of sulfur loss is a stepwise process where a disulfide ion is first formed, combines to higher polysulfides and ultimately forms elemental sulfur.



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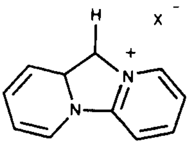
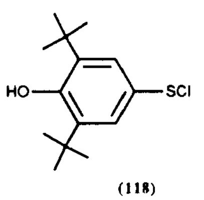


(117)

Pastor[60] discovered that treatment of the sterically hindered sulfenyl chloride, 3,5-di-*t*-butyl-4-hydroxybenzenesulfenyl chloride **118**, with an amine resulted in a dimerization. This occurred with loss of sulfur to give 3,3′,5,5′-tetra-*t*-butyldiphenylquinone **119**.



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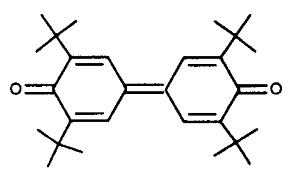
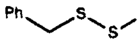


(119)

Benzyl hydrodisulfide[61] **120** and benzhydryl hydrodisulfide[62] **121** reacted with hydroxide ion to produce hydrogen sulfide, the corresponding disulfide and elemental sulfur. With other anions the reaction produces thiols in addition to the products formed with hydroxide.

Benzyl hydrodisulfide **120** and methoxycarbonylsulfenyl chloride **122** reacted to form a mixture, **123**, where the ratio of disulfide (x = 2) to trisulfide (x = 3) was 1:5. Chromatography of the mixture on silica produced a disulfide to trisulfide ratio of 1:2 and sulfur.[63]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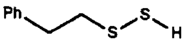
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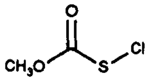
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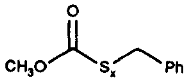

(123)

Wan studied[64] the photolysis of triphenylmethanethiol **124** in benzene and found that it proceeded through a free-radical mechanism with various products produced. These included (major products) hydrogen, bis(triphenylmethyl) sulfide **125**, triphenylmethane and sulfur. The sulfur was possibly formed as a diatomic molecule which combined to form elemental sulfur.

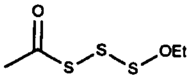
Acyl alkoxy trisulfides **126**, when treated[65] with thiobenzoic acid or *p*-chlorothiobenzoic acid gave a 1:1 mixture of the dibenzoyl trisulfide **127**, diacetyl trisulfide **49** and sulfur. This occurred by loss of a molecule of ethanol to form acetyl benzoyl tetrasulfide **128** which could then rearrange to the trisulfides and sulfur.

$Ph_3C—SH$

(124)

$Ph_3C—S—CPh_3$

(125)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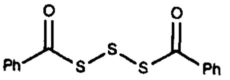
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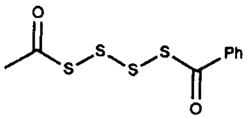
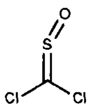

(128)

Rathke[66] studied the hydrolysis of trichloromethanesulfenyl chloride **129** and found that the products were elemental sulfur, carbon dioxide and HCl. It is quickly decomposed by water at 160 °C or in dilute acid solutions.[67] The reaction mechanism was studied and the reaction was proposed to proceed through thiophosgene *S*-oxide **130**.[68]

Chloro-, 1,1-dichloro, and 1,1,1-trichloromethanesulfenyl chloride **131** on treatment with aluminium trichloride form the corresponding chlorinated hydrocarbons **132** and sulfur.[69] The alcohol derivatives of trichloromethanesulfenyl chloride **133** were found to decompose in excess alcohol to produce the carbonate ester, the dialkyl ether, the alkyl chloride, hydrogen chloride, and sulfur.[70]

$CCl_3—S—Cl$

(129)


(130)

$CH_{(3-x)}Cl_x—S—Cl$

(131)

$CH_{(3-x)}Cl_{(x+1)}$

(132)

$CCl_3—S—OR$

(133)

The mercuric salt of trifluoromethanethiol **134** reacted with thionyl chloride to produce mercuric chloride, bis(trifluoromethyl) disulfide **6** and sulfur.[71] Mercury reacts with phenyl tetrasulfide **135** to form mercury bis(phenyldisulfide) **136**. It decomposes[7a] into mercuric sulfide, diphenyl disulfide and sulfur.

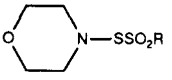
$CF_3S—Hg—SCF_3$ **(134)**

$Ph—S_4—Ph$ **(135)**

$PhSS—Hg—SSPh$ **(136)**

2.3. Y-S_x-Y

Markley and Dunbar observed[72] that aminothiolsulfonates **137** extrude sulfur slowly at room temperature and rapidly at boiling temperatures in polar solvents. The extrusion was observed in acetone, methanol, and 2-propanol to give the corresponding sulfonmorpholides **138**. This reaction is reminiscent of that of the analogous sulfenic sulfonic thioanhydrides **107**.[55] When R = methyl, the conversion also occurred at room temperature in the solid state.



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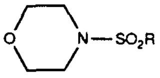
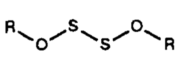


(138)

Sulfanes were observed[73] to decompose slowly into sulfur and hydrogen sulfide at 70.4 °C as 0.2 M solutions in carbon tetrachloride. The decomposition was proposed to occur through a free-radical mechanism.

Thompson[74] found that the primary dialkoxy disulfides **139**, (R = $R'CH_2$) on heating decomposed to the corresponding alcohol, aldehyde and sulfur. Acyclic dialkoxy disulfides **139** are not stable to alumina and decompose with one of the products being elemental sulfur. On standing in solution in chloroform and pyridine hydrochloride, the disulfides decompose with the two major products being sulfur and the sulfite. Dimethoxy disulfide **139** (R = CH_3) when treated with 5,5-dimethyl-1,3-cyclohexanedione **140** and catalytic amounts of potassium *t*-butoxide, gave the dicyclohexyl sulfide **141** along with methanol and sulfur.

Treatment of 1,2-diols with sulfur dichloride results in the formation of polymeric material. Treatment of this material with an alkoxy base results in the formation of starting material, a cyclic sulfite **142**, a cyclic thiosulfite **143** and elemental sulfur.[75]



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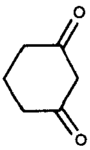

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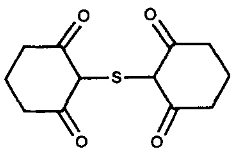

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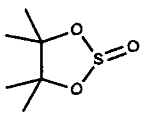

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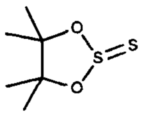
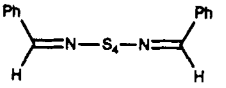


(143)

Kagami and Motoki studied[76] the nucleophilic substitution of dialkoxy disulfides **139** with amines and thiols. Diethoxy disulfide **139** (R = CH_3CH_2), when treated with benzylamine in benzene, gave bis(benzylideneamino) tetrasulfide **144**, ethanol and sulfur. Reaction of diethoxy disulfide with furfurylamine **145** resulted in the formation of the tetrasulfide **146**, ethanol and sulfur. When diethoxy disulfide was treated with thiobenzamide a mixture of benzonitrile, ethanol and sulfur resulted. Reaction with *β*-phenylethylamine **147** or DL-*α*-phenylethylamine **148** formed, after purification by silica gel column chromatography, a thioamide **149** along with sulfur.



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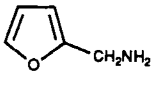

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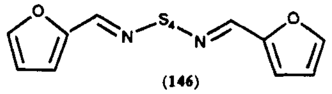

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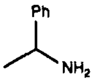

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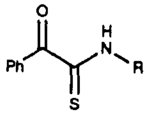


(149)

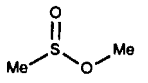
The decomposition of dimethoxy disulfide **139** (R = CH_3) was studied[77] in the presence of a catalytic amount of triethyloxonium fluoroborate **150**. The main decomposition products were found to be sulfur, dimethyl sulfite, methyl methanesulfinate **151**, dimethyl ether and dimethyl sulfate.

Meuwsen and Gebhardt[78] reported the synthesis of the methyl and ethyl sulfoxylate esters **152**. The alkoxide catalyzed decomposition of dialkoxy disulfides **139** leading to the corresponding dialkoxy sulfides and sulfur.

Bis(*N*,*N*-diethylamino) sulfide **153** was reported[79,80] to be hydrolysed into diethylamine, sulfur dioxide and sulfur. Similar results were obtained for corresponding derivatives of dipropyl-, di-*i*-butyl- and di-*i*-amylamine. It was reported that on heating bis(*N*,*N*-diethylamino) disulfide **154** it is converted into sulfide **153** and sulfur.

$\overset{+}{EtO_3}—BF_4^-$

(150)



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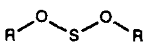

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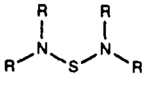

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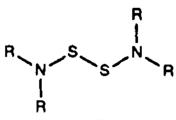
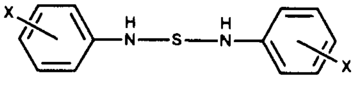


(154)

N,*N*′-Thiodiamines **155** undergo thermal decomposition when heated in benzene at 50 °C for 72 h to form three products; an azobenzene **156**, an arylamine and elemental sulfur.[81] The authors proposed two possible mechanisms to account for the formation of the azobenzene. The first mechanism involved sulfur extrusion from **155** to form hydrazobenzene **157** which could disproportionate to the azobenzene and the amine. This mechanism was discounted as a possibility since under the reaction conditions hydrazobenzene was converted less than 4% to the azobenzene and the absence of absorption peaks for hydrazobenzene in the NMR spectrum. The second mechanism is most likely and first involves a decomposition to the amine and a thionitroso compound **158**. Two thionitroso functionalities could then dimerize forming a four-membered ring which could rearrange to sulfur and the azobenzene. The thionitroso compound was successfully trapped as a Diels-Alder adduct.



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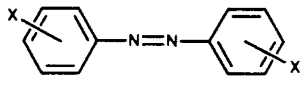

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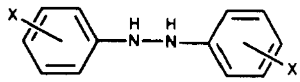

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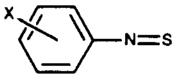
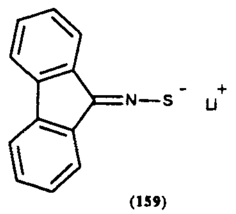


(158)

The anion **159**[82] obtained from the reaction of lithium with the imino disulfide **160** was stable at room temperature in the absence of oxygen. It slowly decomposes in THF with the formation of at least eight compounds as judged by TLC, including sulfur.

The anion **161** obtained from treatment of dimorpholino disulfide **162** with lithium was found to be a stable solid at room temperature under nitrogen.[83] It decomposed rapidly in refluxing tetrahydrofuran giving sulfur and morpholine **100** on work-up. When treated with one equivalent of acetic acid and allowed to warm to room temperature, the expected morpholinethiol **163** decomposed, which eventually resulted in the isolation of sulfur and morpholine.



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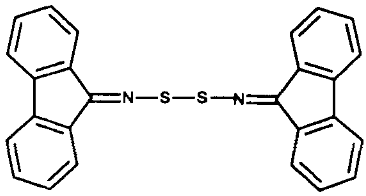

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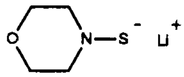

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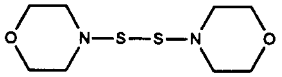

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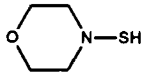
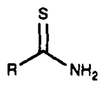


(163)

III. REACTION OF SULFUR COMPOUNDS

Biprotic and monoprotic carbothioamides-thioformamide **164** (R = H), thiobenzamides **164** (R = $C_6H_4R^1$), phenylthioacetamide **164** (R = $CH_2C_6H_5$), quinazoline-4(3*H*)-thione **165**, and pyrrolidine-2(1*H*)-thione **166** condense with ethyl bromocyanoacetate **167** with extrusion of sulfur to form the corresponding olefins **168**, **169** (R = CN) and **170** (R = CN), respectively.[84]

Under basic conditions, ethyl α-chloroacetoacetate **171** reacted with quinazoline-4(3*H*)-thione **165** to form the desulfurized product ethyl α-quinazolineacetate **169** (R = $COCH_3$). Pyrrolidine-2(1*H*)-thione **166** reacted with both ethyl bromomalonate **172** and ethyl α-chloroacetoacetate **171** forming the corresponding unsaturated esters **170** (R = COOEt) and (R = $COCH_3$), respectively, by sulfur extrusion.[85]



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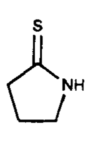

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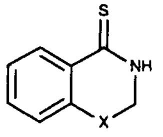

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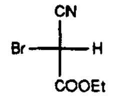

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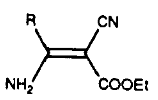

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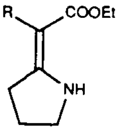

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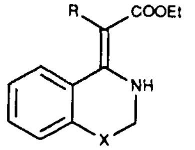

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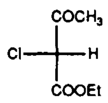

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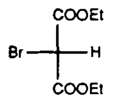
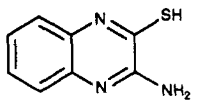


(172)

3-Aminoquinoxaline-2-thione **173** reacts with phenacyl halides to form the reaction products that had lost one atom of sulfur, 2-(quinoxalinyl-3-amino)acetophenones **174**.[86] Quinoxaline-2,3-dithione **175** underwent a similar reaction with the loss of one of the sulfur atoms to form **176**.



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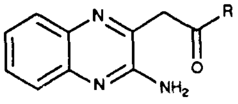

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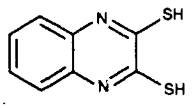

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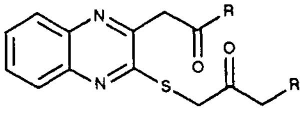
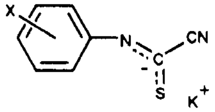


(176)

Mixing equimolar amounts of thioacetamide and ethyl bromocyanoacetate in methanol results in the immediate precipitation of sulfur and the formation of ethyl-α-cyano-β-aminocrotonate **168** (R = CH_3).[87,88] The same product was observed when the reaction was done in the presence of sodium ethoxide or aqueous sodium hydroxide; the reaction gave similar results with other thioamides. Similar sulfur extrusions were observed in the reaction of monoprotic thiocarboxamides [thiobenzanilides, pyrrolidine-2(1*H*)-thione and quinazoline-4(3*H*)-thione] **164**, **165** and **166** forming the unsaturated esters.

Glue and Kay found[89] that anions **177** derived from the addition of potassium cyanide to aryl isothiocyanates **178** are reactive; reaction with ethyl-2-chloroacetoacetate **171** formed 2-(phenylamino)acrylonitriles **179** and sulfur. Similar products were obtained in the reaction of the anions with dimethyl chloromalonate **180** when the mixtures were heated.



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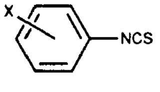

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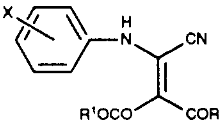

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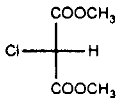
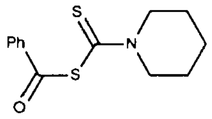


(180)

Boyd,[90] studying ene type reactions involving the transfer of acyl groups, found that *S*-benzoylpiperidine-1-dithiocarboxylic acid **181** and phenyltriazolinedione **182** reacted to give an adduct **183**, whose composition lacked one sulfur atom. It was proposed that the product was formed from the initial adduct through the thiazirinium sulfide **184**. Thiocyanoacetic esters **185** and aldehydes were found to react in moist ether at low temperatures.[91] The major products were the α,β-unsaturated esters and sulfur.



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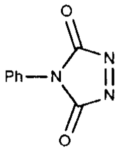

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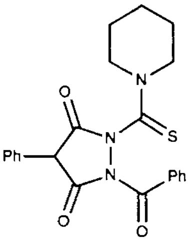

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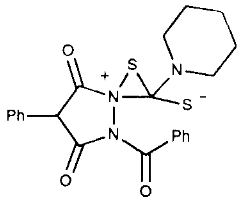

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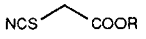
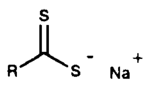


(185)

The oxidative condensation reactions of amines with carbodithioates and xanthates were studied[92] and those which showed sulfur loss are reported below. It was proposed that the initial product of the oxidative condensation of sodium carbodithioates **186** and cyclohexylamine **187** were thioacylsulfenamides **188** which are unstable and decompose immediately with loss of sulfur to form thioamides **189**. Oxidation of a mixture of cyclohexylamine and sodium monothiobenzoate produces an amide **190** probably by the loss of sulfur from the benzoylsulfenamide **191**.

Cyclohexylamine reacted with xanthogen disulfides **70** to form *N*-cyclohexylxanthogenamide **192** and the corresponding xanthogenate **193** with loss of sulfur. Oxidative condensation of cyclohexylamine with sodium trithiocarbonate **194** produced *N*,*N*′-dicyclohexylthiourea likely through the formation of the bis-sulfenamide **195** with immediate loss of sulfur.



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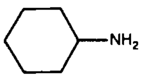

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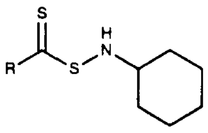

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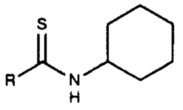

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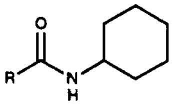
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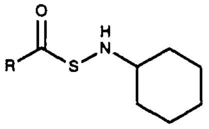
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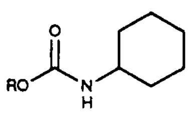
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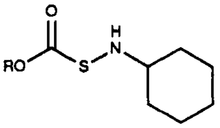
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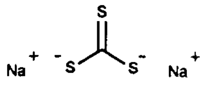
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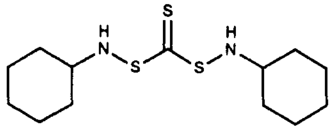
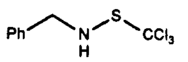

(195)

S-*p*-Toluidinotrichloromethanethiol **196** (R = C_6H_4Me) reacts with an arylamine in inert solvents giving the amine, a tri-s-arylguanidine **197** and sulfur.[93]

S-Aryloxytrichloromethanethiols **198** are obtained by the action of thiocarbonyl tetrachloride **129** on phenols. They are decomposed readily on heating and are slowly hydrolyzed in boiling water and more readily in boiling aqueous alkali to the corresponding phenol. With excess arylamine in inert solvents the triarylguanidine hydrogen chloride **197** is formed along with sulfur.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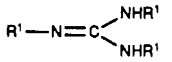
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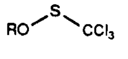
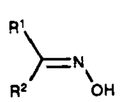

(198)

In 1931 Gheorghiu studies the reaction of isothiocyanates **199** and oximines **200**.[94] On prolonged boiling in an inert solvent decomposition to sulfur and the carbamate **201** occurs. The reaction was reexamined and the urea **202** was found to be the major product of the decomposition, with the carbamate and the other products formed in varying yields.[95] The mechanism of the reaction was studied and was proposed to proceed through a diatomic sulfur intermediate.[96]

$Ph{-}N{=}C{=}S$

(199)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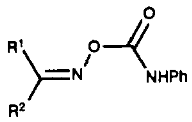
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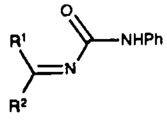
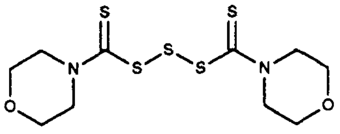

(202)

In 1943 Blake[97] studied the reaction of carbon disulfide with diamino sulfides **153**. Aliphatic diamino sulfides reacted with carbon disulfide to form tetraalkylthiuram disulfides **61** and sulfur. Dimorpholino disulfide **162** reacted with carbon disulfide to give the thiuram trisulfide **203** and sulfur. *N*-Cyclohexyl-2-benzothiazolesulfenamide **204** was found to give a mixture of 2-mercaptobenzothiazole **205**, cyclohexyl isothiocyanate **206** and sulfur, on reaction with carbon disulfide.



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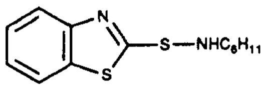

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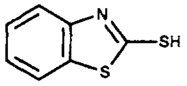

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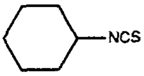
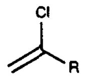


(206)

Reaction[98] of equimolar amounts of α-chloromethyl acrylate **207** (R = $COOCH_3$) and trimethylamine-hydrogen sulfide complex **208** in excess liquid hydrogen sulfide results in the formation of five identified products, trimethylamine hydrogen chloride, sulfur, α-mercaptomethyl propionate **209** (R = $COOCH_3$), di(α-carbomethoxymethyl) trisulfide **210** (R = $COOCH_3$) and di(α-carbomethoxymethyl) disulfide **211** (R = $COOCH_3$). The trisulfide on attempted distillation decomposes into the disulfide and sulfur. Similar results were obtained with α-chloroacrylonitrile **207** (R = CN) which formed trimethylamine hydrogen chloride, sulfur, α-mercaptopropionitrile **209** (R = CN) and a higher boiling mixture, which likely contained the disulfide and the trisulfide.

β-Chloro-α-(acetylthio)propionitrile **212** reacted with dimethylamine to form acrylonitrile **213**, *N*,*N*-dimethylacetamide **214**, dimethylamine hydrogen chloride and sulfur. The possibility of the expulsion of atomic sulfur was considered. Attempts to trap the sulfur atom by having an olefin present during the reaction were unsuccessful.



(207)

$H_2S\text{-}N(CH_3)_3$

(208)

$RCH_2CH_2\text{—}SH$

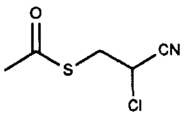
(209)

$RCH_2CH_2\text{—}SSS\text{—}CH_2CH_2R$

(210)

$RCH_2CH_2\text{—}SS\text{—}CH_2CH_2R$

(211)



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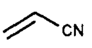

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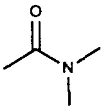
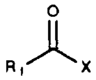


(214)

High-pressure reduction[99] of fluorinated carbonyl compounds, acids **215** (X = COOH) or acid chlorides **215** (X = Cl) and aldehydes **216** (R = H), ketones **216** (R = fluoroalkyl), with hydrogen sulfide results in the formation of the fluorinated thiols **217** and **218**, respectively; also formed as by-products are water and sulfur.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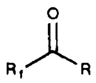
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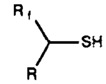
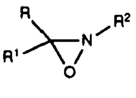

(218)

Oxaziridines **219** were found to be deoxygenated[100] by thiourea, potassium thiocyanate, potassium ethylxanthate and triphenylphosphine sulfide. The reagents did not exhibit similar capabilities and thus specific examples were studied. In all reactions one of the proposed products was elemental sulfur and in several cases the sulfur was isolated.

Oxaziridines **219** were observed to react with carbon disulfide forming elemental sulfur.[101] When 2-*N*-alkyl- or 2-cycloalkyloxaziridine reacted with carbon disulfide the corresponding isothiocyanates were obtained in almost quantitative yield along with the corresponding carbonyl compound and sulfur. Oxaziridines reacted with phenyl isothiocyanate. Sulfur was formed as one of the products only when the *N*-substituent was a *t*-butyl group. When R^2 = isopropyl, the cyclic compound **220** was isolated and on heating found to decompose into two isothiocyanates, *N*-isopropyl-*N*′-phenylcarbodiimide **221** and sulfur.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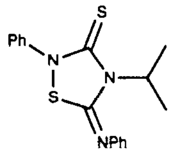
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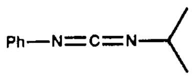
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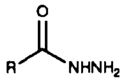
IV. REACTION OF SULFUR CHLORIDES

Acylhydrazines **222** reacted with two equivalents of disulfur dichloride[102] in refluxing solvent to form the corresponding carboxylic acid chlorides, hydrogen chloride, nitrogen and sulfur. Wenschuh and Ritzel studied[103] the reaction of disulfur dichloride and sulfur dichloride with alkoxy(aryloxy)silanes and stannanes. The sulfur chlorides were observed to react with alkoxytrimethylsilanes **223** to produce trimethylsilyl chloride, an alkyl halide, sulfur and dialkoxysulfane **224**.

Thioketones can be prepared by the reaction of hydrazones **225** and sulfur dichloride.[104] The reaction is proposed to proceed through a thioxothioketone **226** intermediate which could collapse to the thioketone and sulfur.

The metal salts of monobasic organic acids react smoothly with disulfur dichloride in neutral solvents.[105,106] The products were found to be the metal chloride and an unstable derivative **227** where the sulfur had replaced the protons. These derivatives were observed to decompose with the formation of the organic anhydride **228**, sulfur dioxide and free sulfur.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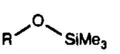
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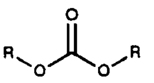
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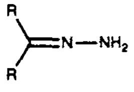

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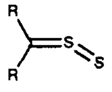

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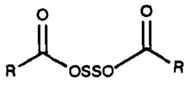

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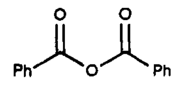

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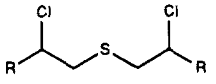
β,β′-Dichloroethyl sulfide **229** (R = H) is formed when disulfur dichloride absorbs ethylene.[107] The other product formed in the reaction with sulfur. The chemistry of β,β′-dichloroethyl sulfide, better known as mustard gas, has been reviewed.[108] Homologues of ethylene, propylene and butylene react in a similar way to form the *bis-β,β′*-dichloroalkyl sulfides **229** (R = CH_3) and (R = CH_3CH_2), respectively.[109]

The interaction of disulfur dichloride and organic acid amides was studied by Naik.[110] He observed that the reaction occurred to form a diamide sulfide **230** and sulfur. Disulfur dichloride was also reported to react with potassium phthalimide **231** to form the diimino disulfide **232**, potassium chloride and sulfur. This observation was later proven to be incorrect by Kalnins.[111]



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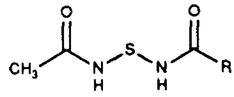

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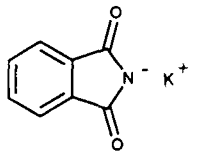

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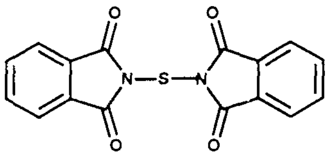
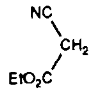


(232)

Naik[112] studied the reaction of disulfur dichloride with cyanoacetic ester **233**, malonic ester **234** and their sodium derivatives **235** and **236**, respectively. Ethyl dicyanosuccinate **237** was the product formed in the reaction from both the cyanoacetic ester and the sodium analogue. Malonic ester formed tetraethyl ethylenetetracarboxylate **238** where the sodium salt formed tetraethyl ethanetetracarboxylate **239**. A separation of sulfur occurred in all the reactions.



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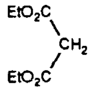

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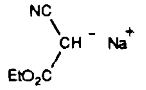

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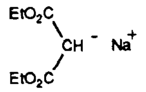

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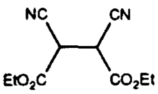

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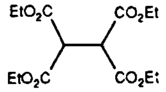

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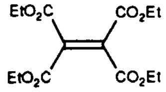


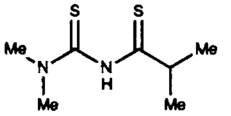
(239)

Metal thiocyanates react with disulfur dichloride to produce sulfur dithiocyanate $S(SCN)_2$, the metal chloride and sulfur.[113]

V. MISCELLANEOUS

1,1,5,5-Tetramethyldithiobiuret **240**, when subjected to air oxidation[114] over a long time, was found to decompose into seven identified compounds and sulfur.

In 1955, Bähr and Schleitzer reported[115] the synthesis of the stable sodium salt of cyanodithioformic acid **241**. The stabilized salt with three molecules of DMF was found to spontaneously dimerize at 25 °C to form disodium dithiolatomaleonitrile **242** and elemental sulfur. The methyl ester **243** also dimerized to give bis(methylthio)maleonitrile **244** and sulfur. Reaction of the ester with catalytic amounts of anions, especially chloride and cyanide ion, led to the dimerized product, **244**, and sulfur.[116]



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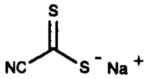

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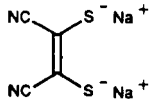

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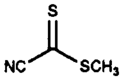

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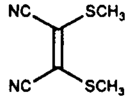


(244)

Ethylammonium dithiocarbamate **245** was reported[117,118] to react with iodine in two ways; both reactions resulted in the formation of elemental sulfur as one of the products. Bis(azidothiocarbonyl) disulfide decomposes into thiocyanogen, nitrogen and sulfur.[119]

Boron sulfides on exposure to moisture were instantly hydrolyzed to a mixture of boric acid and sulfur with loss of hydrogen sulfide (Scheme 1).[120]

$$B_2S_3 + 6H_2O \longrightarrow 3H_3BO_3 + 3H_2S + 2\,\text{'S'}$$

Scheme 1

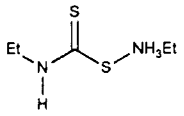
Thiosulfate ion on the addition of dilute acid forms elemental sulfur, sulfur dioxide and water (Scheme 2).[121]

$$SO_4^{2-} + H^+ \longrightarrow H_2O + SO_2 + S_8$$

Scheme 2

Thiols or their sodium salts are oxidized by thionyl chloride to disulfides with the formation of water, sulfur and hydrogen chloride or sodium chloride depending on the starting material.[122]

N-Sulfinylaniline **246** reacts with hydrazobenzene **157** to form azobenzene **156** in addition to sulfur and water.[123]



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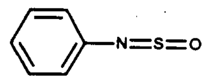


(246)

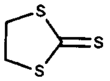
A solution of sulfur dioxide or sodium hydrogen sulfite in boiling cyclohexylamine **187** reacted with hydrogen sulfide to form a mixture which contained elemental sulfur.[124]

A method of producing hydrogen iodide gas is the reaction of hydrogen sulfide with iodine. The other product formed in the reaction is elemental sulfur.

Thiocyanogen cyanide $S(CN)_2$ reacted[125] with hydrogen sulfide with one of the products being sulfur.

Sulfur tetrafluoride reacts with inorganic sulfides resulting in the formation of the corresponding fluorides and sulfur.[126] Sulfur tetrafluoride (SF_4) also has been observed to react with thiocarbonyl compounds to produce the fluorides and sulfur.[127] Ethylene trithiocarbonate **247** reacts smoothly with sulfur tetrafluoride at 100 °C to form 2,2-difluoro-1,3-dithiolane **248** in 82% yield along with sulfur in 90% of the theoretical amount.

Thiuram sulfides **249** react with SF_4 forming the dialkyltrifluoromethylamines **250** and sulfur. Carbon disulfide reacts with SF_4 at 450 °C in the presence of arsenic trifluoride catalyst to form carbon tetrafluoride and sulfur.



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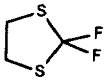

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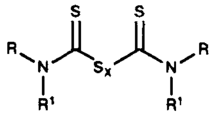

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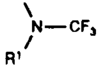

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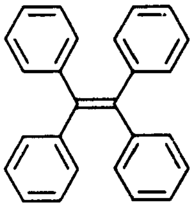
VI. THIOCARBONYLS, OXIDIZED SULFUR MOLECULES AND RELATED COMPOUNDS

Thiocarbonyl compounds undergo reactions in ways similar to the oxygen analogues but in most cases they are more reactive. A reaction observed for some thiocarbonyl compounds is a dimerization accompanied by sulfur extrusion;[128] examples of this process found in the literature are described below.

Thiobenzophenone **73** when heated at 160–170 °C dimerized with the loss of two atoms of sulfur to form tetraphenylethylene **251**.[129] At high temperatures, diethyl 4-thiochelidonate **252** is transformed into tetraethyl 4,4′-dipyrylenetetracarboxylate **253**.[130] The reaction was found to occur slowly at room temperature and was accelerated by light.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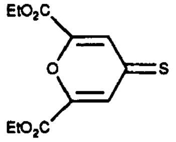

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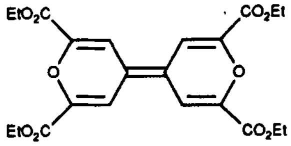
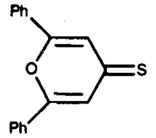


(253)

2,6-Diphenyl-4-thiopyrone **254** (for further reactions involving this functionality see structures **275**, **441**, **515**, **516** and **517**) reacted in a similar fashion to **73** to form 2,2′,6,6′-tetraphenyl-4,4′-dipyrylene **255**.[131] 2,6-Diphenyl-1,4-dithiopyrone **256** when heated at 145 °C formed tetraphenyldithiopyrylene **257**.[132]



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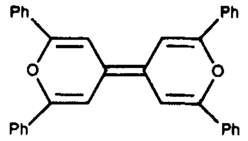

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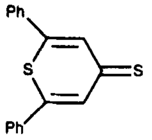

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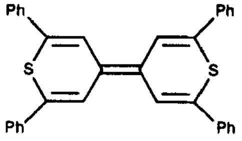
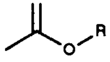


(257)

On irradiation, *O*-alkyl or *O*-aryl thioacetates **258** were found to dimerize with the loss of two atoms of sulfur to form the corresponding alkene **259** in a *cis* to *trans* ratio of three to two.[133] Further study[134] showed that the sulfur produced adds to 1,2-dimethylenecyclohexane **260** to form three products: 1,4,5,6,7,8-hexahydrobenzo[*d*][1,2]dithiin **261**, 1,3,4,5,6,7-hexahydrobenzo[*c*]thiophene **262** and 4,5,6,7-tetrahydrobenzo[*c*]thiophene **263** although in very low yields. The 1,2-dithiin could be formed as a Diels-Alder adduct in the reaction of singlet diatomic sulfur and the diene.



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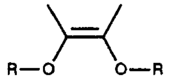

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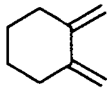
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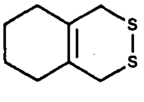

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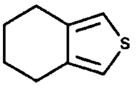

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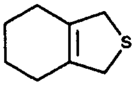
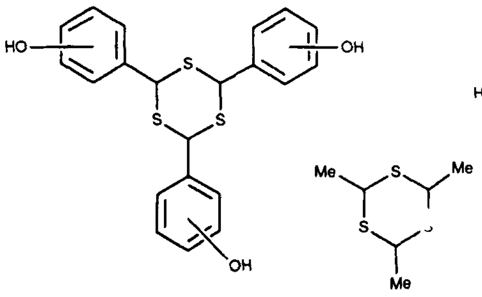
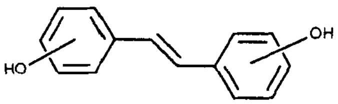


(263)

Until 1987, thioaldehydes were isolated in most cases as trimers which are relatively inert. The trimers of the hydroxythiobenzaldehydes **264**, when heated above their melting points, were found to decompose[135] to the respective hydroxystilbenes **265** and sulfur. Chlorination of *s*-trithiane **266** with disulfur dichloride[136] resulted in the isolation of α,α′-dichlorodimethyl sulfide **267**; also formed were carbon disulfide, hydrogen chloride and sulfur. Reaction with the sulfide as the solvent results in the isolation of the disulfide **268** with the only product being sulfur.[137] Sulfur dichloride on reaction with *s*-trithiane forms similar products; the sulfide and sulfur.[138]



(264) **(266)**



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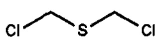

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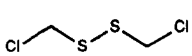
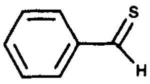


(268)

It was previously reported that dry distillation of thiobenzaldehyde (likely as the trimer) **269** resulted in the formation of stilbene **270** and sulfur.[139]

The first stable thioaldehyde, tris(trimethylsilyl)ethanethial **271**, on irradiation[140] was found to rearrange and lose sulfur and form the diene **272**. This transformation likely occurs through a free-radical mechanism possibly involving a thiirane intermediate.



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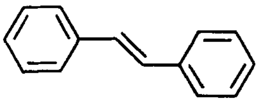

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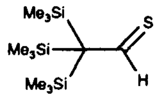

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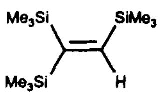
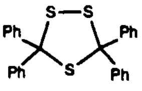


(272)

Thiobenzophenone **73** (R = H) is easily air oxidized[141] at ambient temperature, benzophenone being the major product. A new compound containing three sulfur atoms, **273** (for further chemistry involving this functionality see structures **449** and **537**), was also formed along with sulfur and sulfur dioxide.[142] The oxidation was also observed in the absence of light. For other thioketones, 4,4′-dimethoxythiobenzophenone **274** (R = CH_3O), 4,4′-bis(*N*,*N*-dimethylamino)thiobenzophenone **274** (R = Me_2N), xanthione **275** (X = O) and thioxanthione **275** (X = S), sunlight was necessary for air oxidation to occur. The oxidation produced sulfur, sulfur dioxide and the corresponding ketone.[143]



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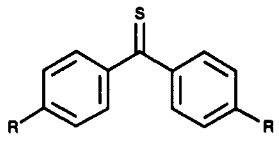

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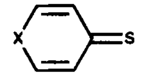
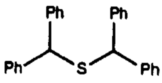


(275)

Thioketones are cleanly converted to the corresponding ketones with an alkoxy base and a catalytic amount of a halogen; sulfur is also formed in the reaction.[144]

Thiobenzophenone when irradiated at 3150 Å in cyclohexane for 20 days formed dibenzhydryl disulfide **71**, dibenzhydryl sulfide **276**, benzhydryl cyclohexyl sulfide **277** and sulfur.[145]

Organic azides reacted[146] with thiobenzophenone to form nitrogen, sulfur and a Schiff base **278**. Hydrogen sulfide reacts with thiobenzophenone to form diphenylmethane and sulfur.[147]



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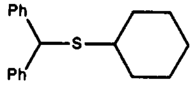


(277)

$Ph_2C{=}N{-}Ph$

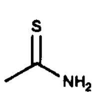
(278)

Hansen and Petersen[148] found that treatment of 4-pyridyldithiocarbamic acid with an amine in methanol, ethanol or chloroform resulted in the formation of elemental sulfur and substituted thioureas.

Thioacetamide **279** reacts[149] with iodine in water to form acetic acid, ammonium iodide, hydrogen iodide and sulfur. In the presence of ethanol the identified products were ethyl acetate, ethyl iodide, ammonium iodide and sulfur.

2,3,7,8-Tetrathiospiro[4.4]nonane 2-sulfide **280** readily loses a sulfur atom, on heating, to form dithiolane **281**.[150]

N-Thionitrosodimethylamine **282** was found[151] to be an unstable compound that decomposes at room temperature with the formation of dimethyl sulfide and sulfur as the two major products. It was also decomposed by acidic materials with the formation of sulfur. Basic material showed no effect on the nature or rate of decomposition.



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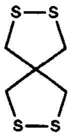

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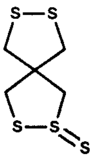

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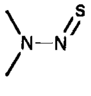
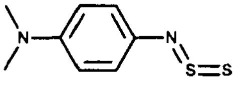


(282)

Barton studied[152] the preparation and properties of *p*-(*N*,*N*-dimethylamino)-*N*-thiosulfinylaniline **283**. Pyrolysis of **283** at 200 °C was found to result in the formation of 4,4′-bis(*N*,*N*-dimethylamino)azobenzene **284** and sulfur. 2,4-Di-*t*-butyl-6-methyl-*N*-thiosulfinylaniline **285** undergoes a number of transformations which result in sulfur extrusion; reaction of **285** with an equimolar amount of bromine formed the corresponding sulfur diimide **286** and sulfur.[153] Irradiation[154] of **283** gave the sulfur diimide **286**, the aniline **287** and sulfur.



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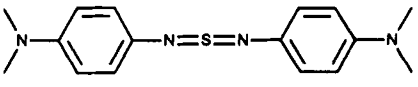

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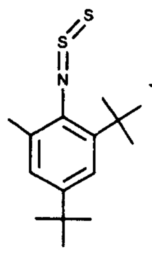

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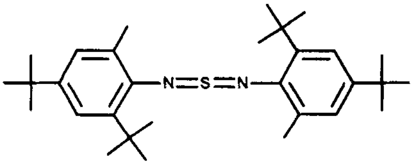

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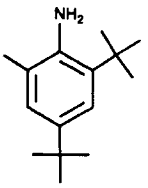
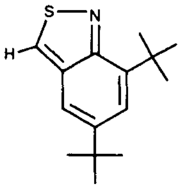


(287)

Thermolysis of **283** in refluxing benzene gives the 2,1-benzisothiazole **288**, the corresponding aniline **287** and sulfur. The thermolysis of 2,4,6-tri-*t*-butyl-*N*-thiosulfinylaniline **289** forms the aniline **290**, sulfur and 4,6-di-*t*-butyl-3(*H*)-1,2,3-benzisothiazole 2-oxide **291**.



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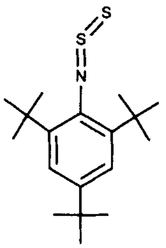

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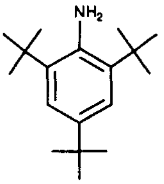

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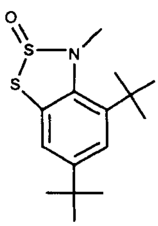
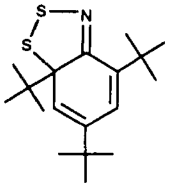


(291)

Oxidation of the equilibrium mixture of 5*H*-1,2,3-dithiazole **292** and 2,4,6-tri-*t*-butyl-*N*-thiosulfinylaniline **289** by *m*-chloroperoxybenzoic acid gave **293** as one of the products.[155] It was found to undergo thermal decomposition in refluxing benzene to form three isolated products **294**, **291** and 2,4,6-tri-*t*-butylaniline **290**. The formation of **291** can be accounted for by the sulfur extrusion of the compound formed from the 1,2-oxygen shift from **293**.



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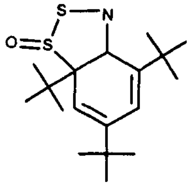

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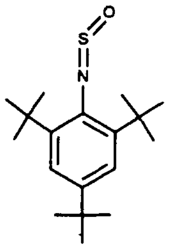


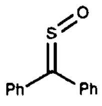
(294)

In many instances, oxidized thiocarbonyl compounds can, under both thermal and photolytic conditions, undergo a sulfur extrusion; the product of such an extrusion is usually the carbonyl analogue. Oxidized sulfur in the form of sulfoxides can also extrude an atom of sulfur to form carbonyl compounds.

Photolysis of thiobenzophenone *S*-oxide **295** quantitatively yields benzophenone and sulfur at room temperature.[156] Photolysis at 85 °K gives two intermediate species which are thermally unstable and decompose into benzophenone and sulfur on warming. Thiobenzophenone *S*-oxide underwent a thermal decomposition in solution at 130 °C, in the absence of oxygen, to form benzophenone and sulfur along with small amounts of thiobenzophenone and sulfur dioxide.[157] Thioacetamide *S*-oxide decomposes into thioacetamide and sulfur.[158] Similar results were obtained for the *N*-substituted[159] and *N*,*N*-disubstituted[160] thioacetamide *S*-oxides.

The lachrymatory factor in onions was determined to be propenethial *S*-oxide which decomposed after several hours at room temperature to sulfur and propenal.[161]

The triethylammonium salts of thiosulfinic acids **296** on treatment[162] with acid undergo a fast conversion to the thiosulfinates **297** by sulfur loss. An intermediate in the conversion was the sulfenic acid which in one case was isolated.



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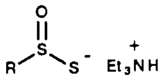

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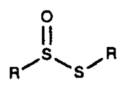
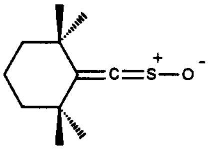


(297)

The gas phase thermolyis[163] of 1,1,3,3-tetramethyl-2-cyclohexanethione *S*-oxide **298** produces a large number of compounds including 1,1,3,3-tetramethyl-2-cyclohexanethione **299** from desulfurization.



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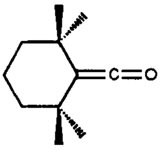
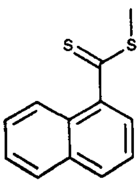


(299)

Oxidation of methyl dithio-1-naphthoate **300** results in the formation of a 1:1 mixture of the *S*-oxide **301** and its epimer. When the mixture was irradiated,[164] a mixture of 70% of *S*-methyl thionaphthoate **302**, 52% free sulfur and 20% recovered starting material is observed.



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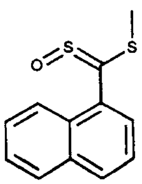

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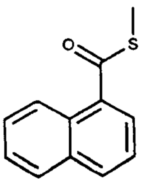
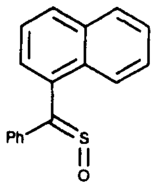


(302)

Schlessinger and Schultz studied[165] the photodesulfurization of the sulfine **303** and found that it could epimerize. Both **303** and its epimer formed a dimeric species, on irradiation, which was not isolated. The dimer decomposed into the corresponding ketone **304** and sulfur.



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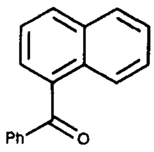
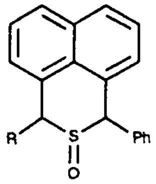


(304)

On sensitized irradiation, 1,3-dihydro-1,3-diphenylacetonaphtho[5,6-*cd*]thiopyran 2-oxide **305** (R = Ph) was observed to be photodesulfurized.[166] The only product from both the *cis* and the *trans* isomer was 1-benzoyl-8-benzylnaphthalene **306**. The desulfurization was reexamined and proposed to proceed through sulfine intermediates **307** and **308** which could be isolated.[167]



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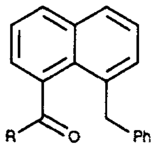

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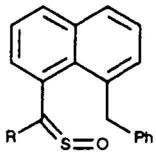

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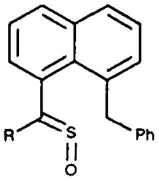
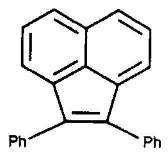


(308)

Photodesulfurization can also be used to convert sulfoxides into aldehydes.[168] The monosubstituted acetonaphtho[5,6-*cd*]thiopyran 2-oxides **305**, (R = H) when irradiated, form the aldehydes **306** when the substitution is methoxy, phenyl or ethyl.

Decomposition of the sulfoxide **305** (R = Ph) at 100 °C gave the hydrocarbon **309** and the episulfide **310**. Heating at 120 °C quantitatively converts the episulfide to the hydrocarbon and sulfur.[169]



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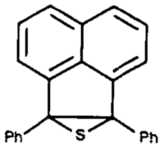
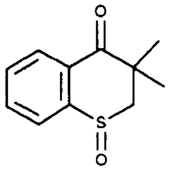


(310)

The irradiation of 3,3-dimethylthiochroman-4-one 1-oxide **311** formed three products, isobutyrophenone **312**, benzoic acid and, by loss of sulfur, 2-methyl-2-benzoylpropanol **313**.[170]



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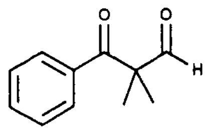

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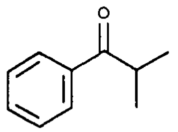
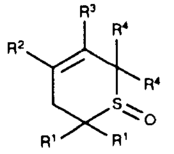


(313)

Irradiation of dihydro-2*H*-thiopyran *S*-oxides **314** in benzene leads to the α,β-unsaturated aldehydes **315**, as mixtures of their E/Z isomers, *via* desulfurization.[171] Deuterium labelling showed that the reaction involved an intramolecular hydrogen transfer.



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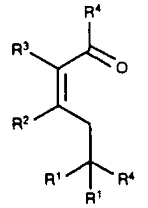
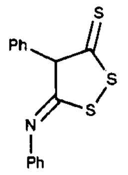


(315)

The reaction of phenyl or methyl isothiocyanate sulfides **316** with certain aliphatic amines in refluxing chloroform forms elemental sulfur, 1-methyl- or 1-phenyl-3-alkylthioureas **317** and 1,3-diphenyl-5-alkyl-2,4-dithiobiurets **318**.[172]



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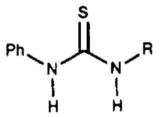

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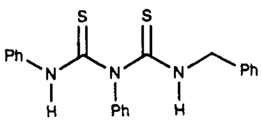
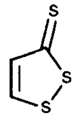


(318)

Trithiones **319** are hydrolysed by alkali to form sulfide, sulfur and an α-alkyl- or α-arylacetoacetic acid which can undergo further hydrolysis.[173] 1,2-Dithiacyclopent-4-ene-3-thione **319** reacts[174] with hot aqueous sodium hydroxide to form a formate, hydrogen sulfide and sulfur. 3*H*-1,2-Benzodithiole-3-thione **320** reacts[175] with diphenyldiazomethane **321** to form the corresponding 4,5-benzo-3-diphenylmethylene-1,2-dithiole **322**.



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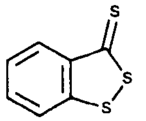
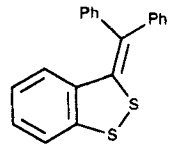


(320)

Ph_2CN_2

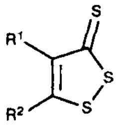
(321)



(322)

Compounds with the *S*-imide structure are susceptible to sulfur extrusion under a variety of conditions. In all cases the extrusion was proposed to proceed through a three-membered ring intermediate.

Substituted 3*H*-1,2-dithiole-3-thiones **323** react with *N*,*N*-dichlorosulfonamides **324** (R = SO_2Ar), *N*,*N*-dichlorourethanes **324** (R = COOAlk), *N*,*N*-dichloro-*N'*,*N'*-dimethylsulfamides **324** (R = $SO_2N(CH_3)_2$), *N*,*N*-dichlorobenzamides **324** (R = COAr) and *N*-chlorobenzamides **324** (R = COAr). The product is the corresponding *N*-substituted 3-imino-1,2-dithiole **325**.[176,177]



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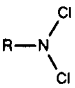

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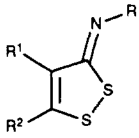

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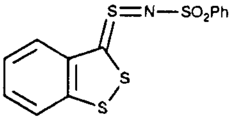
Treatment[178] of the trithiolane **320** with chloramine-B or other similary substituted amines in methanol results in the formation of thiocarbonyl imides **326**. When heated to reflux in various solvents or left standing at room temperature for a month without solvent, a rearranged imine (*N*-benzenesulfonyl-1,2-benzothiole-3-imine) **327**, was obtained. In methanol, the sulfur was isolated in 39% yield. The kinetics of the transformation were studied and found to be first order. It was concluded that the rearrangement took place through the initial ring closure to a three-membered thiaziridine ring **328** followed by loss of sulfur.



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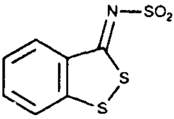

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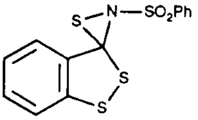

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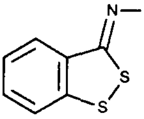


(329)

Treatment of **320** with an equimolar amount of acyl chloride results in the immediate precipitation of elemental sulfur; the imine **326** was isolated.[179]

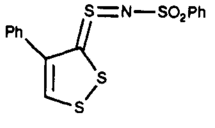
On reaction of **320** with catalytic amounts of inorganic sulfides, thiols and thioacetic or thiobenzoic acid results in the formation of the rearranged product **327** along with benzodithione, sulfonamide and elemental sulfur.[180]

The *N*-phenylsulfonyl thione *S*-imide of 4,5-benzo-1,2-dithiole-3-thione **326** was found to be desulfurized at its decomposition temperature or on the addition of a catalytic amount of acid.[181] The *N*-phenylsulfonyl thione *S*-imide of 4,5-benzo-1,2-dithiole-3-thione **326** reacts with primary or secondary amines, at room temperature, to give

N-benzenesulfonyl-4,5-benzo-1,2-dithiol-3-imine **327**, the amine exchange product **329**, the benzenesulfonamide, elemental sulfur and a small amount of the trithiole **320**.[182]

Treatment of the *S*-imide of 4-phenyl-1,2-dithiole-3-thione **330** with aniline results in the formation of elemental sulfur, the amine exchange product **331** and benzenesulfonamide.

The *S*-tosylimide **332** of chloramine-T and the hindered thioketone **333** on irradiation[183] formed the tosylamine by loss of sulfur.



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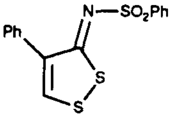

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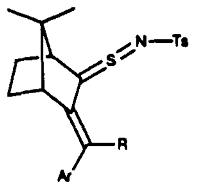

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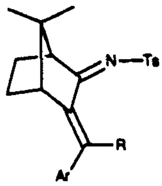
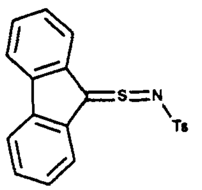


(333)

Fluorenethione *S*-tosylimide **334** reacted with Grignard reagents to form as one of the products the direct addition compound **335**.[184] Sulfur extrusion from **335** accounted for the formation of **336**. The extrusion was also observed in an independent reaction.



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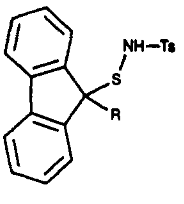

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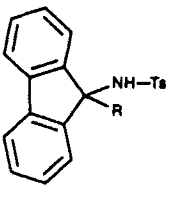
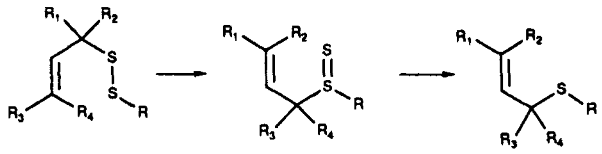


(336)

Thiosulfoxides are the proposed intermediates in several reactions that produce sulfur as one of the products.[185] Reaction of carbon disulfide with **337** forms the sulfide, hydrogen thiocyanate and sulfur.[185] Allylic disulfides **338** rearrange[186] at room temperature to give either disulfides or sulfides. It was proposed that thiosulfoxides **339** are intermediates in the rearrangement. The least substituted allylic disulfides expel the thiono sulfur spontaneously at 25 °C to yield the sulfides **340**.

$R_2C{-}S{=}NH$

(337)



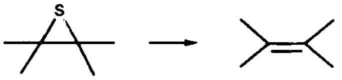
(338) (339) (340)

Thiosulfoxides **226** are also the proposed intermediates when the conversion of sulfoxides into sulfides is conducted using a form of sulfur transfer reagent. It has been proposed that the thiosulfoxide is originally formed and then collapses into the sulfide and elemental sulfur. The reduction of sulfoxides to sulfides has been comprehensively reviewed by Oae[187] and Block.[188]

VII. RINGS

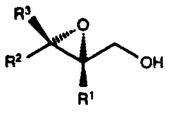
7.1. *Three-Membered Rings*

Thiiranes (or episulfides) are the sulfur analogues of oxiranes (epoxides) and they will undergo many of the normal reactions observed for oxiranes, such as nucleophilic ring opening or olefin formation with phosphorus nucleophiles. However, thiiranes will extrude sulfur under various conditions to form elemental sulfur. An analogous extrusion reaction of oxygen is not found in the chemistry of oxiranes. In many examples of sulfur extrusion, thiiranes are the proposed intermediates; for example, sulfur loss takes place in thiepins with the formation of benzene derivatives; these reactions have been included in the appropriate sections. Below are the examples of direct sulfur extrusion from thiiranes. A reaction common to many thiiranes is thermal decomposition to olefin and elemental sulfur (Scheme 3).



Scheme 3

Several examples are reported in the literature and include 2-heptylthiirane,[189] 2-phenylthiirane or styrene sulfide,[190] acylthiomethylthiiranes,[191] cyclohexene sulfide,[192] 2,3-tetramethylenethiirane,[193] tetrachlorothiirane, diarydichlorothiiranes[194] and other aryl substituted thiiranes.[195] All these thiiranes were observed to form the corresponding olefins and sulfur. At room temperature *trans*-stilbene sulfide was found to decompose into sulfur and *trans*-stilbene.[196] 2,2′-Epithioadamantyladamantanes[197] when treated under a variety of conditions eliminated sulfur to form the corresponding alkenes. Recent examples were observed by Gao and Sharpless[198] who found that 2,3-epithio alcohols **341** decomposed to cinnamyl alcohols **342** and sulfur on standing and by Ando[199] who observed that 1,2,3-butatriene episulfides **343** are desulfurized thermally to the corresponding trienes **344**.



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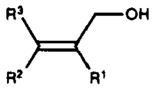

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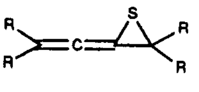

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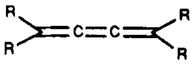
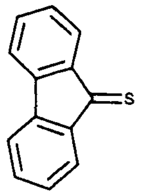


(344)

There are several examples in the literature where attempts to prepare thiiranes resulted only in the formation of olefins and sulfur. These include the reaction of epoxides with various sulfurating agents.[200] For example stilbene oxide reacted with thiourea to form stilbene, sulfur and urea. Another case are the reactions of diazo compounds with thioketones.[201] For example, thiofluorenone **345** and diphenyldiazomethane **321** reacted to form the substituted alkene **346**.



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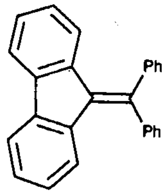
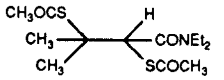


(346)

Treatment of *N*,*N*-diethyl-2,3-bis(thioacetyl)-3-methylbutyramide **347** with aqueous alkali did not give the expected episulfide **348**, but instead gave *N*,*N*-diethyl-3,3-dimethylacrylamide **349** in a 65% yield and an 80% yield of elemental sulfur.[202]



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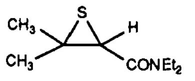

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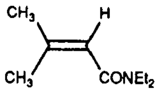
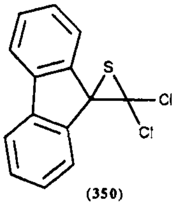


(349)

The thermal decomposition to olefin and sulfur is often proposed to be simply a cheletropic loss of one atom of sulfur. A recent study by Lutz and Biellmann[203] has indicated that this may not be the case as the loss of sulfur from the decomposition of **350** was not found to have first-order kinetics; thus a more complex mechanism may be involved, perhaps with a bridged sulfur species.

An earlier example was observed in the pyrolysis[204] of *cis*- and *trans*-1,2-diethenylthiirane **351** and **352**. It was found that a competition between the observed sulfur extrusion and the thermal synthesis of thienocyclobutadiene **353** occurred. Pyrolysis of the thiiranes at 100 °C resulted only in formation of the corresponding desulfurized olefins **354** and **355**. Sulfur extrusion in solution, at about 0.15 M, initially exhibited second order kinetics which changed to first order as the reaction proceeded. These kinetic studies indicate that the extrusion of sulfur from thiiranes may involve a more complicated mechanism than the simple cheletropic loss of an atom of sulfur.



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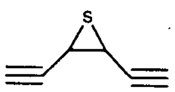

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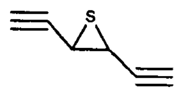

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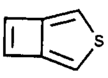
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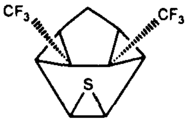
(354)


(355)

There are also examples where thiirane-like compounds lose sulfur thermally. Prinzbach, on studying[205] the *cis*-thia-tris-σ-homobenzene system, found that on heating to 100 °C, thiirane **356** does not undergo the expected transformation to **357**. The system likely extruded sulfur to first form the alkene **358**, which at the reaction temperature, rearranged to the final product **359**.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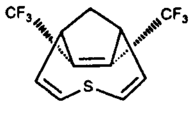
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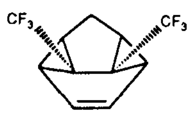
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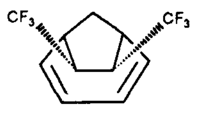
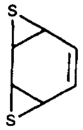

(359)

Vogel, studying[206] the properties of *syn*-3,4:5,6-bis(epithio)-1-cyclohexene **360**, found that, in carbon disulfide or chloroform, it decomposed at 20 °C with a half-life of about 30 minutes. The only products formed were benzene and sulfur. The 1,4-dithiocin-6-yl acetate **361** was found to be more stable than the parent compound **360**. On heating above 50 °C a slow decomposition occurred resulting in the formation of sulfur and phenyl acetate **362**.[207]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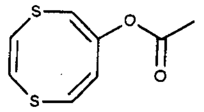
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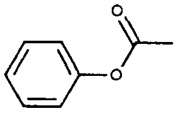
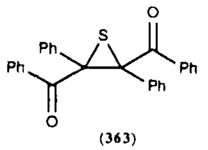

(362)

The extrusion of sulfur from thiiranes was observed to occur in some cases through processes other than the thermally induced processes. *trans*-Dibenzoylstilbene episulfide **363** was found to undergo photodesulfurization.[208] The major products were the *cis* and *trans* isomers of dibenzoylstilbene **364** and **365**. Minor products included the epimer of *cis*-dibenzoylstilbene episulfide **366** and 1-hydroxy-2,3-diphenyl-4-phenoxynaphthalene **367**.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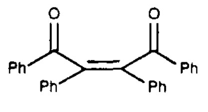
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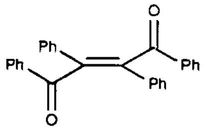
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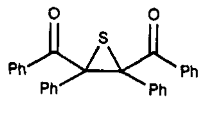

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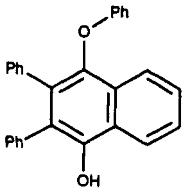
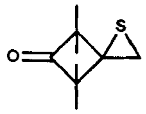


(367)

Methylenecyclobutanone **368** was formed as the major product in the irradiation[209] of 4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexan-5-one **369** in methanol at 2537 Å. The irradiation also produced three minor products **370**, **371** and **372** along with a nonvolatile residue. At wavelengths greater than 2800 Å only the three minor products are observed.



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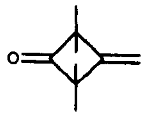

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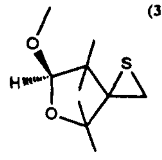

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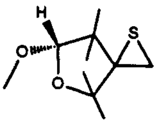

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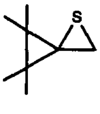
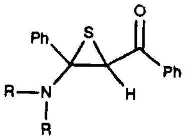


(372)

Thiiranes **373** were formed on treatment of the bromine salt **374**, obtained in the reaction of α-bromoacetophenone and benzothiamides with triethylamine.[210] These were easily desulfurized to enaminoketones **375** by treatment with sodium ethoxide at room temperature.



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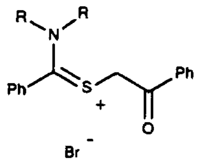

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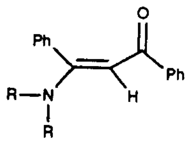
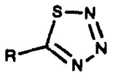


(375)

7.2. *Five-Membered Rings*

7.2.1. 1,2,3,4-Thiatriazoles 1,2,3,4-Thiatriazoles **376** are labile compounds and have been observed to decompose under various conditions.



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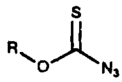


(377)

5-(Carbon substituted) 1,2,3,4-thiatriazoles, (R = aryl or alkyl) are stable at room temperature, but on heating above their melting points vigorously decompose with the formation of nitrogen, sulfur and the corresponding nitrile.[211,212] Some of the thiatriazoles were not isolated in pure form due to decomposition. The photolytic and thermal decomposition of 5-phenyl-1,2,3,4-thiatriazole was studied in the presence of olefins. Isolation of episulfides in the photolysis indicated that sulfur atoms may be formed in the decomposition.[213] No episulfide formation was observed in the thermal decomposition. In 1978 Holm[214] once again studied the mechanism by which 5-phenyl-1,2,3,4-thiatriazole decomposes. He concluded that the decomposition was a three step process via (*E*)-thiobenzoyl azide **377**. The conclusions were based on the lack of any indication of the presence of dinitrogen sulfide. In 1986[215] it was shown that dinitrogen sulfide was an intermediate in the decomposition of 5-phenyl-1,2,3,4-thiatriazole, by the use of infrared spectroscopy, showing the mechanism of Holm to be incorrect. Photoelectron spectroscopy[216] confirmed the presence of dinitrogen sulfide in the decomposition products of 5-phenyl-1,2,3,4-thiatriazole. Photoelectron spectroscopy also showed the presence of diatomic sulfur in the decomposition mixture. From this observation it was concluded that dinitrogen sulfide undergoes a bimolecular decomposition to form one equivalent of diatomic sulfur and two equivalents of nitrogen.

A similar decomposition of 5-amino-1,2,3,4-thiatriazole[217,218] ($R = NH_2$) or 5-alkylamino-1,2,3,4-thiatriazole[219] (R = NHR′) was observed in aqueous solutions or on heating to form nitrogen, sulfur and cyanamide. Reaction with hydroxide results in the precipitation of sulfur and no observed evolution of nitrogen. The 5-amino compound reacted with benzylamine to produce sulfur and various products which were dependent on the molar ratios.

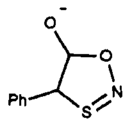
5-Alkoxy-1,2,3,4-thiatriazoles[220] (R = OR′) were found to decompose into nitrogen, alkyl isocyanate and sulfur. All the alkoxy compounds are unstable except the ethoxy derivative (R = OEt) which melted at 44.5–45 °C, but slowly decomposes even at room temperature with the formation of sulfur and the evolution of nitrogen. The decomposition of 5-ethoxy-1,2,3,4-thiatriazole has been studied to determine the primary decomposition products[221,222] and the kinetics[223] which were found to be first-order. Various potential catalysts had practically no effect on the decomposition of the ethoxy derivative. 5-Phenoxy-1,2,3,4-thiatriazole decomposed into nitrogen, sulfur and phenyl cyanate.[224]

5-Thiocyanato-1,2,3,4-thiatriazole (R = SCN) decomposes to nitrogen, sulfur and sulfur dicyanide.[225] The disulfide of 1,2,3,4-thiatriazole-5-thiol (R = SH) gradually decomposes at room temperature with the formation of nitrogen and polymeric thiocyanogen.[226] Solutions of an alkali metal salt of 1,2,3,4-thiatriazole-5-thiol ($R = M^+S^-$) slowly thermally decomposed with the formation of sulfur, nitrogen and thiocyanate ions.[227] The photolysis of 5-aryl-1,2,3,4-thiatriazoles **376** was observed by Kirmse[212] in 1960 resulting in products similar to those of the pyrolysis.

Holm[228] has studied the low-temperature photolysis of 5-arylthiatriazoles **376** and 4-phenyl-1,3,2-oxathiazolylium-5-olate **378**. The thiatriazoles on irradiation lost nitrogen to form a proposed benzonitrile *N*-sulfide intermediate **379**. The mesoionic oxathiazole lost carbon dioxide to form the identical intermediate. Under the reaction conditions a rearrangement occurred forming the isothiocyanate which loses sulfur to ultimately form the nitrile and sulfur. Observed absorptions in the ultraviolet spectrum were attributed to S_2, S_3 and S_4 chains and S_6 and S_7 rings. The authors proposed the formation of singlet sulfur atoms which convert to the triplet state followed by S_2 formation and subsequent polymerization to elemental sulfur, based on the results from the photolysis of carbon oxysulfide in solution.[229]

A thermal degradation of 5-(diphenylmethyleneaminoxy)-1,2,3,4-thiatriazole ($R = Ph_2C = NO$) was observed in refluxing carbon tetrachloride to yield 2-phenyl-4(3*H*)-quinazolinone **380**.[230]

4-Alkyl-5-sulfonylimino-,1,2,3,4-thiatriazolines **381** decompose in inert solvents at 45–80 °C with the formation of sulfur, nitrogen and sulfonyl carbodiimides **382**.[231,232] They also decompose under the influence of bases at room temperature with the formation of sulfur and a substituted urea. Reaction with enamines **383** formed addition adducts which in several cases rearrange with loss of sulfur.



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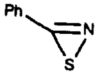

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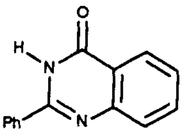

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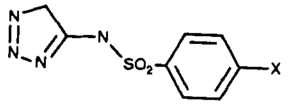

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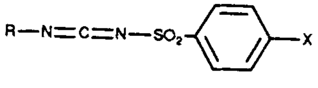

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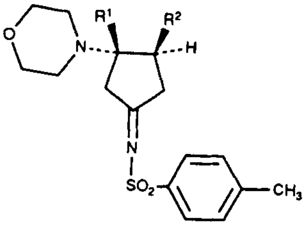
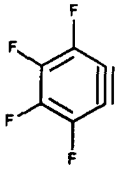


(383)

7.2.2. Thiophenes Thiophenes are five-membered heterocycles which under normal conditions behave as any aromatic system, undergoing reactions such as electrophilic aromatic substitution. However, because of their electronic nature, they can act as dienes and undergo cycloaddition reactions. Those reactions which result in sulfur extrusion are described below.

Wynberg and Bantjes studied[233] the pyrolysis of thiophene at 800–850 °C. They observed the formation of many desulfurized products, but no sulfur was isolated from the reaction mixture. This may be explained by the fact that the sulfur formed at the high temperatures of the experiment would react and not be observed. The reaction of arynes with thiophene has been reviewed,[234] the products isolated in the reaction are those that resulted from desulfurization.

Before 1966 there were several unsuccessful attempts to effect a Diels-Alder reaction with a non-condensed thiophene.[235] The first successful reaction was observed[236] in the reaction of thiophene and tetrafluorobenzyne **384** (formed from pentafluorophenyllithium **385** which at 25 °C cleanly decomposes into the benzyne). The reaction gives 40% 1,2,3,4-tetrafluoronaphthalene **386**, 1% pentafluorothiophenol **387** and 5% of a compound containing both fluorine and sulfur. It gave a proton NMR spectrum corresponding to the bridged sulfide **388**, which on warming decomposed into the tetrafluoronaphthalene **386** and sulfur.



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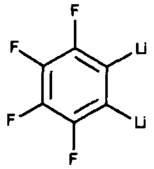

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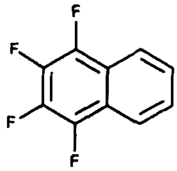

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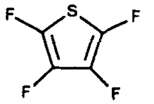

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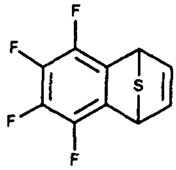
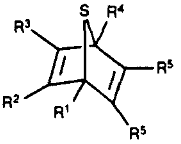


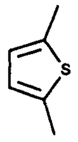
(388)

In 1972 two independent groups reported that substituted thiophenes undergo a Diels-Alder reaction with electron-deficient acetylenes. Helder and Wynberg[237] studied the reaction with dicyanoacetylene, while Kuhn and Gollnick[238] studied the reaction with dimethyl acetylenedicarboxylate, diphenylacetylene and dimethylacetylene. Both researchers proposed a Diels-Alder reaction forming a bridged sulfide **389** which, under the reaction conditions, lost sulfur to form the substituted benzene.



(389)

Singlet oxygen reacted with 2,5-dimethylthiophene **390** in methanol to yield a mixture of *cis*-sulfine **391** and the *trans*-2,5-dione **392**.[239] The reaction was proposed to go through a (4 + 2) cycloaddition reaction to yield a thioozonide **393** which could then decompose through a free-radical mechanism to the sulfine **391** and the *cis*-dione **394**; under the pyrolysis conditions this rearranges to the *trans*-dione. In 1984, isolation of the thioozonide was reported and its decomposition followed at 20 °C in various solvents for the formation of the dione.[240] The reactions were proposed to go through an intermediate **391** which would then lose sulfur, followed by an epimerization. The mechanism by which the ozonide decomposes was further studied in 1986.[241] The authors proposed that the elemental sulfur formed in the reaction was a result of concatenation of sulfur atoms or fragments during the course of the reaction.



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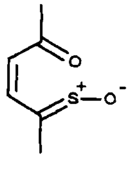

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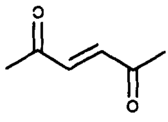

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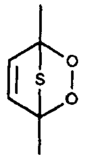

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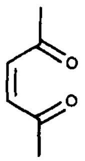
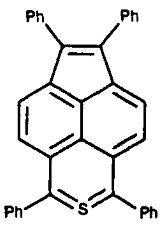


(394)

Irradiation at − 10 °C of an oxygen enriched 30% methanol-chloroform solution of 1,3,6,7-tetraphenylacenaphtho[5,6-*cd*]thiopyran **395** gave the highly unstable thioozonide **396**. The thioozonide, at 40–50 °C, rapidly decomposed into two compounds, the diketone **397** and the thioester **398**, and elemental sulfur.[242]



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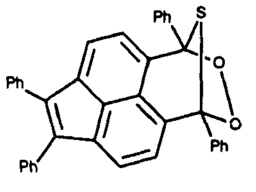

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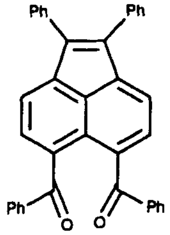

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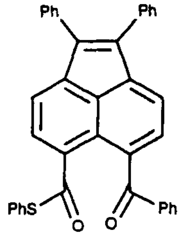
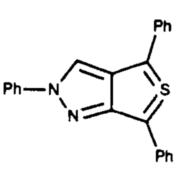


(398)

Potts observed[243] that the tetravalent sulfur heterocycle 2,4,6-triphenylthieno[3,4-*c*]pyrazole (**399**) undergoes a Diels-Alder reaction with acetylenes in refluxing benzene. The proposed mechanism was that the initial adduct **400**, a bridged sulfide **401**, extrudes sulfur forming the isolated heterocycle. 1,3,6-Triphenylimidazo[1,2-*c*]thiazole reacted with alkenes to form 1:1 adducts which extruded sulfur on treatment with sodium ethoxide in methanol or on heating in pyridine.[244]

It was observed[245] that 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-*c*]thiophene **402** undergoes a cycloaddition reaction with dimethyl acetylenedicarboxylate. The product, 5,6-dicarboxymethoxybenzo[*c*]thiophene **403**, was formed by extrusion of sulfur from the initial 1:1 adduct. The parent compound, $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene, was observed to also undergo Diels-Alder reaction forming an adduct which can eliminate sulfur.[246]



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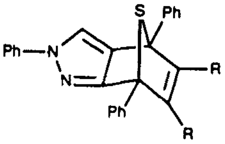

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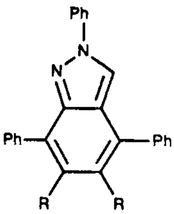

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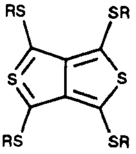

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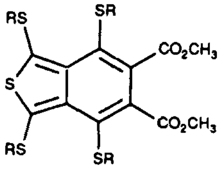
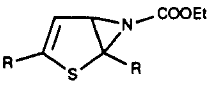


(403)

The thermolysis of the thiophene derivative **404** at 130 °C did not form the expected product but instead the *N*-substituted pyrrole **405** was isolated, formed by loss of the sulfur atom.[247]



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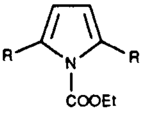
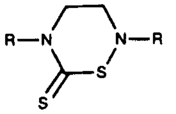


(405)

7.2.3. Thiadiazines The ring contraction of thiadiazines into pyrroles has been reviewed by Radl.[6] Heating 2,5-dialkyltetrahydro-1,2,5-thiadiazine-6-thiones **406** caused decomposition with loss of one sulfur atom to form 1,3-dialkyl-2-imidazolidinethiones **407**.[248] The stability the thiadiazine to temperature was dependent on the size of the alkyl substituent bonded to the nitrogen.



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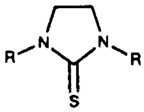
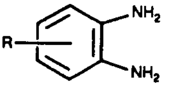


(407)

o-Phenylenediamines **408** react with disulfur dichloride to form 2,1,3-benzothiadiazoles **409**, along with hydrogen chloride and sulfur.[249]



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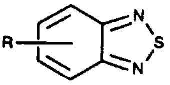
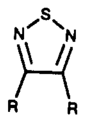
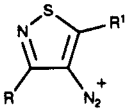


(409)

Cantrell and Haller studied[250] the photolysis of 1,2,5-thiadiazoles **410**; irradiation of 3,4-diphenyl-1,2,5-thiadiazoles **410** (R = Ph) in ether gave benzonitrile and sulfur, while the 3,4-dimethyl compound **410** (R = Me) gave acetonitrile and sulfur. Lee and Volpp observed[251] that when thiourea and an isothiazole-4-diazonium salt **411** are allowed to react, a 1,2,3-thiadiazole **412** is formed along with sulfur.



(**410**)



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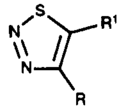
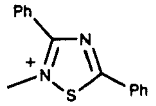
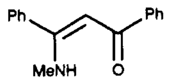


(**412**)

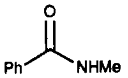
Hydroxide ion attacks the *N*-methyl-1,2,4-thiadiazolium salt **413** to yield as the major products, benzoylamidine **414** and sulfur.[252] Minor products were found to be *N*-methylbenzamide **415**, benzonitrile and the thio analogue of benzoylamidine **416**.



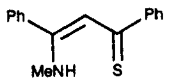
(**413**)



(**414**)

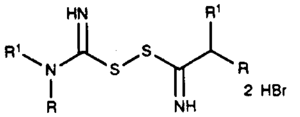


(**415**)



(**416**)

N-Arylthioureas react with bromine to form bis(arylguanyl) disulfide dihydrobromides **417**; treatment of this product with ethanol results in the formation of a mixture of starting material, sulfur and a 1,2,4-thiadiazole derivative **418** when the substitutent is phenyl, benzyl or *p*-chlorophenyl.[253]



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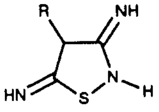
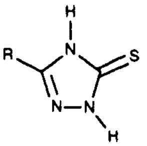


(**418**)

Irradiation[254] of methanolic solutions of 1,2,4-triazoline-3-thione **419** (R = H) gave a near quantitative yield of 1,2,4-triazole **420** (R = H) and sulfur. Both 3,3'-di(1,2,4-triazolyl) disulfide **421** and 3-methylthio-1,2,4-triazoline **422** on irradiation also gave only 1,2,4-triazole **420** and sulfur. 3-Alkyl or -aralkyl-1,2,4-triazoline-5-thiones **419** gave on irradiation the corresponding 3-substituted 1,2,4-triazoles **420** and sulfur.



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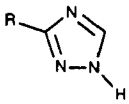

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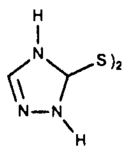
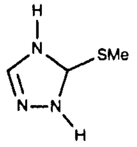
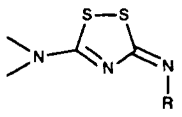


(**421**)



(**422**)

7.2.4. Miscellaneous Five-Membered Rings 5-(*N*,*N*-Dialkylamino)-3-(alkylimino)-1,2,4-dithiazoles **423** decompose thermally by a dimerization process to form **424** with loss of an atom of sulfur[255]. 5-Imino-Δ^3-1,2,4-thiadiazolines **425** are unstable; two molecules undergo a condensation spontaneously to form a new 1,2,4-thiadiazoline **426** and sulfur.[256]



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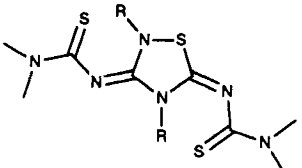

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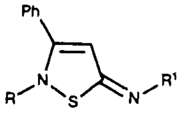

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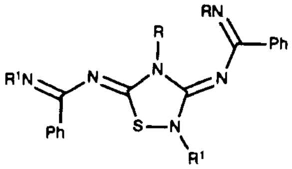
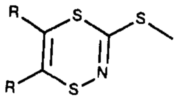


(426)

Fanghänel has studied the synthesis and properties of substituted 1,4,2-dithiazines **427**.[257] These compounds were found to be unstable and undergo decomposition at higher temperatures. The main reaction was elimination of an atom of sulfur to yield the isothiazoles **428**. A secondary reaction can occur when the substitution is trimethylene **429** (R, R′ = $(CH_2)_3$); methyl thiocyanate is eliminated with formation of the dithioketone **430** which can dimerize to the 1,4-dithiin **431** eliminating two atoms of sulfur.



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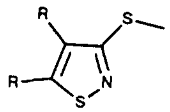

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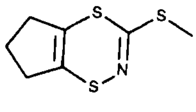

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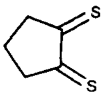

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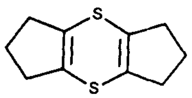


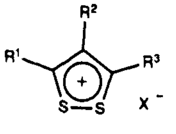
(431)

The chemistry of the 1,2-dithiolium ions **432** has been reviewed.[258,259] 1,2-Dithiolium ion can readily undergo a nucelophilic attack at either position 3 or 5. The resulting reaction is a substitution or a ring opening which is usually accompanied by loss of sulfur which can be isolated. Ring opening is the normal mode of reaction when bases such as hydroxide or amines are used.

The trithiolium salt **433** reacts with thiolate anion *via* ring cleavage and loss of sulfur to form the methyl ester of 1-(alkylthio)cyclopent-1-ene-2-dithiocarboxylic acid **434**.[260] The related dithiazolium cation **435** reacts in a similar way as the 1,2-dithiolium cation. Reaction with ammonia results in ring opening with loss of sulfur.[261]

Azide reacts with 3,5-bis(*N*,*N*-dimethylamino)-1,2,4-dithiazolium chloride **436** in DMF forming the 1,2,4-thiadiazole **437** by loss of nitrogen and sulfur. Other 1,2,4-dithiazolium ions react with azide in a similar way to form the corresponding 1,2,4-thiadiazoles.

The 3,5-disubstituted 1,2,4-dithiazolium cation **436** reacts with potassium cyanate[262] to form bis(*N*,*N*-dialkylamino)-1,3,5-thiadiazin-2-ones **438** by loss of sulfur. The reaction appears to be general, except that under identical conditions 3-(*N*,*N*-dimethylamino)-5-phenyl-1,2,4-dithiazolium perchlorate **439** did not form the expected 1,3,5-thiadiazin-2-one **438** but instead formed 3-(*N*,*N*-dimethylamino)-5-phenyl-1,2,4-thiadiazole **437**.



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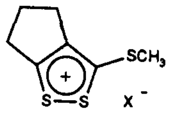

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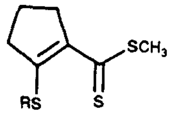

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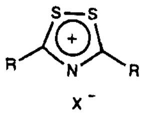

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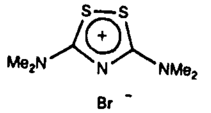

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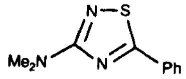

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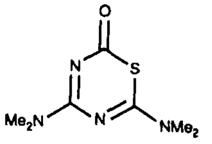

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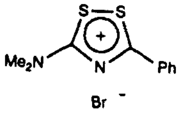
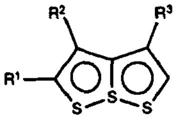


(439)

In the rearrangement of 6*a*-thiathiophthenes **440** to 4*H*-thiapyran-4-thiones **441** by nucleophiles a sulfur loss was proposed, but the sulfur was not isolated.[263] The chemistry of 6*a*-thiathiophthenes, more commonly known as 1,6,6a-S^{iv}-trithiapentalenes, has been reviewed.[264]



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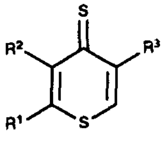


(441)

N-Sulfinylsulfonamides react with thioamides to yield nitriles **442** or a 3,5-disubstituted 1,2,4-thiadiazole **443**; also formed in both reactions was the sulfonamide, sulfur dioxide and sulfur.[265]

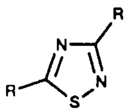
Trifluorothioacetyl fluoride **445** was treated with tetrafluoro-1,2,3,4-tetrathiane **444** at 300 °C and the products found to be 2-(trifluoromethyl)pentafluoro-1,3-dithiolane **446** and sulfur.

Benzonitrile and sulfur are the only products when 5-phenyl-1,3,4-oxathiazol-2-one

447 (R = Ph) is heated in solution at 125 °C.[266,267] Other 5-substituted 1,3,4-oxathiazoles-2-ones can also undergo decomposition to sulfur and the corresponding nitrile.[268]

Ts—N=SO

(442)



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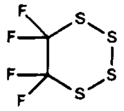

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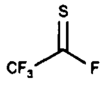

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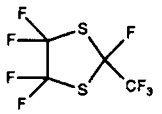

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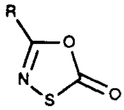


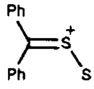
(447)

Staudinger observed[129] that 3,3,5,5-tetraphenyl-1,2,4-trithiolane **273** decomposes above its melting point to give thiobenzophenone **73** and sulfur. This decomposition was studied[269] by Huisgen in order to determine the mechanism of the decomposition. It was concluded that the reaction consists of a 1,3-dipolar cycloreversion to thiobenzophenone *S*-sulfide **448** and thiobenzophenone. The *S*-sulfide, which was successfully trapped, could then abstract more sulfur atoms, ultimately giving thiobenzophenone and cyclooctasulfur.

The pyrolysis of various precursors to generate thiocarbonyl compounds in the gas phase was examined.[270] The parent, 1,2,4-trithiolane **449** (R^1 = R^2 = H), 3,5-dimethyl-1,2,4-trithiolane **449** ($R^1 = CH_3$, R^2 = H), and 3,3,5,5-tetramethyl-1,2,4-trithiolane **449** ($R^1 = R^2 = CH_3$) all generate the corresponding thiocarbonyl compounds with the loss of one sulfur atom in the gas phase.

Boron tribromide or phenylboron dichloride or dibromide were found to react with hydrogen disulfide to produce 1,2,4-trithia-3,5-diborolanes **450** along with the hydrogen halides and sulfur.[271] Boron trichloride was found to undergo a similar reaction with hydrogen disulfide.[272]

Meller observed[273] that 1,3-disubstituted sulfur diimides reacted with 3,5-dialkyl- and 3,5-diaryl-1,2,4-trithia-3,5-diborolanes **450** to give 1,4-dithia-2,6-diaza-3,5-diborinanes **451** and sulfur.



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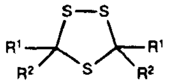

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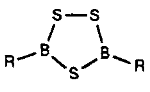

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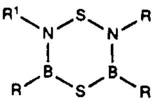


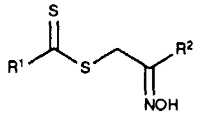
(451)

2-Hydroxyimino-2-phenylethyl arenedithiocarboxylates **452** on treatment with tosyl isocyanate cyclize to isothiazoles **453** and **454** with loss of an atom of sulfur.[274]

Δ^3-Thiazoline-2-thiones **455** eliminated[275] sulfur thermally or photochemically to form vinyl isothiocyanates **456**. The isothiocyanates under the reaction conditions undergo further rearrangements.

The thiopyran anion can undergo an irreversible sulfur extrusion forming the cyclopentadiene anion.[276]

Hydroxylamine reacts with isothiocyanates to yield as proposed intermediates hydroxythioureas **457**. The intermediates dimerize to form oxadiazoles **458**, water and sulfur.[277]



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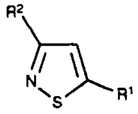

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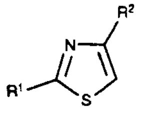

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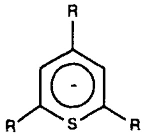

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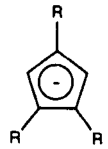

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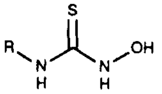

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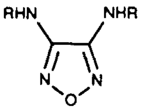


(458)

7.3. *Six-Membered Rings*

7.3.1. Dithiins A common reaction of many dithiins is the loss of an atom of sulfur to form thiophenes. The driving force behind this reaction is the ability of 1,2- and 1,4-dithiins to form a stable aromatic thiophene ring. The reaction is not applicable to 1,3-dithiins because the stable thiophene ring cannot be formed by loss of a sulfur atom. This extrusion from 1,4-dithiins **459** (Scheme 4) was covered in the review by Radl.[6] Not listed in the Radl[6] review was the extrusion from tetrakis(alkoxycarbonyl)-1,4-dithiin **459** (R = CO_2Alk)[278] to form the thiophene. There are fewer extrusion from 1,2-dithiins **460** to form thiophenes and sulfur (Scheme 5) due to their inherent instability.

(Scheme 4)

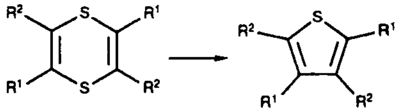
(Scheme 5)

The naturally occurring acetylenic 1,2-dithiins **460** (R = acetylenic) which have been isolated were found to lose an atom of sulfur to form the corresponding thiophene when heated, as well as on photolysis and attempted purification by thin layer chromatography.[279]

A series of substituted 1,2-dithiins **460** (R = aryl) were prepared and studied.[280] All readily lost sulfur on heating or irradiation to form the corresponding substituted thiophenes. The parent compound **460** (R = H) was previously found to lose sulfur with the formation of thiophene.[281]

Below are examples where sulfur extrusion is observed in the formation of various 1,4-dithiins.

Krespan and Brasen[282] in their studies on fluorinated cyclic polysulfides found that octafluoro-1,2,5-trithiepane **461**, on heating to 300 °C, decomposed to octafluoro-1,4-dithiane **462** and sulfur.



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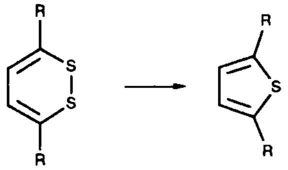
Scheme 4



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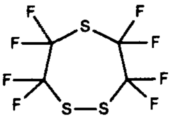
Scheme 5



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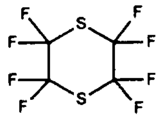
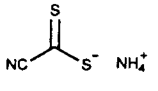


(462)

Tetraethylammonium cyanodithioformate **463** reacts with ethylene dibromide **464** forming 2,3-dicyano-5,6-dihydro-1,4-dithiin **465** and sulfur.[283]



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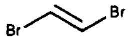

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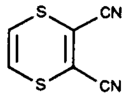
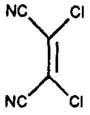


(465)

Disodium maleonitriledithiolate **242** reacts with thionyl chloride in the presence of 1,2-dimethoxyethane (DME) at 0 °C to give tetracyano-1,4-dithiin **459** ($R^1 = R^2 =$ CN), sulfur dioxide, sodium chloride and elemental sulfur.[283,284] The reaction between **242** and dichloromaleonitrile **466** gave the 1,4-dithiin **459** ($R^1 = R^2 =$ CN), the degraded compound **467** and sulfur.[284]

The mesoionic 2,5-diphenyl-1,3-dithiol-4-one **468**, when photolyzed, following the initial loss of carbon oxysulfide, can undergo two reactions;[285] one is dimerization, followed by loss of a second mole of carbon oxysulfide, giving the 1,4-dithiin **459**, or direct extrusion of sulfur to form diphenylacetylene.



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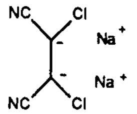

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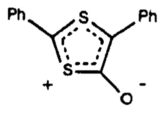
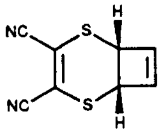


(468)

Compounds with structures similar to dithiins can also extrude sulfur thermally or by another pathway. Coffen, Poon and Lee investigated[286] the possibility of using various compounds to produce 1,4-dithiocins. Thermolysis of compound **469** at 400 °C gives phthalonitrile and a trace of sulfur. Pyrolysis of **470** at 200 °C produces 1,6-benzodithiocin **471**. This compound is converted at 400 °C to naphthalene and sulfur. Direct thermolysis at 400 °C gives a mixture of naphthalene, thiophene, sulfur and four unidentified products. Photolysis of **469** gives a mixture of phthalonitrile and sulfur; pyrolysis of **472** at 400 °C forms benzene, a trace of thiophene, sulfur and diphenyl disulfide.



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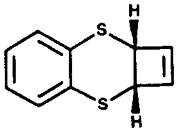

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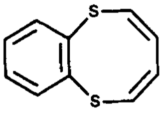

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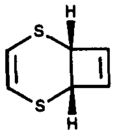

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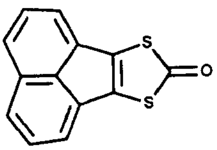
Cava studied[287] the photolysis of the dithiolane **473** which on irradiation gave 1,4-dithiin **474**. The authors proposed that loss of carbon monoxide to form the acenaphthenedithione **475** is the first step in this transformation. The tautomeric form of **475**, the 1,2-dithietane **476**, can undergo a Diels-Alder reaction with **475** to give a proposed bridged disulfide **477**. The disulfide would then decompose by extrusion of diatomic sulfur to form the dithiin **473**.



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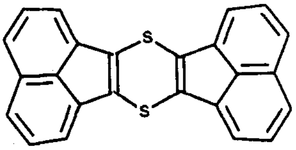

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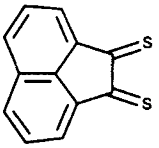

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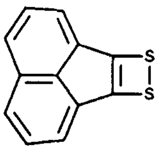

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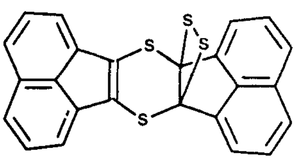

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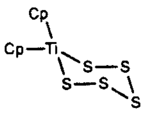
Dicyclopentadienyltitanium pentasulfide **478** reacts with alkynes to form a five-membered ring with two sulfurs and a dithiolene **479** containing the titanium;[288] the sulfur was not isolated.



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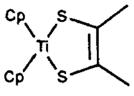
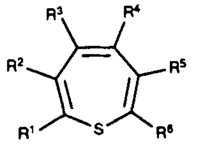


(479)

7.4. *Seven-Membered Rings*

7.4.1. Thiepins Thiepins **480** are seven-membered ring compounds containing three carbon-carbon double bonds and one atom of sulfur. Thiepins, therefore, have eight π electrons and thus by Hückel's rule are considered to be antiaromatic. The resulting instability accounts for the fact that they readily extrude an atom of sulfur to form stable aromatic systems. The formation of thiepins and their reactions including sulfur extrusion have been extensively reviewed and it is not necessary to show all the thiepins from which sulfur extrusion has been observed.



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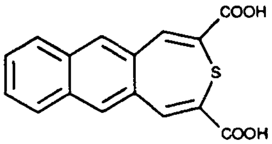

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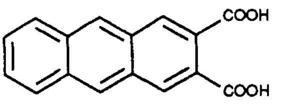
In 1953, Scott[289] prepared the first unsaturated benzothiepin, 3-naphthothiepin-2,4-dicarboxylic acid **481**. It eliminated sulfur on prolonged standing or on refluxing for 2 h in 15% ethanol to form anthracene-2,3-dicarboxylic acid **482**.

The first monocyclic thiepin was reported by Reinhoudt and Kouwenhoven[290] in 1974. It was unstable and was observed to eliminate sulfur at −30 °C; since then many stable thiepins have been reported. The necessary structural requirement for stability was the presence of sterically hindered groups at positions 2 and 7 (**480**, R^1 and R^6, respectively) of the thiepin ring.

Benzothiepins **483** are more stable than the parent thiepins. This can be observed in the stabilities of 1-benzothiepins. The half-lives of desulfurization have been summarized in a review by Reinhoudt.[291] A more recent paper by Gleiter[292] summarized the



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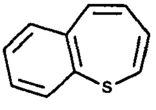
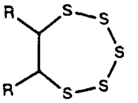


(483)

thermal stabilities of monocyclic thiepins. The authors showed by photoelectron spectroscopic investigations that the loss of a sulfur atom may not be a simple cheletropic elimination. The elimination may involve concatenation of sulfur atoms or form a sulfur chain which could be eliminated as elemental sulfur. This observation is in agreement with a calculation by Miller and Potts.[2] Thiepins can also undergo cycloadditions with the accompanying elimination of sulfur.[293,294]

Pentathiepins **484** have been found to exist in an equilibrium with trithiolanes **485** and sulfur in solution.[295] Bartlett and Ghosh attempted[296] to trap diatomic sulfur in the reaction, but were unsuccessful.



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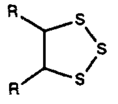

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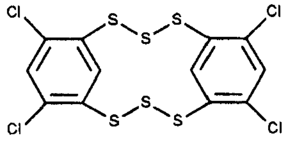
7.5. *Miscellaneous Rings*

Bottino and Pappalardo observed[297] that 5,7,14,16-tetrachloro-1,2,3,10,11,12-hexathia-[3.3]metacyclophane **486**, when refluxed for ten minutes in *o*-dichlorobenzene rearranges with loss of sulfur to form 4,6,12,14,20,22,28,30-octachloro-1,2,9,10,17,18,25,26-octathia[2.2.2.2]metacyclophane **487**. Other substituted cyclophanes did not extrude sulfur under similar conditions.



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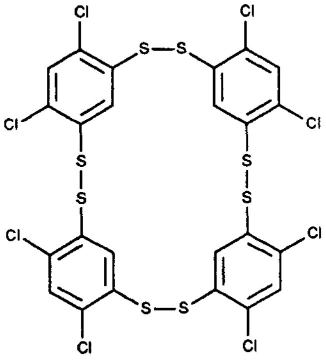

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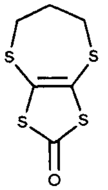
Hartke[298] studied the photolysis of 2,5,7,9-tetrathiabicyclo[4.3.0]non-1-(6)-en-8-one **488** and 2,6,8,10-tetrathiabicyclo[5.3.0]dec-1-(7)-en-9-one **489** and found that each first produced carbon monoxide and proposed as intermediates the corresponding dithioketones, **490** and **491**, respectively. For **488**, the thioketone decomposed into ethylene, a polymeric compound and sulfur, whereas for **489** the products obtained were a polymeric compound and sulfur.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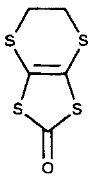
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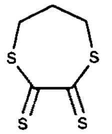
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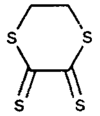
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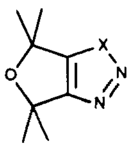
Sterically protected fused 1,2,3-thiadiazole **492** (X = S) and 1,2,3-selenadiazole **492** (X = Se), when heated with molten sulfur, form fused cyclopolysulfides **493** and **494** (X = S or Se).[299] Photolysis of the sulfides in the presence of olefins leads to cycloadducts, likely *via* the initially formed 1,2-dithione **495** (X = S) and 1,2-selenoxothione **495** (X = Se). The authors propose that the compounds lose one chalcogen atom to form either the 1,2,3,4-tetrathiin or the 1-seleno compound. These compounds could then lose a molecule of diatomic sulfur forming either the dithione or the selenoxothione. No indication of attempts to trap the diatomic sulfur was given.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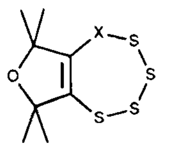
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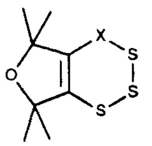
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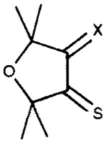
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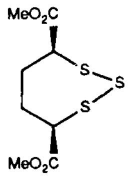
Sulfur extrusion was observed in the attempted preparation of cyclic trisulfides.[300] Two attempts were made to form *cis*-4,7-bis(methoxycarbonyl)-1,2,3-trithiepane **496** but the only products were the corresponding disulfide **497** and sulfur. When dimethyl *meso*-α-α′-dimercaptoadipate **498** was treated with a sulfur transfer reagent, *N,N′*-dibenzimidazolyl sulfide **499**, the only products was the expected benzimidazole **500**, the disulfide **497** and sulfur.

When the disilylated thiol **501** was treated with sulfur dichloride the only products were, once again, the disulfide **497** and sulfur; no mechanistic details were advanced.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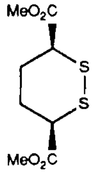
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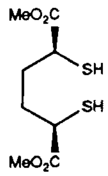
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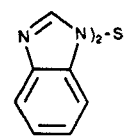

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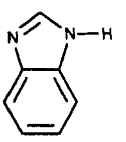

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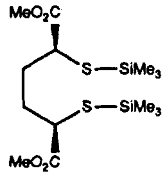

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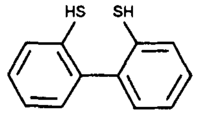
Treatment of the dithiol **502** with a benzothiazole transfer reagent gave a mixture of compounds which when purified by chromatography gave sulfur and a mixture of the trisulfide **503** and the disulfide **504**.



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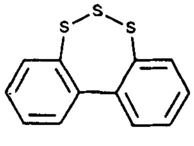

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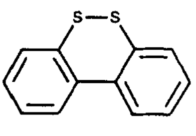
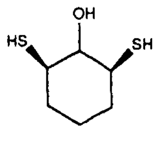


(504)

The reaction between *cis*-2,6-dimercaptocyclohexanol **505** and bis(phthalimido) disulfide **506** did not give the expected trisulfide **507**; the disulfide **508** and sulfur were formed.[301]



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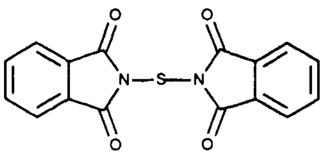

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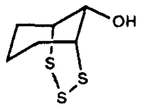

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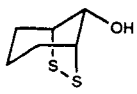
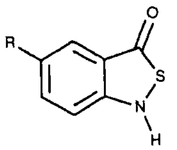


(508)

Benzothiazoles **509** were found to react with isocyanates or isothiocyanates to form a mixture of sulfur and 3,1(4*H*)-benzoxazin-4-ones **510** (X = O) or 3,1(4*H*)-benzothiazin-4-ones **510** (X = S). A similar result was obtained in the reaction of isocyanates with 3-methyl-1,2,4-thiadiazol-5-ol **511** to form 1,3,5-triazine-2,4(1*H*,3*H*)-diones **512**.[302]



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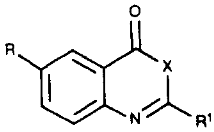

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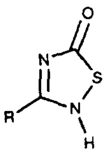

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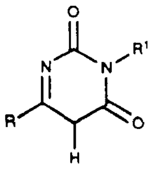
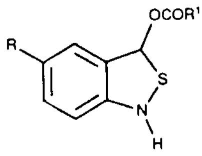


(512)

Acylation of substituted 2,1-benzisothiazolin-3-ones **509** in pyridine initially gave the *O*-acyl derivatives **513** which, under the reaction conditions, rapidly rearranged with extrusion of sulfur to give the ring expanded products, the benzoxazinones **514**.[303] The stabilities vary with the substituents indicated by the half-lives: when R = H $t_{1/2}$ = 20 minutes, R = Cl $t_{1/2}$ = 6 minutes and when R = NO_2 $t_{1/2}$ = 90 seconds. The *O*-benzoyl derivatives were found to be stable in the absence of base and could be isolated.

Treatment overnight with pyridine or heating to 250 °C resulted in sulfur extrusion with ring expansion. A kinetic study of the reaction showed that the rate is enhanced by the addition of low-molecular weight sulfur.[304] Cyclooctasulfur showed no effect on the rate of sulfur extrusion whereas cyclohexasulfur even at very low concentration effected a thousand-fold acceleration of the rate of the extrusion.



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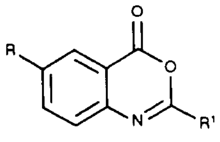
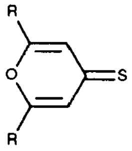


(514)

Elkaschef and Nosseir observed[305] that 2,6-diphenyl-4-thiopyrone **515** (R = Ph) reacted with diazomethane to form the stable dithiole **516** (R = Ph). The dithiole was easily desulfurized to the olefin **517** (R = Ph) with phenyllithium. Reaction of 2,6-di(*p*-methoxyphenyl)-4-thiopyrone **515** (R = *p*-$CH_3OC_6H_4$) with diazomethane gave the olefin **517** (R = *p*-$CH_3OC_6H_4$) directly. The olefin was likely formed by the spontaneous extrusion of thioformaldehyde and sulfur.



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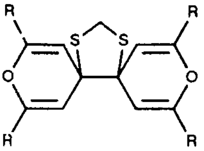

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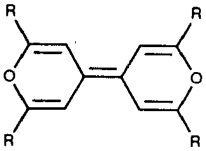
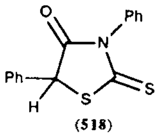


(517)

When a sample of 3,5-diphenyl-4-oxo-2-thiazolidinethione **518** was heated with ammonia at 100 °C for 12 h in a sealed tube, decomposition occurred.[306] The products isolated, along with unchanged starting material, were α-phenylacetamide **519**, ammonium thiocyanate and sulfur.



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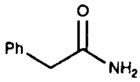
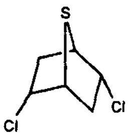


(519)

Treatment of bis-*endo*-1,5-dichloro-7-thiabicyclo[2.2.1]heptane **520** with base resulted in the formation of benzene as the only product.[307] The reaction likely occurred by two steps: the first is loss of two moles of hydrogen chloride, followed by desulfurization to benzene. Benzene was also the only product isolated when 3,4-dibromo-7-thiabicyclo[4.1.0]heptane **521** was treated with base.



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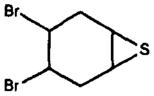

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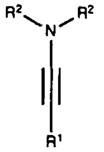
The cycloaddition of ynamines **522** to dehydrodithizone **523** resulted in the formation of a product which was void of a sulfur atom, the pyrazole **524**.[308] The initial adduct likely rearranged into the thiirane which could then extrude the atom of sulfur.



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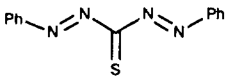

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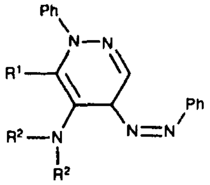
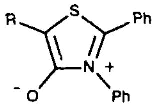


(524)

Potts has studied the cycloaddition reaction between electron deficient acetylenes and sulfur-containing mesoionic heterocycles. The initial report was of the reaction between dimethyl acetylenedicarboxylate and anhydro-2,3-diphenylhydroxythiazolium hydroxides **525**. The heterocycle **526** which was formed was proposed to go through a bridged sulfide **527** which would extrude sulfur.[309] This reaction was expanded to include other acetylenes and different substituents on the mesoionic compound.[310] Other mesoionic compounds also undergo cycloaddition reactions which are accompanied by sulfur extrusion.[311,312,313,314,315]



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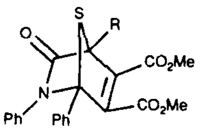

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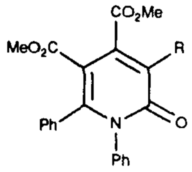
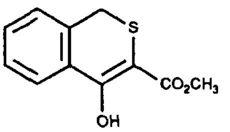


(527)

Irradiation of a basic methanol solution of 3-methoxycarbonylisothiochroman-4-one **528** formed a new ring compound (2-methoxycarbonylindanone **529**) which has lost an atom of sulfur.[316]



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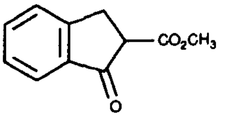
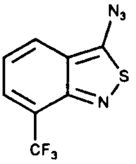


(529)

The azide of 3-amino-7-trifluoromethyl-2,1-benzisothiazole **530** decomposed[317] slowly in low-boiling solvents, but rapidly at 180 °C in *o*-dichlorobenzene to form the sulfur diimide **531**. The diimide is likely formed by dimerization of the intermediate thionitroso compound **532** with loss of sulfur.

Heating the thiatriazole **533** in benzene for long periods or treatment of the 1-(*o*-nitrophenyl)tetrazolethiolate anion **534** in aqueous base, nitrogen and sulfur are lost, and (*o*-nitrophenyl)cyanamide **535** is obtained.[318]



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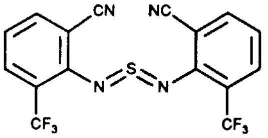

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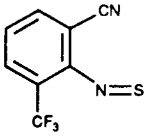

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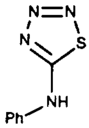

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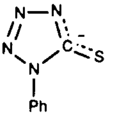

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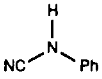
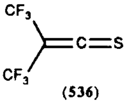


(535)

Heating bis(trifluoromethyl)thioketene **536** with sulfur at 200 °C results in the formation of two adducts which are formed from two molecules of thioketene and one atom of sulfur, **537** and **538**. Both adducts are converted to the thioketene dimer **539** and sulfur on standing in acetone solution.[319]

The thioketene reacted with *N*-methoxy-α-phenylnitrone **540** to form bis(trifluoromethyl)ketene **541**, *o*-methylbenzaldoxime **542** and sulfur.



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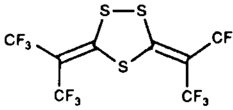

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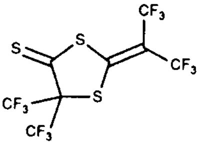

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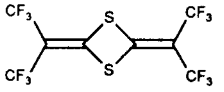

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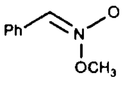

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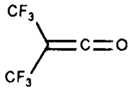

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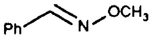
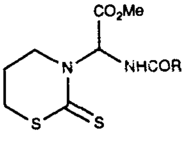


(542)

In 1987 it was reported[320] that treatment of the *N*-substituted thioamide **543** with 5 equivalents of trifluoroacetic acid anhydride in dichloromethane at room temperature resulted in the formation of the corresponding imidazoles **544** and elemental sulfur. The most likely mechanism was proposed to be ring closure to **545** followed by formation of thiirane **546** and subsequent extrusion of sulfur.



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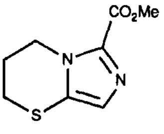

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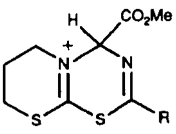

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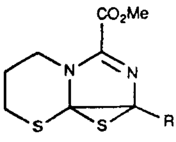
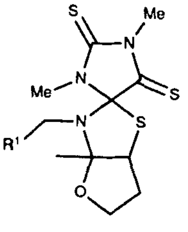


(546)

Cycloaddition of alkyl isothiocyanates with *N*-substituted 4-methyl-5-*β*-hydroxyethylthiazolium ylids resulted in the formation of a fused heterocycle **547**, containing a spiro ring system. Treatment with liquid ammonia at room temperature formed the bridged sulfur compound **548**. This compound could easily be desulfurized by heating in toluene at 100 °C for 30 minutes to give the heterocycle **549**. The conversion from **547** to **549** can be carried out directly by heating in glacial acetic acid at 100 °C or by treatment with sodium ethoxide in ethanol.[321]



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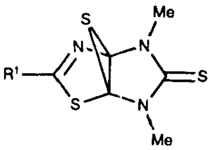

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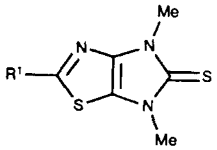
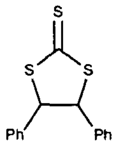


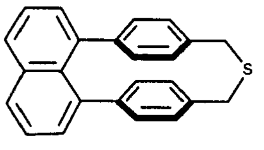
(549)

Stilbene trithiocarbonate **550** on irradiation will lose carbon disulfide and sulfur as well as phenanthrene as the major product.[322]



(550)

The pyrolysis[323] of 2-thia[3.0.0](1,4)benzeno(1,8)naphthalino(1,4)benzenophane **551**, at 650 °C and 10^{-3} torr, caused extrusion of the sulfide sulfur and resulted in the formation of [2.0.0](1,4)benzeno(1,8)naphthalino(1,4)benzenophane **552**.



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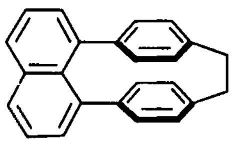
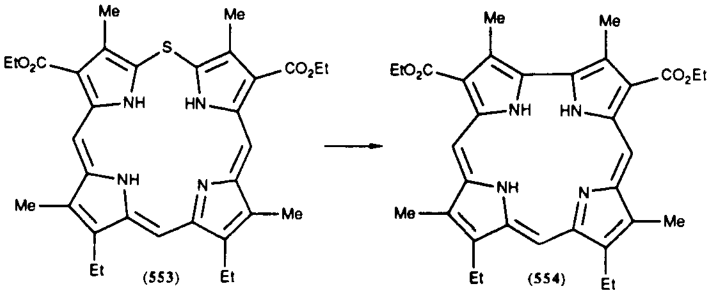


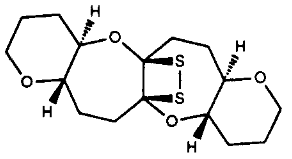
(552)

The mesothiaphlorin **553** underwent a sulfur extrusion, when refluxed in *o*-dichlorobenzene for 2 h, to form the corrole derivative **554**.[324] The reaction was proposed to go through a thiirane intermediate and not a free-radical mechanism. The validity of the proposed mechanism was enhanced by the addition of a radical inhibitor which proved to have no effect on the yield of corrole.



(553) **(554)**

Irradiation[325] of dithiatopazine **555** at room temperature results in extrusion of sulfur with alkene **556** being formed. Similar results are obtained by thermolysis either neat or in xylene at 140 °C.



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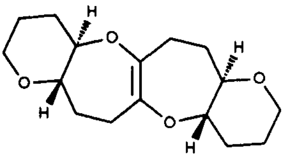
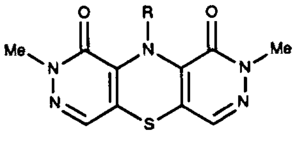


(556)

The condensation[326] between 4-amino-5-mercapto-2-methyl-3(2*H*)-pyridazinne **557** and 4,5-dichloro-2-methyl-3(2*H*)-pyridazinone **558** by heating in DMF, followed by benzylation, forms 10-benzyl-2,7-dimethyl-10*H*-dipyridazino[4,5-*b*:4′,5′-*e*][1,4]thiazine-1,6-(2*H*,7*H*)-dione **559**, and 10-benzyl-2,8-dimethyl-10*H*-dipyridazino[4,5-*b*;4′,4′-*e*][1,4]thiazine-1,9(2*H*,8*H*)-dione **560**. A similar result is obtained in the condensation of **558** with 5-amino-4-mercapto-2-methyl-3(2*H*)-pyridazine **561** to form **562** and **563**. When both condensations are conducted under more vigorous conditions, then the desulfurized product 9-benzyl-2,6-dimethyl-9*H*-dipyridazino[4,5-*b*:4′,5′-*e*]pyrrole-1,5(2*H*,6*H*)-dione **564** is obtained.



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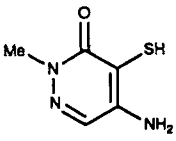

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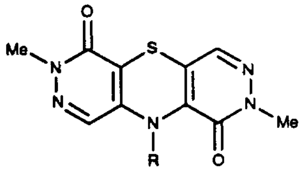

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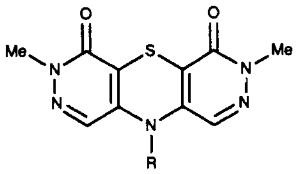

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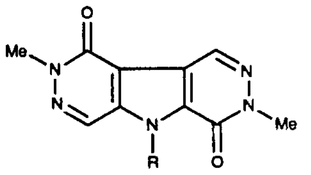
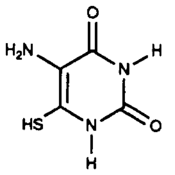


(564)

Fenner and Motschall[327] found that the reaction of 6-thiouracil **565** and *p*-bromophenacyl bromide **566** in ethanol and water resulted in the formation of the 6-phenylpyrimimido[4,5-*b*][1,4]thiazine derivative **567**. Heating (**567**) at 130 °C in DMF resulted in a sulfur extrusion to form the 6-phenyl-2,4-dioxo-tetrahydropyrrole[2,2-*d*]pyrimidine derivative **568**. When the reaction between **565** and **566** is conducted in DMF at 130 °C **568** is obtained directly.



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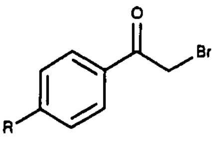

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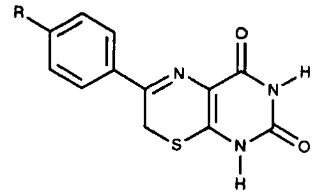

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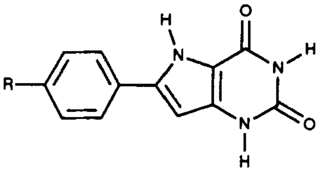
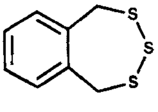


(568)

Singh, Field and Sweetman studied[328] the seven-membered cyclic trisulfide 1,5-dihydro-2,3,4-benzotrithiepin **569** and its related oxides and other analogues. The monoxide of **569**, **570** (n = 1) upon oxidation lost sulfur and gave 1,4-dihydro-2,3-benzodithiin 2-oxide **571** (n = 1). The 2,2-dioxide **570** (n = 2) could not be isolated, but it readily lost an atom of sulfur to form the 2,2-dioxide **571** (n = 2).



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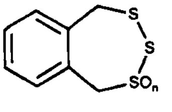

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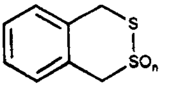
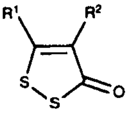


(571)

Photolysis of cyclic disulfides in the presence of hydroxide ion resulted in the formation of the corresponding cyclic sulfide.[329] When the disulfides are photolyzed in the absence of hydroxide only the dithiols are formed. Photolysis of the dithiol in the presence of hydroxide results in the formation of the cyclic sulfide.

Treatment[330] of disubstituted 1,2-dithia-3-cyclopentanones resulted in a dimerization accompanied by loss of sulfur to form the 1,2,5-trithiacycloheptadiene.

The reaction of aromatic amines with sulfur chlorides which lead to the formation of *o*-aminobenzenethiols **574** and the subsequent hydrolysis of the condensation product is known as the Hertz reaction. The reaction of disulfur dichloride with the amine to give a thiazolium chloride is the first step in the reaction. Also formed in the reaction is hydrogen chloride and elemental sulfur. There are a series of reactions of various amines all of which produce elemental sulfur. The Hertz reaction has been reviewed by Warburton[331] and it is not necessary to reiterate the information in this review.



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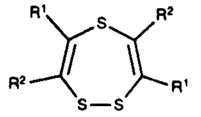

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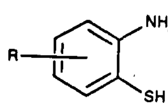
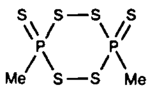


(574)

3,6-Diorganyl-3,6-dithio-1,2,4,5,3,6-tetrathiadiphosphorinanes **575**[332] are relatively stable compounds in the crystalline state, but in solution sulfur eliminations occur. The 3,6-dimethyl compound loses sulfur to form 3,5-dimethyl-3,5-dithio-1,2,4,3,5-trithiadiphospholane **576**. The 3,5-di-*t*-butyl compound decomposes to form the corresponding dithiophosphonic acid anhydride **577**.

o-Biphenylyl isothiocyanate **578** on irradiation[333] forms three products; *o*-biphenylyl isocyanide **579**, 1-azabenz[*b*]azulene **580** and sulfur.



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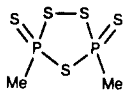

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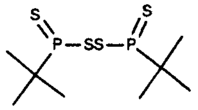

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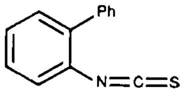

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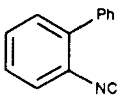

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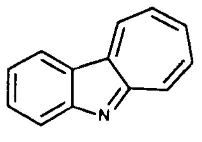


(580)

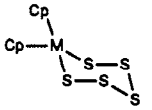
VIII. DIATOMIC SULFUR LOSS

There are only a few examples in the literature where the mechanism by which sulfur is extruded has been clearly expressed. These studies center on the successful trapping of what is thought to be singlet diatomic sulfur. This species was first trapped from the reaction of bis(arylmetal) trisulfides **581** and triphenylphosphine dibromide.[334]

Dicyclopentadienylmetal pentasulfides **582** also react with triphenylphosphine dibromide forming $^1S_2$ which was also successfully trapped.[335] The other products were triphenylphosphine sulfide and (presumably) triarylmetal bromide.

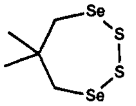
$R_3M{-}SSS{-}MR_3$

(581)

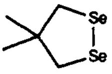


(582)

Diatomic sulfur was trapped from 5,5-dimethyl-1,2-dithia-3,7-diselenacycloheptane **583**, which on heating or slowly at room temperature decomposes into sulfur and 4,4-dimethyl-1,2-diselenacyclopentane **584**.[336]

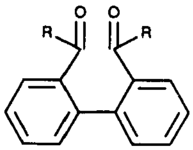


(583)



(584)

Steliou[337] has shown that treatment of the *peri*-diketone **585** under sulfurating conditions results in the formation of the 9,10-substituted phenanthrene **586**; diatomic sulfur is successfully trapped from this reaction with dienes. The reaction likely proceeds through dithioketone **587** which could undergo a head-to-head dimerization to form 1,2-dithietane **588**. This dithietane could then lose diatomic sulfur to form the phenanthrene. It was previously reported that the diketone reacts with phosphorus pentasulfide to proceed directly to the hydrocarbon.[338,339]



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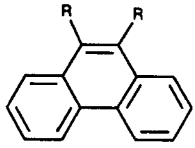

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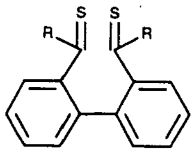

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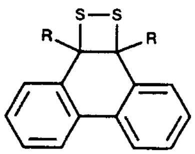
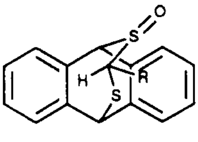


(588)

Ando has claimed[340] that **589** decomposed to the unisolated 9,10-epidithio-9,10-dihydroanthracene **590**. It was proposed to then decompose to anthracene and singlet diatomic sulfur which was trapped. However, yields were based on the amount of anthracene isolated, not on the amount of isolated adduct, thus making the conclusions tentative.



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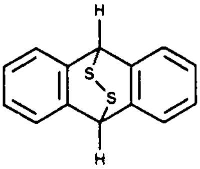
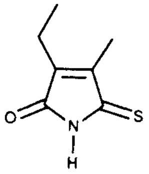


(590)

The most recent example of singlet diatomic sulfur extrusion was published in 1989 by Bishop, Dagam and Rapaport.[341] They observed that 3-ethyl-2-methyl-1-thiomaleimide **591** decomposed into 3-ethyl-2-methylmaleimide **592** and sulfur. Addition of 2,3-dimethyl-1,3-butadiene to the mixture results in the formation of the Diels-Alder adduct with diatomic sulfur; the product was detected by NMR spectroscopy and not isolated. They proposed that the transformation took place with oxygen to form the six-membered ring intermediate **593**.

There are also several examples in the literature where the formation of singlet diatomic sulfur ($^1S_2$) has been indicated. These examples have been included in the appropriate sections because the sulfur production has not been authenticated by successful trapping experiments.[60,96,287,298,301,325]



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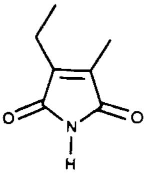

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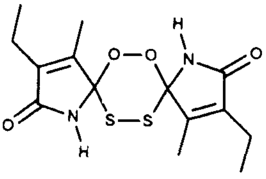


(593)

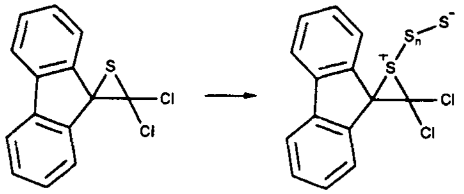
IX. CONCLUSION

As has been shown, there are numerous reactions in which sulfur is lost directly from molecules or in chemical reactions. All of the reactions ultimately produce elemental sulfur and, given the variety of sulfur functionalities, it would appear unlikely that a single mechanism could account for all of the observed extrusions. Yet, we wish to propose that at the very least it is reasonable that branch-bonded sulfur species are involved in most, if not all of these processes. It is possible to write compelling mechanistic pathways for all of these reactions which, starting with a branch-bonded sulfur species, eventually implicate S_2 or longer chains of sulfur atoms before S_8 is formed. In the following paragraphs we will detail what mechanistic efforts that have been uncovered in the literature as well as our own work in this area.

Thermal sulfur loss from thiiranes to form alkenes (Scheme 3),[191,342] from dithiins to form thiophenes (Schemes 4-5)[343] and from thiepins to form stable aromatic systems (Scheme 6),[4,5,293] were proposed to proceed exclusively with the sulfur being lost as a

Scheme 6

singlet sulfur *atom*. The high energy of formation of a singlet sulfur atom would make this mechanism unlikely as a possibility for most reactions.[1] This mechanism, a cheletropic loss of a sulfur atom, would result in the reaction exhibiting first order kinetics. Lutz and Bielmann[203] as well as Vollhardt[204] studied the thermal loss of sulfur from thiiranes; each group concluded that the reaction is not first-order and therefore cannot be a direct extrusion of a singlet sulfur atom. Lutz and Bielmann[203] proposed the possibility of a bridged sulfur species **594** to account for the sulfur loss from **350**.

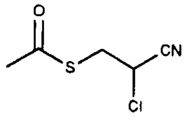


(350) **(594)**

Careful repetition[344] of the experiments of Bielmann and Lutz, while attempting to trap S_2, gave only the alkene, sulfur and unreacted diene trap as isolated products. Other episulfides of similar structure gave no indication of the trapped adducts indicating a singlet sulfur atom formation. It is therefore concluded that Bielmann and Lutz were correct in assuming a bridged sulfur species which would ultimately lose S_8. Thus, S_2 appears not to be formed as an intermediate in the reaction.

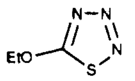
Mueller[98] attempted to trap atomic sulfur in the reaction of β-chloro-α-(acetylthio)-propionitrile **212** and diethylamine, but was unsuccessful. He proposed that the reaction proceeded through a thiirane intermediate which spontaneously lost atomic sulfur. Attempts were also made to trap[345] atomic sulfur in the observed sulfur loss in the oxidation of a phosphothiolate **595** with a peroxy acid to form the phosphate **596**, but were unsuccessful. The photolysis[214] of 5-substituted 1,2,3,4-thiatriazoles **376** in the presence of olefins produced the corresponding episulfides indicating atomic sulfur formation. Thermal decomposition in the presence of olefins gave no evidence for episulfide formation.[214] However, thermal decomposition of 5-ethoxy-1,2,3,4-thiatriazole **376** (R = OEt) in the presence of triphenylphosphine, triphenylarsine or triphenylstibine formed the corresponding sulfides.[223] The results may not be a reaction of sulfur atoms, but may be a nucleophilic attack on the sulfur of the thiatriazole ring with concomitant loss of molecular nitrogen. The photolysis of thiocyanates **597**[346] formed sulfur atoms which were successfully trapped as episulfides. The results from this photolysis are not surprising as the normal method for producing sulfur atoms is the photolysis of carbon oxysulfide (COS).[299]

A second possibility for the mechanism of sulfur loss is by way of a somewhat stable acyclic sulfur species such as diatomic sulfur (S_2) which could combine to form elemental



(212)

(595) **(596)**



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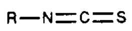
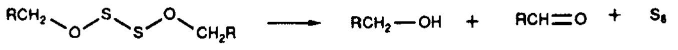


(597)

sulfur; as mentioned in the previous section, there have been several successful trappings of singlet diatomic sulfur. Most of these experiments were designed considering the possible production of diatomic sulfur; this allotrope was proposed as the species produced in numerous reactions, but attempts to trap it from different sulfur loss reactions (as Diels-Alder adducts) have in most instances been unsuccessful. There are other examples were a decomposition reaction produces sulfur atoms which could have been lost as a diatomic species and are shown below.

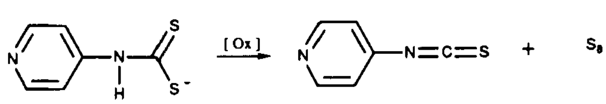
Thompson[74] observed that the decomposition of dialkoxy disulfides **139** with an α-methylene groups produce the corresponding aldehyde, alcohol and two *atoms* of sulfur (Scheme 7). If the decomposition proceeded via the proposed mechanism, a six-membered ring transition state, the sulfur would likely be extruded as a diatomic species.



(139)

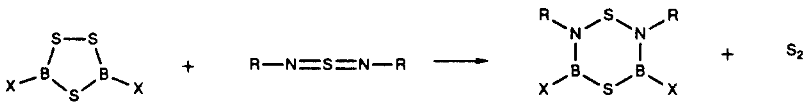
Scheme 7

Hansen and Petersen[148] proposed a similar transition state in the conversion of the dithiocarbamic acid **598** to *N*-alkyl-*N*′-4-pyridylthioureas. Air oxidation would form the intermediates shown which would extrude singlet sulfur to form the intermediate 4-pyridyl isothiocyanate **599** which is converted to the thiourea in the presence of an amine.



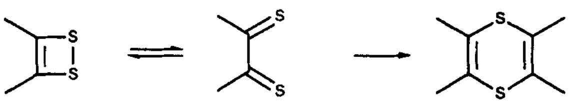
(598) **(599)**

The reaction of sulfur diimides with 1,2,4-trithiaborolanes **450** formed 1,4-dithia-2,6-diaza-3,5-diborinanes **451**; two atoms of sulfur are also proposed products (Scheme 8).[273]



(450) Scheme 8 **(451)**

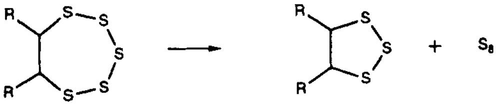
Two atoms of sulfur have often been proposed to be formed in dimerization reactions. There are numerous examples where 1,2-dithietanes or 1,2-dithiodiketones dimerize to form 1,4-dithiins (Scheme 9). Thioketones dimerize with the formation of alkenes and elemental sulfur (Scheme 10).



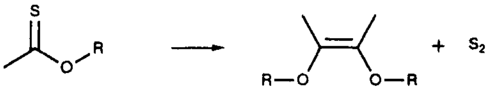
Scheme 9

Scheme 10

Hudson and Dj-Forudian[96] proposed the production of diatomic sulfur in the reaction between ketoximines and phenyl isothiocyanate. Bartlett[296] unsuccessfully attempted to trap diatomic sulfur in the equilibrium reaction between pentathiepins **484** and trithiolanes **485** with elemental sulfur in solution (Scheme 11). The photodimerization of *O*-aryl or *O*-alkyl thioacetates **258** produced an alkene **259** along with elemental sulfur (Scheme 12).[133] Jahn and Schmidt[134] successfully trapped S_2 in the reaction with a diene, but in very low yield.

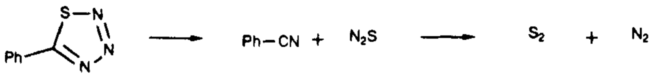


(484) Scheme 11 (485)



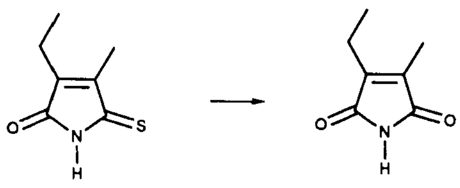
(258) Scheme 12 (259)

Wentrup[217] observed the presence of diatomic sulfur in the decomposition products of 5-phenyl-1,2,3,4-thiatriazole using photoelectron spectroscopy (Scheme 13). The decomposition was observed to originally form dinitrogen sulfide which decomposed through a dimerization reaction to form elemental nitrogen and the observed diatomic sulfur species, although it was not trapped.

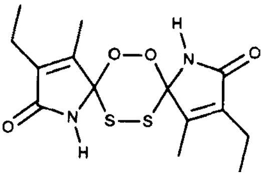


(376) Scheme 13

Very recently, Rapaport[341] observed that 3-ethyl-2-methyl-1-thiomaleimide **591** on stirring in air in ambient light decomposed to 3-ethyl-2-methylmaleimide **592** and elemental sulfur. ^1H NMR evidence of a trapped disulfide indicates that decomposition of the maleimide in the presence of a diene produces a diatomic sulfur species although the resulting adduct was not isolated. The author proposed that the diatomic sulfur formed as the result of a reaction with elemental oxygen giving a six-membered ring compound **593**. In 1928, a similar intermediate **600** was proposed, by Staudinger and Freudenberger[129] in the decomposition of thiobenzophenone with oxygen to form benzophenone and sulfur. Other thioketones were observed to be stable in the presence of oxygen in the dark, but decomposed in sunlight.



(591) **(592)**



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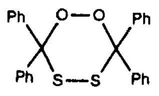
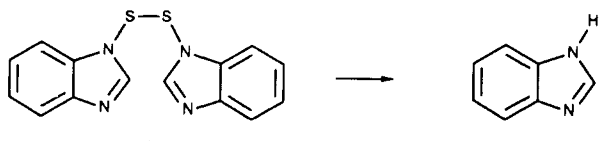
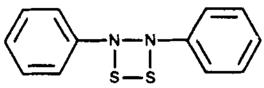


(600)

In our laboratory we have attempted to trap diatomic sulfur in many reactions and some of the attempts are described. The reactions of "sulfur transfer reagents" are excellent methods to prepare sulfides from various precursors. Some of these reactions do not give the expected product but instead form, as one of the products, elemental sulfur.[300,301] Those reactions that can be envisaged to lose two sulfur atoms may be sources of S_2. Reaction of *N,N'*-dithiobisbenzimidazole **601** with hydrazobenzene **157** forms only the expected benzimidazole **602**, sulfur and azobenzene **156**. The sulfur transfer could occur to form the four-membered ring intermediate which could then collapse to the azobenzene and S_2. Such a structure has been postulated in the literature in the decomposition of *N,N'*-thiodiamines.[81] All attempts to trap S_2 in the reaction failed,[347] suggesting that some other mechanism must account for the sulfur formation. Alternatively, the singlet S_2 might simply be converting to the more stable triplet form before trapping.



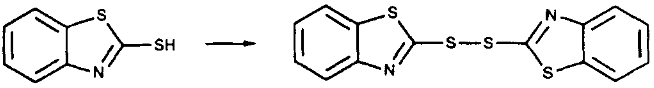
(601) **(602)**



(603)

(156) **(157)**

Reaction of 2-mercaptobenzothiazole **604** with *N*,*N*′-dithiobisbenzimidazole **601** did not form the expected tetrasulfide, but instead disulfide **605** and elemental sulfur. It was thought that the tetrasulfide originally formed, but decomposed to the disulfide **605** and S_2. All attempts to trap the proposed S_2 were unsuccessful.[347]

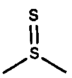


(604) **(605)**

There are numerous coordination complexes, both organometallic and inorganic, which contain a disulfur unit. The chemistry of such units has been reviewed.[348] In our laboratory the complex $(NH_4)_2[Mo_2S_{12}]$ has been used as a sulfur source in the preparation of sulfides and disulfides.[349] The fact that the molybdenum complex has an unusual structure and the knowledge that it releases S_2 in the mass spectrometer made it an attractive possible source for the thermal production of S_2. All attempts to trap the S_2 as a Diels-Alder adduct in the thermal decomposition were unsuccessful.[350]

It has also been postulated that there is no discrete S_2 species, but that the observed disulfides are formed by the transfer of two sulfur atoms.[351] All the successful methods suggested to involve S_2 can be postulated to occur with the transfer of two sulfur atoms from some appropriate intermediate and not by direct S_2 formation.

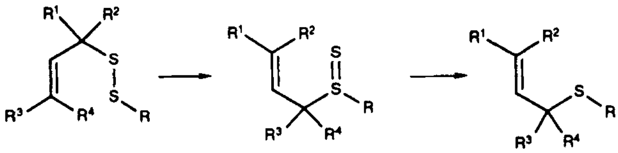
One possibility that has been proposed is the concatenation of sulfur atoms so that the species extruded is stable.[2,3] This would occur through the reaction between two sulfur species with the transfer of a sulfur atom to form a thiosulfoxide-like intermediate **606**. This intermediate could then further react with other molecules until the sulfur chain was six or eight atoms long and could cyclize to S_6 or more likely, S_8.



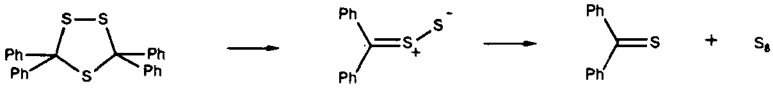
(606)

One reaction that has been observed to readily occur is the formation of sulfides by the loss of sulfur from higher polysulfides (see section on Chains). A common explanation for the observed conversion is the loss of sulfur from a thiosulfoxide intermediate,[8,9,10,185] the intermediate likely formed *via* a rearrangement of the sulfide chain; such a rearrangement has been proposed in solvent,[8] photo-induced[9,10] and in thermally-mediated[185] extrusions. The thiosulfoxide functionality is known and several stable compounds containing it have been isolated and characterized.[74,185,352,353] The intermediacy of thiosulfoxides has been supported by recent results of Strausz.[354]

Allylic disulfides **338** were observed to rearrange to new disulfides at ambient temperature.[186] The rearrangements were proposed to occur through a thiosulfoxide intermediate **339**. For sterically hindered allylic disulfides only rearrangement is observed, while the less substituted allylic disulfides rearrange to the sulfides **340** and sulfur. A possible rationale for less substituted allylic disulfides rearranging to the sulfides and sulfur is the concatenation of sulfur atoms from the thiosulfoxide intermediate. Once reacted, the sulfur species could extend to longer chains and ultimately lose elemental sulfur. Husigen and Rapp[269] in an unrelated experiment successfully trapped molecules which would have a structure similar to the thiosulfoxide intermediate in the thermal decomposition of 3,3,5,5-tetraphenyl-1,2,4-trithiolane, which forms thiobenzophenone and sulfur.



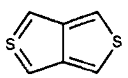
(338) (339) (340)



(449) (448) (73)

As previously stated, Miller and Potts[2] noted in a calculational study that the sulfur loss in the reaction between dicyanoacetylene and thieno[3,4-*c*]thiophenes **608** was unfavorable for the formation of a singlet sulfur atom, but concatenation to form S_6 or S_8 was favorable. A similar conclusion was obtained by Gleiter[292] who studied the loss of sulfur from thiepins using photoelectron spectroscopy. The possibility of a species involving the concatenation of sulfur atoms from the thianorcaradiene intermediate **608** was proposed with **609** as a possible intermediate. That species would ultimately lose elemental sulfur (S_8, *vide infra*).

Such a scheme was proposed by Howe and Shelton[268] to account for the formation of elemental sulfur in the decomposition of nitrile *N*-sulfides. A similar proposal was cited[343] for the observed sulfur loss in the oxidation of a phosphothiolate with a peroxy acid. A related proposal was put forward by Edward[59] in the extrusion of sulfur from dipyrido[1,2-*a*:1′2′-*c*]imidazolium-11-thiolate **116** when it was refluxed in hydrobromic acid. Matturo[241] recently concluded that a similar mechanism must be involved in the extrusion of sulfur in the reaction between dimethylthiophene and singlet oxygen. He proposed that the mechanism involves a concatenation of sulfur atoms or sulfur fragments such as S_2 or S_3.



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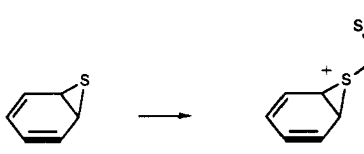

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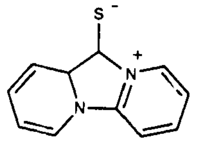

(116)

Of the possible mechanisms considered, it appears that both extrusion of singlet diatomic sulfur and the concatenation of sulfur atoms to ultimately form elemental sulfur are reasonable. The most likely mechanism for sulfur extrusion may be the concatenation of sulfur atoms to form a chain which would ultimately cyclize to form elemental sulfur. Singlet diatomic sulfur therefore may not be formed as a distinct species in any of these reactions.

Steudel[355] has carried out extensive studies on the mechanism of sulfur formation in inorganic systems. He has found that sulfur formed in these systems consisted of several allotropes. An example is in the decomposition of disulfur diiodide[356] (formed from disulfur dichloride and potassium iodide) in which allotropes S_6, S_8, S_{12}, S_{18}, S_{20} and larger homocyclic sulfur molecules are formed. He has also studied the acid decomposition of sodium thiosulfate[357] and discovered that the cyclic molecules S_6, S_7 and S_8 are formed in decreasing yield as listed. This result confirmed the mechanism proposed by Davis in 1958.[121] Ab initio MO calculations were conducted[358] on hypervalent sulfur hydrides and the results were used to discuss the possible pathways in the interconversion reactions of various sulfur cumulated SS bonds (thiosulfoxides). The applicability of the mechanism for elemental sulfur formation in inorganic systems to organic molecules is currently being studied.

In the literature, sulfur allotropes from atoms up to polymers have been studied. Besides elemental sulfur (S_8), the allotrope most often researched has been the sulfur atom. The normal method for the preparation of singlet and triplet sulfur atoms is by photolysis of carbon oxysulfide. Various reactions of these two spin states have been studied in solution[229] and in the gas phase.[359]

It has been known for many years that the chief component of sulfur vapor is diatomic sulfur and this has been studied spectroscopically.[360] Other S_x molecules such as S_3 or S_4 have only been observed in rare gas matrices at low temperature; they can be formed from the photolysis of S_3Cl_2 and S_4Cl_2, respectively.[361]

There are numerous reactions in which sulfur is formed where singlet diatomic sulfur is indicated as the sulfur species produced.[134,148] The first synthetically useful preparation of S_2 did not appear until 1984. The most effective method of preparing S_2 in the literature is that of Steliou[337] involving the reaction of boron trisulfide (prepared *in situ*) with *peri*-diketone **585**. Trapping by dienes with this method gives adducts (cyclic disulfides) in 60–85% isolated yield. The thermal procedure for S_2 production of Schmidt and Görl[336] using, 5,5-dimethyl-1,2-dithia-3,7-diselenacycloheptane **583**, delivered isolated adducts in 48–54% yield. The remaining two synthetically useful methods of preparing singlet diatomic sulfur involve the use of triphenylphosphine dibromide. Reaction of a germanium trisulfide[334] **581** with the dibromide gave trapped adducts in 25–50% yields; the reaction of dicyclopentadienylmetal pentasulfides[335] **582** with the dibromide give 15–22% of trapped adduct.

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