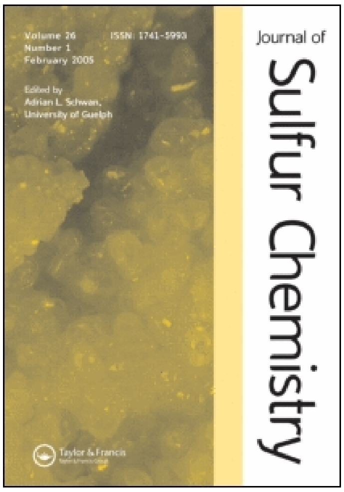


Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Sigmatropic Additions and Cyclosubstitutions in Five-Membered Heterocyclic Compounds Containing Exocyclic Double Bonds

Victor N. Drozd[a]; Nikolai S. Zefirov[b]
[a] Department of Organic Chemistry, K. A. Timiryazev Agricultural Academy, Moscow, USSR [b] Department of Chemistry, Moscow State University, Moscow, USSR

To cite this Article Drozd, Victor N. and Zefirov, Nikolai S.(1981) 'Sigmatropic Additions and Cyclosubstitutions in Five-Membered Heterocyclic Compounds Containing Exocyclic Double Bonds', Journal of Sulfur Chemistry, 1: 5, 271 — 308
To link to this Article: DOI: 10.1080/01961778108082415
URL: http://dx.doi.org/10.1080/01961778108082415

Sulfur Reports
Volume 1 (5), September 1981, pp. 271–314

Printed in the United States of America

SIGMATROPIC ADDITIONS AND CYCLOSUBSTITUTIONS IN FIVE-MEMBERED HETEROCYCLIC COMPOUNDS CONTAINING EXOCYCLIC DOUBLE BONDS

VICTOR N. DROZD
Department of Organic Chemistry, K. A. Timiryazev Agricultural Academy, Moscow 127550, USSR

and NIKOLAI S. ZEFIROV
Department of Chemistry, Moscow State University, Moscow 117234, USSR

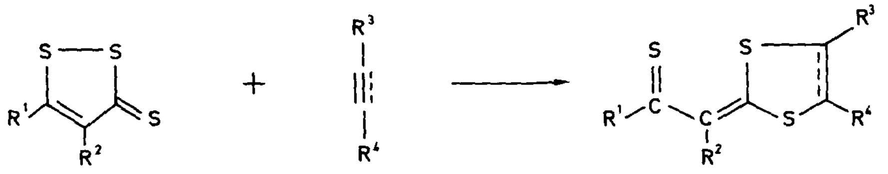
A review of unique pericyclic reactions of five-membered heterocyclic compounds with exocyclic double bonds, i.e. sigmatropic addition and cyclosubstitution reactions, is presented. 3H-1,2-Dithiole-3-, 3H-1,2,4-dithiazole-3-, isothiazoline-3- and isothiazoline-5-thiones and their imines as well as Δ^3-1,2,4-thiadiazoline-5-imines and 4-imino-4,5-dihydro-1,2S^{IV},3-oxathiazole 2-oxides exibit the reactions of the first type and 1,3-dithiolane-2-thiones and related compounds exhibit the reactions of cyclosubstitutions (147 references).

Contents

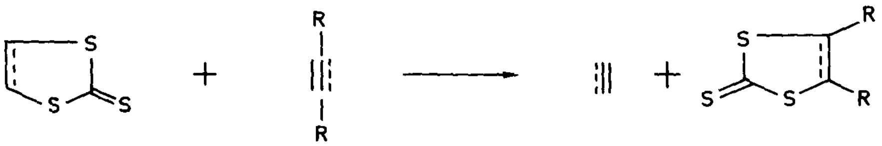
I. INTRODUCTION

The remarkably fast development of the chemistry of five-membered heterocyclic ketones, thiones, and imines, mainly the derivatives of 1,3- and 3H-1,2-dithioles containing a double-bonded exocyclic heteroatom, in the past decade or so has been caused by several factors. Firstly, these compounds are hetero analogs of tropone or fulvene and, consequently, possess aromatic properties. Secondly, the ability of S-containing heterocycles to give charge-transfer complexes with suitable acceptors provided the additional stimulus for the study of such structures since the complexes obtained exhibit metal-like conductivity[1] in quite a number of cases. Thirdly, dithiolethiones as well as their hetero analogs may enter into various cycloaddition reactions which makes these compounds valuable starting materials in the synthesis of complex heterocycles. Besides, the periselectivity[2-4] of these reactions determined by the reagent structure may vary considerably which leads to changes in the reaction path and to a great variety of obtainable structures. Finally, dithiolethiones and their hetero analogs may enter into pericyclic reactions of a unique type. Consider two reactions of 3H-1,2-dithiole-3-thiones (1) and 1,3-dithiolane-2-thiones (2) with an olefin or acetylene, activated by electron-withdrawing groups occurring in accordance with the schemes:

(1)



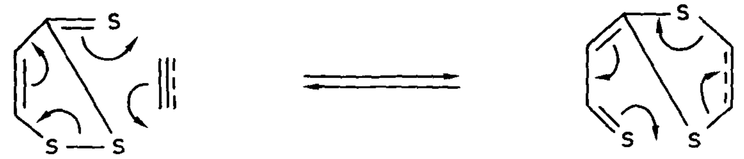
(2)



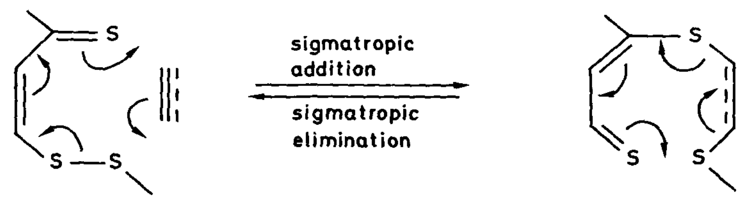
The outstanding peculiarity of the first reaction is that the one with olefin resembles cycloaddition, yet due to the structural characteristics of the starting dithiolethione the reaction must inevitably be accompanied by a sigmatropic rearrangement with S—S bond cleavage and, consequently, by opening of the starting heterocycle. The classification of such a process within the conventional framework presents difficulties.

Earlier, N. S. Zefirov and S. S. Trach[5-9] formulated and developed a system of classification of reactions based on the formal-logical approach. Within the framework of this system the given reaction (1) represents a *sigmatropic addition*.[6,7] Consider this problem in greater detail. In order to perform the classification consider the structural changes in the process by placing *all* bonds which change their order in the course of the transformation on the polygon perimeter (Scheme 3). It is easy to see that the process discussed is the combination of addition to a double (triple) bond with migration of a bond from a double-bonded sulfur atom to one of the "disulfide" sulfur atoms. After exclusion of "diagonal" or "peripheral" bonds (Scheme 4) one can see that the arrangement and order

(3)



(4)



of bonds at eight centers are changed, but not a single of them changes its formal valence (constant "pericyclic number")[5,7] and the process as a whole is described as a monocyclic electron transfer. The consideration of the number of components and reaction fragments,[6–9] *i.e.* the sets of those reaction centers of reaction systems which are connected by bonds of non-zero order situated on the edges of an octagon, shows that the initial system is constructed from two linear components and the final system from one linear component. Thus, this interconversion belongs to the type of chain ⇌ multi-chain transformations[6–9] which represent the formation or fragmentation of linear systems (reactions of addition and elimination; see examples in Ref. 9).

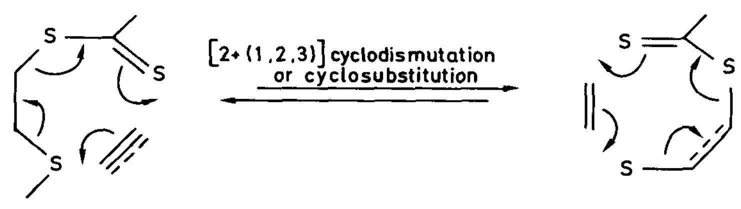
The next step of this classification is the evaluation of the type and number of fragments[6] for every component. By reaction fragment one understands an individual reaction center of a group of centers linked together by bonds of non-zero order which behave as a unified whole in a process.[6] Two types of the fragments, namely I and A fragments, have been introduced. The A fragment possesses the characteristic that electron transfer leads to simultaneous formation or rupture of two single bonds between the terminal atoms of this fragment (*e.g.* $\cdot{=}\cdot \rightleftharpoons -\cdot-\cdot-$). In Eq. 4 the left reaction system is the two-component one. The component $\cdot{=}\cdot$ may be regarded as the A fragment in the chain form ($^{c}A_2$ fragment). The right reaction system of Eq. 4 contains this A fragment in a ring form ($-{}^{r}A_2-$). An I_n fragment, where n is the number of reaction centers, has the characteristic that the electron transfer leads to migration of a single bond from one terminal center of this fragment to another terminal center ($I_n- \rightleftharpoons -I_n$). The six-centered component on the left side of Eq. 4 may be regarded as the combination of two I fragments, I_5–I_1. Thus, the reaction of Eq. 4 may be described in terms of reaction fragments as $I_5\text{–}I_1 + {}^{c}A_2 \rightleftharpoons I_5-{}^{r}A_2-I_1$, and hence it may be classified as a process of *eight-centered isodesmic [2+(1,5)]-sigmatropic addition* (sigmatropic elimination is the reverse reaction) in the case of alkenes, or [2′+(1,5)]-sigmatropic addition (elimination) in the case of alkynes.

It should be stressed that sigmatropic addition reactions (for definition, see[6,7]) have been studied very little; the best known examples are the processes of six-centered [2+(1,3)]-sigmatropic addition (ene reactions or fragmentations of β-ketoacids). Thus, the process considered is of utmost theoretical significance.

Consider the problem of classification of the reaction in Scheme 2. This reaction is another example of an eight-centered process which may be classified according to the Zefirov and Trach approach by placing all the bonds that change their pericyclic number on the perimeter of an octagon (Scheme 5) and then by excluding diagonal bonds (Scheme 6).

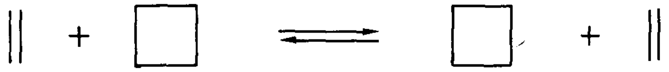
(5)

(6)



It may be seen from Scheme 5 that both the initial and final systems are multi- (two) component ones and hence, one deals with the process of *cyclodismutation.*[6,7] The consideration of fragments allows to finally classify it as an ***eight-centered isodesmic process of** [2+(1,2,3)]-dismutation* (for alkenes); in the case of acetylenes this is a derived process[7] of [2′+(1,2,3)]-cyclodismutation. The simplest analog of this process in a six-centered system is the [2+(1,2,1)]-dismutation (Scheme 7). Earlier we have proposed to call this subtype of cyclodismutation reactions cyclosubstitution.[6] This term will be used throughout the paper.

(7)



Thus, the present review is devoted to the consideration of two unique pericyclic processes for dithiolethiones and their analogs, sigmatropic addition reactions, *i.e.* elimination and cyclosubstitution; in a number of cases these reactions go extremely smoothly which allows one to use them as a tool in the rational synthesis of heterocyclic systems.

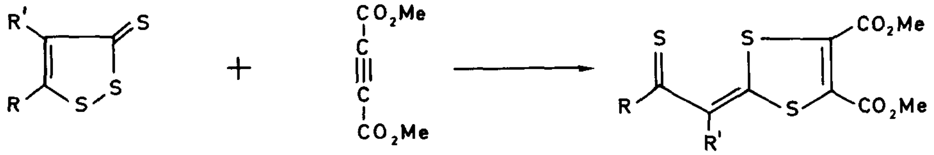
As a matter of fact a recent review on the chemistry of four- and five-membered cyclic disulfides very briefly considers reactions of a similar type for 3H-1,2-dithiole-3-thiones and their imines.[10] We should like to emphasize here the relevance of these reactions for other heterocyclic systems as well. We do not touch upon cycloaddition reactions where fragmentation of a heterocycle occurs before or after the initial act of cycloaddition.

2. SIGMATROPIC ADDITION REACTIONS

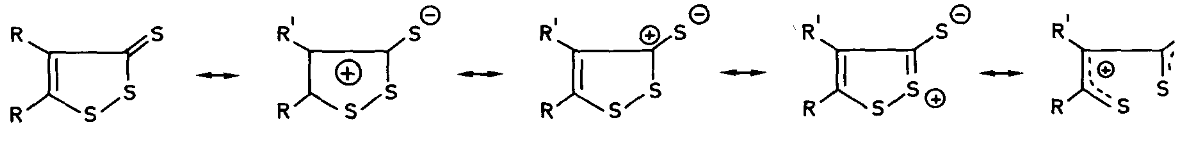
2.1. 3H-1,2-Dithiole-3-thiones (trithiones) and -imines

A short communication by Lehot and Vialle about the formation of 1 : 1 adducts between 5-aryl-3H-1,2-dithiole-3-thiones and phenylacetylene appeared as early as in 1964.[11] Yet, the structures of these adducts were not determined and there was apparently a mistake since the adduct of 5-phenyl-3H-1,2-dithiole-3-thione and phenylacetylene upon desulfuration with Raney nickel gives 2-methyl-1,4-diphenylbutane. It was also noted that 4-substituted trithiones do not enter into the reaction.

In 1965 Behringer and Wiedenmann[12] and later independently Easton and Leaver[13] showed that trithiones of various structures readily react with acetylenes containing electron-withdrawing groups:

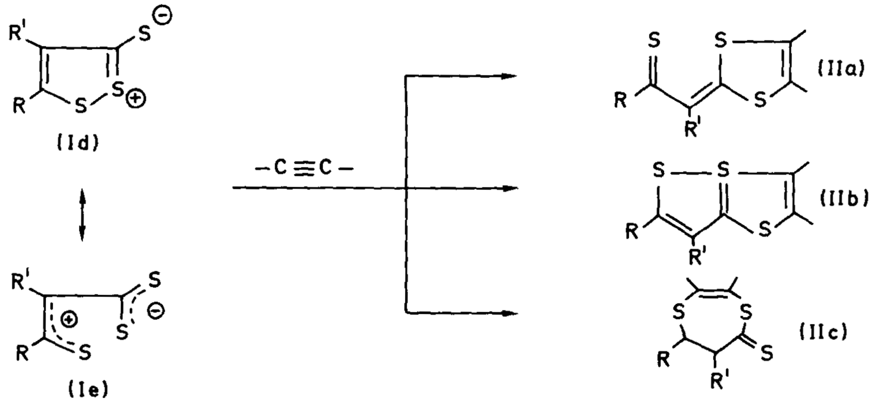


Discussing the structure of the adducts formed, the authors proposed to consider the following resonance structures of the initial trithiones (I a–e):



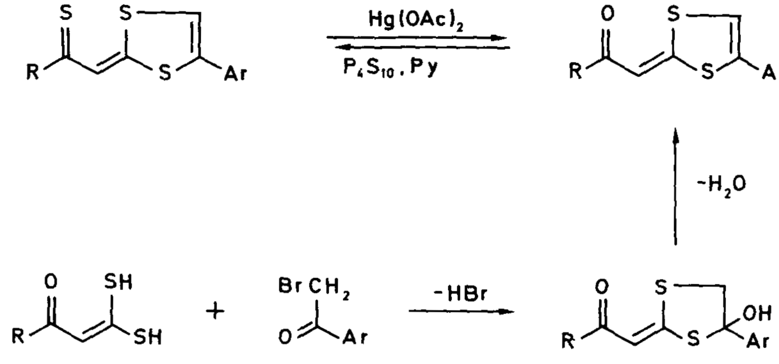
(Ia) (Ib) (Ic) (Id) (Ie)

The adduct of 5-phenyl-3H-1,2-dithiole-3-thione and diethyl acetylenedicarboxylate upon desulfuration with Raney nickel gives propylbenzène and diethyl succinate due to which only (II a–c) were discussed as possible structures since their formation can be explained through resonance structures (I d–e).

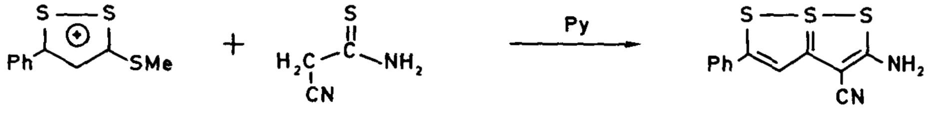


The main evidence to the effect that the adduct structure is that of a 2-(thioacylmethylene)-1,3-dithiole was derived by chemical transformations.[12,14–16]

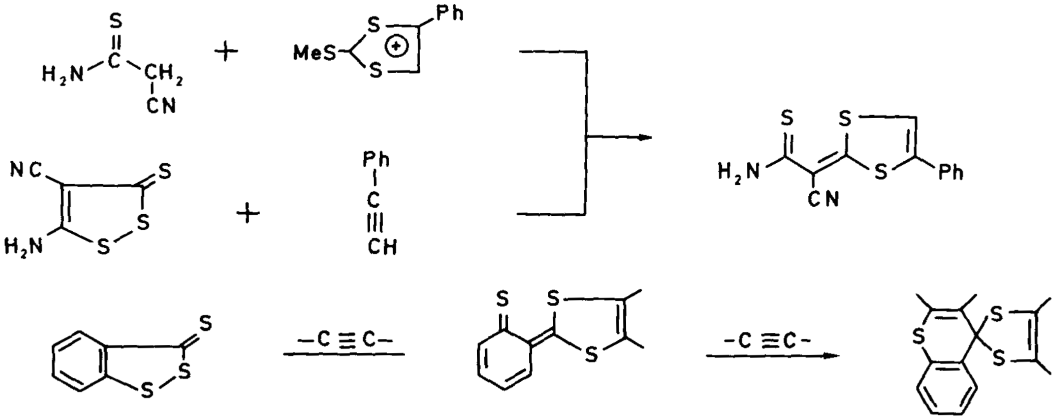
Interaction of β,β-dimercaptovinyl ketones and α-bromomethyl ketones gives 2-(acylmethylene)-1,3-dithioles, transformed by treatment with phosphorus pentasulfide into the corresponding thioketones identical to those obtained by interaction of arylacetylenes with 5-R-3H-1,2-dithiole-3-thiones.[15,16] The reverse transformation of a thione functionality into a ketone is easily carried out either with mercury acetate[15] or by oxidation with permanganate.[12,14]



Interaction of 3-methylthio-5-phenyl-1,2-dithiolium iodide and its analog, 2-methylthio-4-phenyl-1,3-dithiolium iodide, with α-cyanothioacetamide gives two isomeric trisulfides, the latter being identical with the one obtained from the interaction of 5-amino-4-cyano-3H-1,2-dithiole-3-thione with phenylacetylene.[12,14]



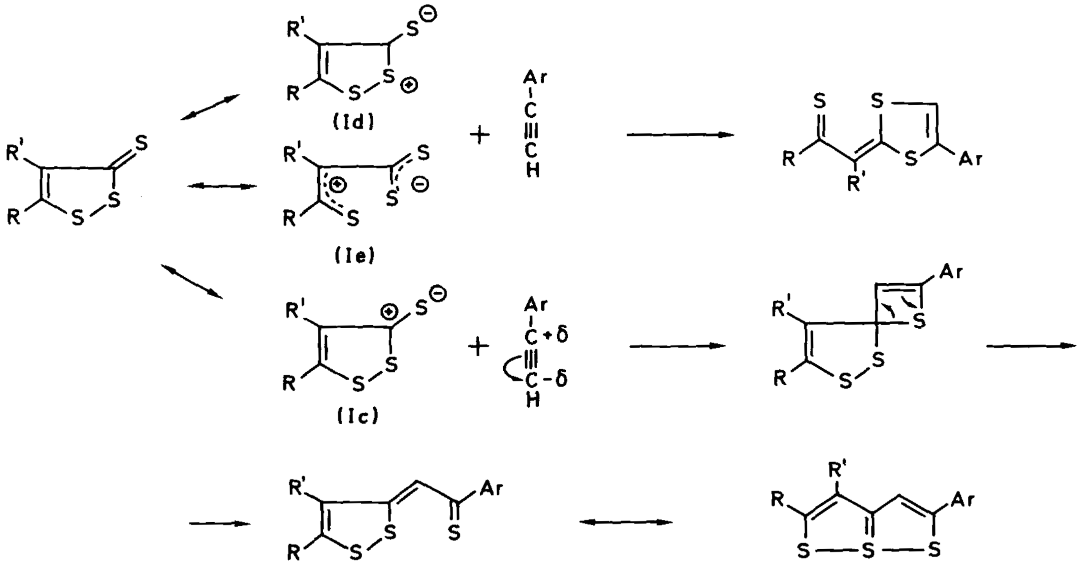
A $1,3aS^{IV},4$-trithiapentalene structure (II b) for these cycloadducts could be excluded since no 1 : 1 adduct could be obtained by interaction of 3H-1,2-benzodithiole-3-thione with acetylenes. Due to the instability of the intermediate ortho-quinoid structure the reaction then proceeds with addition of a second molecule of acetylene and formation of the corresponding spirane:[12,13,17]



In the case of dimethyl acetylenedicarboxylate the spirane structure was confirmed by formation of a mixture of dimethyl succinate and dimethyl benzylsuccinate upon desulfuration with Raney nickel.[17]

On the other hand, 1 : 1 adducts should be stable if the structure II b with hypervalent sulfur was present, since $2,3$-benzo-$1,6,6aS^{IV}$-thithiapentalene is quite stable.[12]

In 1966 Vialle *et al.* were the first to note that acetylenes with less powerful electron-withdrawing groups, namely arylacetylenes, form $1,6,6aS^{IV}$-trithiapentalenes via an initial [2+2]-cycloaddition of the acetylenes to the trithione thiocarbonyl group followed by a [2+2]-cycloreversion and a sigmatropic addition:[15]

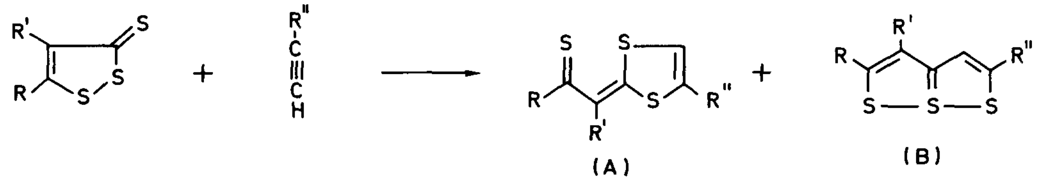


These authors noted that the reaction conditions influence the pathway of adduct formation considerably, *i.e.* more 1,6,6aS$^{\mathrm{IV}}$-trithiapentalene is formed in boiling xylene than in xylene saturated with HCl. Thus, phenylacetylene and 5-phenyl-3H-1,2-dithiole-3-thione under neutral conditions (12–14 hrs boiling) yields only 2,5-diphenyl-1,6,6aS$^{\mathrm{IV}}$-trithiapentalene (30%) while with acid catalysis (4 hrs boiling) 4-phenyl-2-(thiobenzoylmethylene)-1,3-dithiole (30%) is formed.[15–16] On the other hand, Behringer *et al.* found in contrast to this only the latter compound in 42% yield in the same reaction with 5 hrs boiling.[14]

Similar differences were observed in the reaction between 5-p-chlorophenyl-3H-1,2-dithiole-3-thione and phenylacetylene (Table I). The conclusion may be drawn from Table

TABLE I

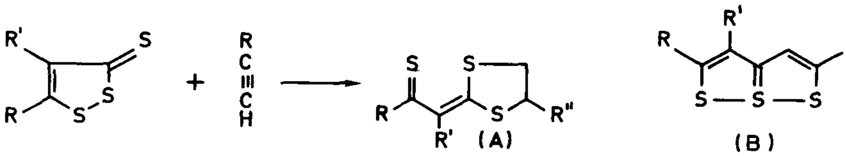
Competitive Pathways for the Reactions of Trithiones with Arylacetylenes:



R	R′	R″	solvent^a	Yields, % A	Yields, % B	Refs
1	2	3	4	5	6	7
Ph	H	Ph	xylene	—	45,30	15,16
Ph	H	Ph	xylene	42	—	12,14
Ph	H	Ph	xylene, sat. HCl	30	—	15,16
Ph	H	p-BrC$_6$H$_4$	xylene	15	20	16
Ph	H	p-ClC$_6$H$_4$	xylene	10	5	16
Ph	H	p-NO$_2$C$_6$H$_4$	dioxan	39	—	12,14
Ph	H	p-MeOC$_6$H$_4$	xylene	—	48	14
p-BrC$_6$H$_4$	H	Ph	xylene	20	20	16
p-BrC$_6$H$_4$	H	Ph	xylene, sat. HCl	25	—	16
p-ClC$_6$H$_4$	H	Ph	xylene	25	25	16
p-ClC$_6$H$_4$	H	Ph	xylene	52	—	12,14
p-ClC$_6$H$_4$	H	p-MeOC$_6$H$_4$	tolyene	58	—	12,14
p-MeOC$_6$H$_4$	H	Ph	xylene	—	50	15,16
p-MeOC$_6$H$_4$	H	Ph	xylene, sat. HCl	60	10	16
Ph	Me	Ph	xylene	—	50	16
Ph	Me	Ph	xylene, sat. HCl	10	20	16
p-MeOC$_6$H$_4$	Me	Ph	xylene	—	50	16
p-MeOC$_6$H$_4$	Me	Ph	xylene, sat. HCl	15	15	16
MeS	Me	MeS	xylene	—	42	20
MeS	Ph	MeS	xylene	43	—	20
MeS	p-MeC$_6$H$_4$	MeS	xylene	38	42	20

[a] The reactions were carried out in the boiling solvents.

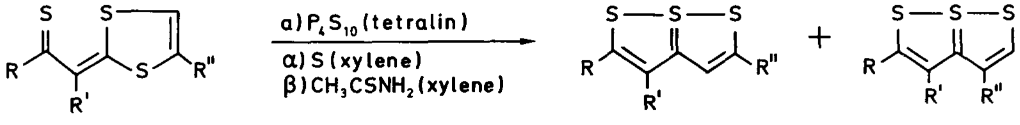
I that the increase in steric demands for the cyclization, *e.g.* introduction of a methyl group into position 4 of 5-aryl-3H-1,2-dithiole-3-thiones hinders the formation of 1,6,6aS^{IV}-trithiapentalenes. Tolane, which does not react in boiling xylene, interacts with 5-phenyl-3H-1,2-dithiole-3-thione in boiling DMF with formation of 2,3,5-triphenyl-1,6,6aS^{IV}-trithiapentalene (41%)[12,14] while 4-methyl-5-phenyl-3H-1,2-dithiole-3-thione under the same conditions only gives traces of 4,5-diphenyl-2-(α-thiobenzoylethylidene)-1,3-dithiole.[18,19] Due to certain contradictions in the cited papers 12, 14 and 15, 16 it is difficult to estimate the influence of para-substituents of the phenyl rings of arylacetylenes and of 5-aryl-3H-1,2-dithiole-3-thiones on this dichotomy of cycloaddition. Of interest is the influence of the nature of substituents in position 4 of 5-methylthio-4-R-3H-1,2-dithiole-3-thiones on the addition to methylthioacetylene[20] (Table I).



Photochemical excitation of trithiones promotes the reaction with less active acetylenes (phenylacetylene, tolane, dimethylacetylene) the reaction predominantly following a sigmatropic addition pathway.[18,19]

Brownish-green 2-(α-thioacylalkylidene)-1,3-dithioles and crimson 1,6,6aS^{IV}-trithiapentalenes can readily be identified by their electronic spectra and chromatographic behavior.

It should be noted that both reaction products, in the absence of catalysts, do not transform into each other (boiling in tetralin for 3 hrs). Yet, Vialle *et al.* succeeded in transforming 2-(α-thioacylalkylidene)-1,3-dithioles into the corresponding 1,6,6aS^{IV}-trithiapentalenes by heating them with phosphorus pentasulfide in tetralin.[16,20]

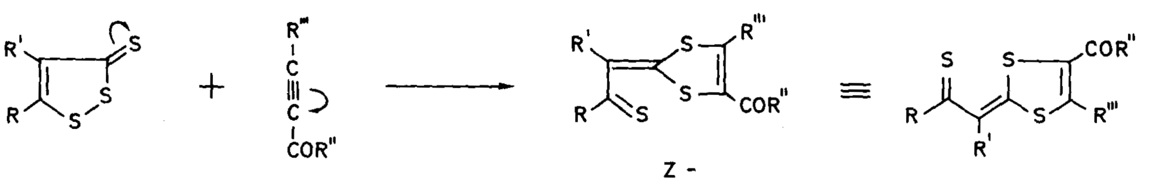


(A) (B) (B')

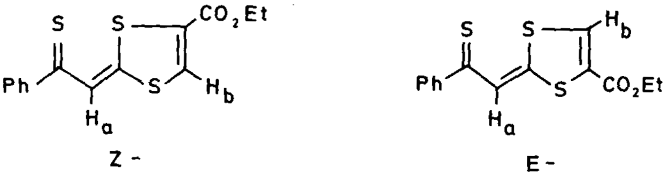
Sulfur in boiling xylene was later suggested as isomerization catalyst.[21] The presence of traces of sulfur may perhaps account for the above-mentioned differences in the adduct formation of arylacetylenes and trithiones. Thioacetamide was found to be the most effective catalyst.[22,23] The second isomeric 1,6,6aS^{IV}-trithiapentalene B' corresponding to the adducts A given in Table I is not observed.

Later the reaction between trithiones and acetylenes was extended to a diversity of compounds. The activity of acetylene compounds in these reactions decreases in the order $R'COC{\equiv}CCOR > HC{\equiv}CCOR \sim Ar(Alk)C{\equiv}CCOR > ArC{\equiv}CH > ArC{\equiv}CAr$. When acetylenes with at least one carbonyl or carbalkoxy group are used the reaction usually only takes place with formation of 2-(α-thioacylalkylidene)-1,3-dithioles.

Adduct formation with asymmetric acetylenes $R'C{\equiv}CCOR$ proceeds to give a mixture of (Z)- and (E)-2-(α-thioacylalkylidene)-1,3-dithioles, though only the (Z)-isomer ought to be expected.[14,23,24]



Such a mixture of isomers was found, for example, to result from the interaction of 5-aryl- and 4,5-diphenyl-3H-1,2-dithiole-3-thiones with methyl and ethyl propiolate.[23,24]

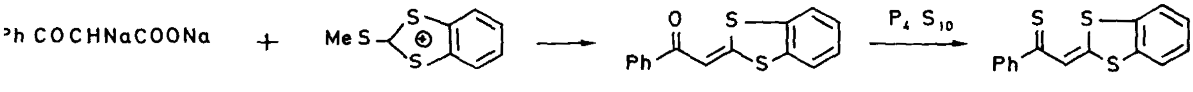


The NMR spectrum of 2-thiophenacylidene-4-carbethoxy-1,3-dithiole in $CDBr_3$ at 40–110°C contains the signals of the H_a and H_b protons of both isomers (4 : 6 isomer ratio), but at 140°C the signals merge due to the rapid isomerization. When this mixture is heated in the presence of thioacetamide a mixture of isomeric 2- and 3-carbethoxy-5-phenyl-1,6,6aS^{IV}-trithiapentalenes is formed.[23]

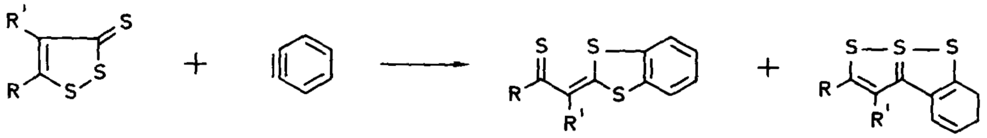
Interaction between 3H-1,2-dithiole-3-thione and 4-R-3H-1,2-dithiole-3-thiones, respectively, and acetylenes containing electron-withdrawing groups gives 2-(α-thioformylalkylidene)-1,3-dithioles.[17,25,27]

Dehydrobenzene also readily reacts with trithiones.[13,17–19,28,29]

The structure of 2-thiophenacylidene-1,3-benzodithiole for the product of the reaction between dehydrobenzene and 5-phenyl-3H-1,2-dithiole-3-thione was acertained by independent synthesis.[17]



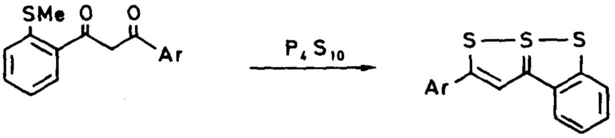
It was later shown that various amounts of 2,3-benzo-1,6,6aS^{IV}-trithiapentalene derivatives are formed with dehydrobenzene together with the adduct generated by sigmatropic addition.[28]



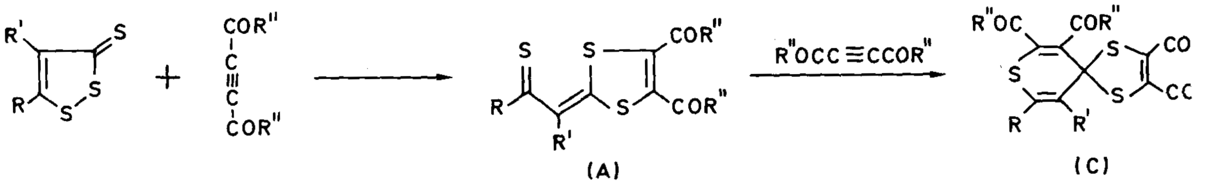
(A) (B)

It should be noted that in this case it is impossible to transform (A) into (B) by boiling in naphthalene, DME, or THF nor catalytically in the presence of sulfur or thioacetamide.

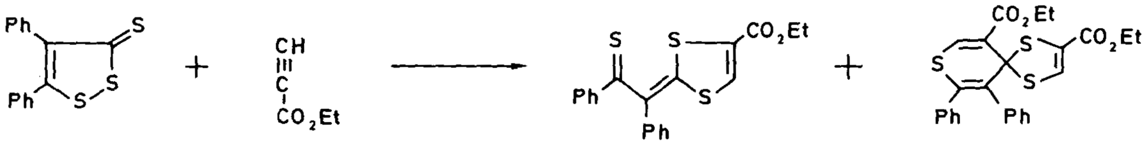
The adduct structure (B) was ascertained by independent synthesis from 1-(o-methylthiophenyl)-3-arylpropanediones-1,3:



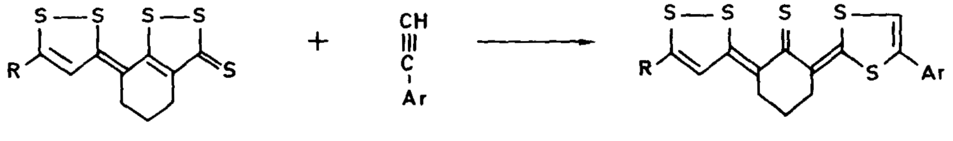
The interaction of trithiones with excess of the most active acetylenes like acetylenedicarboxylic acid esters or dibenzoylacetylene gives not only brownish-green 1 : 1 adducts, but also pale-yellow 1 : 2 adducts (C) with a spirane structure.[13,17,24]



The structure of the 1 : 2 adduct from 5-phenyl-3H-1,2-dithiole-3-thione and dimethyl acetylenedicarboxylate was ascertained by isolation of dimethyl succinate and dimethyl 3-phenylpropylsuccinate after desulfurization with Raney nickel.[18] The ethyl esters of methyl- and phenylpropiolic acid form only 1 : 1 adducts,[18] while the propiolic ester gives both 1 : 1 and 1 : 2 adducts with 4,5-diphenyl-3H-1,2-dithiole-3-thione:[24]

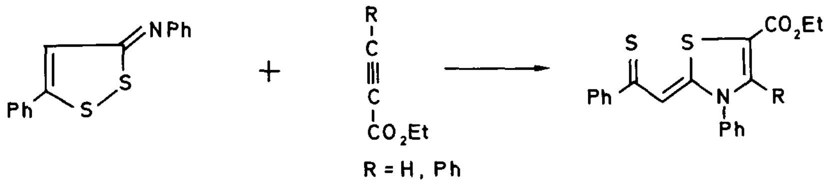


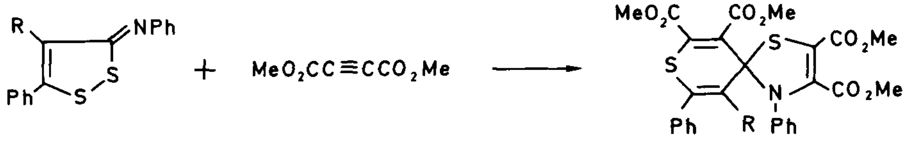
2-(5-R-3H-1,2-dithiolidene-3)-6-(4-Ar-1,3-dithiolidene-2)-cyclohexanethiones are formed by interaction of 7-(5-R-3H-1,2-dithiolidene-3)-4,5,6,7-tetrahydro-3H-1,2-benzodithiole-3-thiones with arylacetylenes.[30]



The reaction with acetylenes is now so well understood that it has been used as a criterion for the 3H-1,2-dithiole-3-thione structure of newly obtained compounds when there is some doubt.[31,32]

Unlike 3H-1,2-dithiole-3-thiones 3H-1,2-dithiole-3-ones do not react with acetylenes. On the other hand, 5-phenyl- and 4,5-diphenyl-3H-1,2-dithiole-3-phenylimine give 1 : 2 adducts with dimethyl acetylene-dicarboxylate.[24] The less active ethyl esters of propiolic and phenylpropiolic acid react only with 5-phenyl-3H-1,2-dithiole-3-phenylimine in boiling benzene or xylene with formation of 2-(thiobenzoylmethylene)-5-carbethoxythiazolines.[24]

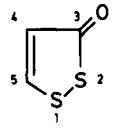
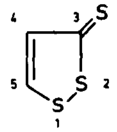
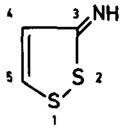




At our request Yu. M. Udachin (K. A. Timiryazev Agricultural Academy) has carried out quantum-mechanical calculations (MO-SCF, PPP approximation) of the 3H-1,2-dithiole-3-one, -thione and -imine molecules. The results obtained are shown in Table II. Inspection of the values of the HOMOs of the heterocycles and of the LUMOs of the acetylenes (Table II) predicts the same order of reactivity 3-thione > -imine > -one which is observed experimentally.

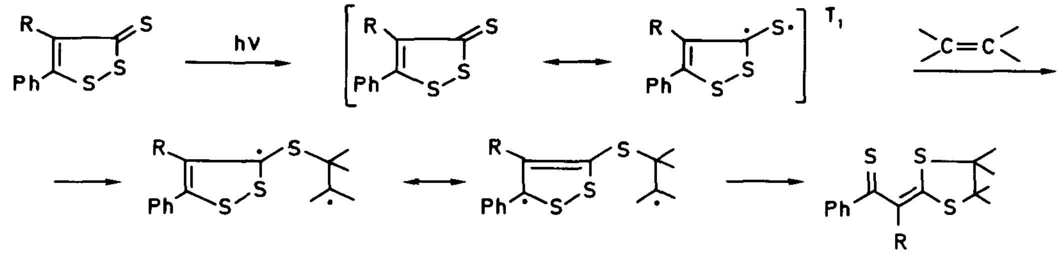
TABLE II

Results of MO-SCF (PPP) Calculations

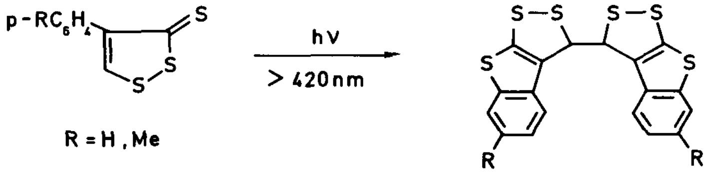
Compound	atom	q	HOMO c	HOMO E (eV)	LUMO c	LUMO E (eV)
	O	−0.447	0.451	−9.587	0.405	−1.810
	S^2	0.084	−0.362		0.173	
	exo-S	−0.417	0.764	−8.695	0.495	−2.691
	S^2	0.111	−0.293		0.217	
	N	−0.323	0.573	−9.132	0.476	−1.828
	S^2	0.078	−0.369		0.169	

Unlike acetylenes alkenes do not react thermally with trithiones. However, in 1972 Inamoto *et al.* found that alkyl substituted olefins react photochemically with 5-aryl-3H-

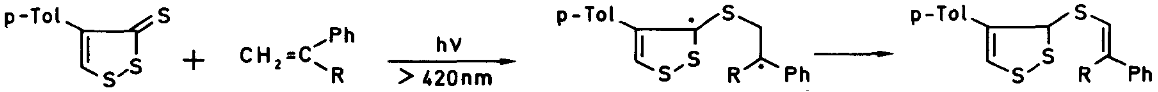
1,2-dithiole-3-thiones in benzene giving 2-(thioaroylmethylene)-1,3-dithiolanes.[33,34] The following picture of this transformation is proposed:



While 5-aryl-3H-1,2-dithiole-3-thiones are photochemically stable,[35] 4-aryl substituted compounds undergo photochemical transformation when irradiated by light with >420 nm wavelength.[36]

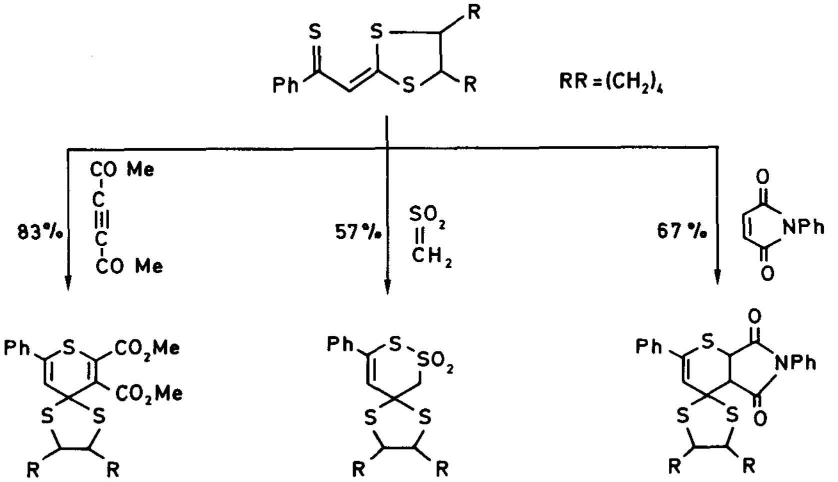


Upon irradiation in the presence of 1,1-diphenylethylene or α-methylstyrene adducts still containing the 1,2-dithiole ring are formed.

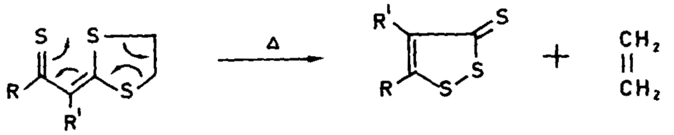


Various alkyl substituted olefins have been subjected to photochemical reaction with 5-aryl-3H-1,2-dithiole-3-thiones, namely cis- and trans-2-butene, cyclopentene, cyclohexene, cis-cyclooctene, norbornene, and norbornadiene.[34] Strained olefins (1,3,3-trimethylcyclopropene, norbornadiene, and, to a smaller extent, norbornene) can react in the absence of photochemical excitation.[29,37] 3H-1,2-Dithiole-3-ones do not react photochemically with olefins.[34]

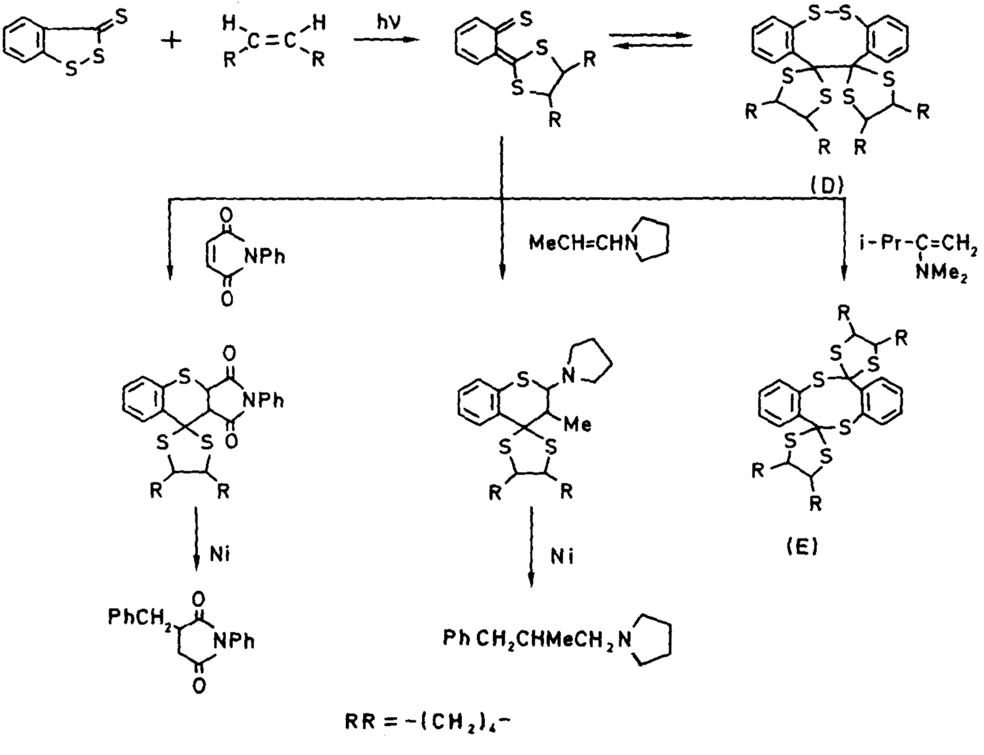
The 2-(thioaroylmethylene)-1,3-dithiolanes formed react with various dienophiles, like other thioacetals of thioacylketenes, by [4+2]-cycloaddition.[38,39]



Thermolysis of 2-(α-thioacylalkylidene)-1,3-dithiolanes at 180°C leads to sigmatropic elimination with formation of the corresponding 3H-1,2-dithiole-3-thiones and ethylene.[40]



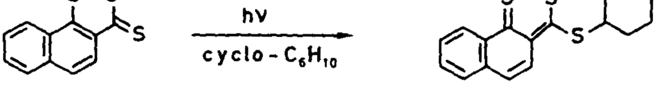
Upon irradiation of a 3H-1,2-benzodithiole-3-thione and cyclo-olefin mixture rather stable blue o-thioquinonemethides which are in equilibrium with their colorless ("head-to-head") dimer forms (D) were obtained for the first time.[41–44]



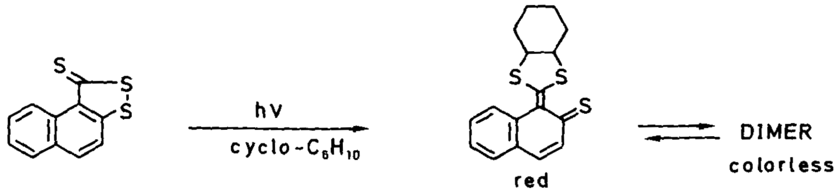
Upon dissolution of the colorless crystals of the dimer (D) the formation of blue solutions is observed due to a dimer-monomer equilibrium. The monomer structure is confirmed by formation of adducts with N-phenylmaleinimide and 1-pyrrolidinopropene, desulfurization of which with Raney nickel gives N-phenyl-benzylsuccinimide[43,44] and 1-pyrrolidino-2-methyl-3-phenylpropane,[45,46] respectively. In the presence of 2-N,N-dimethylamino-3-methyl-1-butene irreversible dimerization of the o-thioquinonemethides to ("head-to-tail") dimers (E) is observed.[42,47]

The stereo- and regioselectivity of the cycloaddition reactions of o-thioquinonemethides have also been studied.[42,48]

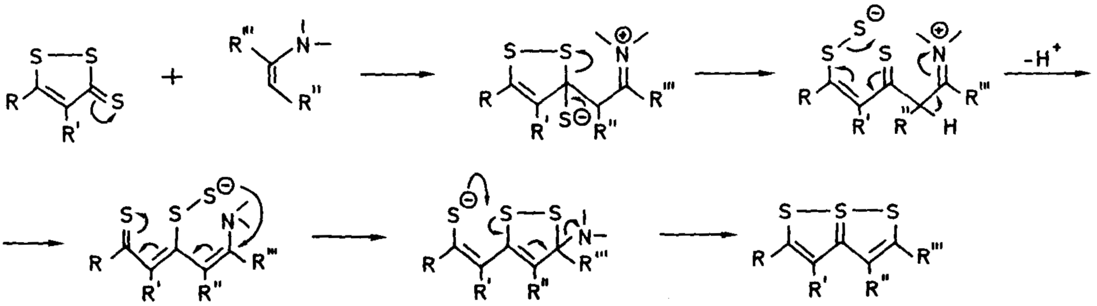
Photochemical reaction of naphtho[2,1-d]-3H-1,2-dithiole-3-thione with cyclohexene leads to the formation of a stable dark purple o-thioquinonemethide:[49]



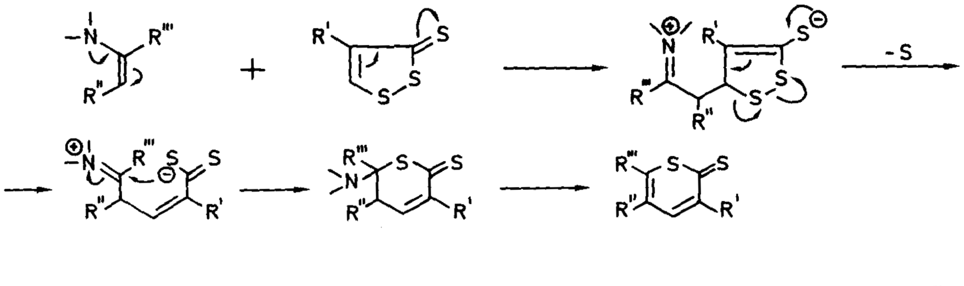
The o-thioquinonemethide formed from the isomeric naphtho[1,2-d]-3H-1,2-dithiole-3-thione is less stable and is in equilibrium with its dimer:[49]



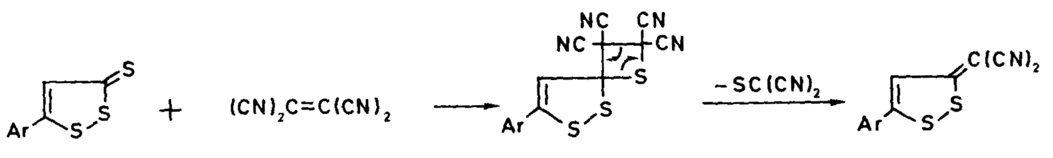
Basic olefins such as enamines react with trithiones via nucleophilic attack at position 3 or 5; the reaction is carried out in boiling acetonitrile.[50,51] With a substituent present in position 5 the attack takes place at position 3 with further formation of 1,6,6aS^{IV}-trithiapentalenes, albeit in low yield, according to:



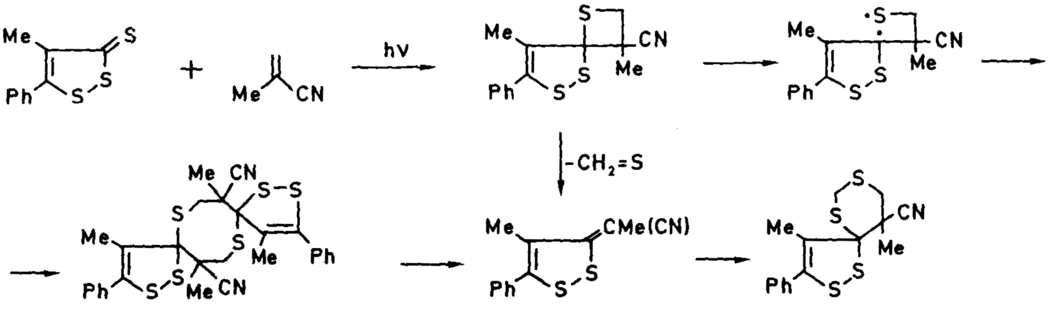
Attack at a free position 5 leads to formation of 2-thiopyranethiones in good yield:



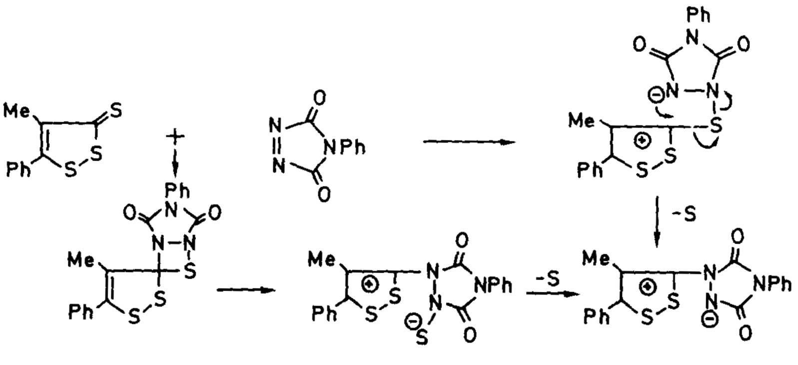
On the other hand, the reaction with the electron deficient tetracyanoethylene first proceeds as a [2+2]-cycloaddition to the thiocarbonyl group followed by cyclofragmentation and 3H-1,2-dithiolidene-3-malononitrile formation:[52]



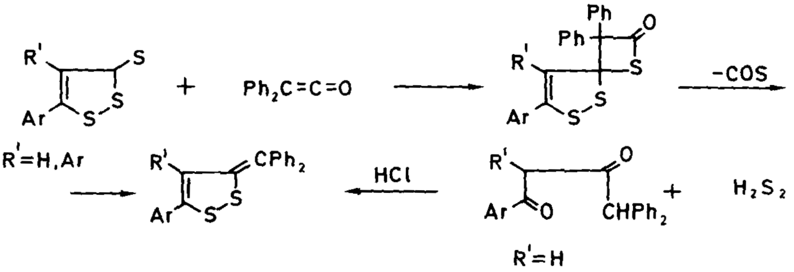
The reaction with methacrylonitrile requires photochemical excitation of the 3H-1,2-dithiole-3-thione and proceeds as follows:[18,37]



Interaction of 4-methyl-5-phenyl-3H-1,2-dithiole-3-thione with one of the most active dienophiles, 4-phenyl-1,2,4-triazoline-3,5-dione, leads to the formation of the zwitterionic 4-phenyl-1-[3-(4-methyl-5-phenyl-1,2-dithiolio)] triazolide shown below:[29,53,54]

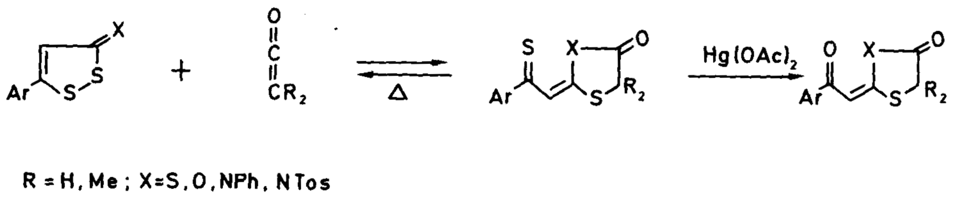


Let us now consider the behavior of heterocumulenes in reactions with trithiones. Ketenes readily react not only with 3H-1,2-dithiole-3-thiones, but also with 3H-1,2-dithiole-3-ones and 3-imines.[55-58] Diphenylketene in boiling xylene reacts with trithiones to give 3-diphenylmethylene-3H-1,2-dithioles.[55] In chloroform a colorless unstable intermediate appears for which the structure of a [2+2]-cycloadduct of the ketene to the thiocarbonyl group was proposed originally.[56]

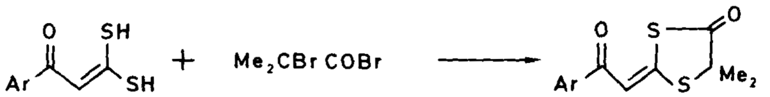


An independent synthesis of the final reaction products has been carried out by condensation of disulfane with 1-aryl-4,4-diphenyl-1,3-butanediones.

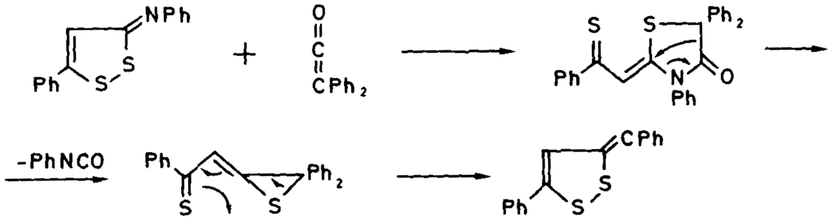
Ketene and dimethylketene in the cold react with 5-aryl-3H-1,2-dithiole-3-thiones, -ones and -imines by sigmatropic addition, the reaction being reversible, and upon heating the adducts decompose into the initial components.[21,58]



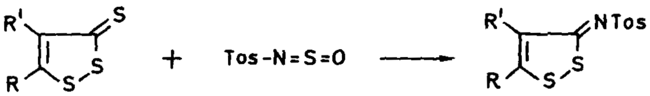
The 2-α-thioaroylalkylidene derivatives so formed can be transformed to 2-α-aroyl derivatives by treatment with mercury acetate. Condensation of the corresponding β,β-dimercaptovinyl aryl ketones with α-bromoisobutyryl bromide affords an independent synthesis of the adducts obtained from trithiones and dimethyl ketene.[58]



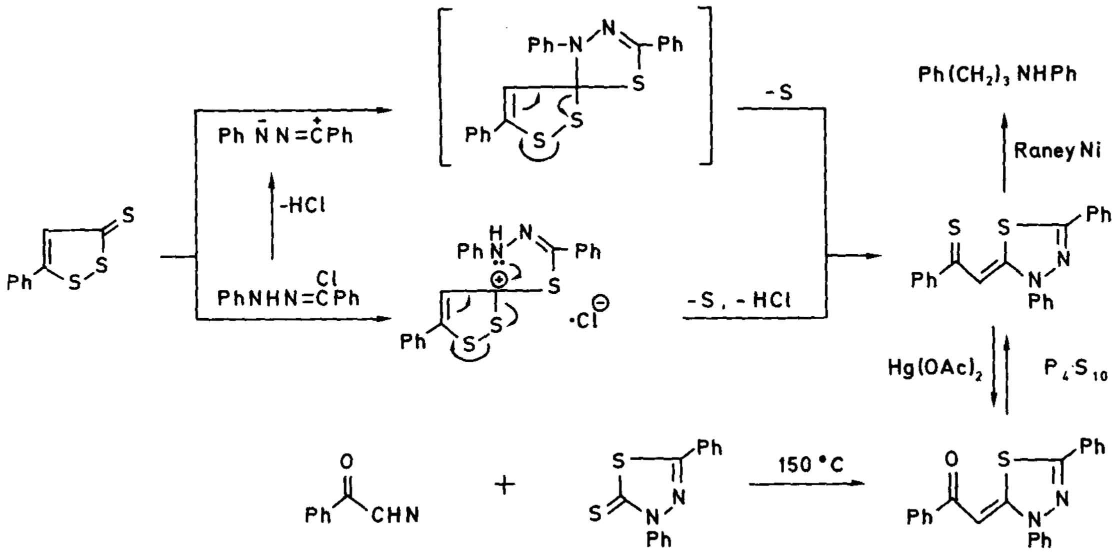
The reaction between 5-phenyl-3H-1,2-dithiole-3-phenylimine and diphenylketene yields a relatively stable intermediate, *i.e.* 3,5,5-triphenyl-2-(thiobenzoylmethylene)-1,3-thiazolidone-4; at room temperature it gradually decomposes to 5-phenyl-3-diphenylmethylene-3H-1,2-dithiole and phenyl isocyanate due to which the structure of the primary intermediate formed from trithiones and diphenyl ketene was revised:[58]



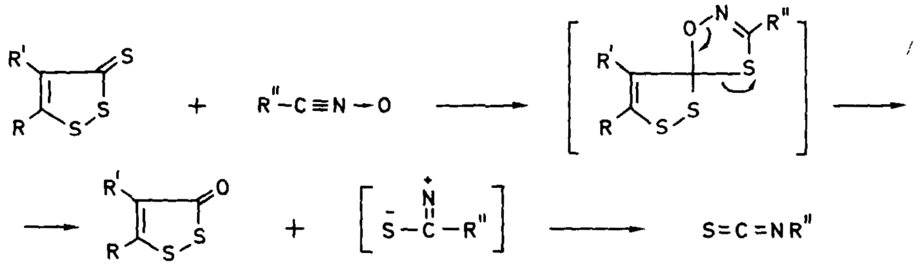
The interaction of trithiones with N-sulfinyl-p-toluenesulfonamide leads to formation of 3H-1,2-dithiol-3-tosylimines.[59]



The interaction of trithiones with 1,3-dipoles initially takes place at the thiocarbonyl group. Thus, 5-phenyl-3H-1,2-dithiole-3-thione with α-chlorobenzylidenephenylhydrazine in boiling xylene gives 3,5-diphenyl-2-(thiobenzoylmethylene)-Δ^4-1,3,4-thiadiazoline.[60,61]



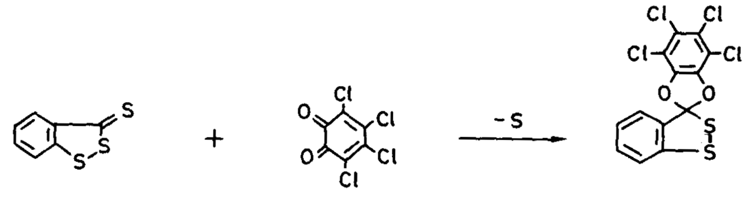
The reaction path may be represented in two ways: as cycloaddition of the 1,3-dipole to the thiocarbonyl group or as electrophilic attack at the exocyclic sulfur atom with subsequent closure of a thiadiazoline ring and opening of the dithiole ring. The product structure was confirmed by desulfurization with Raney nickel (γ-phenylpropylaniline is formed) and by independent synthesis, *i.e.* condensation of diazoacetophenone with 3,5-diphenyl-Δ^4-1,3,4-thiadiazoline-2-thione and further treatment of the ketone obtained with phosphorus pentasulfide.



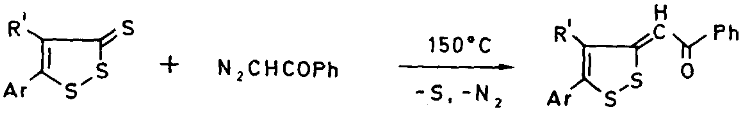
The reaction of trithiones with nitrile oxides leads to formation of 3H-1,2-dithiole-3-ones.[62]

Intermediate spiranes of similar structure are isolated as products of the interaction of 3-aryl-1,4,2-dithiazoline-5-thiones with benzonitrile oxide.[63]

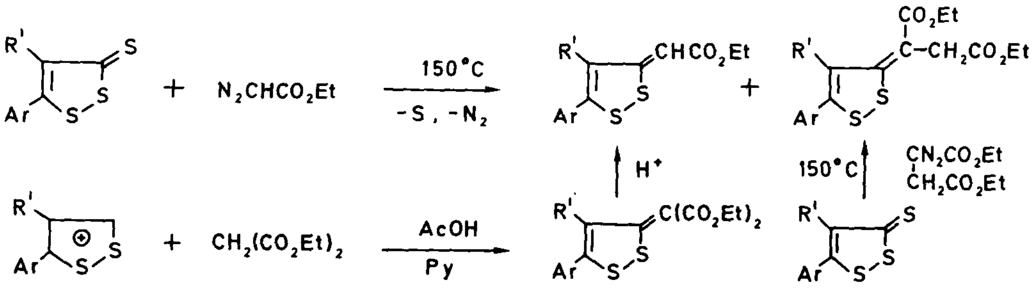
3H-1,2-Benzodithiole-3-thione and tetrachloro-o-benzoquinone gives spiro-1,3-tetrachlorbenzodioxolo-2,3′-[3H-1,2]benzodithiole; a rationalization of the reaction pathway has not been presented.[64]



The initial reaction of trithiones with carbenes and nitrenes probably proceeds as a [2+2]-cycloaddition to the thiocarbonyl group or as an electrophilic attack at the exocyclic sulfur atom. The thermal or photochemical reactions with diphenyldiazomethane proceed with loss of a sulfur atom and formation of 3-diphenylmethylene-3H-1,2-dithioles; in the first case tetraphenylethylene is also obtained while the second gives tetraphenylthiirane.[65,66] The reaction with diazoketones goes along the same pathway:

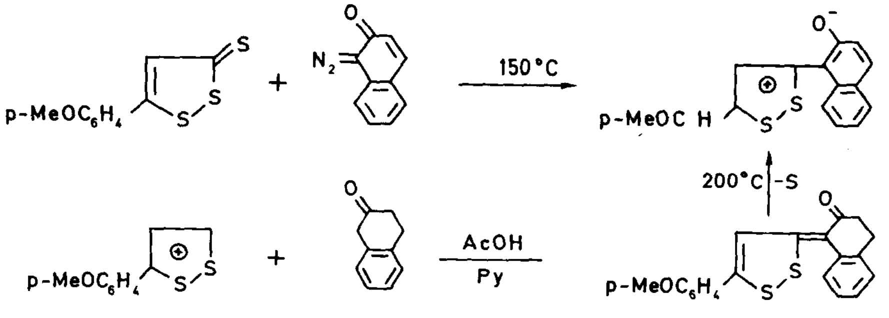


The reaction with diazoacetic ester gives a 1 : 1 and 1 : 2 adduct mixture:

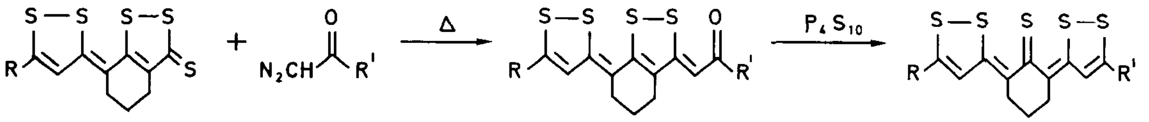


The independent synthesis of the first adduct was achieved by condensation of 1,2-dithiolium salts and malonic ester and that of the second by thermal condensation of the starting thione with diethyl diazosuccinate.[65] The interaction of diphenyldiazomethane with 3H-1,2-benzodithiole-3-selone (3 hrs, 60°C) unexpectedly proceeds with extrusion of the endocyclic sulfur atom and formation of 3-diphenylmethylene-3H-1,2-benzothiaselenole while 3H-1,2-benzodithiole-3-thione labelled with ^{35}S at the exocyclic sulfur atom reacts mainly with ejection of this particular atom.[67]

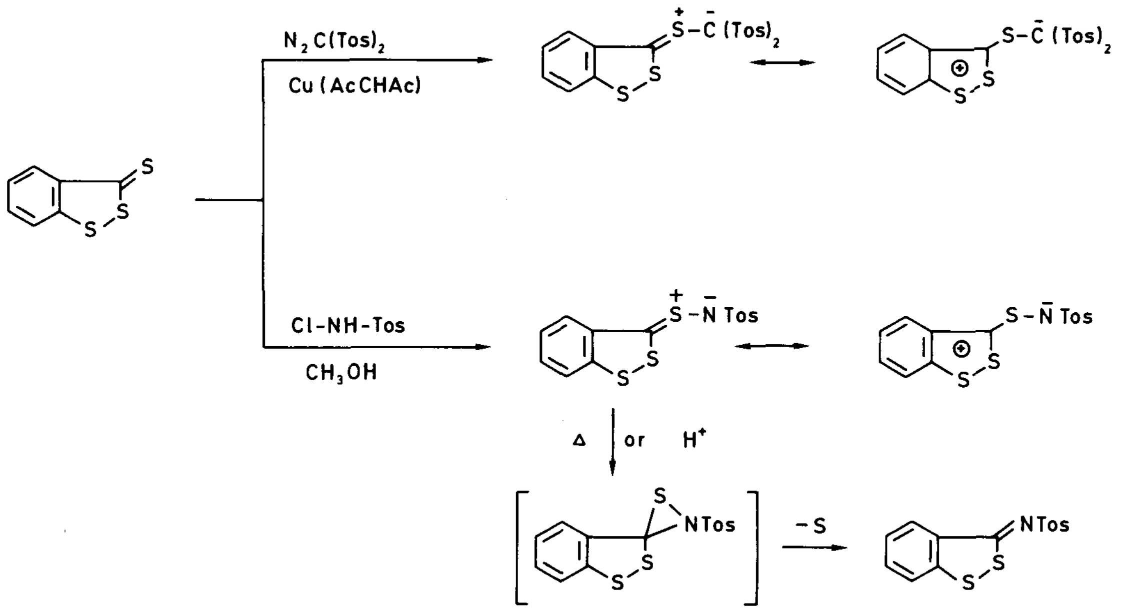
The reaction between 5-p-anisyl-3H-1,2-dithiol-3-thione and 1-diazo-1H-2-naphthalenone at 150°C gave 1-(5-p-anisyl-1,2-dithiolium-3)-2-naphtholate (7% yield), independently synthesized from 3-p-anisyl-1,2-dithiolium perchlorate and β-tetralone with subsequent dehydrogenation of the ketone formed with sulfur at 200°C.[65,68]



The reaction with diazoketones has been used for the synthesis of 2,6-bis(1,2-dithiolidene-3)-cyclohexanethione which is of certain theoretical interest.[69]

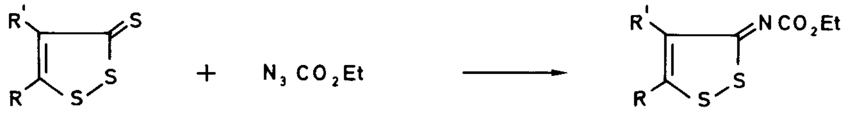


The treatment of 4-phenyl- and 3H-1,2-benzodithiole-3-thiones with stabilized carbenes and nitrenes led to the synthesis of the first stable thiocarbonyl ylides and imides which can be accounted for by the additional delocalization of the positive charge by the dithiole ring.[70,71]



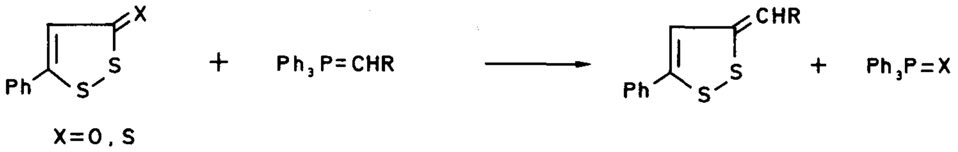
Upon heating or in the presence of acids,[70,71] acid chlorides,[72] thiols,[73] or secondary amines[74] these thiocarbonyl ylides lose a sulfur atom giving the corresponding imines, while a mixture of two imines is formed in their interaction with primary amines.[74] It has been shown by ^{35}S label experiments that the reaction involves extrusion of the thiocarbonyl sulfur atom.[75] In the case of the corresponding selenocarbonyl ylides the reaction follows another pathway, *i.e.* extrusion of the endocyclic sulfur atom and formation of 3H-1,2-thiaselenole-3-imines.[75,76]

It should be noted that the oxidation of 3H-1,2-benzodithiole-3-selone by benzoyl peroxide also triggers a rearrangement and formation of 3H-1,2-benzothiaselenole-3-one.[77] The transformation of thiones to imines can also be carried out using N,N-dichlorosulfamides[78] or N,N-dichlorobenzamides.[79] The reaction between trithiones and ethyl azidoformate also leads to imines



The same treatment transforms 4-phenyl-3H-1,2-dithiole-3-one 2-carbethoxy-4-phenyl-1,2-thiazolidone.[80]

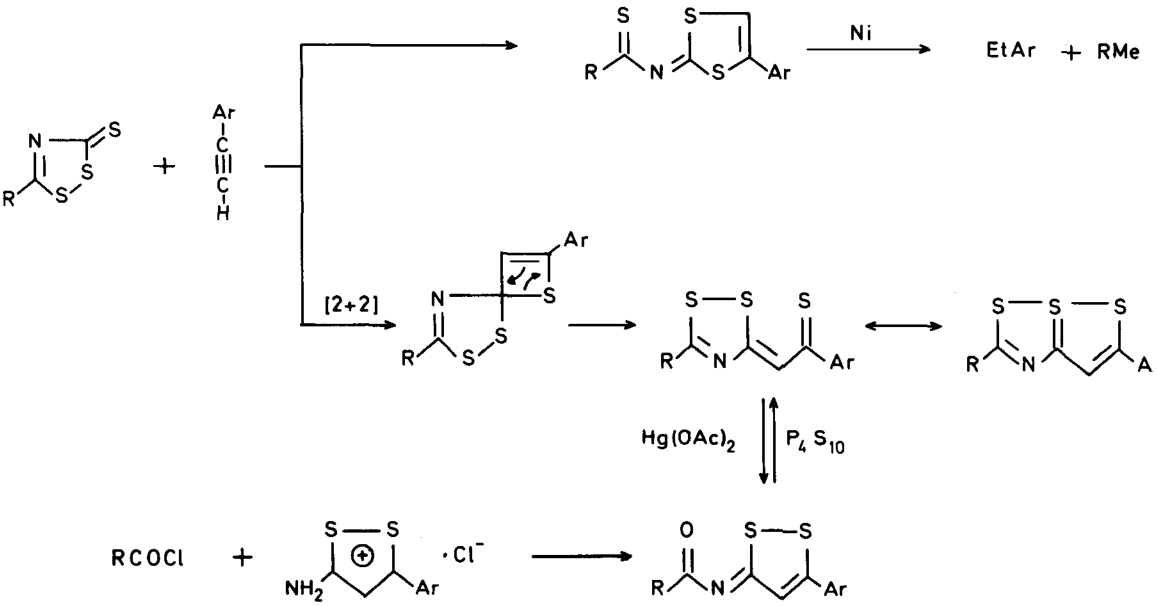
3H-1,2-Dithiol-3-ones or -thiones and phosphoranes react by substitution of the exocyclic heteroatom by a methylene group.[81]



2.2 3H-1,2,4-Dithiazole-3-thiones and -imines

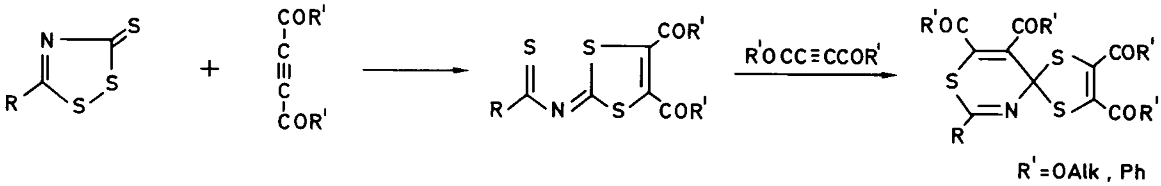
The behavior of 3H-1,2,4-dithiazole-3-thiones, the 4-aza analogs of trithiones in reactions with acetylenes is very similar.

The reaction with arylacetylenes gives a mixture of 2-thioacylimino-1,3-dithioles and 3-aza-1,6,6aS^{IV}-trithiapentalenes with a 3- to 10-fold predominance of the former; moreover the latter are not formed at all in the presence of HCl.[82,83]



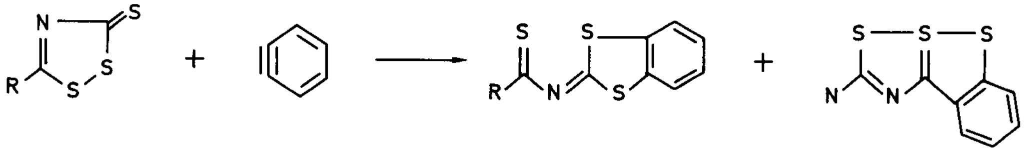
The 3-aza-1,6,6aS^{IV}-trithiapentalene structure was proven by independent synthesis: condensation of 3-amino-1,2-dithiolium chlorides with acyl chlorides and further treatment of the amides obtained with phosphorus pentasulfide.

Interaction with the more active acetylenic dienophiles acetylenedicarboxylic acid esters,[14,63,83–86] dibenzoylacetylene,[25] propynal,[14] and hexafluoro-2-butyne[24] gives only 2-thioacylimino-1,3-dithioles; use of excess acetylenedicarboxylic esters[83] or dibenzoylacetylene[25] under more severe conditions leads to 1:2 adduct formation.

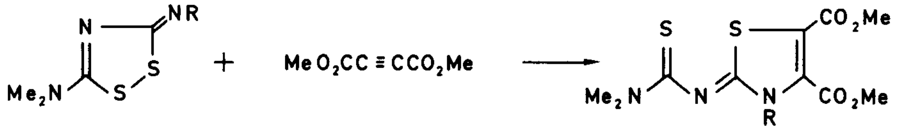


The isomeric 1,3,4-dithiazole-2-thiones do not react with acetylenes[14,84] (see, however 63). It should be noted that a relatively rapid rotation around the C=N bond (on the NMR time scale) has been observed in 2-thioacylimino-1,3-dithioles.[24]

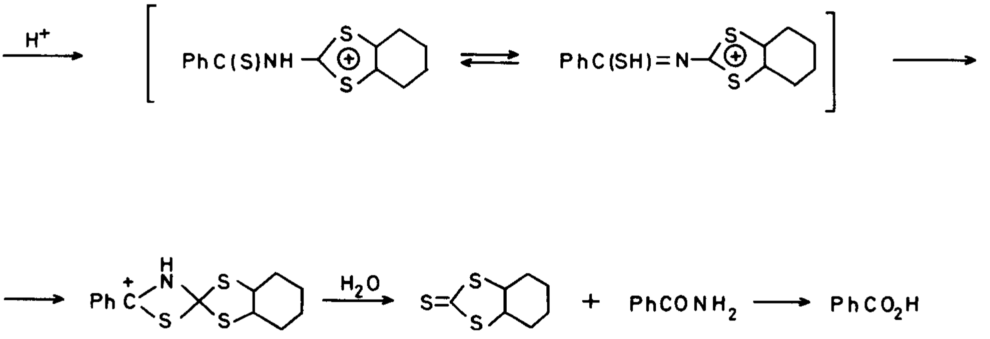
Dehydrobenzene takes part in sigmatropic additions like the acylacetylenes.[28]



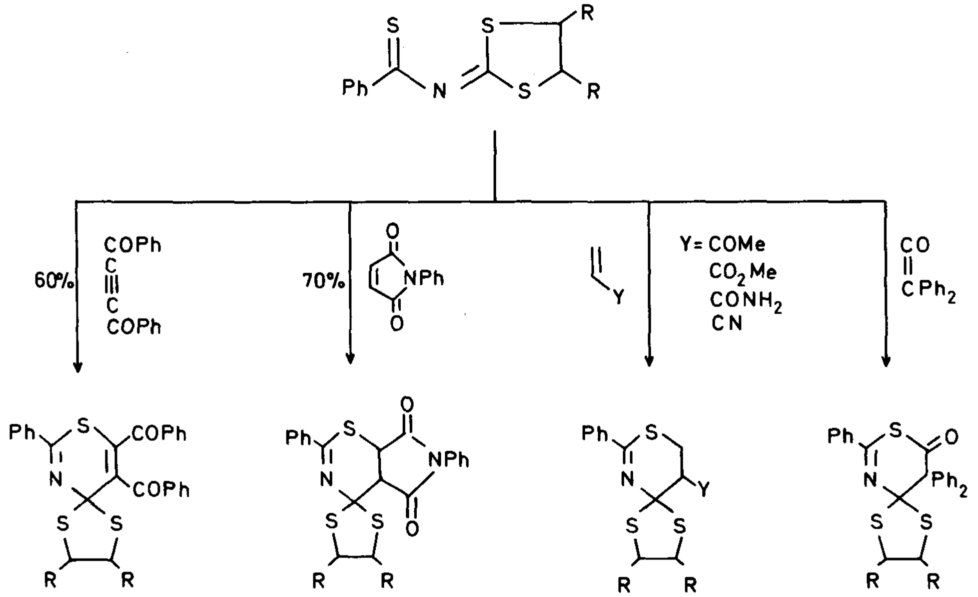
3H-1,2,4-Dithiazole-3-alkyl(aryl) imines react with acetylenedicarboxylic acid esters even in the cold.[83,86,87]



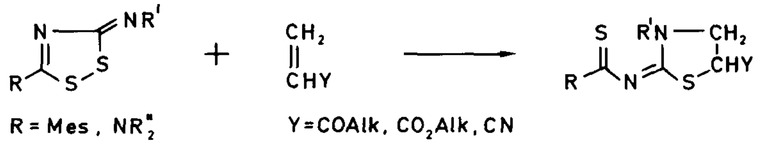
Like trithiones, 3H-1,2,4-dithiazole-3-thiones react photochemically with olefins[34,88] *e.g.*



The structure of the adduct between 5-phenyl-3H-1,2,4-dithiazole-3-thione and cyclohexene has been proven by acid hydrolysis which leads to cis-1,2-cyclohexenetrithiocarbonate and benzoic acid. The N-thioacyldithioimidocarbonates thus obtained can be used as heterodienes in [4+2]-cycloadditions.[39,89]

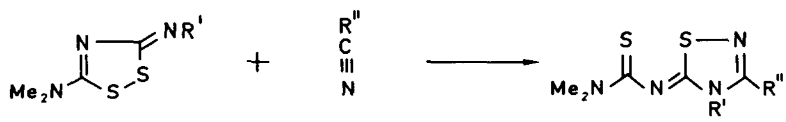


The greater activity of the 3H-1,2,4-dithiazole system in sigmatropic additions as compared to the 1,2-dithiole system is indicated by the fact that 3H-1,2,4-dithiazole-3-imines react thermally with olefins containing electron-withdrawing groups (60–90°C, 3 hrs).[90]

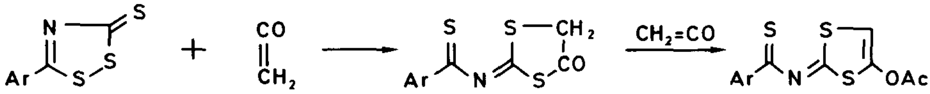


The stereospecificity of the reaction is evident in the case of sigmatropic addition to fumaric and maleic acid esters.

The sigmatropic addition to nitriles of these systems is also unique.[91]

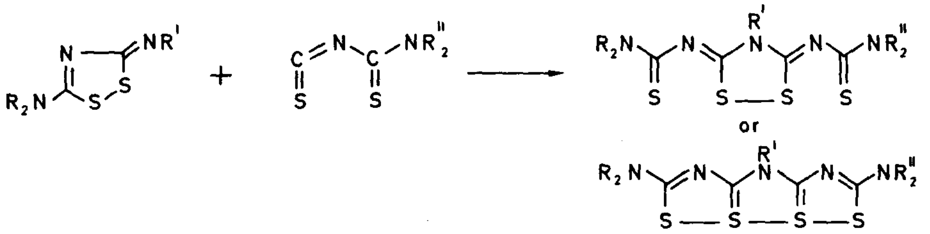


Sigmatropic addition of ketenes to 5-aryl-3H-1,2,4-dithiazole-3-thiones follows the same pathway and is as facile as with trithiones.[58]



The number of heterocumulenes reacting in the same manner with 3H-1,2,4-dithiazole-3-imines is greater. These reactions were studied mainly by the groups of Goerdeler and Oliver.

It was found in 1972 that the orange-colored substances formed by autoxidation of 1,1,5-trisubstituted 2,4-dithiobiurets in solution can be synthesized by interaction of 5-N,N-dialkylamino-3H-1,2,4-dithiazole-3-imines with N,N-dialkylthiocarbamoyl isothiocyanates.[92,93]



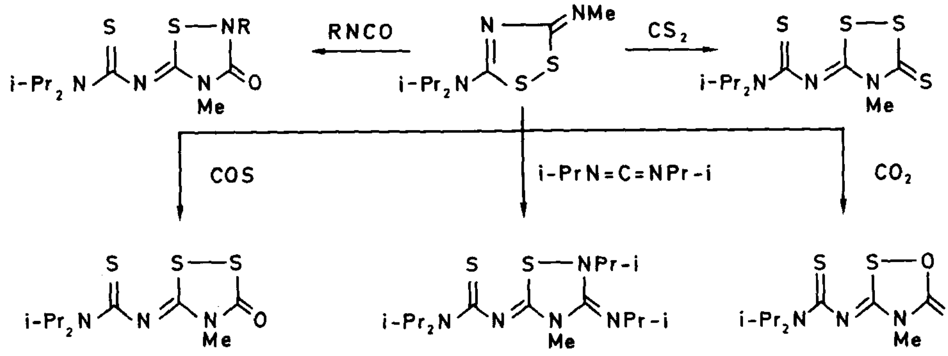
It has been discussed which of the structures—monocyclic or tricyclic with two hypervalent central sulfur atoms—is closer to the real structure of the compound. X-Ray structure determinations have shown that the former is closer since the distance between the central sulfur atoms is 2.2 Å while the distance between the central and the terminal ones is 1.8 Å. Yet, the contribution of the latter is also important since the molecule is planar, all four sulfur atoms are aligned and the 2.8 Å distance is considerably smaller than the sum of two van der Waals radii of covalent sulfur.[94-96] It should also be noted that substitution of one of the central sulfur atoms by a NMe group forces one thiocarbamoyl group out of the plane of the molecule.[97]

The reaction has been extended to isothiocyanates of various structures.[86,98]

Relative to 5-ethoxy-3H-1,2,4-dithiazole-3-phenylimine they show the following order of reactivity: RCO—NCS > RS(NR)—NCS > R—NCS (R = Alk and Ar).[98]

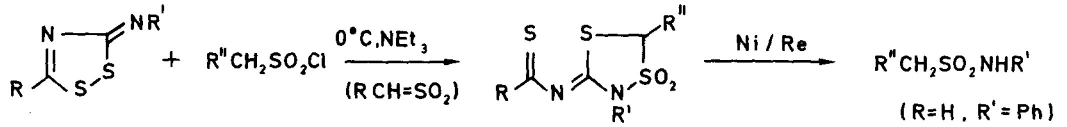
In contrast to imines 5-N,N-dimethylamino-3H-1,2,4-dithiazole-3-thione does not react with isothiocyanates.[86]

Other heterocumulenes have also been used, namely isocyanates,[92,98,99] carbon disulfide,[86,99] carbon oxysulfide, carbon dioxide, and carbodiimides,[99] *e.g.*

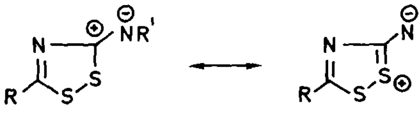


The reactivity of these heterocumulenes decreases in the order: R—NCS > R—NCO > CS_2 > RN=C=NR > CO_2;[99] more active heterocumulenes can replace the less active ones in their adducts. The imine reactivity in reactions with heterocumulene changes as follows: alkylimines > arylimines > acylimines ≈ N,N-dimethylaminoimines. Thus, in contrast to the N-methylimine, 2-ethoxy-3H-1,2,4-dithiazole-3-phenylimine does not react with carbon disulfide and diisopropylcarbodiimide and its adduct with methyl isocyanate dissociates upon heating.[99] 3H-1,2,4-Dithiazole-3-alkylimines react with carbon disulfide exothermally, arylimines react only upon heating while carbethoxy- and N,N-dimethylaminoimines do not react at all.[86]

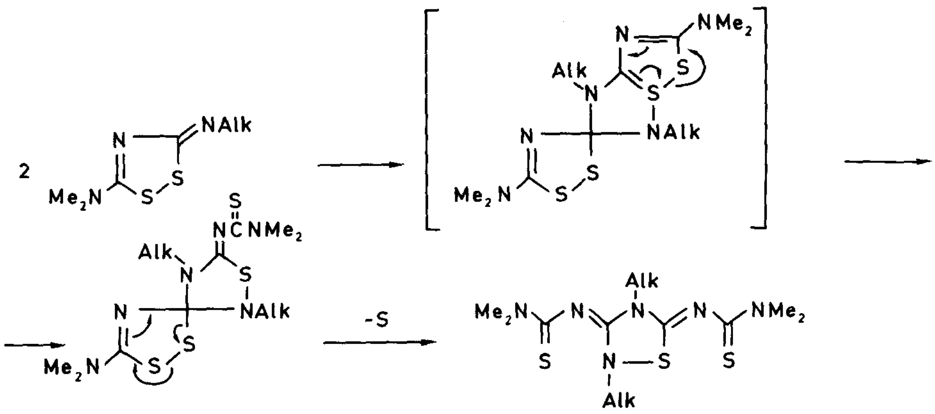
3H-1,2,4-Dithiazole-3-alkyl- and arylimines interact with sulfenes giving five-membered sultams[100] the structure of which has been confirmed by desulfurization with Raney nickel with the formation of the corresponding sulfamides.



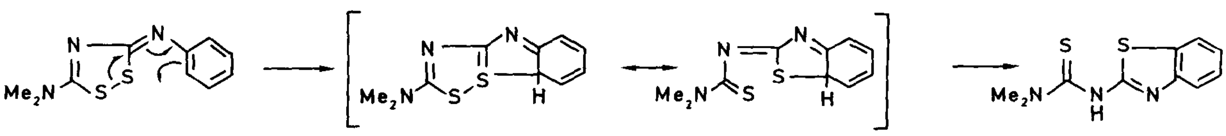
When one considers the limiting structures (IIIa) and (IIIb) of 3H-1,2,4-dithiazole-3-imine it appears likely that dimerization is possible with the first molecule acting as dipolarphile and the second as 1,3-dipole. This dimerization is actually observed upon heating of 5-N,N-dimethylamino-3H-1,2,4-dithiazole-3-alkylimines.[97]



(IIIa) (IIIb)

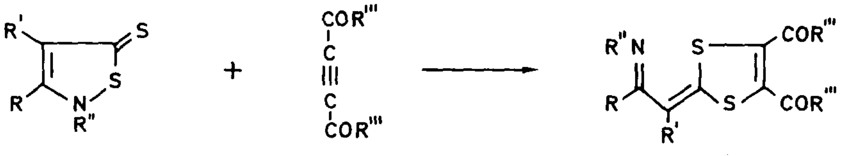


The thermal decomposition of 5-N,N-dimethylamino-3H-1,2,4-dithiazole-3-phenylimine proceeds intermolecularly due to an electrocyclic process involving electrophilic attack of the endocyclic sulfur on the phenyl ring.[97]

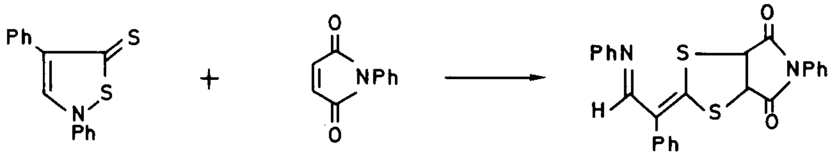


2.3. *Isothiazoline-3- and -5-thiones and their imines*

Isothiazoline-3- and -5-thiones react with dienophiles via sigmatropic addition with opening of the isothiazoline ring due to S—N bond cleavage. N-Alkyl-[101,102] and N-arylisothiazoline-5-thiones[102,103] readily react with acetylenedicarboxylic acid esters and dibenzoylacetylene while 2,4-diphenylisothiazoline-5-thione also reacts with N-phenylmaleinimide (76% yield).[102]

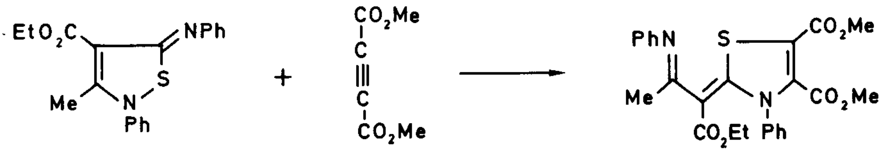


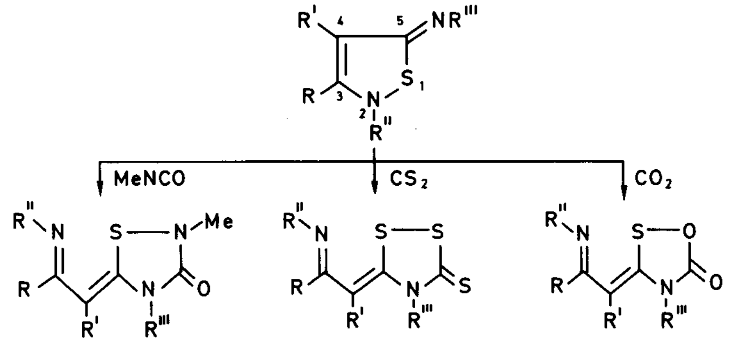
$R''' =$ OAlk, Ph



The reaction of 3-methyl-2-phenyl-4-carbethoxyisothiazoline-5-phenylimine with acetylenedicarboxylic acid esters proceeds similarly to give isothiazoline-5-thiones.[101]

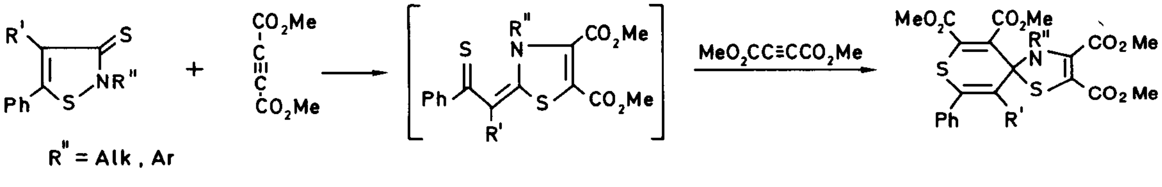
Isothiazoline-5-imines react with heterocumulenes such as isocyanates, carbon disulfide, and carbon dioxide, with the reactivity order RNCO > CS_2 > CO_2.



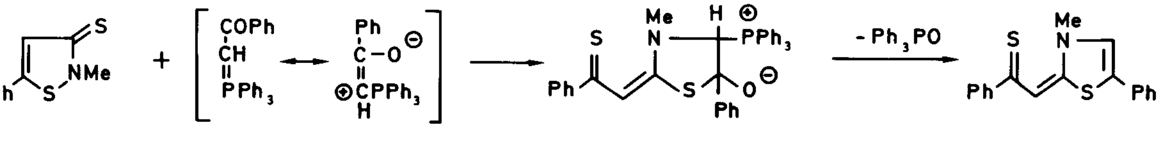


While N-alkyl-, N-aryl- and N-benzoylimines react with methyl isocyanate, N-benzoylimines do not enter into the reaction with carbon disulfide and carbon dioxide, and N-alkyl- and N-arylimines with a carbethoxy group in position 4 do not react with the latter.[99]

Isothiazoline-3-thiones and -5-thiones react with acetylenecarboxylic acid esters to form a 1 : 1 adduct which is more active as a diene than the starting thione and thus a 1 : 2 adduct is always formed in this reaction.[87]



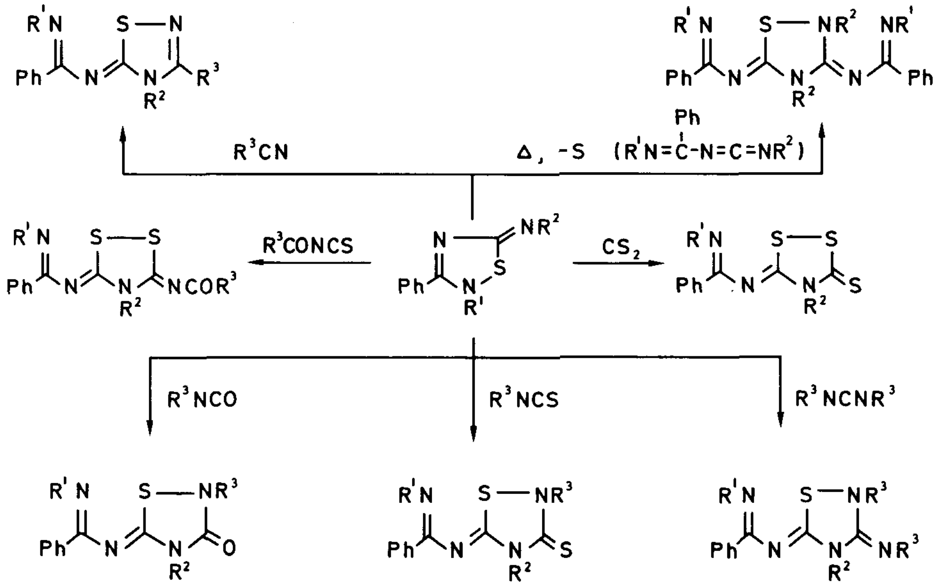
The reaction of phenacylidenetriphenylphosphorane with 2-methyl-5-phenyl-isothiazoline-3-thione is a sigmatropic addition with subsequent extrusion of triphenylphosphine oxide.[102]



The reaction of the same thione with benzonitrile oxide gives an unstable adduct which decomposes to yield 2-methyl-5-phenylisothiazoline-3-one and phenyl isothiocyanate.[104]

2.4 Δ^3-*1,2,4-Thiadiazoline-5-imines*

Δ^3-1,2,4-Thiadiazoline-5-imines react readily with various heterocumulenes by sigmatropic addition, methylimines being more reactive than phenylimines. Heterocumulenes exhibit the following order of reactivity: PhNCO, MeNCO > Me_2N-CO-NCS > PhNCS > MeNCS ≫ i-Pr-NCS ≫ t-Bu-NCS.[105]

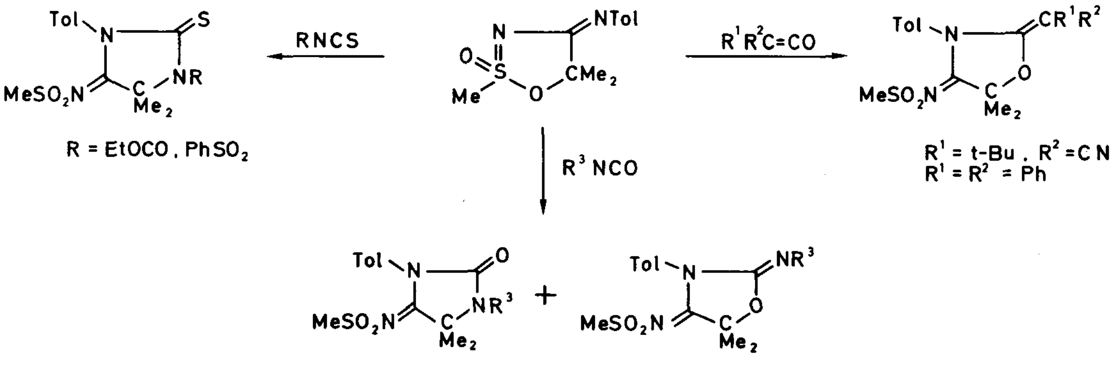


Analogously, 3H-1,2,4-dithiazoline-3-imines and Δ^3-1,2,4-thiadiazoline-5-imines represent yet another heterocyclic system which reacts with nitriles according to the same pattern.[105]

Upon heating Δ^3-1,2,4-thiazolidine-5-imines lose their sulfur atom giving the corresponding carbodiimide which cycloadds to another molecule of the starting compound.[106]

2.5 *4-Imino-4,5-dihydro-1,2,*S^{IV}*,3-oxathiazole 2-oxides*

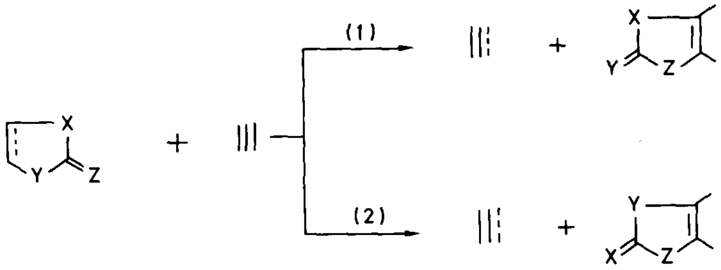
The interaction of 2,5,5-trimethyl-4-p-tolylimino-4,5-dihydro-1,2,S^{IV},3-oxathiazole 2-oxide with isocyanates and ketenes is a sigmatropic addition involving cleavage of the C—O bond of the ring; the formation of a sulfonyl group evidently promotes the reaction.[107]



In the case of isocyanates two regioisomers are formed due to the participation of both C=O and RN=C bonds in the ring formation. The relative reactivity of isocyanates follows the order: $PhSO_2NCO > PhCONCO > PhNCO$. Phenyl and t-butyl isothiocyanate, dicyclohexyl-carbodiimide, dimethyl acetylenedicarboxylate, methyl acrylate, acrylonitrile, methyl vinyl ketone, nitriles, ketones, thioketones, enamines, and isonitriles do not enter into the reaction.

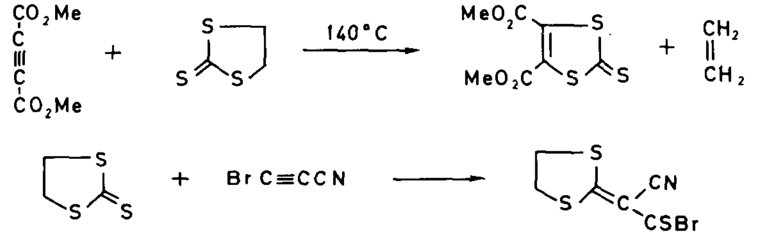
3. 1,3-DITHIOLANE-2-THIONES AND RELATED COMPOUNDS IN CYCLOSUBSTITUTIONS

As has been noted in the Introduction, 1,3-dithiolane-2-thiones and related compounds react with acetylenes, activated by electron-withdrawing groups, by cyclosubstitution:



The first example of this reaction was found in 1965 by Easton and Leaver who obtained 4,5-dicarbomethoxy-1,3-dithiole-2-thione in almost quantitative yield by heating 1,3-dithiolane-2-thione with dimethyl acetylenedicarboxylate at 140°C.[13,17] This reaction was utilized for the synthesis of tetrathiafulvalenes.[108,109]

4-Acetylamino-1,3-dithiolane-2-thiones react in DMSO at 80°C.[110] Similar reactions take place with hexafluoro-2-butyne and cyanoacetylene; acetylene itself gives 1,3-dithiolane-2-thione in 2–5% yield. The reaction of bromocyanoacetylene is anomalous.[111]

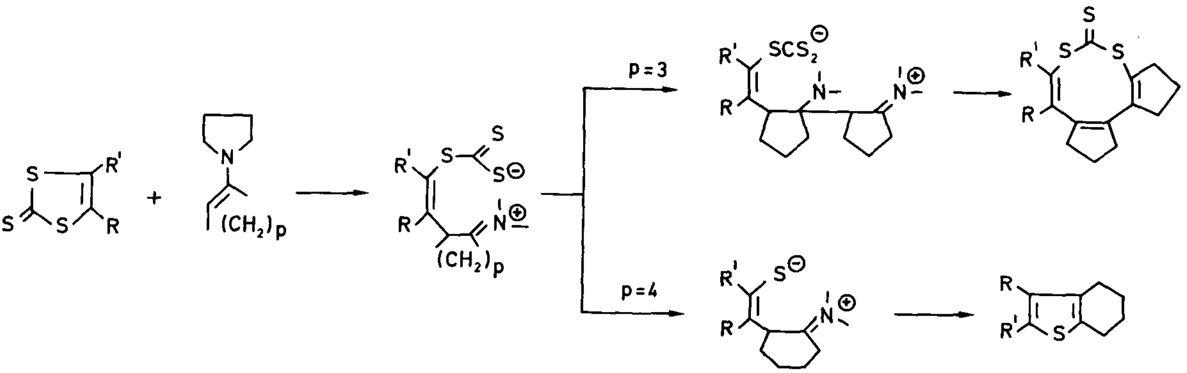


The stereospecificity of the reaction was studied by observing the interaction of trans- and cis-4,5-diphenyl-1,3-dithiolane-2-thione with dimethyl acetylenedicarboxylate: pure trans-stilbene is obtained in the first case, and a mixture of cis- and trans-isomers in the second.[13,17,111]

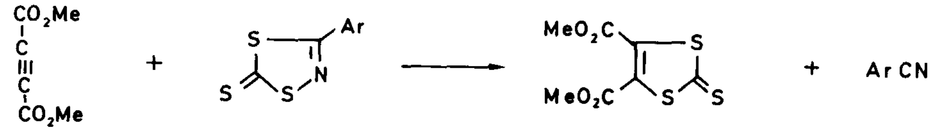
Dehydrobenzene obtained by oxidation of 1-aminobenzotriazole with lead tetraacetate or by thermal decomposition of diphenyliodonium-2-carboxylate reacts with 1,3-dithiolane-2-thione to give 1,3-benzodithiole-2-thione in 13 and 9% yield, respectively.[13,17]

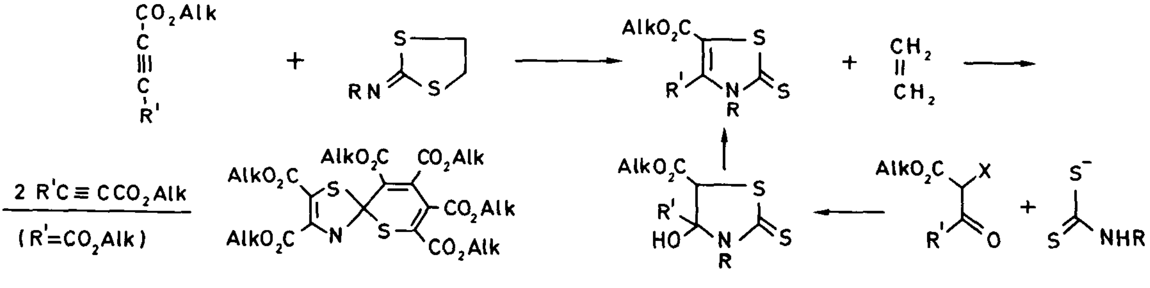
Tolane and methylphenylacetylene react similarly, but only upon photochemical excitation of the acetylene.[112]

The reaction of 1,3-dithiole-2-thiones with enamines, paralleling the case of 3H-1,2-dithiole-3-thiones, is not a cyclosubstitution, but starts as a nucleophilic attack of the β-C-enamine atom at the C-4(5)-thione atom to give 1,3-dithiocine-2-thiones in the case of 1-pyrrolidinocyclopentene and 4,5,6,7-tetrahydrobenzothiophenes in the case of 1-pyrrolidinocyclohexene.[113]



In 1967 Noël and Vialle[55] reported the interaction of 3-aryl-1,4,2-dithiazoline-5-thiones with dimethyl acetylenedicarboxylate to be a cyclosubstitution as proven by the isolation of a nitrile. However, later Behringer *et al.* could not confirm these results.[14]

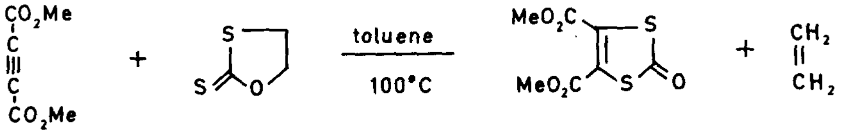




1,3-Dithiolane-2-alkylimines react with esters of acetylenedicarboxylic, propiolic, and phenylpropiolic acid; the corresponding arylimines do not react with the less active phenylpropiolic acid esters.[114]

In excess acetylenedicarboxylic acid ester the Δ^4-1,3-thiazoline-2-thione formed adds two molecules of the ester to the thiocarbonyl group giving a spirane. The structure of the corresponding Δ^4-1,3-thiazoline-2-thiones was confirmed by an independent synthesis from α-halogenocarbonyl compounds and dithiocarbamates.

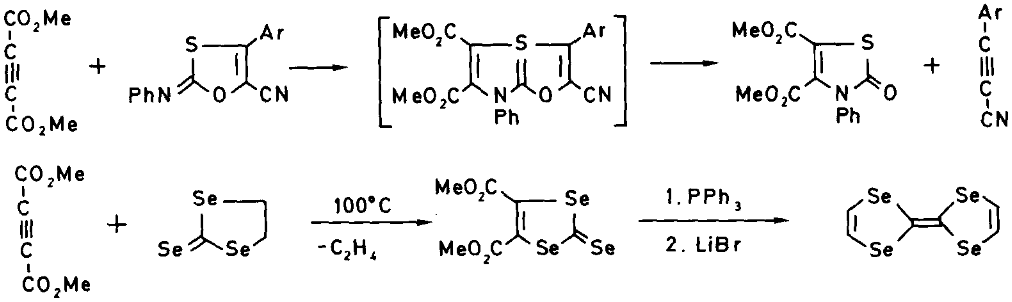
O,S-Ethylenedithiocarbonate reacts with dimethyl acetylenedicarboxylate with formation of 4,5-dicarbomethoxy-1,3-dithiole-2-one, another example of cyclosubstitution.[111]



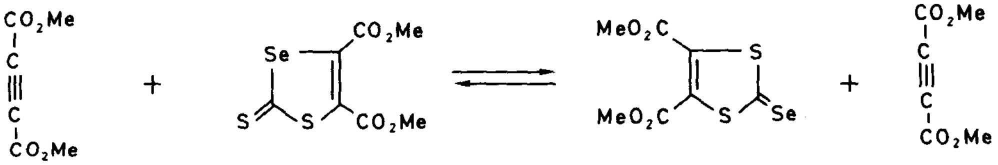
The authors suppose that the driving force of the reaction is the transformation of the thionocarbonate group into a thiolocarbonate group which is accompanied by a 24 kcal/mol energy gain. Indeed, S,S'-ethylenedithiocarbonate and O,O'-ethylenethiocarbonate, under the same or even more severe conditions do not enter into the reaction.

5-Cyano-4-aryl-1,3-oxathiole-2-phenylimines similarly react with dimethyl acetylenedicarboxylate to give the corresponding thiazoline and cyanoarylacetylenes; the authors suppose the intermediate formation of unstable bicyclic adducts with hypervalent sulfur[115] and thus this [2'+(1,2,3)]-sigmatropic addition is considered as two consecutive reactions of [2'+3α]-cycloaddition and cyclofragmentation.

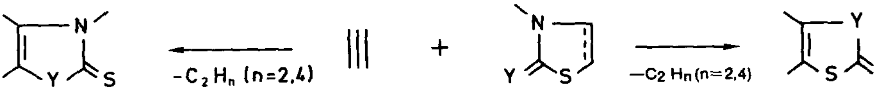
The interaction of 1,3-diselenane-2-selone with dimethyl acetylenedicarboxylate was used for the synthesis of tetraselenafulvalene.[116]



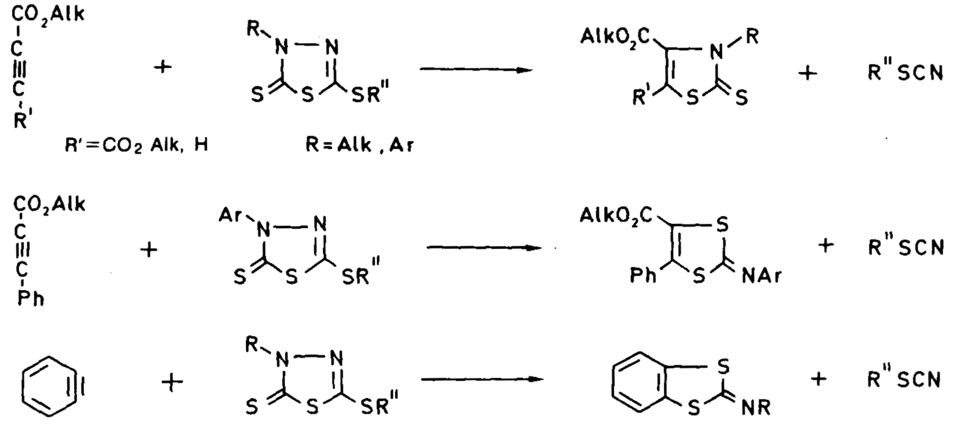
The similar reaction of 1,3-diselenolane-2-thione gives 4,5-dicarbomethoxy-1,3-thiaselenole-3-selone[117] while 1,3-thiaselenolane-2-thione and 1,3-dithiolane-2-selone form the same mixture of 4,5-dicarbomethoxy-1,3-dithiole-3-selone and 1,3-thiaselenole-3-thione[118] due to a reversible reaction in the reaction mixture:



Inspection of the 2-thiazoline systems leads to the expectation that both the nitrogen or the sulfur atom of the ring will participate in the formation of the bond with the dienophile which leads to the formation of two regioisomers:



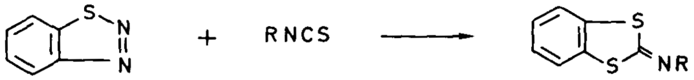
Though such reactions are not known for these systems, their aza-analog, the Δ^2-1,3,4-thiadiazoline system, reacts in this manner since the course of the reaction is facilitated by the cleavage of an N—N bond which is weaker than an N—C bond. The reaction of 2-alkylthio-Δ^2-1,3,4-thiadiazoline-5-thiones with acetylenedicarboxylic and propiolic acid esters takes place with participation of the nitrogen atom of the ring.[114]



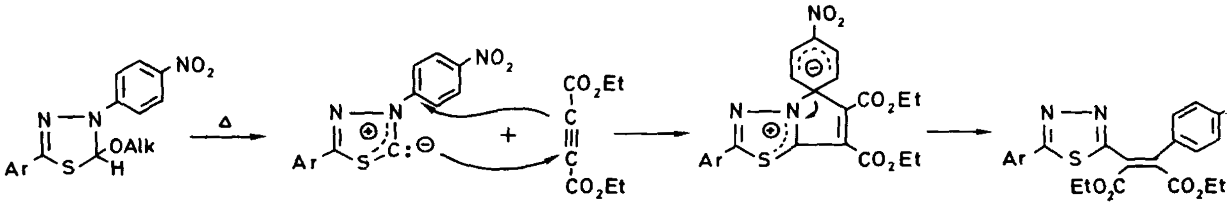
The reaction with phenylpropiolic acid esters is similar if N-4 carries an alkyl substituent; with an aryl substituent the reaction proceeds mainly with participation of the ring sulfur atom.[114]

The reaction with dehydrobenzene also occurs at the sulfur atom.

The independent synthesis of the 1,3-benzodithiole-2-imines formed was achieved as follows:[28]



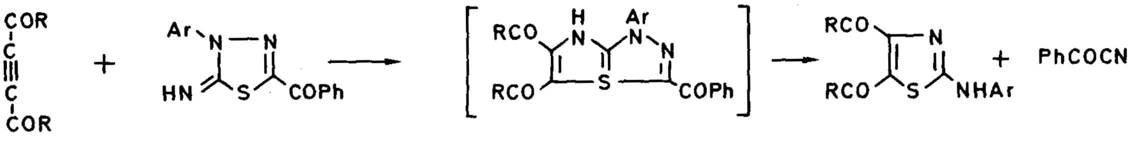
Nucleophilic carbenes formed by thermolysis of 2-alkoxy-3-p-nitrophenyl-5-aryl-1,3,4-thiadiazolines react with diethyl acetylenedicarboxylate without opening of the thiadiazoline ring and with migration of the p-nitrophenyl group to a carbon atom of the acetylenedicarboxylic acid ester.[114]

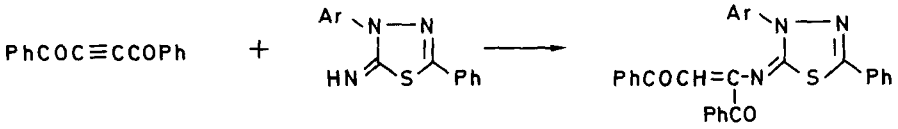


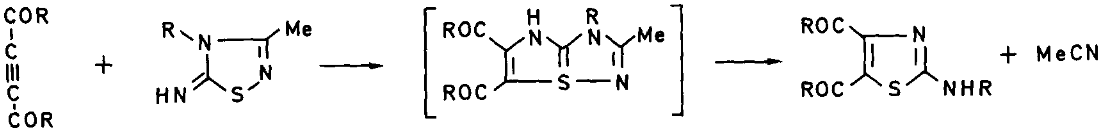
4-Aryl-2-benzoyl-Δ^2-1,3,4-thiadiazoline-5-imines also react with reactive acetylenes, dialkyl acetylenedicarboxylates, and dibenzoylacetylene, giving the corresponding 2-arylaminothiazoles *i.e.* the cyclosubstitution involves the sulfur atom and not the ring nitrogen.[120,121]

On the other hand, in the presence of a phenyl group in position 2 one observes simple addition of dibenzoylacetylene to the imino group.[121]

3,4-Diphenylthiazoline-2-imine reacts with acetylenes in a similar way.[122]

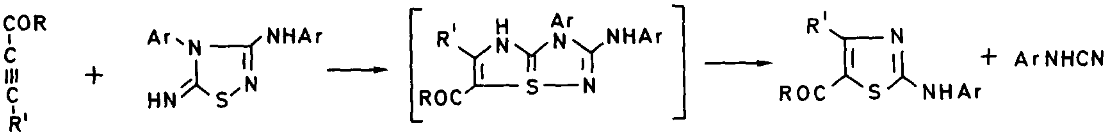






Δ^2-1,2,4-Thiadiazoline-5-imines readily react with reactive acetylenes with ring sulfur atom participation, but the reaction proceeds with cleavage of the S—N bond.[120,122]

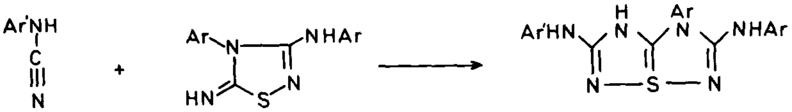
Hector's bases for which the structure of 4-aryl-3-arylimino-5-imino-1,2,4-thiadiazolines was assumed previously, react with reactive acetylenes by cyclosubstitution with participation of the ring sulfur atom and the unsubstituted imino group to form 2-arylaminothiazoles and N-arylcyanamides.[120,122]

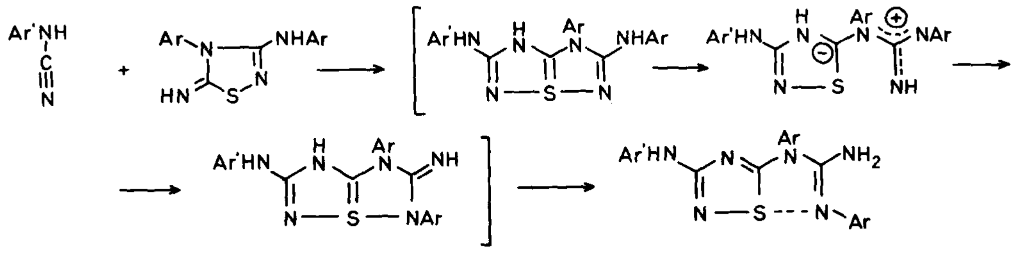


R=OMe, R'=CO_2Me
R=Ph, R'=COPh
R=OMe, R'=Ph

The reactions with dimethyl acetylenedicarboxylate and dibenzoylacetylene in chloroform take place at room temperature, with methyl phenylpropiolate 48 hrs boiling in dichloroethane is required. The independent synthesis of the 2-arylaminothiazoles formed was accomplished as follows:

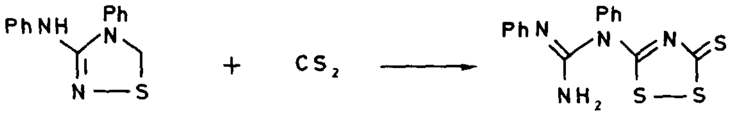
It should be noted that the proposed intermediates with hypervalent sulfur have never been observed (for details, see 123). The formation of the first stable structures of this kind was proposed for the adducts of Hector's bases with N-arylcyanamides.[122] However, X-ray analysis[124] and ^{13}C—NMR[125] showed that the real structure of these adducts is different from the one initially proposed.[126]



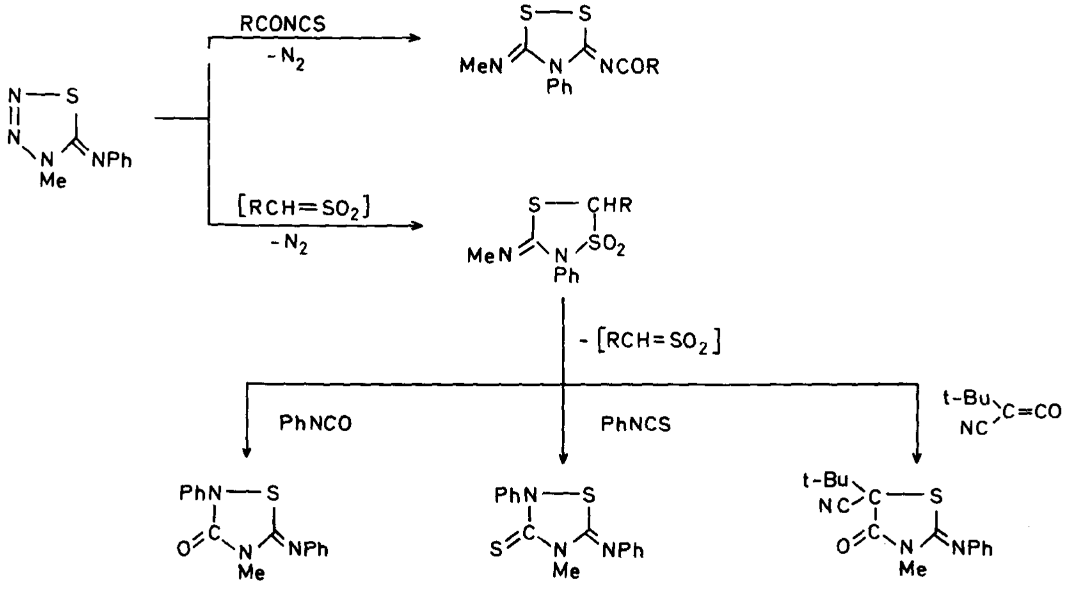


Thus, the framework $N—\overset{\|}{S}—N$ with hypervalent sulfur is not present in this case though the S—NAr distance (2.54 Å) is less than the sum of the van der Waals radii of nitrogen and sulfur (3.35 Å).

Later X-ray studies showed that Hector's base obtained by oxidation of phenylurea has the molecular structure of 5-imino-4-phenyl-3-phenylimino-4H-1,2,4-thiadiazoline in the crystalline solid.[127,128] Thus, it was established that the 1 : 1 adduct of this Hector's base with carbon disulfide obtained as early as 1908,[129] possesses the molecular structure of 5-(1,2-diphenylguanidino)-3H-1,2,4-dithiazole-3-thione.[130–132]



The reaction of 4-alkyl-5-arylimino-1,2,3,4-thiatriazolines with acyl isothiocyanates and sulfenes generated in situ is a cyclosubstitution with participation of the endocyclic sulfur atom and the exocyclic nitrogen atom with extrusion of a nitrogen molecule. In turn, the sultams so formed may react further with phenyl isocyanate, phenyl isothiocyanate, and t-butylcyanoketene in the same manner, but with elimination of sulfene.[133]



4. CONCLUDING REMARKS

In this review we have tried to demonstrate the synthetic importance of [2+(1,5)]-sigmatropic addition-elimination reactions for five-membered heterocycles with exocyclic double bonds. In conclusion we should like to emphasize that the formal logical consideration and classification of sigmatropic addition processes can serve as a starting point for the explanation of the reaction paths of a large number of heterocycles as well as for the search for new types of processes (*cf.* 8,9).

General equations for sigmatropic addition-elimination (1) and sigmatropic oligoaddition and oligofragmentation (2) (j,k > 1) were given in paper.[6]

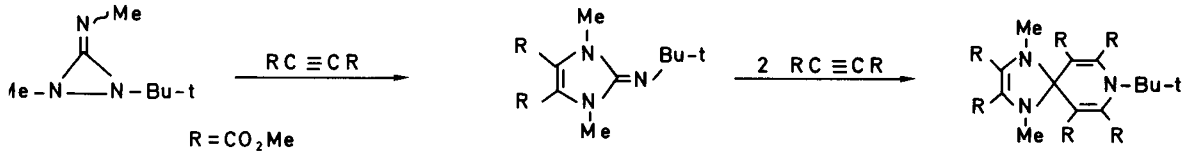
$$(1)\quad {}^{c}A_i + I_j - I_k \rightleftharpoons I_j - {}^{r}A_i - I_k$$

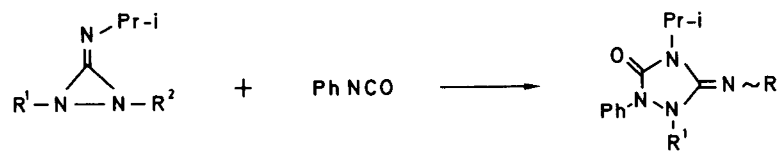
$$(2)\quad p\,{}^{c}A_i + I_j - I_k \rightleftharpoons I_j - ({}^{r}A_i)_p - I_k;\ p \geqslant 2$$

It follows that we are dealing with families of related processes described by different symbolic Eqs.[7–9] Thus, we have considered eight-centered [2+(1,5)]-sigmatropic addition-elimination processes. It is obvious that the [2+(1,3)]-six-centered process is the simplest isodesmic sigmatropic addition-elimination. In fact, such reactions are encountered in the literature.

Within this framework it is of interest to consider the interaction of the three-membered heterocyclic system in diaziridinimines with dimethyl acetylenedicarboxylate which first involves a sigmatropic addition; then follows the addition of another two molecules of acetylenedicarboxylic acid ester.[134,135]

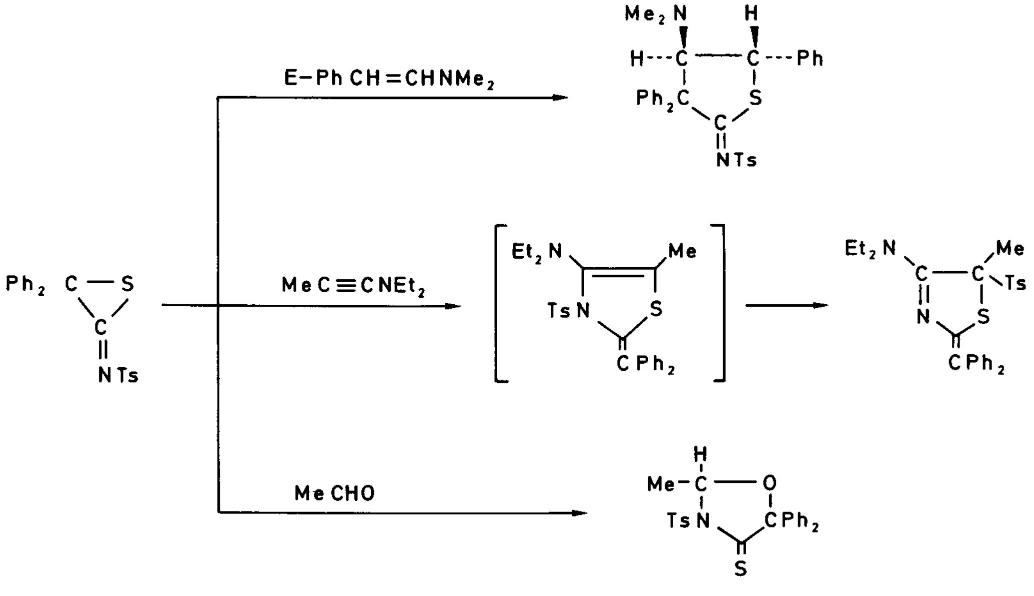
Diaziridinimines readily react with phenyl isocyanate by sigmatropic addition.[136]

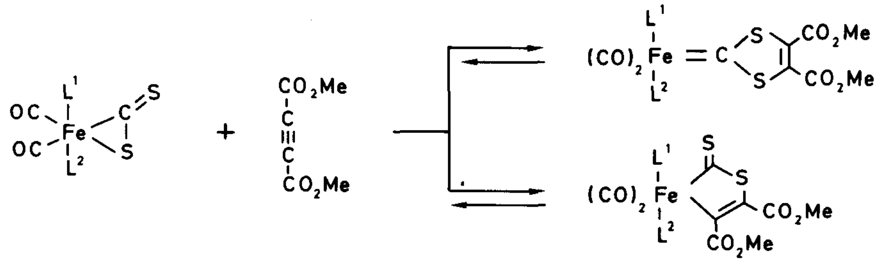




Reactions of 3,3-diphenylthiirane-2-arylsulfonylimines depending on the reagents can follow three different pathways the two latter reactions constituting [2+(1,3)]-sigmatropic additions.[137]

Thus, the definition of the [2+(1,3)]-sigmatropic addition-elimination process as a classificational unit has promoted the search for reactions of this type.

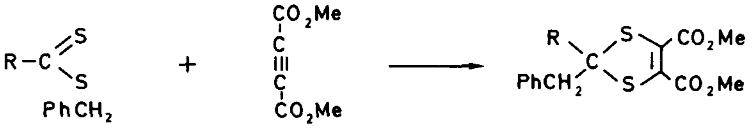


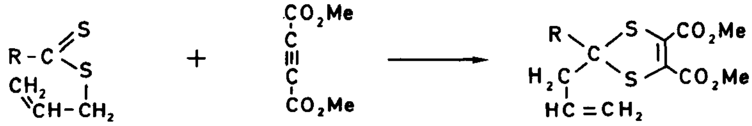


Transformations of interest were found among organometallic compounds of transition metals as for example the interaction of η^2-CS_2-iron complexes with dimethyl acetylenedicarboxylate.[138–140]

The reaction consists of a [2+(1,3)]-sigmatropic addition with participation of the exocyclic sulfur atom and simultaneous opening of the starting three-membered heterocycle, a metal-carbene complex being formed, and a competing insertion of an acetylenedicarboxylic acid ester molecule into an Fe—S bond with formation of a new five-membered metallocycle. The adduct of the first type is formed faster, but the equilibrium between the two adducts is determined by the electron-donating properties of the phosphine ligands L^1 and L^2.

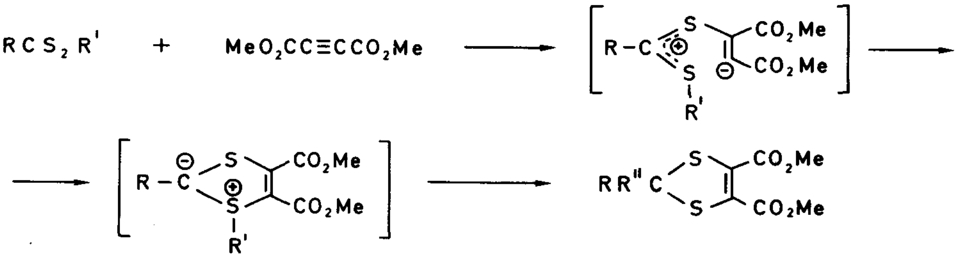
We have not considered sigmatropic additions to carbocyclic systems (*e.g.* methylenecyclopropane[141]) in the presence of transition metal compounds which involve simultaneous opening of the initial ring although these reactions are important both practically and theoretically.[142]



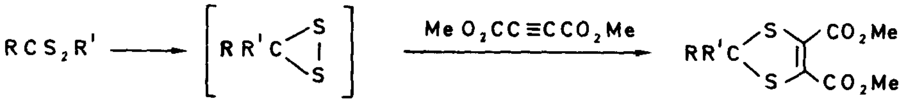


Six-centered [2+2+(1,1)]- and eight-centered [2+2+(1,3)]-processes are the simplest examples of an isodesmic sigmatropic oligoaddition-oligofragmentation as described by Eq. (2). Such reactions were found by V. N. Drozd and O. A. Popova when investigating the interaction of dimethyl acetylenedicarboxylate with dithiocarboxylic benzyl and allyl esters.[143–145]

The authors proposed the following mechanism for these reactions:[145]



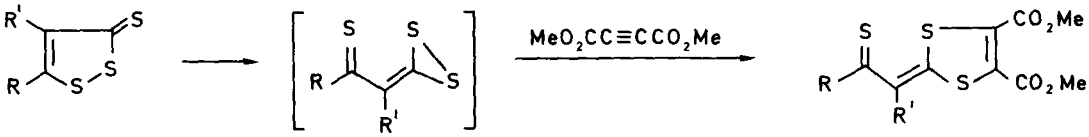
On the other hand, A. Senning put forward the interesting suggestion that the driving force of the reactions is the preceding rearrangement of the dithioesters into unstable dithiiranes:[146]



It is important to stress again that the formal-logical approach is used as a purely classificational tool and does not deal with the description of the real mechanisms of the reactions.

The reactions considered above were found mainly in five-membered heterocycles representing isoelectronic heteroanalogs of tropone for which the contribution of the polar structure with the negative end of the dipole at the exocyclic heteroatom and the positive charge within the heterocycle is considerable. It seems possible that a non-synchronous addition really takes place with initial nucleophilic attack of the negative dipole end on the triple bond of the acetylene with further electronic rearrangement within the zwitterion formed. L'abbé *et al.* suggested to call such compounds "masked 1,3-dipoles."[107,133] For calculation of synchronous sigmatropic addition reactions of 3H-1,2-dithiole-3-thione and its aza-analogs to acetylenes by the PMO method in the CNDO/2 approximation see 147.

There also exist some other mechanistical possibilities. For example, A. Senning considers the intermediate formation of dithiiranes from 3H-1,2-dithiole-3-thiones in the pre-equilibrium step in the reaction of these thiones with acetylenes.[146]



In conclusion we would like to note that though the first examples ot sigmatropic addition and cyclosubstitution were found only 15 years ago this field of organic chemistry is developing extremely rapidly and one should expect new synthetic and theoretical discoveries in the course of this development.

REFERENCES

1. J. H. Perlstein, *Angew. Chem.*, **89**, 534 (1977).
2. K. N. Houk, L. J. Luskus and N. S. Bhacca, *J. Amer. Chem. Soc.*, **92**, 6392 (1970).
3. K. N. Houk, J. Sims, C. R. Watts and L. J. Luskus, *J. Amer. Chem. Soc.*, **95**, 7301 (1973).
4. K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975).
5. N. S. Zefirov and S. S. Trach, *Zh. Org. Khim.*, **11**, 225 (1975).
6. N. S. Zefirov and S. S. Trach, *Zh. Org. Khim.*, **11**, 1785 (1975).
7. N. S. Zefirov and S. S. Trach, *Zh. Org. Khim.*, **12**, 7 (1976).
8. N. S. Zefirov and S. S. Trach, *Zh. Org. Khim.*, **12**, 697 (1976).
9. N. S. Zefirov and S. S. Trach, *Chem. Scripta*, **15**, 4 (1980).
10. T. P. Vasil'eva, M. G. Lin'kova and O. V. Kil'disheva, *Usp. Khim.*, **45**, 1269 (1976).
11. A. Lehot et J. Vialle, *Bull. Soc. Chim. Fr.*, **1964**, 1173.
12. H. Behringer and R. Wiedenmann, *Tetrahedron Letters*, **1965**, 3705.
13. D. B. J. Easton and D. Leaver, *J. Chem. Soc., Chem. Commun.*, **1965**, 585.

14. H. Behringer, D. Bender, J. Falkenberg and R. Wiedenmann, *Chem. Ber.*, **101**, 1428 (1968).
15. H. Davy, M. Demuynck, D. Paquer, A. Rouessac and J. Vialle, *Bull. Soc. Chim. Fr.*, **1966**, 1150.
16. H. Davy, M. Demuynck, D. Paquer, A. Rouessac and J. Vialle, *Bull. Soc. Chim. Fr.*, **1968**, 2057.
17. D. B. J. Easton, D. Leaver and T. J. Rawlings, *J. Chem. Soc., Perkin Trans. I*, **1972**, 41.
18. V. N. Drozd, G. S. Bogomolova and Yu. M. Udachin, *Zh. Org. Khim.*, **14**, 2459 (1978).
19. V. N. Drozd, Yu. M. Udachin, G. S. Bogomolova and V. V. Sergeichuk, *Zh. Org. Khim.*, **16**, 883 (1980).
20. C. Portail and J. Vialle, *Bull. Soc. Chim. Fr.*, **1966**, 3187.
21. C. Davidson and D. Leaver, *J. Chem. Soc., Chem. Commun.*, **1972**, 540.
22. H. Davy and J. Vialle, *C. R. Acad. Soc.*, **275C**, 625 (1972).
23. H. Davy and J. M. Decrouen, *Bull. Soc. Chim. Fr.*, **1976**, 115.
24. J. M. Buchshriber, D. M. McKinnon and M. Ahmed, *Can. J. Chem.*, **47**, 2039 (1969).
25. M. Ahmed, J. M. Buchshriber and D. M. McKinnon, *Can. J. Chem.*, **48**, 1991 (1970).
26. D. M. McKinnon and J. M. Buchshriber, *Can. J. Chem.*, **49**, 3299 (1971).
27. H. Davy and J. Vialle, *Bull. Soc. Chim. Fr.*, **1975**, 1435.
28. D. Paquer and R. Pou, *Bull. Soc. Chim. Fr.*, **1976**, 120.
29. V. N. Drozd and G. S. Bogomolova, *Zh. Org. Khim.*, **13**, 2012 (1977).
30. M. Stavaux, *Bull. Soc. Chim. Fr.*, **1971**, 4426.
31. C. T. Pedersen, *Acta Chem. Scand.*, **28B**, 367 (1974).
32. N. A. Bunina, M. L. Petrov and A. A. Petrov, *Zh. Org. Khim.*, **16**, 13 (1980).
33. R. Okazaki, F. Ishii, K. Ozawa and N. Inamoto, *Chem. Letters*, **1972**, 9.
34. R. Okazaki, F. Ishii, K. Okawa, K. Ozawa and N. Inamoto, *J. Chem. Soc., Perkin Trans. I*, **1975**, 270.
35. E. Klingsberg, *J. Amer. Chem. Soc.*, **83**, 2934 (1961).
36. P. de Mayo and H. Y. Ng, *Tetrahedron Letters*, **1973**, 1561.
37. V. N. Drozd, Yu. M. Udachin, V. V. Sergeichuk and G. S. Bogomolova, *Zh. Org. Khim.*, **16**, 443 (1980).
38. R. Okazaki, A. Kitamura and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, **1975**, 257.
39. M. O-oka, A. Kitamura, R. Okazaki and N. Inamoto, *Bull. Chem. Soc. Japan*, **51**, 301 (1978).
40. J. Maignan and J. Vialle, *Bull. Soc. Chim. Fr.*, **1973**, 2388.
41. R. Okazaki and N. Inamoto, *Chem. Letters*, **1974**, 1439.
42. R. Okazaki, K. Sunagawa, K. T. Kang and N. Inamoto, *Bull. Chem. Soc. Japan*, **52**, 496 (1979).
43. P. de Mayo and N. Y. Ng, *J. Chem. Soc.*, **1974**, 877.
44. P. de Mayo and N. Y. Ng, *Can. J. Chem.*, **55**, 3763, (1977).
45. F. Ishii, R. Okazaki and N. Inamoto, *Tetrahedron Letters*, **1976**, 4283.
46. R. Okazaki, F. Ishii and N. Inamoto, *Bull. Chem. Soc. Japan*, **51**, 309 (1978).
47. R. Okazaki, F. Ishii, K. Sunagawa and N. Inamoto, *Chem. Letters*, **1978**, 51.
48. R. Okazaki, K. T. Kang, K. Sunagawa and N. Inamoto, *Chem. Letters*, **1978**, 55.
49. R. Okazaki, K. Sunagawa, M. Kotera and N. Inamoto, *Tetrahedron Letters*, **1976**, 3815.
50. F. Ishii, M. Stavaux and N. Lozac'h, *Tetrahedron Letters*, **1975**, 1473.
51. F. Ishii, M. Stavaux and N. Lozac'h, *Bull. Soc. Chim. Fr.*, **1977**, 1142.
52. A. Rouessac and J. Vialle, *Bull. Soc. Chim. Fr.*, **1968**, 2054.
53. G. G. Alexandrov, Yu. T. Strachkov, A. E. Kalinin, A. A. Tsherbakov, G. S. Bogomolova and V. N. Drozd, *Isv. Akad. Nauk SSSR, Ser. Khim.*, **1979**, 545.
54. V. N. Drozd, V. M. Fedoseev, G. S. Bogomolova, V. V. Sergeichuk, N. M. Semenenko and A. A. Mandrugin, *Zh. Org. Khim.*, 16, **198** (1980).
55. P. Rioult and J. Vialle, *Bull. Soc. Chim. Fr.*, **1966**, 2707.
56. P. Rioult and J. Vialle, *Bull. Soc. Chim. Fr.*, **1967**, 2883.
57. G. Hervieu, P. Rioult and J. Vialle, *Bull. Soc. Chim. Fr.*, **1971**, 4375.
58. G. Hervieu, P. Rioult and J. Vialle, *Bull. Soc. Chim. Fr.*, **1971**, 4380.
59. G. Kresze and A. Horn, *Chem. Ber.*, **100**, 1655 (1967).
60. Y. Poirier, *Bull. Soc. Chim. Fr.*, **1968**, 1203.
61. M. Maguet, Y. Poirier and J. Teste, *Bull. Soc. Chim. Fr.*, **1970**, 1503.
62. F. Boberg and J. Knoop, *Liebigs Ann. Chem.*, **708**, 148 (1967).
63. D. Noël and J. Vialle, *Bull. Soc. Chim. Fr.*, **1967**, 2239.
64. N. Latif, A. Nada, H. El-Namaky and B. Haggag, *Chem. Ind.*, **1975**, 706.
65. Y. Poirier and N. Lozac'h, *Bull. Soc. Chim. Fr.*, **1967**, 2090.
66. M. Elkaschef, F. M. Abdel-Megeid and A. A. Elbarbary, *Acta Chim. Acad. Sci. Hung.*, **93**, 157 (1977).
67. S. Tamagaki, R. Ichihara and S. Oae, *Bull. Chem. Soc. Japan*, **48**, 355 (1975).
68. D. Barillier, C. Gy, P. Rioult and J. Vialle, *Bull. Soc. Chim. Fr.*, **1973**, 277.
69. M. Stavaux, *Bull. Soc. Chim. Fr.*, **1971**, 4429.
70. S. Tamagaki and S. Oae, *Tetrahedron Letters*, **1972**, 1159.
71. S. Tamagaki, K. Sakaki and S. Oae, *Bull. Chem. Soc. Japan*, **46**, 2608 (1973).

72. S. Tamagaki, K. Sakaki and S. Oae, *Bull. Chem. Soc. Japan,* **48,** 2983 (1975).
73. S. Tamagaki, K. Sakaki and S. Oae, *Bull. Chem. Soc. Japan,* **48,** 2985 (1975).
74. S. Tamagaki, K. Sakaki and S. Oae, *Bull. Chem. Soc. Japan,* **47,** 3084 (1974).
75. S. Tamagaki, K. Sakaki and S. Oae, *Heterocycles,* **2,** 39 (1974).
76. S. Tamagaki, K. Sakaki and S. Oae, *Tetrahedron Letters,* **1974,** 1059.
77. S. Tamagaki, K. Sakaki and S. Oae, *Heterocycles,* **2,** 45 (1974).
78. F. Boberg, G. J. Wentrup and M. Koerke, *Synthesis,* **1975,** 502.
79. G. J. Wentrup and F. Boberg, *J. Liebigs Ann. Chem.,* **1978,** 387.
80. M. S. Chauhan and D. M. McKinnon, *Can. J. Chem.,* **54,** 3879 (1977).
81. R. S. Tewari and K. C. A. Gupta, *Synth. Comm.,* **8,** 315 (1978).
82. A. Grandin and J. Vialle, *Bull. Soc. Chim. Fr.,* **1967,** 1851.
83. G. Lang and J. Vialle, *Bull. Soc. Chim. Fr.,* **1967,** 2865.
84. H. Behringer and D. Deichmann, *Tetrahedron Letters,* **1967,** 1013.
85. J. W. McDonald and D. M. McKinnon, *Can. J. Chem.,* **45,** 1225 (1967).
86. J. E. Oliver and R. T. Brown, *J. Org. Chem.,* **39,** 2228 (1974).
87. J. Vialle, *Quart. Rep. Sulfur Chem.,* **5,** 151 (1970).
88. R. Okazaki, K. Okawa and N. Inamoto, *J. Chem. Soc., Chem. Commun.,* **1971,** 843.
89. R. Okazaki, M. O-oka and N. Inamoto, *J. Chem. Soc., Chem. Commun.,* **1976,** 562.
90. J. Goerdeler and H. W. Linden, *Tetrahedron Letters,* **1975,** 3387.
91. J. E. Oliver and A. B. DeMilo, *J. Org. Chem.,* **39,** 2225 (1974).
92. J. Goerdeler and J. Ulmen, *Chem. Ber.,* **105,** 1568 (1972).
93. J. E. Oliver and J. B. Stokes, *Int. J. Sulfur Chem.,* (A) **2,** 105 (1972).
94. J. E. Oliver, J. L. Flippen and J. Karle, *J. Chem. Soc., Chem. Commun.,* **1972,** 1153.
95. J. L. Flippen, *J. Amer. Chem. Soc.,* **95,** 6073 (1973).
96. J. Sletten, *Acta Chem. Scand.,* **A28,** 989 (1974).
97. J. E. Oliver and J. L. Flippen, *J. Org. Chem.,* **39,** 2233 (1974).
98. J. Goerdeler, W. Kunnes and F. M. Panshiri, *Chem. Ber.,* **109,** 848 (1976).
99. J. Goerdeler, R. Büchler and S. Solyom, *Chem. Ber.,* **110,** 285 (1977).
100. H. W. Linden and J. Goerdeler, *Tetrahedron Letters,* **1977,** 1729.
101. H. Behringer, J. Kilger and R. Wiedenmann, *Tetrahedron Letters,* **1968,** 1185.
102. M. S. Chauhan, M. E. Hassan and D. M. McKinnon, *Can. J. Chem.,* **52,** 1738 (1974).
103. G. E. Bachers, D. M. McKinnon and J. M. Buchshriber, *Can. J. Chem.,* **50,** 2568 (1972).
104. G. LeCoustumer and Y. Mollier, *C. R. Acad. Sci.,* **270G,** 433 (1970).
105. J. Goerdeler and W. Löbach, *Chem. Ber.,* **112,** 517 (1979).
106. J. Goerdeler, J. Haag and W. Löbach, *Chem. Ber.,* **112,** 1288 (1979).
107. G. L'abbé, C. C. Yu and S. Toppett, *J. Org. Chem.,* **44,** 3991 (1979).
108. L. R. Melby, H. D. Hartzler and W. A. Sheppard, *J. Org. Chem.,* **39,** 2456 (1974).
109. C. U. Pittman, M. Narita and Y. E. Liang, *J. Org. Chem.,* **41,** 2855 (1976).
110. S. Hoff and A. P. Blok, *Rec. Trav. Chim.,* **93,** 75 (1974).
111. B. R. O'Connor and F. N. Jones, *J. Org. Chem.,* **35,** 2002 (1970).
112. M. Ohashi, N. Mino, N. Nakayama and S. Yamada, *Chem. Letters,* **1978,** 1189.
113. F. Ishii, R. Okazaki and N. Inamoto, *Heterocycles,* **6,** 313 (1977).
114. C. Gueden and J. Vialle, *Bull. Soc. Chim. Fr.,* **1973,** 270.
115. M. Brady and A. Robert, *J. Chem. Soc., Chem. Commun.,* **1976,** 912.
116. M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.,* **41,** 882 (1976).
117. M. V. Lakshmikantham, M. P. Cava and A. F. Garito, *J. Chem. Soc., Chem. Commun.,* **1975,** 383.
118. M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.,* **41,** 879 (1976).
119. G. Scherowsky, K. Dünnbier and G. Höfle, *Tetrahedron Letters,* **1977,** 2095.
120. K. Akiba, T. Tsuchiya and N. Inamoto, *Heterocycles,* **3,** 1143 (1975).
121. K. Akiba, T. Tsuchiya and N. Inamoto, *Tetrahedron Letters,* **1976,** 1877.
122. K. Akiba, M. Ochimi, T. Tsuchiya and N. Inamoto, *Tetrahedron Letters,* **1975,** 459.
123. R. Gleiter and R. Gygax, *Top. Current Chem.,* **63,** 49 (1976).
124. K. Akiba, T. Tsuchiya, N. Inamoto, K. Onuma, N. Nagashima and A. Nakamura, *Chem. Letters,* **1976,** 723.
125. K. Akiba, T. Tsuchiya and N. Inamoto, *Tetrahedron Letters,* **1976,** 3819.
126. T. Tsuchiya, S. Arai, Y. Murata, K. Akiba and N. Inamoto, *Heterocycles,* **4,** 1840 (1976).
127. A. R. Butler, C. Gleidewell and D. C. Liles, *J. Chem. Soc., Chem. Comm.,* **1978,** 652.
128. A. R. Butler, C. Gleidewell and D. C. Liles, *Acta Crystallogr.,* **B34,** 3241 (1978).
129. E. Fromm and R. Heyder, *Ber.,* **42,** 3804 (1909).
130. A. R. Butler, *J. Chem. Res.* (*S*), **1978,** 50.

131. A. R. Butler, *J. Chem. Res. (M)*, **1978**, 855.
132. A. R. Butler, C. Gleidewell and D. C. Liles, *Acta Crystallogr.*, **B34**, 2570 (1978).
133. G. L'abbé, A. Timmerman, C. Martens and S. Toppett, *J. Org. Chem.*, **43**, 4951 (1978).
134. H. Quast, K. H. Roβ, E. Spiegel, K. Peters and H. G. von Schnering, *Agnew. Chem.*, **89**, 202 (1977).
135. H. Quast and E. Spiegel, *Tetrahedron Letters*, **1977**, 2705.
136. H. Quast and E. Spiegel, *Angew. Chem.*, **89**, 112 (1977).
137. G. L'abbé, J. P. Dekerk, S. Toppett, J. P. Declercq, G. Germain and M. Van Meerssche, *Tetrahedron Letters*, **1979**, 1819.
138. H. Le Bozec, A. Gorgues and P. Dixneuf, *J. Chem. Soc., Chem. Commun.*, **1978**, 573.
139. H. Le Bozec, A. Gorgues and P. Dixneuf, *J. Am. Chem. Soc.*, **100**, 3946 (1978).
140. A. Gorgues and A. Le Coq, *Tetrahedron Letters*, **1979**, 4829.
141. R. Noyori and M. Yamakawa, *Tetrahedron Letters*, **1978**, 4823.
142. K. C. Bishop, *Chem. Rev.*, **76**, 461 (1979).
143. V. N. Drozd, *Zh. Org. Khim.*, **15**, 1106 (1979).
144. V. N. Drozd and O. A. Popova, *Tetrahedron Letters*, **1979**, 4491.
145. V. N. Drozd and O. A. Popova, *Zh. Org. Khim.*, **16**, 2047 (1980).
146. A. Senning, *Angew. Chem.*, **91**, 1006 (1979); Organic Sulfur Chemistry (Ed. R. Kh. Freidlina and A. E. Skorova), Pergamon Press, Oxford, 1981 in press.
147. R. Pinel, M. Gelize-Duvigneau, M. Z. Benabdallah and J. Arriau, *Bull. Soc. Chim. Belg.*, **89**, 187 (1980).