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Four- and Five-membered Cyclic Disulphides

T.P.Vasil'eva, M.G.Lin'kova, and O.V.Kil'disheva

The principal methods for synthesising 1,2-dithiolans are surveyed, together with their advantages and disadvantages. Information is given on the geometry of the 1,2-dithiolan ring. The polarography, photolysis, and spectra of 1,2-dithiolans are discussed, and results are given for their polymerisation, reduction, oxidation, and chlorolysis, as well as the removal of a sulphur atom. Data are presented on the biological importance and application of 1,2-dithiolans. The major part of the review is devoted to the chemistry of unsaturated five-membered cyclic disulphides—the 3-thiones, 3-ones, 3-imines, and 3-ylidenes of 1,2-dithiolens—with methods of preparation and both chemical and physical properties. A detailed examination is made of their reactions with electrophilic and nucleophilic reagents, as well as condensations. Fields of practical application of 1,2-dithiolens are surveyed. The review concludes with 233 references.

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I. INTRODUCTION

The chemistry of saturated and unsaturated four- and five-membered cyclic disulphides forms a new field, widely developed during the past decade. Saturated and unsaturated five-membered disulphides (1,2-dithiolans and 1,2-dithiolens) are present as fragments in certain antibiotics (gliotoxin, thiolutin, holomycin) and naturally occurring physiologically active compounds (α-lipoic and asparagusic acids, nereistoxin, brugine, etc.). Certain compounds find application as insecticides, antioxidants, and colorants.

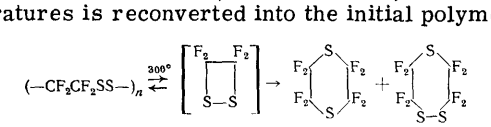
II. 1,2-DITHIETANS AND 1,2-DITHIETENS

Four-membered cyclic disulphides, 1,2-dithietans (I)



(I)

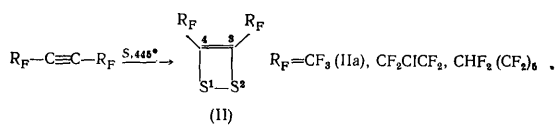
have not yet been obtained. It is known only that, when the pressure is lowered in the pyrolysis of polymeric perfluoroethylene disulphide, dithian and trithiepan are obtained. The mass spectra suggest the intermediate formation of tetrafluoro-1,2-dithietan (Ia), which at low temperatures is reconverted into the initial polymer[1]:



(Ia)

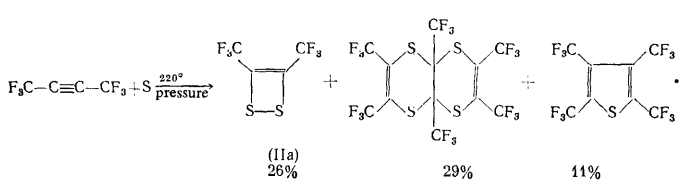
The instability of the almost planar 1,2-dithietan ring (I) is attributed to strong repulsion of the p,π electrons of the neighbouring sulphur atoms[1]. However, unsaturated four-membered cyclic disulphides, 1,2-dithietens (II), are more stable than the saturated analogues (I) because of the presence in the ring of an "aromatic" sextet of electrons[2].

Perfluorinated 1,2-dithietens (II) were first obtained by Krespan[3] by the action of sulphur on polyfluorinated alkynes[3,4]:



(II)

A yield of 80% of bistrifluoromethyl-1,2-dithieten (IIa) was prepared in this way[3]. At lower temperatures the yield does not exceed 26% owing to the formation of secondary condensation products[4]:

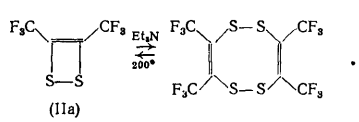


(IIa) 26% 29% 11%

However, 1,2-dithietens (II) cannot be obtained from acetylene and dimethyl acetylenedicarboxylate[4]. The first report that benzo-1,2-dithieten had been obtained[5] has proved to be erroneous[4].

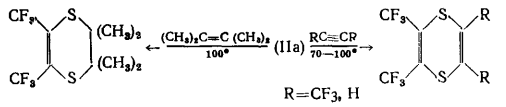
The 1,2-dithieten ring exhibits characteristic ultraviolet absorption in two ranges—at 231–243 and 334–340 nm[4].

The chemical properties of 1,2-dithietens are determined by the labile disulphide bond. Thus (IIa) dimerises slowly at 25°C, rapidly in the presence of weakly basic catalysts (triethylamine, ethanol); (IIa) is reformed when the dimer is heated to 200°C:[3,4]



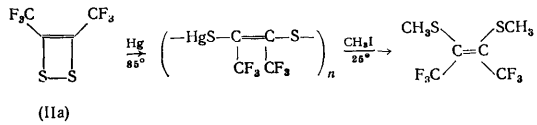
(IIa)

Cycloaddition at the disulphide bond occurs readily with alkenes and alkynes [3,4,6]:



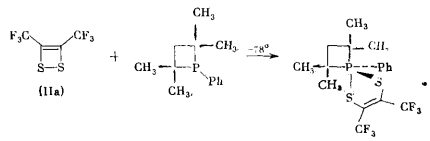
R=CF_3, H

The presence of electron-donor substituents in the unsaturated hydrocarbons facilitates cycloaddition [6]. The action of mercury converts (IIa) into a polymer, which with iodomethane forms 2,3-bismethylthioperfluorobut-2-ene [6]:



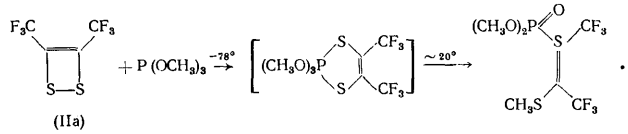
(IIa)

With phosphines and phosphites (IIa) yields sulphur-containing phosphorans [7]:



(IIa)

Methyl *o*-phenylene hydrogen, ethyl methyl hydrogen, and trimethyl phosphites react similarly. In the latter two cases the adducts are unstable, and undergo the Arbuzov rearrangement even at 20°C: [7]

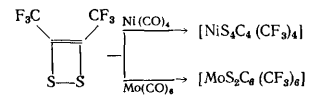


(IIa)

With transition-metal carbonyls (IIa) form complexes also with cleavage of the cyclic disulphide bond. Thus it gives a trimeric complex with octacarbonyldicobalt [8]:

$$Co_2(CO)_8 + (IIa) \rightarrow [(CF_3)_2C_2S_2Co(CO)]_3 .$$

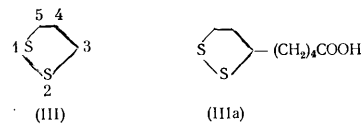
Nickel, molybdenum, chromium, and tungsten carbonyls form with (IIa) metal complexes from which the carbonyl group is absent [9]:



(IIa)

III. 1,2-DITHIOLANS

This survey of the literature on 1,2-dithiolans (III) mainly covers the period after 1963, for earlier investigations were summarised in a monograph [10]. Because of the great biological importance of α-lipoic (thioctic) acid (IIIa)



(III) (IIIa)

results for this compound have been segregated as an independent topic [10], and will not be considered in detail here.

1. Methods of Preparation

(*a*) Oxidation of 1,3-dithiols

The most general method for obtaining 1,2-dithiolans is the intramolecular oxidation of 1,3-dithiols (Table 1). [10-23] Thus a substituted 1,2-dithiolan was first obtained by Reissert in 1906, by oxidising the dianilide of dithiomalonic acid [10]:

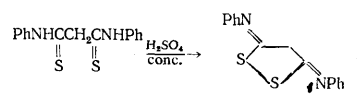
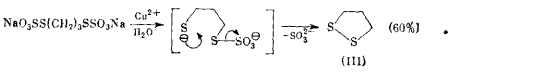


Table 1. 1,2-Dithiolans obtained by the oxidation of 1,3-dithiols.

1,2-Dithiolan	Oxidant (temp., °C)	Yield, %	Ref.	1,2-Dithiolan	Oxidant	Yield, %	Ref.
(III)	H_2O_2—KI (25°)	35*	12	4-(=O)	I_2—Et_3N	—	13
	H_2O_2—KI (75°)	70*	12		I_2	—	10
	H_2O_2—KI (115°)	0	12	3,5-(=O)$_2$-4-$(CH_3)_2$		57	17
	I_2—$FeCl_3$	26*	12	3,5-(=O)$_2$-4-$(C_2H_5)_2$	I_2, pyridine	80	17
	Pb $(OAc)_4$ (80°)	36*	12	3,5-(=O)$_2$-4-$(CH_2)_3$		82	17
	Pb $(OAc)_4$ (25°)	21—40*	12	3-(=O)-4-NHCOPh-5-$(CH_3)_2$	$FeCl_3$	50	10
3-$(CH_3)_2$**	I_2—Et_3N	56*	13	3-CH_2COOH	O_2, Fe^{3+}	10	10
4-N $(CH_3)_2$	*t*-BuOOH, Fe^{3+}	50	10	3-CH_2COOH-4-(=O)	I_2	24	18, 19
3-COOH	air	—	14	4-$(CH_2)_3$COOH	O_2—$FeCl_3$	1	20
	O_2, Fe^{3+}	66	10	4-$(CH_2)_3$ COOH	O_2—$FeCl_3$	42	20
	air, $FeCl_3$	74***	15	3,5-$(COOH)_2$	I_2	65	21
	H_2O_2, Fe^{3+}	15	10		O_2, Fe^{3+}	77	10
4-COOH	H_2O_2	17	16	4-$(NH_2 \cdot HCl)$	I_2—KI	60	22
	H_2O_2—KI (75°)	57	16	3-[$(CH_2)_4$COOH]-4-(=O)	I_2	59	18
	I_2—Et_3N	40	16		I_2—KI	30	23
	$K_3Fe(CN)_6$	32	16	3-[$(CH_2)_4CO_2CH_3$]-4-OH	I_2—KI	75	23
4-CH_2OH	H_2O_2 (75°)	70	16	4-CO $(CH_2)_3CO_2R$	I_2—KI	10	23
4-$(CH_2OH)_2$	I_2	—	10				
4-C_6H_5	I_2—Et_3N	73	13				
4-SO_3H	I_2—H_2O	—	10				

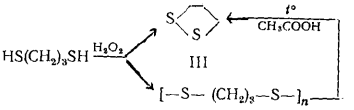
*Yield determined from concentration in solution (by ultraviolet spectrometry).
**Here and below the numeral indicates the position of the substituent in the ring (III).
***Yield of crude product.

The early attempts at synthesising unsubstituted (III) usually yielded solid polymers or dimers, and only in 1950 did Affleck obtain (III)—in benzene solution—by the action of copper(II) chloride on trimethylene bisthiosulphate[11]:

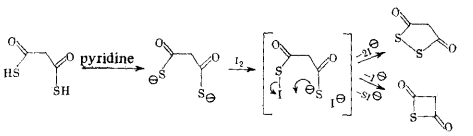


(III)

A disadvantage of this method is secondary intermolecular oxidation to poly-1,2-dithiolans; on prolonged heating in acetic acid these are converted into (III):[12]

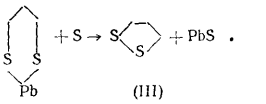


Intermediate formation of a monosulphenyl iodide is postulated in the oxidation of 1,3-dithiols (or 1,3-bisthiolic acids) to 1,2-dithiolans: e.g.[17]



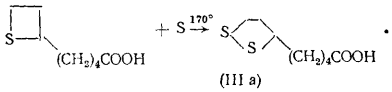
The intermediate undergoes either conversion into the cyclic disulphide or, with elimination of an SI^- ion, cyclisation to a four-membered sulphide[17].

High yields of various derivatives of 1,2-dithiolan (III) are obtained by the action of sulphur on the corresponding lead dithiolates[24]:



(III)

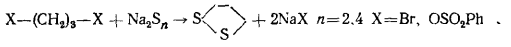
It is noteworthy that α-lipoic acid (IIIa) and its methyl ester can be prepared by introducing a second sulphur atom into the corresponding thietan derivatives[25]:



(III a)

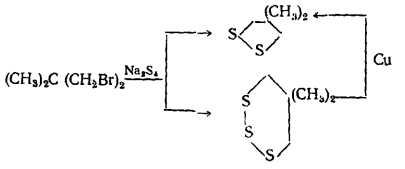
(*b*) Condensation of 1,3-dihalogeno-derivatives with alkali-metal polysulphides

The lower yields are responsible for the less frequent use made of the cyclisation of 1,3-dihalides (or bisarenesulphonic esters of 1,3-glycols) by means of alkali-metal polysulphides (Table 2):[26-28]



(III)

Higher yields of (III) are obtained with Na_2S_4 than with Na_2S_2. Use of the latter yields thietans as byproducts[10], whereas Na_2S_4 gives cyclic trisulphides, which are converted into disulphides (III) by boiling with copper powder[27]:



(*c*) Intramolecular cyclisation of β-mercaptothio-carboxylic acids

The most general method for obtaining 1,2-dithiolan-3-ones is intramolecular acylation of β-thiothiols (or their acetyl derivatives) containing an activated carboxyl:

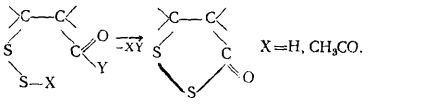
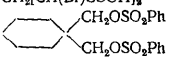


Table 2.

1,2-Dithiolan (III)	Initial compound	Reagent	Yield, %	Ref.
Unsubstituted	$Br(CH_2)_3Br$	Na_2S_2	9	
4-$(CH_3)_2$	$(CH_3)_2C(CH_2Br)_2$	K_2S_2	55	10
3,5-$(COOH)_2$	$CH_2[CH(Br)COONa]_2$	Na_2S_2	22	
Ditto	$CH_2[CH(Br)COOH]_2$	Na_2S_2	11	26
4-$(CH_2)_5$		Na_2S_4	47	27
4-$(CH_2OH)_2$	$(HOCH_2)_2C(CH_2Br)_2$	Na_2S_4 Na_2S_2	94 57	10
3-$(CH_3)_4CONH_2$	$Cl(CH_2)_2CH(Cl)(CH_2)_4CONH_2$	Na_2S_2	83	10
3,3,5,5-$(CH_3)_4$-4-(=O)	$O=C[C(CH_3)_2Br]_2$	Na_2S_2	35	28

The disulphides to be cyclised are readily formed and are used without isolation in pure form, by the action of hydrogen sulphide on β-chlorosulphenyl-carboxylic acids, when cyclisation occurs sometimes spontaneously[29], and sometimes in the presence of an organic base[30]:

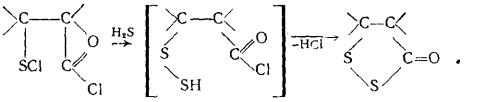
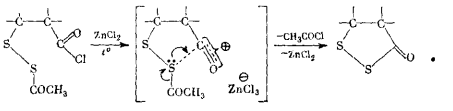


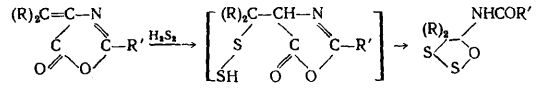
Table 3. Cyclisation of β-acetyldithio-carbonyl chlorides by zinc chloride[32].

1,2-Dithiolan-3-one	Unsubstituted	5-C_6H_5-	4-CH_3-	5-CH_3-	4-Cl-	4-Cl-4-CH_3
Yield, %	50	70	67	71	89	86

1,2-Dithiolan-3-ones are formed especially readily by intramolecular transacylation of the chlorides of β-acetyldithio-carboxylic acids (Table 3) catalysed by zinc chloride, with removal of acetyl chloride from the reaction zone[31,32]:



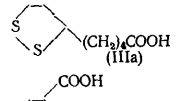
An example is the intramolecular transacylation of a 4-mercaptothiomethyl-1,3-oxazolin-5-one: [33]



2. Physical Properties

Crystallographic examination of the structure of 1,2-dithiolan-4-carboxylic acid has shown [10] that the molecule is non-planar and unsymmetrical. The angle between the $C_{(5)}-S_{(1)}-S_{(2)}$ and the $S_{(1)}-S_{(2)}-C_{(3)}$ planes is 26.6°—not the 90° found in open-chain disulphides [34]—which leads to repulsion of the unshared p-electrons of the sulphur atom and instability of the 1,2-dithiolan ring [35]. The angle at a sulphur atom is also smaller (92° instead of the 107° in linear disulphides) [36], so that the S–S bond is longer in 1,2-dithiolans than in open-chain disulphides (2.1 instead of 2.044 Å) [10].

Table 4.

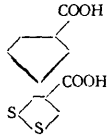
1,2-Dithiolan	Stress, kcal mole^{-1}	Method of determination	Ref.
5 4 / 1 S 3 / (III) S 2	14–18	calculation of deformation of bond angles	37
	27	from shift of λ_{max} in ultraviolet	10,38
	6.5	kinetic measurements of $C_6H_5CH_2SH$-(III) equilibrium	10,38
	4*	calorimetrically from heat of reaction**	10,38
 (IIIa)	3.5	calorimetrically from heat of reaction***	10,38
	11	crystallographic structure analysis	10,38
	16–30	conformational analysis	10,38

*The stress in 1,2-dithian determined by the same method was 0.5 kcal mole^{-1}. [38]

** $HS(CH_2)_3SH \xrightarrow{I_2}$ (III).

*** $HS(CH_2)_3CH(CH_2)_4CO_2H \rightarrow$ (IIIa).
SH

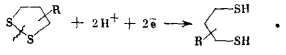
Table 4a.

	μ, D	pK_a
	1.70	4.93
	3.15	3.82

The stress in the 1,2-dithiolan ring has been determined by many workers using various methods (Table 4). Strongly divergent values have been obtained. The underestimates given by chemical methods may be due either to the presence of a polymer in the specimens or to the fact that the comparable reactions were conducted in solution, not in the vapour phase [10,37,38].

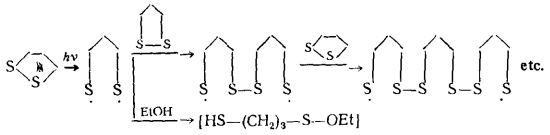
In conformity with the negative inductive effect of the disulphide group the measured dipole moments and the acidity of 1,2-dithiolan-4-carboxylic acids exceed those of cyclopentanecarboxylic acids (Table 4a) [39].

1,2-Dithiolans are reduced polarographically (mostly at pH ~ 2.2) by a two-electron mechanism via intermediate mercury complexes to dithiols [10,40,41]:

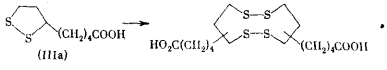


The half-wave potential $E_{1/2}$ is higher for 1,2-dithiolans than for linear and more macrocyclic disulphides [40,41].

On photolysis 1,2-dithiolans readily polymerise [42], and in alcohol they react with the solvent [35]:



Exposure of aqueous α-lipoic acid (IIIa) leads to rapid dimerisation [43]:

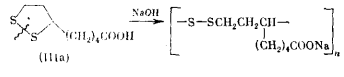


The ultraviolet spectra of 1,2-dithiolans have been studied ($\lambda_{max} \simeq 310-350$ nm). [36] In contrast to cyclic disulphides, polymeric linear disulphides absorb at 230 to 250 nm. [22] 1,2-Dithiolancarboxylic acids are exceptions, absorbing at 250–280 nm, with only weak absorption at 330 nm. [10] 1,2-Dithiolan-3-ones exhibit carbonyl absorption in the infrared (at 1710–1720 cm^{-1}). [32]

3. Chemical Properties

(a) Polymerisation

The most characteristic property of 1,2-dithiolans is their ease of polymerisation to linear disulphides, especially when heated or in the absence of a solvent, the activation energy of polymerisation being very low (8.6 kcal mole^{-1}). [36] All monosubstituted 1,2-dithiolans—the 4-amine [22], 3-carboxylic acid [44,45], methyl 3-carboxylate [41], 3-one [32], 4-one [24], and 4-hydroxymethyl derivative [46]—tend to polymerise, as well as certain disubstituted derivatives, 3,3-dimethyldithiolan [37] and the 4-methyl-3-valeric acid [23]. 3,3,5,5-Tetramethyl-1,2-dithiolan polymerises only in the presence of a catalyst (H^+, RS^-, OH^-, $AlCl_3$). [37] On addition of an aqueous alkali the compound (IIIa) also forms a polymer [47]:

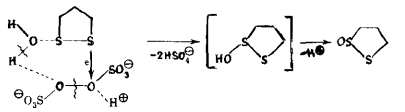


(b) Reduction and oxidation

In the presence of zinc in hydrochloric acid [21], zinc in aqueous ammonia, sodium in liquid ammonia, and sodium tetrahydroborate [44,45], 1,2-dithiolans are readily reduced at the disulphide bond to 1,3-dithiols (Table 5). [10]

1,2-Dithiolans are more easily oxidised than are linear or macrocyclic disulphides [41]. Under controlled conditions both cyclic thiosulphinates (1-oxides) and thiosultones (1,1-dioxides) can be obtained (Table 6). Thiosultones are

most stable compounds [41]. Oxidation with hydrogen peroxide more often gives 1-oxides, but 1,1-dioxides are formed when the ring contains electron-donor substituents or in the presence of a catalyst (Table 6). The oxidation of 1,2-dithiolans (e.g. by a persulphate) proceeds by a mechanism of one-electron transfer [20,36]:



The primary oxidation products of 1,2-dithiolans are thiosulphinates, which can then be oxidised further to 1,1-dioxides (Table 7). [20,49]

Table 5. Reduction of 1,2-dithiolans.

1,2-Dithiolan	1,3-Dithiol	Reagent	Yield, %
	$HS(CH_2)_3SH$	Zn, HCl	100
-4-COOH	$(HSCH_2)_2CHCOOH$	Zn, NH_4OH	—
-3,5-$(COOH)_2$	$HO_2CCH(SH)CH_2CH(SH)CO_2H$	Zn, HCl	90
-4-$(CH_3)_2$	$(CH_3)_2C(CH_2SH)_2$	Na, NH_3	94
-4-$(CH_2OH)_2$	$(HOCH_2)_2C(CH_2SH)_2$	Na, NH_3 H_2, CO_2S_x	87.5 71

Table 6. Oxidation products from 1,2-dithiolans.

1-Oxide	Oxidant (temp., °C)	Yield, %	Ref.
	H_2O_2 (75°)	76	11
	$NaIO_4$ H_2O_2 (5°)	— 72*	43 15
	H_2O_2 ($t°$)	77	39
	H_2O_2 or $(NH_4)_2S_2O_8$	—	19
	H_2O_2 (t)	76	39
	$NaIO_4$	86	45

1,1-Dioxide	Oxidant (temp., °C)	Yield, %	Ref.
	H_2O_2, tungstic acid (25°)	33	12
	H_2O_2 (75°)	16	16
	H_2O_2 (20°)	35	48
	*m*-ClC_6H_4COOH	good	49

*Mixture of *anti*- and *syn*-sulphoxides (in the proportions 77 : 23). [46]

1,2-Dithiolan 1,1-dioxide can be oxidised further by hydrogen peroxide in the presence of tungstic acid to the stable 1,1,2,2-tetroxide [12]:

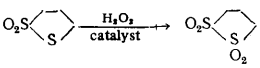


Table 7. Products of the oxidation of 1,2-dithiolan 1-oxides.

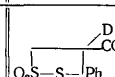
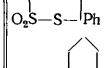
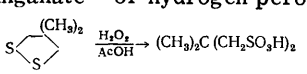
1,1-Dioxide	Reagent	Yield, %	Ref.	1,1-Dioxide	Reagent	Yield, %	Ref.
	H_2O_2	20	11		$R-CO_3H$	—	49
	H_2O_2, $t°$	54	39				
					H_2O_2	—	41

Table 8. Products of the cleavage of 1,2-dithiolan-3-ones by sulphuryl [50] or sulphenyl [51] chlorides.

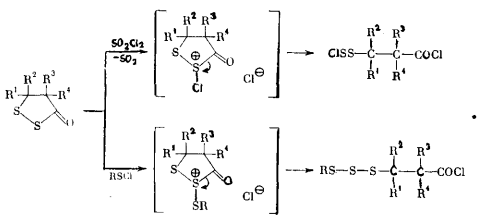
Substituents	Reagent	Cleavage product	Yield, %
4-Methyl	SO_2Cl_2	$ClSSCH_2CH(CH_3)COCl$	70
	PhSCl	$PhS_2CH_2CH(CH_3)COCl$	60
5-Methyl	SO_2Cl_2	$ClSSCH(CH_3)CH_2COCl$	78
	CH_3SCl	$CH_3S_2CH(CH_3)CH_2COCl$	76
	PhSCl	$PhS_2CH(CH_3)CH_2COCl$	75
4-Chloro	SO_2Cl_2	$ClSSCH_2CH(Cl)COCl$	90
4-Chloro-4-methyl	SO_2Cl_2	$ClSSCH_2C(CH_3)(Cl)COCl$	85
	CH_3SCl	$CH_3S_2CH_2C(CH_3)(Cl)COCl$	89
	PhSCl	$PhS_2CH_2C(CH_3)(Cl)COCl$	64

The oxidation of 4,4-bishydroxymethyl-1,2-dithiolan by hydrogen peroxide to the 1,1,2,2-tetroxide is usually accompanied by ring cleavage to give disulphonic acids [10]. Better yields of the latter are obtained from alkylated 1,2-dithiolans by the prolonged action of excess of potassium permanganate [41] or hydrogen peroxide [10]:

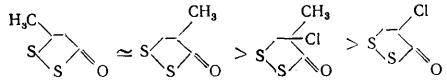


(*c*) Reactions with electrophilic reagents

It has recently been shown that the chlorolysis of 1,2-dithiolan-3-ones by sulphuryl or sulphenyl chlorides involves selective cleavage of only the CO–S bond (Table 8) [50,51]:



These dithiolanones form the sequence



according to ease of rupture of the CO–S bond.

(*d*) Removal of a sulphur atom

A novel reaction of 1,2-dithiolans is the removal of a sulphur atom by trisdiethylaminophosphine [13,52] or triphenylphosphine [17,53] with the formation of four-membered heterocycles—thietans, β-thiolactones, and thietan-2,4-diones (Table 9). The process is a second-order reaction accompanied by inversion (S_N2), with intermediate formation of an internal phosphonium salt [13,52]:

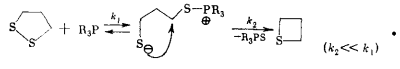
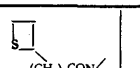
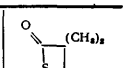
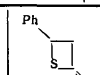
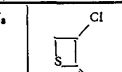
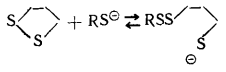


Table 9. Thietans from 1,2-dithiolans.

Thietan				
Reagent	$(Et_2N)_3P$	$(Et_2N)_3P$	$(Et_2N)_3P$	Ph_3P
Temperature, °C	20—80°	20—80°	20—80°	60°
Yield, %	82	64	87	86
Reference	13,52	13,52	13,52	17
Thietan				 
Reagent	Ph_3P	Ph_3P	Ph_3P	Ph_3P	Ph_3P
Temperature, °C	60°	60°	5—20°	5—20°	5—20°
Yield, %	83	87	98	34	24
Reference	17	17	53	53	53

(*e*) Reactions with metal alkyl sulphides and with inorganic salts

Thiols cleave 1,2-dithiolans very slowly:



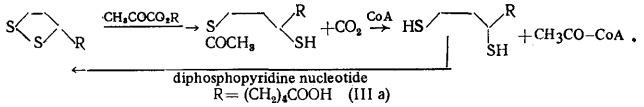
(III)

The rate of reaction increases in the presence of a weak base (the acetate ion) [10,54]. The rate of cleavage of the disulphide bond by sodium cyanide depends on the structure of (III). Thus unsubstituted (III) is cleaved rapidly and completely, the 3,3-dimethyl derivative slowly, and 3,3,5,5-tetramethyl-1,3-dithiolan does not react with sodium cyanide [10,37].

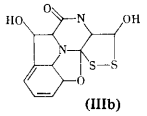
The antibiotic gliotoxin (IIIb), which contains a 1,2-dithiolan ring, is cleaved at the disulphide bond when heated with potassium sulphide [33]. With mercury(II) chloride and bromide substituted 1,2-dithiolans form crystalline adducts, but their nature is still obscure [10,55,56].

4. Biological Importance and Application

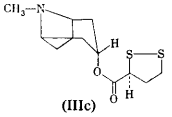
Of all the compounds containing a cyclic disulphide bond α-lipoic acid (IIIa) is the most important: it is a growth factor, and is involved in the oxidation of pyruvate and in photosynthesis [57]. In the organism reductive cleavage of (IIIa) gives a dithiol [58]:



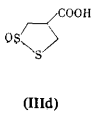
Gliotoxin (IIIb)—an antibiotic in which nitrogen atoms are attached to positions 3 and 4 of a 1,2-dithiolan ring—has an antitubercular and bacteriostatic action. 4-Acylamino-1,2-dithiolan-3-ones also possess tuberculostatic and cytotoxic activity [33]. 4-Amino-1,2-dithiolans are insecticidal [59]. 4-Dimethylamino-1,2-dithiolan—nereistoxin, isolated from marine worms—exerts a selective toxic action on harmful insects [60]. Intensive research is being conducted on its synthesis [22,61–63].



(IIIb)



(IIIc)



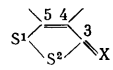
(IIId)

Bruguine—the tropinyl 1,2-dithiolan-3-carboxylate (IIIc) isolated from Cinchona—is an antitumour alkaloid [64,65]. 4-Hydroxy-1,2-dithiolan *trans*- and *cis*-1-oxides (brugierol and isobrugierol) [66], 1,2-dithiolan-3-carboxylic acid [67], and the 4-carboxylic (asparagusic) acid and its sulphoxide (IIId) also occur in plants; they inhibit the growth of lettuce, rice, radish, etc. [46,48]

All functionally substituted 1,2-dithiolans are potential protective agents against radiation [16].

IV. 1,2-DITHIOLENS

Unsubstituted 1,2-dithiolen and its 3,3-disubstituted analogues are known. The 3-thiones (trithiones) (IVa), 3-ones (IVb), 3-imines (IVc), and 3-ylidenes (IVd) are discussed below.



(IV)

a) X=S c) X=NR
b) X=O d) X=CR_2



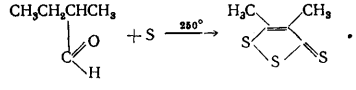
(V)

Several reviews have appeared on the chemistry of 1,2-dithiolium (V) salts [10,69,70], which therefore will not be considered in detail here. The literature on 1,2-dithiolens (IV) up to 1963 was examined in Breslow's monograph [10].

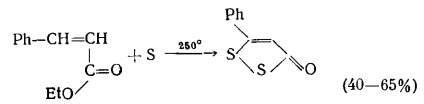
1. Methods of Preparation

(*a*) Sulphurisation of various types of organic compounds (with sulphur, phosphorus pentasulphide, and carbon disulphide)

4,5-Dimethyltrithione was first obtained in 1884 by Barbagliya by the action of sulphur on isovaleraldehyde [10]:

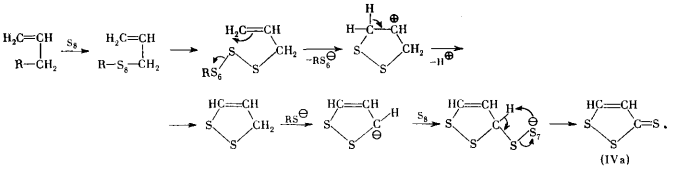


Although the corresponding reaction with ethyl cinnamate gives 5-phenyl-1,2-dithiolen-3-one [71]



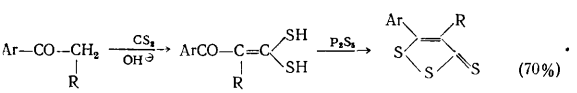
the α-methyl and α-ethyl-cinnamates yield the alkyl trithione-4-carboxylates or thiophens [10]. Sulphurisation of carbonyl (or thiocarbonyl) derivatives with sulphur and (or) phosphorus pentasulphide has so far remained the most general method for obtaining the 3-thiones (IVa), 3-ones (IVb), and 3-ylidenes (IVd) of 1,2-dithiolens (Table 10) [72-90]. The yields of trithiones from the reactions of hydrocarbons and halogenated hydrocarbons with sulphur (Table 11) [91-100] improve in the presence of basic catalysts (diphenylguanidine, mercury acetamide) [95].

The mechanism of the formation of trithiones (IVa) from alkenes [101] is



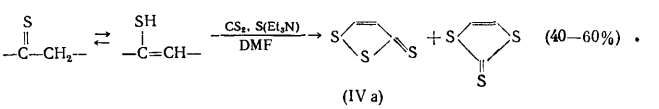
The use of phosphorus pentasulphide enables the temperature of this reaction to be lowered from 500° to 200°C. [91,92,101]

Sulphurisation of saturated and unsaturated hydrocarbons often produces difficultly separable mixtures of thiols, disulphides, thiophens, etc., so that the yields of (IV), especially from aliphatic compounds, rarely exceed 20% (Table 11). 5-Aryltrithiones are formed in higher yields, especially by the action of phosphorus pentasulphide on products of the condensation of aryl ketones with carbon disulphide (Table 10): [10,101]



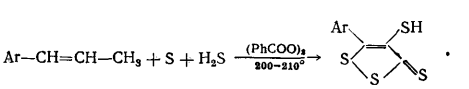
The action of sulphur and carbon disulphide in dimethylformamide on nitrogen-containing derivatives of hydrocarbons—ketimines, enamines, nitriles—also yields trithiones, together with isothiazolines (Table 12). [76,102-106]

With aliphatic thioketones (enethiols) carbon disulphide and sulphur give mixtures of isomeric 1,2-dithiolen-3-thiones (IVa) and 1,3-dithiolen-2-thiones [107]:



(IV a)

The sulphurisation of propenylbenzene in an atmosphere of hydrogen sulphide produces 4-mercaptotrithiones [10]:



In the presence of basic catalysts 5-alkenyltrithiones react with sulphur to form bicyclic thienotrithiones [108,109]:

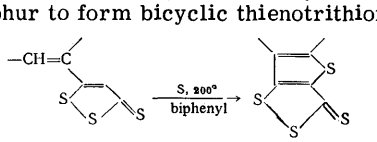
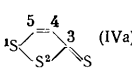
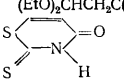
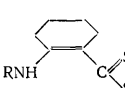
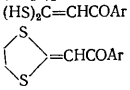
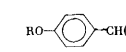
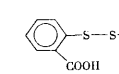
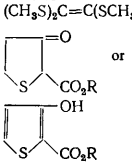
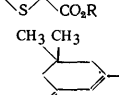


Table 10. 1,2-Dithiolens by the sulphurisation of carbonyl and thiocarbonyl derivatives.

1,2-Dithiolen (IVa, b, d)	Reagent, condition	Initial compound	Yield, %	Ref.
 (IVa)	S, P_2S_5, 135°	R—CO—CH=C(SR')$_2$ or (EtO)$_2$CHCH$_2$C(SEt)$_3$	47	72
	P_2S_5, C_5H_5N, t°		30	73
4,5-(Cl)$_2$-(IVb)	S, $AlCl_3$	CCl_2=CCl—COCl	48	74
4-R-(IVa)	P_2S_5, boiling xylene	$(CH_3S)_2$CHCH(R)CO_2Et	27—39	75
4-R-4-R'-(IVa)	P_2S_5, boiling xylene	R'—CS—CH(R)CO_2Et	31—60	75
4,5-(CH$_2$)$_4$-(IVa)	S, DMF, 20°		50	76
5-EtO$_2$C-(IVb)	S, t°	EtO$_2$C—CH=CH—CO$_2$Et	9	10
		$(CH_3S)_2$C=CHCOAr	87	10
5-Ar-(IVa)	P_2S_5, boiling xylene	$(HS)_2$C=CHCOAr	78	10
			96	10
4-R-5-Ar-(IVa)	S, 200°	Ar—CO—CR=C(SR)$_2$	1—6	77
	P_2S_5, boiling benzene		46	78
4-p-RO-C$_6$H$_4$-(IVa)	S, t°, catalysis		5—75	79
4,5-(—CH=CH—)$_2$-(IVb)	S, 300°		65	80
4-X-5-R-(IVa) (X=Cl, CN, CO$_2$Et)	P_2S_5, toluene	RCOCH(X)CO$_2$Et (X=Cl, CN, CO$_2$Et)	40—70	81
4-Ph-5-EtO$_2$C-(IVa)	P_2S_5	EtO$_2$C—CH(Ph)—CO$_2$Et	20	82
5-Ph-(IVa)+Z *	S, P_2S_5	Ph—CO—CH$_2$—C(NR$_2$)=NH	—	83
4-RCO-5-R'-(IVa)	S, 220°, PhCO$_2$Et	R—CO—C(CH$_3$)=CH—R'	20—38	84
4-ArCO-5-Ar'-(IVa)	S, 215°, PhCO$_2$Et	Ar—CO—C(CH$_3$)=CH—Ar'	45	10, 85
4-Ar'CH$_2$-5-Ar-(IVa)	S, P_2S_5, 200°		—	85
3-[=C(CO$_2$R)$_2$]-5-Ar-(IVd)	S, 250°	Ar—CH=CH—CH=C(CO$_2$R)$_2$	9—23	86
3-(=CHCOR')-5-R-(IVd) + Z	S, 200°	R—(CH=CH)$_2$—CO—R'	5—40	87
4-Ar-5-CH$_3$S-(IVa)	P_2S_5, xylene	$(CH_3S)_2$C=C(Ar)CO$_2$R	70—80	88
4-CH$_3$S-5-Ph-(IVa)	P_2S_5, t°	$(CH_3S)_2$C=C(SCH$_3$)COPh	45	10
4,5-(—CH=CH—S—)-(IVa)	P_2S_5, C_5H_5N	 or	8	89
4,5-[—COCH$_2$C(CH$_3$)$_2$CH$_2$]-(IVa)+ +4,5-[CH$_3$COCH$_2$C(CH$_3$)$_2$—]-(IVa)+Z	S, 200—250°		—	90

*Z represents a secondary product not containing 1,2-dithiolen.

(*b*) Cyclisation of derivatives of β-acetyldithio-carboxylic acids

Good yields of arylated and poor yields of alkylated 1,2-dithiolen-3-ones are obtained by the action of hydrogen chloride on β-acetyldithio-acrylic esters (in boiling methanol) [110].

When β-acetyldithio-β-chloro-carboxylic acids are heated in the presence of a zinc chloride catalyst without a solvent, high yields of alkylated and of halogenated

Table 11. Preparation of trithiones by the sulphurisation of hydrocarbons and halogenated hydrocarbons.

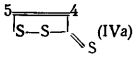
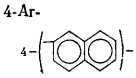
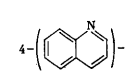
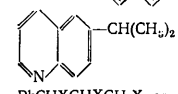
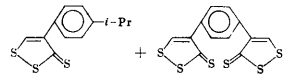
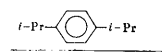
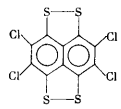
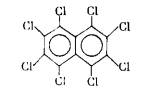
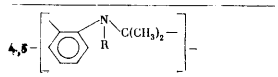
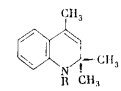
Trithione	Reagent, conditions	Initial compound	Yield, %	Ref.
 (IVa)	S, 550°, N_2	CH_3—CH=CH_2	56	91, 92
4-CH_3-	$S(SO_2)$, 195°	$(CH_3)_2C=CH_2$	39—42	10
4-Cl-		CH_3—C(Cl)=CH—Cl	44	93
4-F-	S, 500°, N_2	CH_3—C(F)=CH_2	46	93
4-CF_3-		CH_3—C(CF_3)=CH_2	46	93
4-CN-		CH_3=C(CH_3)—CN	19	93
4-C_6H_5-	S, 190—220°	PhCX(CH_3)$_2$ or PhCH(CH_3)CH_2X, or PhCX(CH_3)CH_2X, or PhCHX(CH_2)CHX_2 (X=Hal)	<40	94
4-Ar-	S, 190°, catalyst	Ar$CH(CH_3)_2$	22—40	95
	S, 190°, catalyst	$(CH_3)_2$CH— 	56	96
	S, 190°, catalyst		49	96
5-C_6H_5	S, 190—220°	PhCHXCHXCH$_2$X or PhCH$_2$CHXCH$_2$X, or PhCHXCH$_2$CH$_3$, or PhCH$_2$CHXCH$_3$, or Ph(CH_2)$_3$X (X=Hal)	11—18	94
4-C_6H_5-5-CH_3-	S, 190°, catalyst	PhCH(CH_3)CH_2CH_3	1	96
4-C_6H_5-5-HS-	S, DMF, $t°$ (Me_2NH)	$(CH_3)_2$CHPh	52	97
4,5-(C_6H_5)$_2$-	S, 190°, catalyst	PhCH$_2$CH(Ph)CH_3	27	96
4,5-(—CH_2—)$_4$-	S, 130°		—	98
4,5-(—CH=CH—)$_2$-	S, 400°	Ph—CH_3	0.05	98
	S, 400—500°		—	91
	S, 320°, N_2		85	99
	S, $t°$		19—36	100

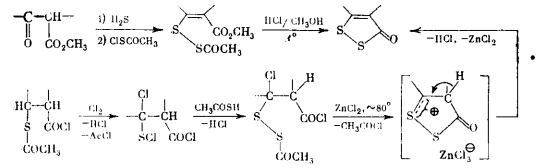
Table 12. Sulphurisation of nitrogen-containing compounds by a mixture of carbon disulphide and sulphur (in dimethylformamide at 20°C).

Trithione	Initial compound	Yield, %	Ref.
4-C_6H_5-	Et—CH=CHNR_2	50	102
4-C_6H_5-	PhCH=CH—NR_2	30	102
5-C_6H_5-	CH_3=C(Ph)NR_2	30	102
4-OCH_3-5-NH_2	NC—CH_2—CO_2CH_3*	38	103
4,5-(NH_2)$_2$-	NC—CH_2CONH_2*	27	103
4-CN-5-NH_2	CH_2(CN)$_2$	70	104
4,5-(—CH_2—)$_3$-		60	105
4,5-(—CH_2—)$_4$-		30—40	76
4,5-(—CH_2—)$_n$- + Z**; n=3—5	CH=C—NR_2 ( ) (CH_2)$_n$ n=3.5	30—50	102, 106

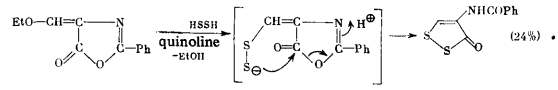
*Reaction with carbon disulphide in presence of sodium methoxide.

**Z represents a secondary product.

1,2-dithiolen-3-ones are obtained, and even of the unsubstituted carbonyl compound (Table 13):[32]



4-Acylamino-1,2-dithiolen-3-ones are obtained by the reaction of 4-ethoxymethylenoxazol-5-one with hydrogen sulphide and sulphur in the presence of quinoline[111]:



(*c*) Other methods

The condensation of disulphane with derivatives of phenylpropionic acid during exposure to ultraviolet radiation gives 5-phenyl-1,2-dithiolens (this reaction cannot be accomplished with the aliphatic analogues) [10]:

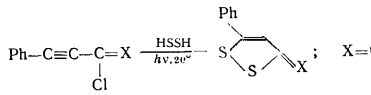
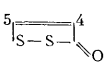
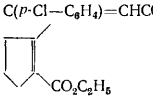
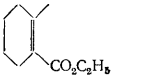
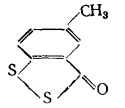
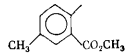
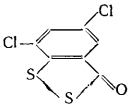
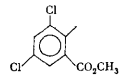
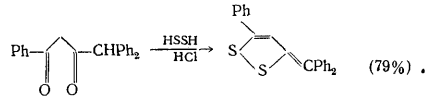


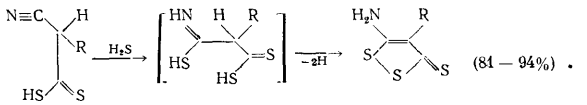
Table 13. Cyclisation of derivatives of β-acetyldithiocarboxylic acids CH_3COSSR by methanolic hydrogen chloride [110] or by zinc chloride [32].

1,2-Dithiolen-3-one	R	Yield, %	Ref.
	$CHClCH_2COCl$	87	32
4-CH_3-	$CHClCH_2(CH_3)COCl$	92	32
5-CH_3-	$CCl(CH_3)CH_2COCl$	90	32
5-CH_3	$C(CH_3)=CHCO_2C_2H_5$	20	110
4-Cl-	$CHClCHClCOCl$	68	32
4,5-$(CH_3)_2$-	$C(CH_3)=C(CH_3)CO_2C_2H_5$	17	110
5-C_6H_5-	$C(Ph)=CHCO_2C_2H_5$	80	110
5-(*p*-C_6H_4)-	$C(p\text{-}CH_3C_6H_4)=CHCO_2C_2H_5$	76	110
5-(*p*-Cl-C_6H_4)-	$C(p\text{-}Cl{-}C_6H_4)=CHCO_2C_2H_5$	81	110
4,5-$(CH_2)_3$-		9	110
4,5-$(CH_2)_4$-		30	110
4,5-$(CH{=}CH)_2$-		95	110
		88	110
		76	110

The reaction of disulphane with arylated 1,3-diketones yields 1,2-dithiolylidene compounds [112]:



5-Aminotrithiones are formed from α-cyano-carboxylic acids containing two sulphur atoms by the action of hydrogen sulphide and bromine water [113]:

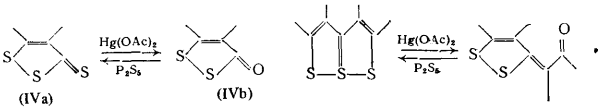


R=CN, CO_2CH_3, $CONH_2$

(*d*) Interconversion of 1,2-dithiolen derivatives

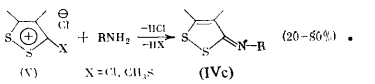
1,2-Dithiolens themselves are often the starting materials for obtaining other compounds of this type.

Thus 1,2-dithiolen-3-thiones (IVa) are easily converted into the 3-ones (IVb) by the action of mercury acetate [72,114] or chlorides of hydroxamic acids [115]; and the action of phosphorus pentasulphide converts (IVb) back into (IVa); dithiolylidene ketones and thiothiophthens are interconverted similarly [116]:



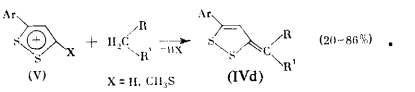
(IVa) (IVb)

1,2-Dithiolen-3-imines (IVc) are obtained by the reaction of 3-chloro- or 3-methylthio-1,2-dithiolium salts (V) with amines [117-120] or with *NN*-dichlorobenzamides [121], the yield of (IVc) depending on the basicity of the amine:



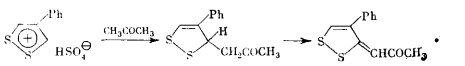
(V) X = Cl, CH_3S (IVc)

1,2-Dithiolylidenes (IVd) are usually obtained by condensing 1,2-dithiolium salts (V) with compounds containing active methylene groups [122-124]:

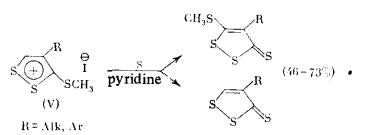


(V) X = H, CH_3S (IVd)

However, the reaction of a 4-phenyl-1,2-dithiolium salt with acetone gives a stable 3-monosubstituted 1,2-dithiolen, which forms a dithiolylidene ketone (IVd) only in the presence of chloranil [125,126]:



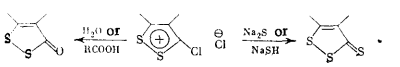
Sulphur acts on 1,2-dithiolium salts under mild conditions to form trithiones; in the case of 3-methylthio-1,2-dithiolium salts (V) this reaction gives a mixture of the expected 5-methylthiotrithione and a trithione formed by demethylation of the initial compound (V): [127-129,159]



(V)

R = Alk, Ar

More nucleophilic bases convert 3-chloro-1,2-dithiolium salts into trithiones, and the less nucleophilic bases yield 1,2-dithiolen-3-ones [74,130]:

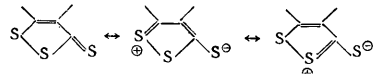


2. Physical Properties

1,2-Dithiolens have a planar *cis*-configuration of the disulphide bond, which would appear to be energetically less favourable than in 1,2-dithiolans, and still less than in open-chain disulphides (dihedral angle between the planes of the valencies of the sulphur atoms respectively 0°, 27°, and 90°). Actually, however, unsaturated five-membered cyclic disulphides are far more stable than the saturated rings, because the energy of repulsion of the unshared *p* electrons of the sulphur atoms is balanced by the conjugation energy of *p* and π electrons [34].

The structures of trithione [131] and 4-methyltrithione [132] have been established by means of X-rays. The molecules are planar [10], with carbon–carbon and carbon–sulphur bond lengths closely similar to those in benzene and in

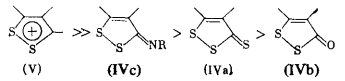
thiophen, but the sulphur–sulphur bond length in trithiones (2.04 Å) is identical with that in S_8 and R_2S_2 molecules. The structure of trithiones is therefore a hybrid of the resonance structures



in the proportions 5 : 4 : 1.[133]

According to LCAO-MO calculations, trithione and its 4- and 5-phenyl analogues have a low π-order of the S–S bond (0.07–0.08,[133] 0.242 [34]) and a higher order of the $C_{(4)}-C_{(5)}$ π-bond (~0.8).[134] In contrast to the $C_{(3)}$ and $C_{(5)}$ atoms the $C_{(4)}$ atom of trithiones bears a fractional negative charge (about −0.06).[133,134] The considerable negative charge on the exocyclic sulphur atom (about −0.28) is explained by the tendency of trithione to acquire an aromatic configuration by repelling the "spare" π-electron[133].

1,2-Dithiolen-3-ones and -thiones are analogues of the non-alternant tropone and tropothione systems. A clear comparison of the aromaticities of the various types of 1,2-dithiolens (IVa–c) and (V) can be obtained from their energies calculated by the LCAO-MO method (Table 14).[134] According to their DE/n values these compounds form the sequence of diminishing aromaticity



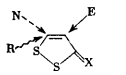
(V) (IVc) (IVa) (IVb)

Table 14. Energies of 1,2-dithiolens (in β-units)*.

No.	System	n	DE	W	DE/n
(IVb)	1,2-Dithiolen-3-one	8	1.063	12.527	0.133
(IVc)	1,2-Dithiolen-3-imine	8	1.096	10.332	0.137
(IVa)	1,2-Dithiolen-3-thione	8	1.057	9.425	0.132
(V)	1,2-Dithiolium ion	6	1.57÷2.05	7.57÷8.13	0.198÷0.342

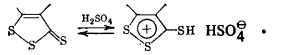
*DE = delocalisation energy; n = number of π-electrons; W = total π-electron energy.

From the molecular diagrams for (IVa–c) it is predicted that centres of electrophilic, nucleophilic, and radical reactivity—E, N, and R —will have the locations[134]

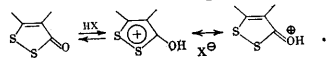


(IVa–c) (X = S, O, NR)

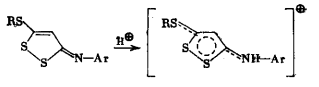
Because of the high electron density on the thiocarbonyl sulphur atom (1.576,[135] 1.433 [134]) trithiones exhibit basic properties and dissolve readily in acids[135]:



Protonation of the less basic 1,2-dithiolen-3-ones leads to a greater proportion of the oxonium form than of the 1,2-dithiolium structure (according to ^{1}H-n.m.r. data)[70,136]:

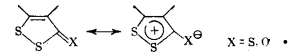


1,2-Dithiolen-3-imines are fairly strong bases. Thus for *N*-aryl-5-methylthio-1,2-dithiolen-3-imines

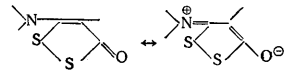


pK_b = 2.57 (the value for aniline is 3.69).[118]

Both trithiones and 1,2-dithiolen-3-ones have considerable dipole moments, although higher for similarly substituted trithiones because of the greater importance of the limiting polar structure[137,138]:

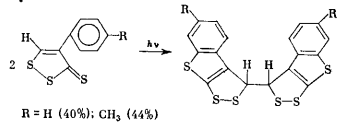


Thus the measured dipole moments of the two groups lie in the ranges 3.3–5.5 and 2.8–4.9 D. The measured "apparent" conductivities are also higher for the former than for the latter group ($10^5\kappa$ is respectively 8.3–52 and 2.6 to 30 ohm^{-1} cm^{-1}).[137] The calculated dipole moment of unsubstituted trithione is 5.25 D.[133] 4-Halogeno- and 5-aryl-1,2-dithiolens have higher dipole moments than the corresponding 5-halogenated and 4-arylated compounds[138]. 1,2-Dithiolen-3-ones containing a tertiary amino-group at position 5 have extremely high dipole moments (4.74 to 6.73 D):[137,138]



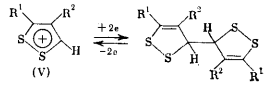
The surprisingly high melting points of trithiones[10] may be due to their high polarity.

The photochemical behaviour of 1,2-dithiolens is influenced by the position of the substituent. Whereas 5-phenyltrithione is photochemically stable[139], 4-*p*-tolyl- and 4-phenyl-trithiones undergo photochemical reactions at the C=S bond[140]:



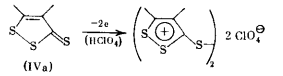
R = H (40%); CH_3 (44%)

1,2-Dithiolium ions (V) and bi-1,2-dithiolen-3-yls are interconverted electrochemically at a platinum electrode in acetonitrile[141]:



(V)

The preparative anodic oxidation of trithiones (IVa) yields bis-1,2-dithiolium disulphide[142]:



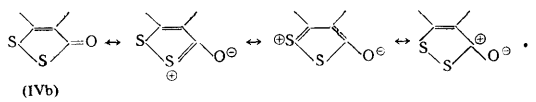
(IVa)

Trithiones are oxidised at potentials of ~0.8–1.32 V, and 1,2-dithiolium salts are reduced between about +0.32 and −0.06 V. Substituents in the ring affect both oxidation and reduction potentials: monosubstituted derivatives are oxidised and reduced far more easily than are disubstituted derivatives[142]. Polarographic reduction of trithiones gives a cathodic wave having a half-wave potential of −0.9 V.[101]

Ultraviolet and visible spectra. Trithiones exhibit strong absorption bands at 225, 250, 280, 335, and 417 nm,[101] which are somewhat displaced in the arylated compounds[10].

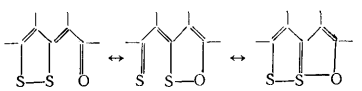
Infrared spectra. The 1,2-dithiolen framework shows characteristic absorption bands at 504–561 and 1508–1567 cm^{-1} (sulphur–sulphur and carbon–carbon vibrations of the ring)[143]. Later results reveal characteristic infrared lines at 405–420 and 430–450 cm^{-1} (planar deformation vibrations of the ring) and at 1305 to 1350 and 1490–1565 cm^{-1} (stretching vibrations of the ring). Sulphur–sulphur stretching vibrations of 1,2-dithiolens[144] appear at 480–525 cm^{-1}.

1,2-Dithiolens-3-ones exhibit a low carbonyl frequency (1610–1685 cm^{-1}),[32,115] like their analogue tropone (1638 cm^{-1}), as a consequence of the electron displacement[138,144]

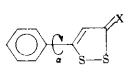


(IVb)

Therefore (IVb) with a tertiary amino-group at position 5 have the lowest carbonyl frequency (1610–1635 cm^{-1}).[138] The thiocarbonyl group in trithiones[115] absorbs at 1110 to 1190 cm^{-1}. The carbonyl frequency of α-1,2-dithiol-3-ylidene ketones is located in a very low range (1550–1600 cm^{-1}), owing to interaction of the carbonyl oxygen with a cyclic sulphur atom[145,146]:



Proton magnetic resonance spectra. The signals of the ring protons, especially the fragment =CH–S, in 1,2-dithiolen-3-ones and -thiones are situated down-field ($\delta \simeq 6.3-8.4$ p.p.m.) from those for cycloalkenes (for cyclopentene $\delta_{CH} = 4.4$ p.p.m.), owing to conjugation of the carbonyl (or thiocarbonyl) group and the heteroatoms[32,147]. The chemical shifts of the aromatic protons in 5-aryl-1,2-dithiolens indicate that the rings are non-coplanar



X=O, S;

with the preferred deformation $\alpha = 30°$. The electron-acceptor inductive contributions found experimentally for 1,2-dithiolens with respect to the aryl substituent are −0.13 and −0.16 according as X = O or S.[148]

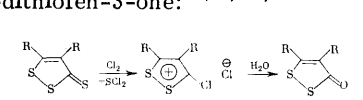
Mass spectra. 1,2-Dithiolens exhibit an intense peak due to the molecular ion, which may also indicate the aromaticity of these compounds[149,150].

3. Chemical Properties

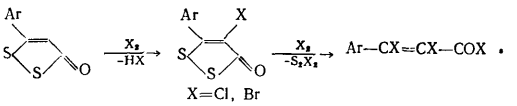
Trithiones are more reactive than 1,2-dithiolen-3-ones because of the greater polarisability of the thiocarbonyl group[151].

(*a*) Reactions with electrophilic reagents

Under mild conditions alkylated 1,2-dithiolen-3-thiones react readily with chlorine only at the thiocarbonyl bond to form a dithiolium salt, which is easily converted by interaction with the solvent (water, acetic acid) into the corresponding 1,2-dithiolen-3-one:[74,80,152,153]



As the system becomes more strongly aromatic, the ring also undergoes chlorination: the halogenation of 4-arylated or (under more severe conditions) 5-arylated 1,2-dithiolen-3-thiones, for example, yields the corresponding 5- or 4-halogenated 3-ones.[10,120,154,155] Under still more severe conditions (prolonged action of excess of halogen in boiling tetrachloromethane), however, substitutive halogenation is accompanied by ring cleavage with loss of both sulphur atoms and formation of the corresponding derivatives of $\alpha\beta$-dihalogenocinnamic acids[156,157]:



X=Cl, Br

Even under mild conditions unsubstituted and alkylated 1,2-dithiolen-3-ones undergo only ring fission with sulphuryl chloride, sulphenyl chlorides, and chlorine, at the S–CO bond with the chlorides and at both S–CO and S–S bonds with chlorine (Table 15):[50,51]

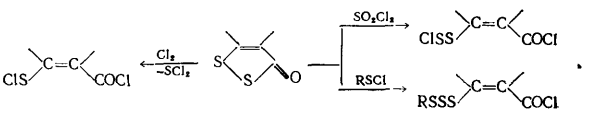
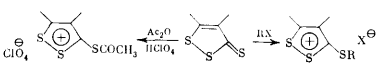


Table 15. Products of the cleavage of 1,2-dithiolen-3-ones by SO_2Cl_2,[50] RSCl,[51] and Cl_2.[50]

1,2-Dithiolen-3-one	Reagent	Product	Yield, %
	SO_2Cl_2	ClSSCH=CHCOCl	50
	Cl_2	ClSCH=CHCOCl	72
	CH_3SCl	CH_3S_2CH=CHCOCl	43
	C_6H_5SCl	$C_6H_5S_2CH$=CHCOCl	83
4-Methyl-	SO_2Cl_2	ClSSCH=C(CH_3)COCl	68
5-Methyl-	SO_2Cl_2	ClSSC(CH_3)=CHCOCl	79

(*b*) Formation of 1,2-dithiolium salts

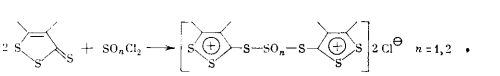
Alkylated[10,135,158–160] and acylated[105] trithiones usually yield 1,2-dithiolium salts:



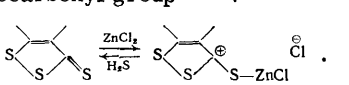
X = I, Br, Cl, HSO_4, HgI_3 etc.
R = Alk, CH_2COR[158] etc.

1,2-Dithiolen-3-ones react similarly with acetic anhydride[105] and with triethyloxonium fluoroborate[161,162]. Trithiones are converted into 3-chloro-1,2-dithiolium salts by the action of oxalyl chloride, trichloromethyl isocyanide dichloride, or thiocarbonyl chloride ten times as easily as are 1,2-dithiolen-3-ones[105,151]. These salts are formed also from 1,2-dithiolen-3-ones and phosphorus pentachloride or phosphoryl chloride[80,163], but not with phosphorus trichloride or thionyl chloride[80].

Under mild conditions trithiones form 2 : 1 ionic adducts with oxalyl[80], thionyl, or sulphuryl[101,164] chloride:



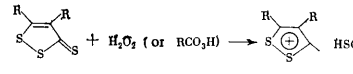
Halides of heavy and transition metals ($HgCl_2$, $HgBr_2$, HgI_2, $CdCl_2$, CdI_2, $ZnCl_2$, $FeCl_3$, $AgNO_3$, $SbCl_3$, $CuCl_2$, Cu_2Br_2, $AuCl_4$, $PdCl_2$, $PtCl_4$, $BiCl_3$, and $SnCl_4$) form with trithiones yellow crystalline complexes (1 : 1 or 1 : 2) also involving the thiocarbonyl group[10,101]:



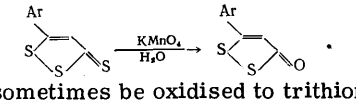
Trithiones form with 1,2-dithiolen-3-ones 1 : 2 donor–acceptor complexes[164].

(*c*) Oxidation and reduction

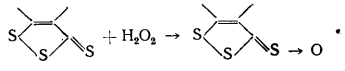
Oxidising agents convert alkylated trithiones into 1,2-dithiolium salts [128,139,165,166]



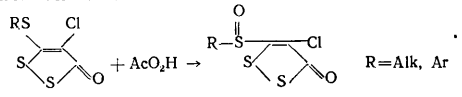
and arylated trithiones into 1,2-dithiolen-3-ones [120]



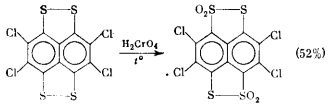
Trithiones can sometimes be oxidised to trithione *S*-oxides [167,168]:



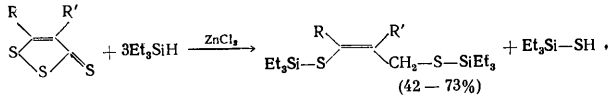
5-Alkyl(and aryl)thio-1,2-dithiolen-3-ones are oxidised only at the exocyclic sulphur atom with the formation of sulphinyl derivatives [118,169]:



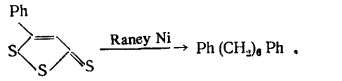
Heating with chromic and nitric acids oxidises 4,5-dimethyltrithione to acetic acid, and 5-*p*-methoxyphenyltrithione to anisic acid [101]. The only known example of oxidation of a dithiole sulphur atom is the formation of thiosultones from naphthobisdithioles and chromic acid [99]:



The reduction of trithiones by triethylsilane involves both thiocarbonyl and disulphide bonds [170]:

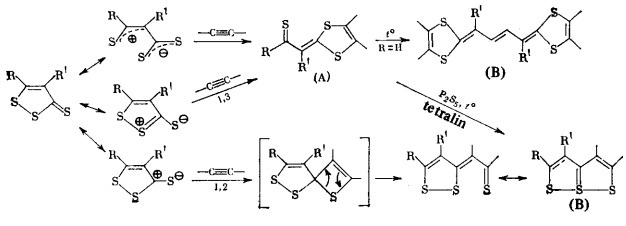


Sulphur is completely removed when trithiones undergo hydrogenation in the presence of Raney nickel, and the hydrocarbon residues dimerise [101]:



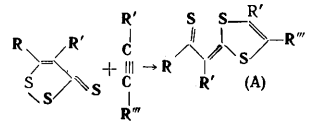
(*d*) Condensation

Alkynes. The discovery in 1964 of the reaction of trithiones with alkynes showed [171] that, depending on the reaction conditions and the nature of the substituents, the trithiones can react in one of the possible resonance structures, with the formation of compounds of types (A) and (B):



The former type are mostly formed, especially under conditions of acid catalysis [172] (Table 16). [173–179] 5-Substituted thiones are more reactive [171]. In the absence of a 5-substituent thioaldehydes (A: R = H) are formed; these are unstable, and when heated readily lose sulphur with the formation of biadducts of type (C). [174,179] In the absence of acids either a mixture of isomeric compounds (A) and (B) or solely (B) is produced (Table 17). [172–180] The isomers differ in their ultraviolet spectra [177]. 1,3-Dithiolylidene thioketones (A) are easily isomerised to thiothiophthens (B) by heating with phosphorus pentasulphide [176].

Table 16.

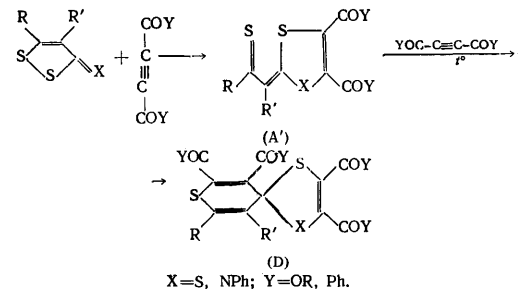


R	R′	R″	R‴	Conditions, °C	Yield of (A), %	Ref.
Ph	H	CO_2Me	CO_2Me	20°	82	173–176
				dioxan, *t*°	82	177
Ph	H	CO_2Et	CO_2Et	$CHCl_3$, *t*°	84	175, 177
Ph	H	H	CHO	20°	92	175, 177
				xylene, *t*°	42	175, 177
Ph	H	Ph	H	xylene, HCl, *t*°	30	172, 176
Ph	H	H	*p*-O_2N—C_6H_4	dioxan, *t*°	39	175, 177
Ph	H	$CONH_2$	$CONH_2$	80°	81	177
Ph	H	CO_2Et	Ph	dioxan, *t*°	75, 92	174, 175, 177
Ph	H	PhCO	Ph	dioxan, *t*°	79	177
Ph	H	CO_2Et	CH_3	benzene, *t*°	74	174
Ph	H	CH=CH—CH=CH		benzene, *t*°	28	173
»	»			catalyst, $Pb(OAc)_4$	55	174
Ph	Ph	CO_2Et	Ph	*t*°	56	
p-Br-C_6H_4	H	Ph	H	HCl	25	176
		H	Ph	dioxan, *t*°	52	177
p-Cl-C_6H_4	H	CO_2Me	CO_2Me	dioxan, *t*°	75	177
		H	*p*-$CH_3OC_6H_4$	toluene, *t*°	58	177
Ph	*p*-$CH_3OC_6H_4CO$	CO_2Me	CO_2Me	$CHCl_3$, *t*°	73	177
H_2N	CN	CO_2Me	CO_2Me	DMF, *t*°	44	177
		H	Ph	DMF, *t*°	40	177
		CO_2H	H	60°	90	177
$CH_2CH_2CH_2$		CO_2Et	Ph	130°	40	177
		PhCO	Ph	toluene, *t*°	82	177
CH_3S	Ph	H	SCH_3	140°	43	178
H	Ph	CO_2Me	CO_2Me	—	85	179
CH_3CH_2	CH_3	CO_2Me	CO_2Me	—	65	174
		CO_2Me	CO_2Me	20°	74	179
H	H	PhCO	PhCO	20°	70	
		$CO_2H(CO_2Me)$	H	—	60	92

The reactivity of acetylenic compounds in these condensations falls in the sequence [175,176]

$$RO_2C{-}C{\equiv}C{-}CO_2R > HC{\equiv}C{-}CO_2R > Ar{-}C{\equiv}C{-}CO_2R > Ar{-}C{\equiv}C{-}H > Ar{-}C{\equiv}C{-}Ar\,.$$

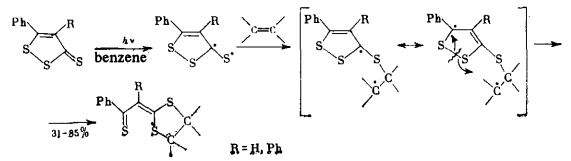
Acetylenedicarboxylic esters are able to form not only 1:1 (A′) but also 2:1 (D) adducts or their mixtures in proportions depending on the reactivity of the alkyne and the temperature (Table 18): [173,174,176]



(D)

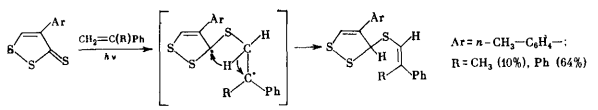
X=S, NPh; Y=OR, Ph.

Alkenes. Trithiones react with alkenes, in contrast to alkynes, only on irradiation, forming equimolecular adducts. Whereas 5-phenylated trithiones give 1,3-cycloaddition products with cleavage of the cyclic disulphide bond [181]



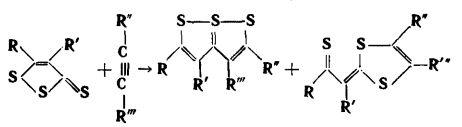
R = H, Ph

the 4-*p*-tolyl derivatives form adducts in which the ring remains intact [140]



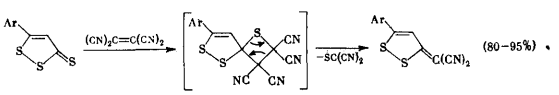
Ar = *n*-CH_3—C_6H_4—; R = CH_3 (10%), Ph (64%)

Table 17.



R	R′	R″	R‴	Conditions	Yield, % (B)	Yield, % (A)	Ref.
		Ph	H	xylene, *t*°	30	0	172, 176
		p-Cl-C_6H_4	H	xylene, *t*°	5	10	176, 180
Ph	H	*p*-Br-C_6H_4	H	xylene, *t*°	20	15	176, 180
		Ph	Ph	DMF, *t*°	41	0	177
		p-$CH_3OC_6H_4$	H	xylene, *t*°	48	0	180
p-$CH_3OC_6H_4$	H	Ph	H	xylene, *t*°	50	0	172, 176
p-Br-C_6H_4	H	Ph	H	xylene, HCl, *t*°	10	60	172, 176
				xylene, *t*°	20	20	176
p-$CH_3OC_6H_4$	CH_3	Ph	H	xylene, *t*°	50	0	176
				xylene, HCl, *t*°	15	15	176
Ph	CH_3	Ph	H	xylene, HCl, *t*°	20	10	176
				xylene, *t*°	50	0	176
p-Cl-C_6H_4	H	Ph	H	xylene, *t*°	25	25	176
CH_2S	CH_3	CH_2S	H	140°	42	0	178
CH_2S	*p*-$CH_3C_6H_4$	CH_2S	H	140°	38	0	178

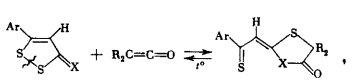
The condensation of 5-aryltrithiones with the electron-deficient tetracyanoethylene does not require exposure [182]:



(80–95%)

In contrast to trithiones, 1,2-dithiolen-3-ones do not react with alkynes and alkenes [175,181].

Ketens. 1,2-Dithiolens containing exocyclic C=S, C=O, and C=NR double bonds react readily in the cold with ketens—more reactive unsaturated compounds—to form equimolecular addition products. However, this reaction is reversible, and at higher temperatures the adducts break down into the initial components [111,183–185]:



R = H, CH_3; X = S (30–70%); O (40%); NPh (65–90%)

Certain adducts rearrange into 1,2-dithiolylidenes on standing [112,184]:

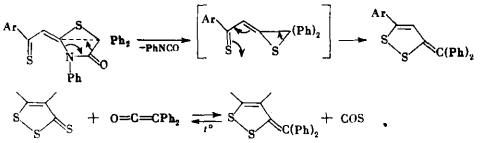
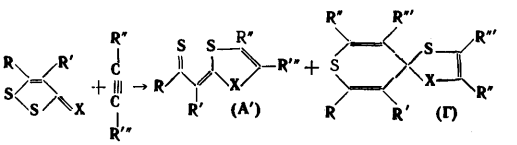
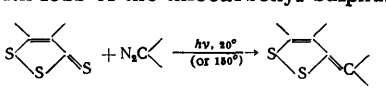


Table 18.

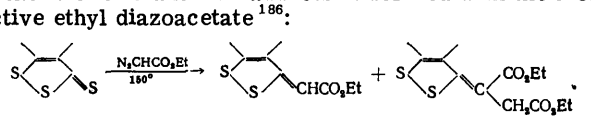


R	R′	X	R″	R‴	Conditions	Yield, % (A′)	Yield, % (D)	Ref.
Ph	H	NPh	CO_2Et	H	—	75	0	176
Ph	H	NPh	CO_2Et	Ph	—	64	0	176
Ph	H	NPh	CO_2Me	CO_2Me	—	0	63	176
Ph	Ph	NPh	CO_2Me	CO_2Me	heat	0	75	176
					20°	43	44	174
Ph	H	S	CO_2Me	CO_2Me	heat	0	93	173, 174, 176
Ph	H	S	COPh	COPh	—	71	14	179
Ph	Ph	S	CO_2Me	CO_2Me	20°	70	0	173, 174, 176
			ditto	ditto	heat	0	66	173, 174, 176
Ph	Ph	S	H	CO_2Et	heat	29	70	176
—$(CH_2)_3$—		S	CO_2Me	CO_2Me	—	78	9.5	174
—$(CH_2)_4$—		S	CO_2Me	CO_2Me	—	17	56	174
CH_3CH_2	CH_3	S	CO_2Me	CO_2Me	excess of reagent	0	96	174

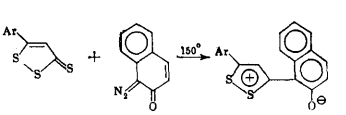
Carbenes and nitrens. Trithiones react extraordinarily readily with carbenes. Thus with diazoketones and with diphenyldiazomethane 1,2-dithiolylidenes are formed with loss of the thiocarbonyl sulphur [186]:



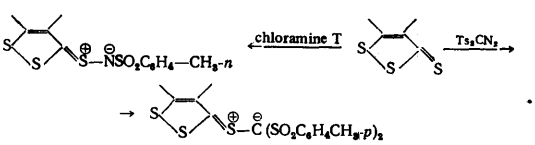
A mixture of 1 : 1 and 1 : 2 adducts is formed with the more reactive ethyl diazoacetate [186]:



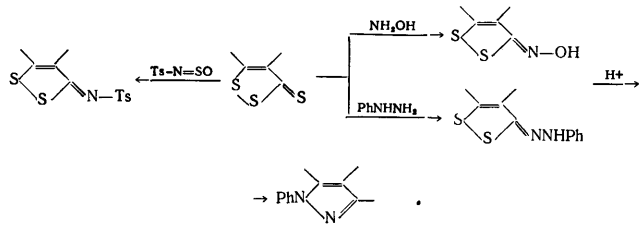
1-(1,2-Dithiolio)-2-naphthoxides are obtained from 1-diazodihydronaphthalen-2-one [186,187]



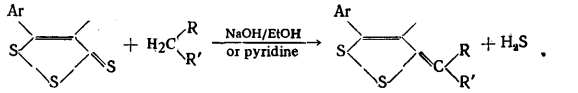
In some cases the thiocarbonyl group is preserved in the reaction of 4-phenyl- and benzo-trithiones with carbenes and nitrens. For the first time good yields have been obtained of stable thiocarbonyl ylides and their nitrogen analogues—imines [188]:



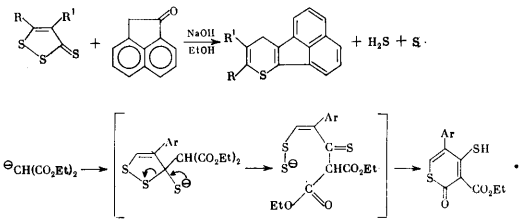
Hydroxylamine[10,189,190], phenylhydrazine[101], and *N*-sulphinyltoluene-*p*-sulphonamide[191]. Like ketones and thioketones, 1,2-dithiolen-3-thiones and -ones condense with these compounds to form the corresponding 3-imine derivatives. Phenylhydrazones are readily converted into pyrazoles[101]:



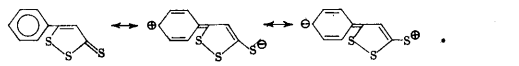
CH-Acids. Like thioketones, 5-aryltrithiones react readily with CH-acids—malononitrile, acenaphthenone, and malonic and cyanoacetic esters[101,192]—and with α-bromo-ketones[160] to form 1,2-dithiol-3-ylidenes[10,101]:



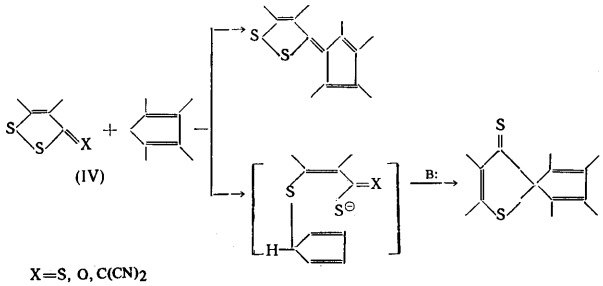
In contrast to the 5-aryl derivatives, the reaction of other trithiones with CH-acids usually involves cleavage of the ring[10,101,192]:



The great stability of 5-aryltrithiones towards cleavage is attributed to resonance stabilisation, which is impossible with the 4-aryl compounds:

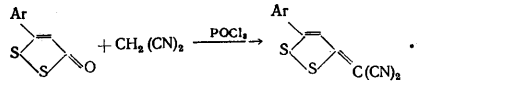


1,2-Dithiolen-3-thiones, -ones, and -ylidenes (IV) give with tetraphenylcyclopentadiene (or fluorene) in an alkaline medium a mixture of condensation and ring-cleavage products—dithiafulvalenes and spiro-compounds[123]:



X=S, O, C(CN)2

In contrast to 5-aryl-1,2-dithiolen-3-thiones, the 3-ones can be condensed with malononitrile in the presence of phosphoryl chloride[125]:



(*e*) Substitution with preservation of the ring

Numerous reactions of 5-chloro- and 4,5-dichloro-1,2-dithiolen-3-ones and -imines have shown that the 5-halogen is very easily substituted by any nucleophile[193–198], but a 4-halogen is not replaced even with excess of a nucleophile[196] (Tables 19–21):[118,120,121,170,193–197]

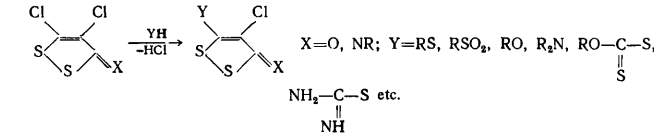
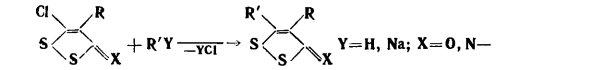
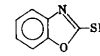
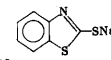
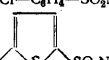
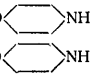


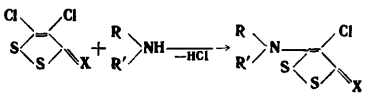
Table 19. Reaction of 5-chloro-1,2-dithiolens with thiols, sulphinates, alkoxides, and amines:



X	R	R'Y	Yield, %	Ref.
O	Ph	CH_3SH	45	118
O	Ph	EtSH	25	118
O	Ph		36	118
O	Ph		37	118
N-SO_2—C_6H_4—CH_3-*p*	Cl	PhSH	72	193
N-CO_2Et	Cl	PhSH	62	193
N-SO_2—Ph	Cl	CH_3ONa	76	193
N-SO_2—C_6H_4—CH_3-*p*	Cl	CH_3ONa	66	193
N-CO_2Et	Cl	CH_3ONa	66	193
N-SO_2—Ph	Cl	*p*-CH_3—C_6H_4—SO_2Na	94	193
N-CO_2—Et	Cl	*p*-CH_3—C_6H_4—SO_2Na	82	193
N-CH_3	Cl	*p*-CH_3—C_6H_4—SO_2Na	47	193
N-CO—C_6H_4—NO_2-*o*	Cl	$PhSO_2Na$	77	121
N-CO—$C_6H_3(NO_2)_2$-*o*, *p*	Cl	$PhSO_2Na$	76	121
O	Cl	CH_3SO_2Na	70	118
O	Cl	$EtSO_2Na$	84	118
O	Cl	$(CH_3)_2CHSO_2Na$	61	118
O	Cl	$ClCH_2SO_2Na$	55	118
O	Cl	$PhSO_2Na$	97	118
O	Cl	*p*-CH_3—C_6H_4—SO_2Na	92	118
O	Cl	*p*-Cl—C_6H_4—SO_2Na	89	118
O	*p*-CH_3—C_6H_4		57	118
O	Ph	CH_3SO_2Na	75	118
O	Ph	$PhSO_2Na$	62	118
O	*p*-CH_3—C_6H_4	$PhNH_2$	<1	197
O	Ph	*o*-CH_3—C_6H_4—NH_2	40	197
O	*p*-CH_3—C_6H_4	*o*-CH_3—C_6H_4—NH_2	21	197
O	Ph	*p*-CH_3—C_6H_4—NH_2	47	197
O	*p*-$CH_3C_6H_4$	*p*-CH_3—C_6H_4—NH_2	25	197
O	Ph	*p*-OCH_3—C_6H_4—NH_2	50	197
O	*p*-CH_3—C_6H_4	*p*-OCH_3—C_6H_4—NH_2	52	197
O	Ph	*o*-OEt—C_6H_4—NH_2	70	197
O	*p*-CH_3—C_6H_4	*o*-OEt—C_6H_4—NH_2	59	197
O	Ph	*p*-OEt—C_6H_4—NH_2	40	197
O	*p*-CH_3—C_6H_4	*p*-OEt—C_6H_4—NH_2	47	197
O	Ph		54	197
O	*p*-CH_3—C_6H_4		32	197

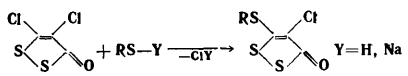
The difference in reactivity between substituents at positions 4 and 5 is attributed to the difference in polarity between the $C_{(4)}$ and $C_{(5)}$ carbon atoms (see above)[133]; great activity of the 5-halogen is indicated also by the vinylogy principle, since 5-chloro-1,2-dithiolen-3-one is a vinylogue of carboxylic acid chlorides[193].

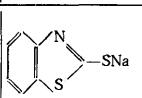
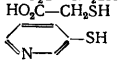
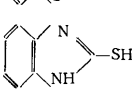
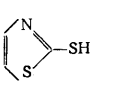
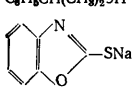
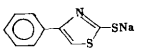
Table 20. 5-Alkylamino-4-chloro-1,2-dithiolens from 4,5-dichloro-1,2-dithiolens:



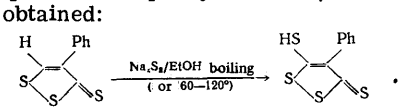
X	R	R′	Yield, %	Ref.	X	R	R′	Yield, %	Ref.
O	H	*o*-CH_3—C_6H_4	60	196	N—SO_2—C_6H_5	H	C_6H_5	57	193
O	H	*m*-CH_3—C_6H_4	85	196	N—$SO_2C_6H_4CH_3$-*p*	H	CH_3	36	193
O	H	*p*-CH_3—C_6H_4	85	196	ditto	H	*n*-C_3H_7	34	193
O	H	*o*-CH_3O—C_6H_4	77	196	ditto	H	*n*-C_4H_9	58	193
O	H	*m*-$CH_3OC_6H_4$	88	196	ditto	H	*n*-$C_{18}H_{37}$	58	193
O	H	*p*-CH_3O—C_6H_4	99	196	ditto	H	cyclo-C_6H_{11}	67	193
O	H	*o*-EtO—C_6H_4	69	196	ditto	H	$HO(CH_2)_2$	37	193
O	H	*p*-EtO—C_6H_4	98	196	ditto	H	$H_2N(CH_2)_2$	7.0	193
O	C_2H_5	C_2H_5	20	196	ditto	H	$C_6H_5CH_2$	64	193
O	H	Ph	94	196	ditto	H	C_6H_5	79	193
CH_3N	$(CH_2)_2$—O—$(CH_2)_2$		12	193	ditto	H	*p*-$CH_3C_6H_4$	61	193
NSO_2CH_3	$(CH_2)_2$—O—$(CH_2)_2$		87	193	ditto	H	*o*-OH—C_6H_4	34	193
NSO_2Ph	H	CH_3	44	193	ditto	CH_3	CH_3	53	193
ditto	H	*n*-C_3H_7	40	193	ditto	$(CH_2)_4$		80	193
ditto	H	*n*-C_4H_9	54	193	ditto	$(CH_2)_5$		77	193
ditto	H	*n*-C_8H_{17}	40	193	ditto	$(CH_2)_2$—O—$(CH_2)_2$		79	193
ditto	H	cyclo-C_6H_{11}	54	193	N—$SO_2C_6H_4CH_3$-*p*	H	C_6H_5NH	85	193
ditto	H	$HO(CH_2)_2$	33	193	N—CO_2Et	H	Ph	78	193
ditto	H	$C_6H_5CH_2$	44	193	N—CO_2Et	$(CH_2)_2$—O—$(CH_2)_2$		67	193
ditto	H	C_6H_5	72	193	$NCOC_6H_4NO_2$-*o*	H	*p*-$CH_3C_6H_4$	54	121
ditto	H	*p*-CH_3—C_6H_4	62	193	$NCOC_6H_4NO_2$-*o*	H	*p*-OEtC_6H_4	62	121
ditto	H	*o*-OH—C_6H_4	51	193	$NCOC_6H_4NO_2$-*o*	$(CH_2)_2$—O—$(CH_2)_2$		91	121
ditto	CH_3	CH_3	92	193	$NCOC_6H_3(NO_2)_2$-*o*, *p*	H	*p*-CH_3—C_6H_4	18	121
ditto	C_2H_5	C_2H_5	85	193	ditto	H	*p*-OCH_3—C_6H_4	24	121
ditto	CH_3	C_6H_5	35	193	ditto	H	*p*-OC_2H_5—C_6H_4	15	121
ditto	$(CH_2)_4$		76	193	ditto	$(CH_2)_4$		39	121
ditto	$(CH_2)_5$		73	193	ditto	$(CH_2)_2$—O—$(CH_2)_2$		56	121
ditto	$(CH_2)_2$—O—$(CH_2)_2$		87	193					

Table 21. Reaction of 4,5-dichloro-1,2-dithiolen-3-ones with thiols:

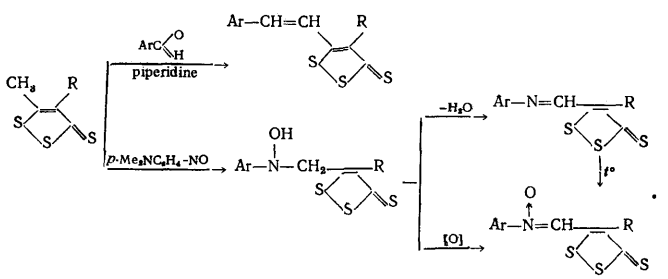


RSY	Yield, %	Ref.	RSY	Yield, %	Ref.
p-Cl-C_6H_4—SH	84	170, 195		76	120
$PhCH_2CH_2SH$	93	195, 118			
EtO_2C—CH_2SH	75,5	195			
MeO_2C—CH_2SH	53; 89	195, 118			
HO_2C—CH_2SH	32; 91	195, 118			
	97	195		88	120
CH_3SH	70	118			
$EtSH$	79	118			
$HO(CH_2)_2SH$	54	118			
iso-PrO_2C—CH_2—SH	58	118			
n-$C_{18}H_{28}O_2C$—CH_2—SH	52	118		71	120
C_6H_5SH	84	118			
p-$CH_3C_6H_4SH$	78	118			
p-$NO_2C_6H_4SH$	89	120			
$C_6H_5CH_2SH$	89	120			
o-Cl-$C_6H_4CH_2SH$	70	120			
$C_6H_5CH(CH_3)_2SH$	94	120			
	82	120		63	120

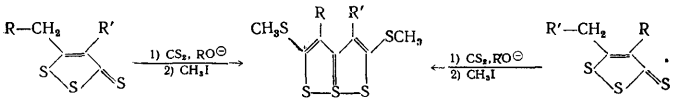
An unusual reaction has been reported[199] between sodium disulphide and 4-phenyltrithione, when 5-mercaptotrithione is obtained:



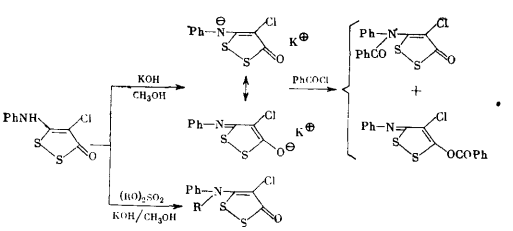
Trithiones containing a methyl or substituted methyl group at position 5 react with aromatic aldehydes to form aldol condensation products; an anil and a nitrone are obtained with *p*-nitroso-*NN*-dimethylaniline[10,81,101]:



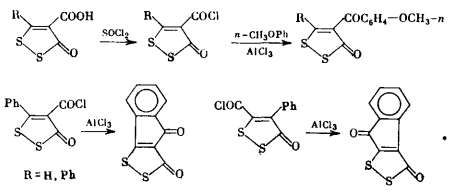
The condensation with carbon disulphide of trithiones containing a substituted methyl group at position 5, in the presence[178] or the absence[200] of a base, gives after methylation bismethylthiothiophthens:



A 5-amino-group present in a 1,2-dithiolen-3-one may be both acylated and alkylated[196,201]:

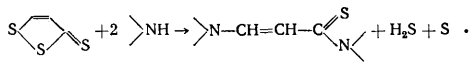


The stability of the 1,2-dithiolen ring is demonstrated by Friedel–Crafts reactions [82,202,203]:

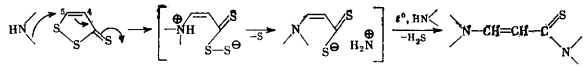


(*f*) Reactions with nucleophilic reagents accompanied by ring fission

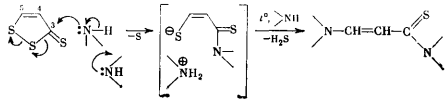
The action of nucleophiles on reactive 1,2-dithiolen-3-thiones opens the ring. Thus β-aminothioacrylamides are formed from unsubstituted trithione and its 4-cyano-derivative with excess of such amines as aniline, *p*-toluidine, and morpholine [204]:



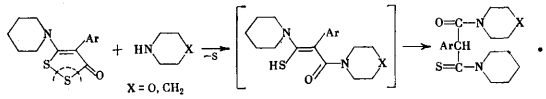
However, the authors' assumption of initial rupture of the $C_{(5)}-S_{(1)}$ bond



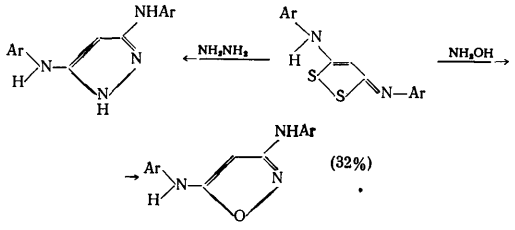
appears questionable. A more probable mechanism involves synchronous cleavage of C(S)–S and S–S bonds, with the amine attacking not $C_{(5)}$ but the thiocarbonyl $C_{(3)}$ atom:



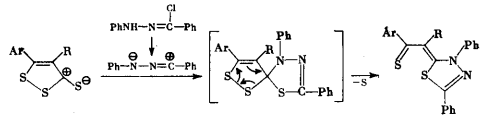
The proposed mechanism is consistent with the cleavage of 4-aryl-5-piperidino-1,2-dithiolen-3-ones by morpholine and piperidine, when diamides of arylmonothiomalonic acids are formed [197]:



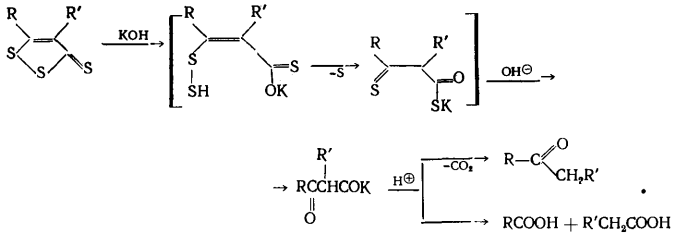
The reactions of 5-arylamino-1,2-dithiolen-3-imines with hydrazine (or phenylhydrazine) and with hydroxylamine involve ring opening with formation of a pyrazole and a 1,2-oxazole [191,205]:



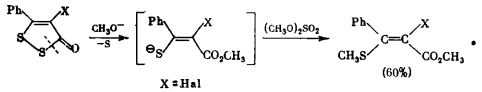
5-Aryltrithiones react similarly with α-chlorobenzylidene-phenylhydrazine to form thia-3,4-diazolines [206]:



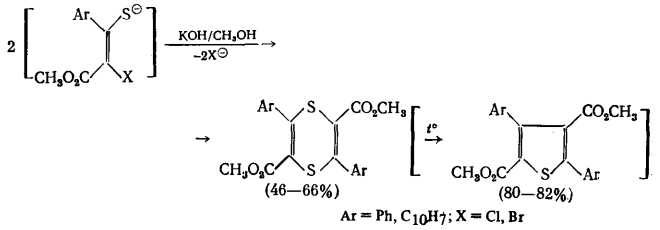
The 1,2-dithiolen ring is cleaved by alkalis [207] still more easily than by amines. Hydrolysis of trithiones with excess of alkali yields derivatives of acetoacetic acid, which then split into a ketone or the corresponding acids [10,101]:



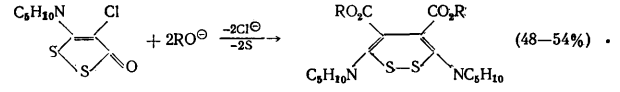
The hydrolysis of 5-phenyl-1,2-dithiolen-3-one by excess of potassium hydroxide gives acetophenone [71]. However, the action of an equimolecular quantity of methanolic alkali yields the β-methylthio-cinnamic ester [208]:



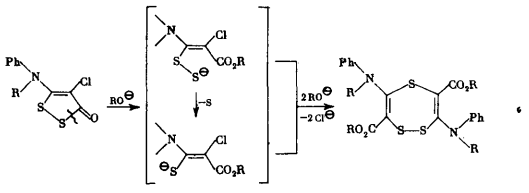
In the alkaline cleavage of 5-aryl-4-halogeno-1,2-dithiolen-3-ones the resulting fragments undergo "head to tail" condensation to 1,4-dithiacyclohexadiene derivatives with liberation of halide ions [120,207]:



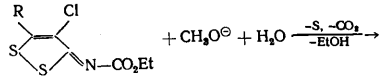
When 4-chloro-5-piperidino-1,2-dithiolen-3-ones are hydrolysed, such fragments undergo "head to head" dimerisation with formation of 1,2-dithiacyclohexadiene derivatives [208,209]:

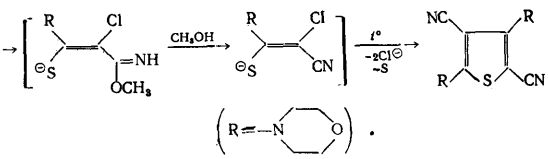


In the reaction of 5-*N*-alkylanilino-4-chloro-1,2-dithiolen-3-ones with alcoholic alkali the primary product of cleavage of the cyclic S–CO bond is preserved in only one unit of the resulting 1,2,5-trithiacycloheptadiene structure [194,210]:

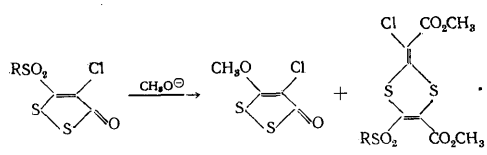


4-Chloro-1,2-dithiolen-3-imines are far more stable and are broken down only by boiling methanolic alkali, with the formation of thiophen derivatives [193]:

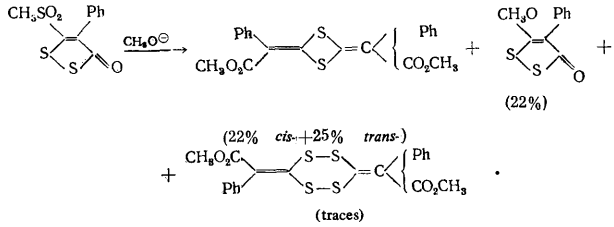




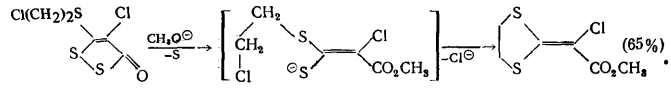
The reaction of 4-chloro-5-sulphonyl-1,2-dithiolen-3-ones with alkoxides gives 1,3-dithiafulvalenes together with the 5-alkoxy-4-chloro-1,2-dithiolen-3-one:[211]



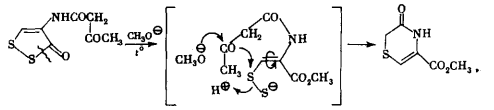
In the absence of a 4-chloro-substituent competing reactions lead to the formation of several compounds, with 2,4-dialkylidene-1,3-dithietans predominating[211]:



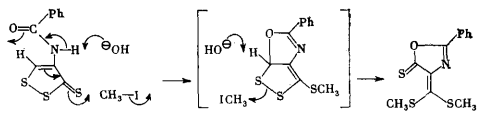
The alkaline cleavage of 4-chloro-5,2′-chloroethylthio-1,2-dithiolen-3-one yields a 2-alkylidene-1,3-dithiolan[211]:



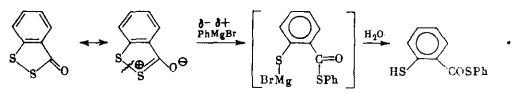
Under these conditions 4-acylamino-1,2-dithiolen-3-ones form nitrogen heterocycles. Thus the 4-acetoacetamido-derivative gives a low yield of a 3-oxodihydrothiazine derivative[212]:



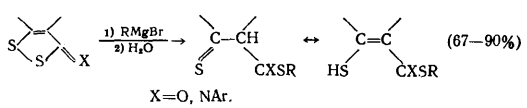
However, methylation of 4-acylamino-trithiones in the presence of potassium t-butoxide or hydroxide gives oxazoline-5-thiones[213]:



4,5-Benzo-1,2-dithiolen-3-one is cleaved by phenylmagnesium bromide at the disulphide bond with the formation of *o*-mercaptothiobenzoic *S*-esters[214]:

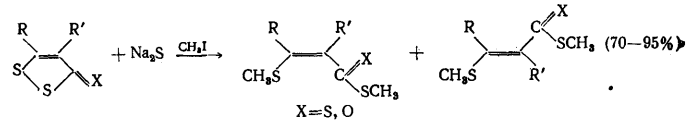


5-Amino-1,2-dithiolen-3-ones and the 5-aryl-3-imines react similarly with Grignard reagents, but the cleavage products exist predominantly in the thioketone—not the thioenolic—form[215,216]:



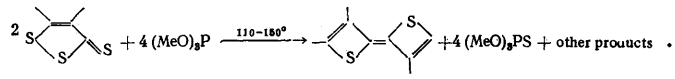
X=O, NAr.

The reaction of trithiones and 1,2-dithiolen-3-ones with sodium sulphide also involves rupture of the disulphide bond with formation of unsaturated mono- or di-thioesters[217]:



X=S, O

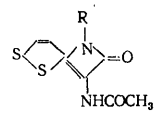
Heating alkylated trithiones with excess of an organic phosphorus(III) compound is assumed to yield a thietenylidene[218]:



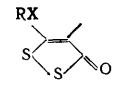
4. Applications

(*a*) Medicinals

Trithiones occur in Nature (in plants)[95]. The 1,2-dithiolen ring forms a fragment of the antibiotics thiolutin (VIa), holomycin (VIb), etc.[212] Several thiones are used in medicine to stimulate the functioning of the liver and the gall-bladder[95]. 5-*p*-Methoxyphenyl-1,2-dithiolen-thione—Sulfarlem (DDR)[219]—and -3-one[220] are non-toxic bile-producing preparations, but the 4-aryltrithiones are less effective[219]. Trithiones, especially those containing a thiophen residue at position 5, have a diuretic effect[221].



(VI); R=CH_3 (a), H(b)



(VII); X=SO_2 (a), SO (b), S (c)

(*b*) Insecticides

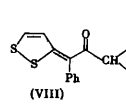
4-Aroyl-5-aryltrithiones[85], 5-chloro-4-phenyl-1,2-dithiolen-3-ones[222], and *N*-aryl-4,5-dichloro-1,2-dithiolen-3-imines[223] are fungicides suitable for the treatment of grain. 1,2-Benzodithiolen-3-thiones and -oximes both possess antifungal properties[189,190,224]. 5-Alkyl-sulphonyl-, -sulphinyl, and -thio-1,2-dithiolen-3-ones (VIIa–c)[170,195,225–227] are bactericides and fungicides effective against moulds and pathogenic fungi[170,195], as are also 5-aminated 4-chloro-1,2-dithiolen-3-ones[225,226] and -3-phenylimines[119]. 5-Methoxycarbonylthio- and 5-morpholinothio-4-phenyltrithiones are used as insecticides and fungicides[228,229].

(*c*) Additives to lubricating oils

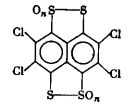
Alkylated trithiones can be used in lubricating oils as antioxidant and anti-seizing additives. 4-Neopentyl-5-t-butyltrithione is especially effective because of its better solubility in petroleum oils[230]. Trithione *S*-oxides[168,169] and products of the reaction of trithiones with polyamines[231] and phosphites[218] are multipurpose additives for lubricating oils. 4-Substituted trithiones act as corrosion inhibitors in lubricating oils[93].

(*d*) Other fields

Chlorinated 3-acylmethylene-1,2-dithiolens (VIII),[126] chlorinated naphthodithioles (IXa), and dioxides of the latter (IXb)[99]



(VIII)



(IX); $n = 0$ (a), 2 (b)

are used as yellow colorants for thermoplastics. Compounds (IX) are employed also as semiconductors and dielectrics[99]. 5-Methoxycarbonylthio- and 5-morpholinothio-4-phenyltrithiones find application as vulcanisation accelerators[228,229].

Phenylated trithiones are used in analytical practice for the extraction and the photometric or gravimetric determination of platinum(II) or mercury(II) as water-insoluble orange complexes $M^{II}Cl_2R_2$.[103,232,233]

REFERENCES

1. C.Krespan, J.Org.Chem., 27, 3995 (1962).
2. D.Dittmer, P.Chang, F.Davis, J.Stamos, and K.Takahashi, J.Org.Chem., 37, 1116 (1972).
3. C.Krespan, B.McKusick, and T.Cairns, J.Amer. Chem.Soc., 82, 1515 (1960).
4. C.Krespan, J.Amer.Chem.Soc., 83, 3434 (1961).
5. P.Guha and M.Chaklader, Quart.J.Indian Chem. Soc., 2, 318 (1925).
6. C.Krespan and B.McKusick, J.Amer.Chem.Soc., 83, 3438 (1961).
7. N.De'Ath and D.Denney, Chem.Comm., 395 (1972).
8. R.King and F.Korendowski, Chem.Comm., 771 (1966).
9. A.Davidson and R.Holm, Inorg.Synth., 10, 8 (1967).
10. D.Breslow and H.Skolnik, "Multi-sulphur and Sulfur and Oxygen 5- and 6-Membered Heterocycles", Interscience, New York, 1966, Part 1, pp.313, 347.
11. J.Affleck and G.Dougherty, J.Org.Chem., 15, 865 (1950).
12. L.Field and R.Barbee, J.Org.Chem., 34, 36 (1969).
13. D.Harpp and J.Gleason, J.Org.Chem., 35, 3259 (1970).
14. K.Konishi, Agric.and Biol.Chem.(Japan), 32, 1199 (1968); Chem.Abs., 70, 19997 (1968).
15. G.Claeson, Arkiv Kemi, 30, 277 (1969).
16. L.Field and J.Khim, J.Org.Chem., 37, 2710 (1972).
17. J.Schauble and J.Williams, J.Org.Chem., 37, 2514 (1972).
18. C.Goran and T.Arne, Arkiv Kemi, 29, 311 (1968).
19. G.Claeson and A.Thalen, Acta Chem.Scand., 17, 2763 (1963).
20. C.Frisell and G.Bergson, Arkiv Kemi, 25, 263 (1966).
21. M.Hedblom, Tetrahedron Letters, 5159 (1970).
22. A.Thalen and G.Claeson, Arkiv Kemi, 24, 462 (1965).
23. U.Schmidt, P.Grafen, and H.Goedde, Annalen, 670, 157 (1963).
24. R.Cragg and A.Weston, Tetrahedron Letters, 655 (1973).
25. S.Yurugi, H.Yonemoto, T.Fushimi, and M.Murata, Yakugaku Zasshi, 80, 1691 (1960); Chem.Abs., 55, 12288 (1961).
26. L.Schotte, Acta Chem.Scand., 8, 130 (1954).
27. G.Bergson and A.Biezais, Arkiv Kemi, 22, 475 (1964).
28. G.Claeson and A.Thalen, Acta Chem.Scand., 17, 1172 (1963).
29. T.P.Vasil'eva, M.G.Lin'kova, O.V.Kil'disheva, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser. Khim., 209 (1973).
30. M.G.Lin'kova and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1889 (1968).
31. T.P.Vasil'eva, M.G.Lin'kova, O.V.Kil'disheva, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser. Khim., 489 (1972).
32. T.P.Vasil'eva, M.G.Lin'kova, O.V.Kil'disheva, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser. Khim., 700 (1974).
33. J.Johnson, The Roger Adams Symposium, New York, 1955, p.60.
34. A.Hordvik, Acta Chem.Scand., 20, 1885 (1966).
35. J.Barltrop, P.Hayes, and M.Calvin, J.Amer. Chem.Soc., 76, 4348 (1954).
36. U.Schmidt, P.Grafen, and H.Goelde, Angew. Chem., 77, 900 (1965).
37. A.Schöberl and H.Gräfje, Annalen, 614, 66 (1958).
38. S.Sunner, Nature, 176, 217 (1955).
39. M.Krackov, G.Bergson, A.Biezais, and H.Mautner, J.Amer.Chem.Soc., 88, 1759 (1966).
40. Y.Asahi, K.Terada, and M.Ichio, Rev.Polarogr., 14, 328 (1967); Chem.Abs., 71, 21598 (1969).
41. B.Lindberg and G.Bergson, Arkiv Kemi, 23, 319 (1965).
42. P.Brown and J.Edwards, J.Org.Chem., 34, 3131 (1969).
43. T.Owen and A.Wilbraham, J.Amer.Chem.Soc., 91, 3365 (1969).
44. G.Claeson, Acta Chem.Scand., 9, 178 (1955).
45. T.Akira, M.Kentaro, and I.Teruyuki, Chem.and Pharm.Bull.(Japan), 19, 1022 (1971).
46. H.Yanagawa, T.Kato, and Y.Kitahara, Tetrahedron Letters, 1073 (1973).
47. Y.Fukuhara, Jap.P.6805820 (1968); Chem.Abs., 69, 52650 (1968).
48. E.Goethals, J.Huylebroeck, and W.Smolders, Bull.Soc.chim.belges, 78, 191 (1969).
49. F.Wudl, R.Gruber, and A.Padwa, Tetrahedron Letters, 2133 (1969).
50. T.P.Vasil'eva, M.G.Lin'kova, O.V.Kil'disheva, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser. Khim., 643 (1974).
51. T.P.Vasil'eva, M.G.Lin'kova, O.V.Kil'disheva, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser. Khim., 2610 (1975).
52. D.Harpp and J.Gleason, J.Amer.Chem.Soc., 93, 2437 (1971).
53. I.L.Knunyants, O.V.Kil'disheva, M.G.Lin'kova, and T.P.Vasil'eva, Dokl.Akad.Nauk SSSR, 224, 99 (1975).
54. A.Fava, A.Iliceto, and E.Camera, J.Amer.Chem. Soc., 79, 836 (1957).
55. P.Brown and J.Edwards, Biochemistry, 8, 1200 (1969).
56. P.Brown and J.Edwards, J.Inorg.Nuclear Chem., 32, 2671 (1970).
57. F.Challenger, "Aspects of the Organic Chemistry of Sulphur" (Translated into Russian), Mir, Moscow, 1963, p.15.
58. P.Sadler, Chem.Rev., 60, 575 (1960).
59. S.Chiba, Y.Saji, Y.Takeo, T.Yui, and Y.Aramaki, Japan.J.Pharmacol., 17, 491 (1967); Chem.Abs., 68, 11172 (1968).
60. K.Konishi, Agric.and Biol.Chem.(Japan), 32, 1199 (1968); Chem.Abs., 70, 19997 (1969).

61. N. Mitsuo and H. Hukoichi, Chem. and Pharm. Bull. (Japan), 16, 311 (1968); Chem. Abs., 69, 19056 (1968).
62. M. Sakai, Biochem. Toxicol. Insectic., 13 (1969); Chem. Abs., 73, 65284 (1970).
63. K. Konishi, Agric. and Biol. Chem. (Japan), 34, 935 (1970); Chem. Abs., 73, 45386 (1970).
64. J. W. Loder, G. B. Russell, and G. Graeme, Austral. J. Chem., 22, 1271 (1969).
65. J. W. Loder and G. B. Russell, Tetrahedron Letters, 6327 (1966).
66. K. Atsushi and N. Mitsuo, Tetrahedron Letters, 203 (1972).
67. G. Claeson and J. Pedersen, Tetrahedron Letters, 3975 (1968).
68. H. Janagawa, T. Kato, Y. Kitahara, N. Takahashi, and Y. Kato, Tetrahedron Letters, 2549 (1972).
69. N. Lozac'h and J. Vialle, Org. Sulfur Comp., 2, 257 (1966).
70. H. Prinabach and E. Futterer, Adv. Heterocyclic Chem., 7, 39 (1966).
71. E. Baumann and E. Fromm, Ber., 30, 110 (1897).
72. R. Beer and R. Slater, J. Chem. Soc., 4069 (1964).
73. R. Warrener and E. Cain, Chem. and Ind., 289 (1966).
74. F. Bôberg, Annalen, 679. 109 (1964).
75. P. Mouchel and A. Thuillier, Bull. Soc. chim. France, 482 (1966).
76. R. Mayer and J. Jentzsch, J. prakt. Chem., 23, 113 (1964).
77. J. Brelivet and J. Teste, Compt. rend., 263, 495 (1966).
78. D. Duguay and T. Quiniou, Bull. Soc. chim. France, 637 (1972).
79. M. G. Voronkov and T. V. Lapina, Khim. Geterotsikl. Soed., 592 (1970).
80. J. Faust and R. Mayer, Annalen, 688, 150 (1965).
81. C. Trebaul and J. Teste, Bull. Soc. chim. France, 2456 (1969).
82. C. Trebaul, Bull. Soc. chim. France, 721 (1973).
83. A. Bruno and G. Purrello, Gazzetta, 96, 1009 (1966).
84. M. Cadec, C. Trebaul, and J. Teste, Bull. Soc. chim. France, 2964 (1968).
85. M. Francois, French P. 6400267 (1964); Chem. Abs., 62, 564 (1965).
86. H. Quiniou and N. Lozac'h, Bull. Soc. chim. France, 1171 (1963).
87. G. Peister-Guillouzo and N. Lozac'h, Bull. Soc. chim. France, 153 (1963).
88. M. Marceau and A. Thuillier, Compt. rend., 262C, 147 (1966).
89. J. Brelivet, P. Appriou, and J. Teste, Bull. Soc. chim. France, 1344 (1971).
90. M. Ebel, L. Legrand, and N. Lozac'h, Bull. Soc. chim. France, 161 (1963).
91. R. Hodgson, BRD P. 1275068 (1968); Chem. Abs., 69, 86999 (1968).
92. H. Davy and J. Vialle, Compt. rend., 275C, 625 (1972).
93. R. Hodson and E. Smutny, US P. 3394146 (1968); Chem. Abs., 69, 67326 (1968).
94. M. G. Voronkov, T. V. Lapina, and E. P. Popova, Khim. Geterotsikl. Soed., 633 (1967).
95. M. G. Voronkov and T. V. Lapina, Khim. Geterotsikl. Soed., 342 (1965).
96. M. G. Voronkov, T. V. Lapina, and Zh. Z. Minkina, Khim. Geterotsikl. Soed., 999 (1971).
97. J. Brown, J. Chem. Soc. (C), 1077 (1968).
98. R. Mayer, E. Hoffmann, and J. Faust, J. prakt. Chem., 23, 77 (1964).
99. E. Klingsberg, US P. 363048 (1972).
100. J. Brown, J. Chem. Soc. (C), 1074 (1968).
101. P. Landis, Chem. Rev., 65, 237 (1965).
102. R. Mayer, P. Wittig, J. Fabian, and R. Heitmüller, Chem. Ber., 97, 654 (1964).
103. K. Gewald, Chem. Ber., 101, 383 (1968)
104. K. Gewald, Z. Chem., 3, 26 (1963).
105. R. Mayer and H. Hartmann, Chem. Ber., 97, 1886 (1964).
106. J. Fabian, K. Gewald, and R. Mayer, Angew. Chem., 75, 90 (1963).
107. R. Couturier, D. Paquer, and A. Thuillier, Compt. rend., 270C, 1878 (1970).
108. J. Brelivet, P. Appriou, and J. Teste, Compt. rend., 265C, 1010 (1967).
109. P. Appriou, J. Brelivet, and J. Teste, Bull. Soc. chim. France, 1497 (1970).
110. P. Raoul and J. Vialle, Bull. Soc. chim. France, 1670 (1959).
111. R. Brown and J. Rae, Austral. J. Chem., 17, 447 (1964).
112. R. Rioult and J. Vialle, Bull. Soc. chim. France, 2883 (1967).
113. M. Yokoyama, Bull. Chem. Soc. Japan, 43, 2938 (1970).
114. R. Mayer and J. Faust, Chem. Ber., 96, 2702 (1963).
115. F. Boberg and J. Knoop, Annalen, 708, 148 (1967).
116. M. Stavaux and N. Lozac'h, Bull. Soc. chim. France, 2082 (1967).
117. R. Wiedermann, W. Gentzkow, and F. Boberg, Annalen, 742, 103 (1970).
118. J. Bader, Helv. Chim. Acta, 51, 1409 (1968).
119. J. Bader and K. Gaetzi, Swiss P. 1928871 (1970); Chem. Abs., 72, 90437 (1970).
120. A. Marei and M. El Sukkary, J. Chem. U.A.R., 14, 101 (1971).
121. F. Boberg and G. Wentrup, Annalen, 241 (1973).
122. R. Pinel, Y. Mollier, and N. Lozac'h, Bull. Soc. chim. France, 1049 (1966).
123. A. Lüttringhaus, E. Futterer, and H. Prinzbach, Tetrahedron Letters, 1209 (1963).
124. Y. Mollier, N. Lozac'h, and F. Terrier, Bull. Soc. chim. France, 157 (1963).
125. E. Klingsberg, J. Org. Chem., 31, 3489 (1966).
126. E. Klingsberg, US P. 3361764 (1968); Chem. Abs., 69, 19140 (1968).
127. A. Grandin, C. Bouillon, and J. Vialle, Bull. Soc. chim. France, 4555 (1968).
128. E. Klingsberg, "Organosulfur Chemistry—Reviews of Current Research" (Edited by M. Janssen), New York, 1967, p. 171.
129. C. Bouillon and J. Vialle, Bull. Soc. chim. France, 1173 (1964).
130. J. Faust, H. Spies, and R. Mayer, Z. Chem., 7, 275 (1967).
131. A. Hordvik, Acta Chem. Scand., 17, 1809 (1963).
132. W. Kehl and G. Jeffrey, Acta Cryst., 11, 813 (1958).
133. M. G. Voronkov, V. I. Minkin, O. A. Osipov, M. G. Kogan, and T. V. Lapina, Khim. Geterotsikl. Soed., 758 (1967).
134. R. Zahradnik and J. Koutecký, Coll. Czech. Chem. Comm., 28, 1117 (1963).
135. R. Mayer, see Ref. 128, p. 219.
136. A. Lüttringhaus, Tetrahedron Letters, 19, 1209 (1962).
137. H. Eicke, F. Boberg, and J. Knoop, Z. Naturforsch., 23b, 413 (1968).

138. F. Boberg, Annalen, **693**, 212 (1966).
139. E. Klingsberg, J. Amer. Chem. Soc., **83**, 2934 (1961).
140. P. Mayo, Tetrahedron Letters, 1561 (1973).
141. C. Pedersen and V. Parker, Tetrahedron Letters, 767 (1972).
142. C. Pedersen and V. Parker, Tetrahedron Letters, 777 (1972).
143. J. Fabian and R. Mayer, Chem. and Ind., 1262 (1966).
144. T. V. Lapina and M. G. Voronkov, "Tezisy Dokladov XII Nauchnoi Sessii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei" (Abstracts of Papers at the Twelfth Scientific Congress on the Chemistry and the Technology of Organic Sulphur Compounds and of Sulphur-containing Petroleums), Riga, 1971, p. 222.
145. Y. Mollier, F. Terrier, and N. Lozac'h, Bull. Soc. chim. France, 1778 (1964).
146. R. Pinel and Y. Mollier, Bull. Soc. chim. France, 1385 (1972).
147. R. Brown, I. Rae, and S. Sternhell, Austral. J. Chem., **18**, 1211 (1965).
148. A. Dorange, F. Tonnard, and F. Venien, Compt. rend., **276C**, 1057 (1973).
149. C. Pedersen and J. Møller, Acta Chem. Scand., **26**, 250 (1972).
150. C. Pedersen, N. Huaman, R. Pinel, and J. Møller, Acta Chem. Scand., **26**, 1305 (1972).
151. F. Boberg and W. Gentzkow, Annalen, **766**, 1 (1972).
152. F. Challenger, E. Mason, E. Holdsworth, and R. Emmott, J. Chem. Soc., 292 (1953).
153. P. Landis and L. Hamilton, J. Org. Chem., **25**, 1742 (1960).
154. K. Brack, Belg. P. 586 027 (1959); see Ref. 80.
155. H. Quiniou and N. Lozac'h, Bull. Soc. chim. France, 1167 (1963).
156. F. Boberg, Angew. Chem., **73**, 579 (1961).
157. F. Boberg, Annalen, **678**, 66 (1964).
158. M. Paulmier, Bull. Soc. chim. France, 954 (1963).
159. E. Klingsberg, J. Org. Chem., **28**, 529 (1963).
160. G. Cailland and Y. Mollier, Bull. Soc. chim. France, 2018 (1970).
161. J. Faust and J. Fabian, Z. Naturforsch., **24b**, 577 (1969).
162. C. Bouillon and J. Vialle, Bull. Soc. chim. France, 4560 (1968).
163. G. Reynolds, BRD P. 1 807 360 (1969); Chem. Abs., **71**, 81 334 (1969).
164. H. Eicke and J. Knoop, Z. Naturforsch., **23b**, 163 (1968).
165. J. Poite, A. Perichaut, and J. Roggero, Compt. rend., **270C**, 1677 (1970).
166. A. Perichaud, J. Poite, G. Mille, and J. Roggero, Bull. Soc. chim. France, 3830 (1972).
167. D. Anderson, US P. 3 364 232 (1968); Chem. Abs., **68**, 60 776 (1968).
168. D. Anderson, US P. 3 376 225 (1968); Chem. Abs., **68**, 106 655 (1968).
169. S. Agripat, Franch P. 1 528 170 (1968); Chem. Abs., **71**, 61 428 (1969).
170. F. Blazy and J. Bonastre, Bull. Soc. chim. France, 4247 (1968).
171. M. Lenot and J. Vialle, Bull. Soc. chim. France, 1173 (1964).
172. H. Davy, M. Demuynck, D. Paquer, A. Rouessac, and J. Vialle, Bull. Soc. chim. France, 1150 (1966).
173. D. Easton and D. Leaver, Chem. Comm., 585 (1965).
174. D. Easton, D. Leaver, and T. Rawlings, J. Chem. Soc., Perkin I, 41 (1972).
175. H. Behringer and R. Wiedenmann, Tetrahedron Letters, 3705 (1965).
176. J. Buchshriber, D. McKinnon, and M. Ahmed, Canad. J. Chem., **47**, 2039 (1969).
177. H. Behringer, D. Bender, J. Falkenberg, and R. Wiedenmann, Chem. Ber., **101**, 1428 (1968).
178. C. Portail and J. Vialle, Bull. Soc. chim. France, 3187 (1966).
179. D. McKinnon and J. Buchshriber, Canad. J. Chem., **49**, 3299 (1971).
180. H. Davy, M. Demuynck, and D. Paquer, Bull. Soc. chim. France, 2057 (1968).
181. R. Okazaki, F. Ishii, K. Ozawa, and N. Inamoto, Chem. Letters, 9 (1972).
182. A. Rouessac and J. Vialle, Bull. Soc. chim. France, 2054 (1968).
183. G. Hervieu, P. Rioult, and J. Vialle, Bull. Soc. chim. France, 4375 (1971).
184. G. Hervieu, P. Rioult, and J. Vialle, Bull. Soc. chim. France, 4380 (1971).
185. J. Vialle, Bull. Soc. chim. France, 2707 (1966).
186. Y. Poirier and N. Lozac'h, Bull. Soc. chim. France, 2090 (1967).
187. D. Barillier, C. Gy, P. Rioult, and J. Vialle, Bull. Soc. chim. France, 277 (1973).
188. S. Tamagaki and S. Oae, Tetrahedron Letters, 1159 (1972).
189. J. Montagne and B. Cross, B. P. 1 104 893 (1968); Chem. Abs., **69**, 59 218 (1968).
190. French P. 1 504 150 (1967); Chem. Abs., **70**, 47 426 (1969).
191. G. Kresze and A. Horn, Chem. Ber., **100**, 1655 (1967).
192. J. Adelfang, J. Org. Chem., **31**, 2389 (1966).
193. F. Boberg and R. Wiedermann, Annalen, **734**, 164 (1970).
194. F. Boberg, Angew. Chem., **76**, 575 (1964).
195. J. Bader, Swiss P. 513 898 (1971).
196. F. Boberg, Annalen, **681**, 169 (1965).
197. F. Boberg and A. Marei, Annalen, **666**, 88 (1963).
198. J. Faust and R. Mayer, Angew. Chem., **75**, 573 (1963).
199. J. Bader and K. Gatzi, US P. 3 636 222 (1972).
200. M. Portail and J. Vialle, Bull. Soc. chim. France, 451 (1964).
201. F. Boberg, Annalen, **681**, 178 (1965).
202. C. Trebaul, Bull. Soc. chim. France, 1840 (1972).
203. J. Faust and R. Mayer, Z. Chem., **7**, 275 (1967).
204. E. Smutny, W. Turner, E. Morgan, and R. Robinson, Tetrahedron, **23**, 3785 (1967).
205. G. Barnikow, Chem. Ber., **100**, 1389 (1967).
206. Y. Poirier, Bull. Soc. chim. France, 1203 (1968).
207. F. Boberg, Annalen, **679**, 118 (1964).
208. F. Boberg, H. Niemann, and K. Kirchhoff, Annalen, **728**, 32 (1969).
209. F. Boberg, H. Niemann, and J. Jovanovic, Annalen, **717**, 154 (1968).
210. F. Boberg, Annalen, **683**, 132 (1965).
211. J. Bader, Helv. Chim. Acta, **51**, 1421 (1968).
212. R. Brown and I. Rae, Austral. J. Chem., **18**, 1071 (1965).
213. R. Brown, I. Rae, and S. Sternell, Austral. J. Chem., **18**, 61 (1965).
214. F. Boberg and R. Schardt, Annalen, **728**, 44 (1969).
215. F. Boberg and R. Schardt, Annalen, **734**, 173 (1970).
216. F. Boberg and W. Gentzkow, Annalen, **247** (1973).
217. J. Maignan and J. Vialle, Bull. Soc. chim. France, 1973 (1973).
218. D. Anderson, US P. 3 427 246 (1969); Chem. Abs., **70**, 79 768 (1969).

219. M.G.Voronkov, T.V.Lapina, A.S.Saratikov, M.I.Solov'eva, and L.I.Dubro, Khim.-farm.Zhur., 18 (1967).
220. F.Koss and W.Lamprecht, Europ.J.Pharmacol., 4, 215 (1968).
221. B.Dartigues, C.Trebaul, A.Bebaud, and C.Peyraud, Compt.rend.Soc.Biol., 163, 1947 (1969).
222. M.Makram and S.Sidky, Agric.Res.Rev.(Cairo), 46, 123 (1968).
223. J.Bader and K.Gaetzi, BRD P.1 928 889 (1969); Chem.Abs., 72, 79 006 (1970).
224. L.Amoretti, F.Mossini, and V.Plazzi, Farmaco, Ed.Sci., 2, 23, 583 (1968).
225. J.Bader and G.Karl, BRD P.1 278 701 (1968); Chem.Abs., 70, 115 147 (1969).
226. S.Agripat, B.P.1 136 793 (1968); Chem.Abs., 70, 105 438 (1969).
227. J.Bader and G.Karl, Swiss P.447 207 (1968); Chem.Abs., 69, 59 216 (1968).
228. J.Brown, B.P.1 183 645 (1970); Chem.Abs., 72, 111 447 (1970).
229. J.Brown, B.P.1 188 858 (1970); Chem.Abs., 72, 3942 (1970).
230. T.A.Burtseva, I.E.Vinogradova, A.F.Plate, and T.A.Danilova, Khim.Tekhnol.Topliv Masel, 34 (1965).
231. B.P.1 117 500 (1968); Chem.Abs., 69, 45 108 (1968).
232. A.I.Busev, V.V.Evsikov, and F.A.Khromova, Vestnik Moskov.Univ., Khim., 99 (1969).
233. A.I.Busev and V.V.Evsikov, Vestnik Moskov.Univ., Khim., 81 (1972).

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