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The synthesis and properties of thioaldehydes

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ABSTRACT. Data on the synthesis of thioaldehydes, a little investigated class of organic sulphur compounds, are described systematically and surveyed. Various types of relatively unstable thioaldehydes and thioaldehydes stabilised by electronic and steric factors are examined. Their physical, spectroscopic, and chemical properties are discussed. The important role of thioformyl compounds as intermediates and synthons is demonstrated.

The bibliography includes 92 references.

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I. Introduction

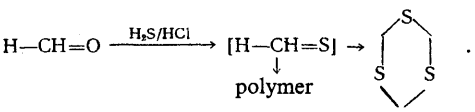
The chemistry of aldehydes has been developing successfully since the beginning of the past century. They are used widely in the synthesis of acetals, oximes, hydrazones, carboxylic acids, amines, alcohols, diols, etc., and in the manufacture of polymers, medicinal preparations and perfumes, dyes, pesticides, explosives, etc.[1] However, their sulphur analogues, thioaldehydes (TA), were ignored for a long time. This was because for historical reasons the view was established that TA are extremely unstable and that their synthesis and study are therefore difficult.

The first communications on stable TA appeared as late as 1960.[2,3] They probably in fact initiated the development of the chemistry of this class of compound. The role of TA as important intermediates and synthons in organic chemistry and also as practically useful substances became increasingly clear from the individual publications which appeared in the second half of the present century. For example, 5-thioformyldipyrrolylmethane has been used as a key compound in the total synthesis of chlorophyll.[3] Penicillins have been converted into biosynthetically important peptides through TA derived from mercaptoazetidinone;[4,5] thioformylmethylene derivatives of heterocyclic bases have begun to be used in the synthesis of photosensitive materials.[3] At the present time, there has been an appreciable growth of interest in TA. Communications about the generation and reactions of thioformaldehyde, thioacetaldehyde (Section II), thioacrolein, and thiobenzaldehyde (Section IV), which previously did not attract attention because of their extreme instability, are being published with increasing frequency. Modern physicochemical methods have made it possible to establish the lifetimes of these compounds, to obtain their spectroscopic characteristics, and to discover their involvement as intermediates in many chemical reactions. A trend has arisen towards the specific synthesis of fairly stable TA stabilised by electronic (Section IV) or steric (Section V) factors associated with substituents. Increasing attention is being devoted to the study of the properties of TA.

The chemistry of TA has been developing mainly abroad and chapters in several reviews in the German language have already been devoted to them,[6–12] but unfortunately they have by no means covered all the available data. The present review is being published because of a wish to draw the attention of Soviet investigators to compounds of this class.

II. Thioformaldehyde and thioacetaldehyde

The simplest representative of TA, thioformaldehyde, is extremely unstable. Its half life is ~6 min at a pressure of 0.01–0.05 Pa.[11] One of the initial (1868) synthetic approaches to thioformaldehyde was based on what has now become the classical reaction of formaldehyde with hydrogen sulphide in the presence of acid catalysts:[6]



The thioformaldehyde reaction products, which are, depending on the reaction conditions, 1,3,5-trithiane (trithioformaldehyde) or polymethylene sulphides, have served as indirect evidence for the primary formation of thioformaldehyde. Subsequently, the successful development of the methods of synthesis of thioformaldehyde in combination with modern physicochemical research methods made it possible to establish unambiguously the possibility of the existence of monomeric thioformaldehyde.[7,8,10] The use of the pulse thermolysis technique, whose undoubted advantages are a very short reaction time (at a reduced pressure) and the possibility of analysing the pyrolysis product in the gas phase, should be regarded as one of the most productive achievements in this field. Monomeric thioformaldehyde has been obtained by the thermolysis of various sulphur compounds, for example thietan, dimethyl disulphide, 1,2,4-trithiolan, and methanesulphenyl chloride.[10,13]

It is very remarkable that thioformaldehyde has been detected in cosmic space.[10] The prolonged existence of such highly reactive molecules in the interstellar vacuum and cold is possible because of the large intermolecular distances. Such conditions in fact ensure the

stability of individual thioformaldehyde molecules, which usually exhibit a high tendency towards oligomerisation and polymerisation.

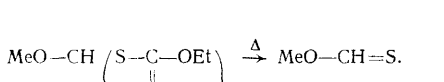
The closest homologue of thioformaldehyde, namely thioacetaldehyde, is also very unstable. In contrast to thioformaldehyde, it can exist in the tautomeric enethiol form (ethenethiol):

$$CH_3{-}CH{=}S \rightleftarrows CH_2{=}CH{-}SH.$$

Thioacetaldehyde is generated in different ways: photochemically by adding hydrogen sulphide to acetylene,[10] by the thermolysis of ethane-1,2-dithiol[10] and dimethyl sulphide,[14] and by the reaction of vinyl chloride with an excess of hydrogen sulphide.[14] On thermal decomposition of 2-vinylthiotetrahydropyran, the isomeric α- and β-trithioacetaldehydes were isolated.[15]

III. Alkoxy-, acyl-, and alkoxycarbonylthioformaldehydes

O-Substituted thioformates (RO−CH = S), which can be regarded as alkoxythioformaldehydes, are interesting not only as unusual representatives of thiocarbonyl compounds but also as reagents for the introduction of the thioaldehyde group.[16,17] *O*-Ethyl thioformate was first obtained in 33% yield by the hydrothiolysis of ethyl orthoformate.[18] Later a new, simple, and more effective procedure, starting with the readily available 1,1-dichloromethyl methyl ether, was proposed for the synthesis of *O*-alkyl thioformates using the *O*-methyl derivative as an example.[19] Heating potassium *gem*-bis(*O*-ethyl dithiocarbonate) (I), obtained by the reaction of dichloromethyl methyl ether with *O*-ethyl dithiocarbonate, to 200−220 °C leads to *O*-methyl thioformate. This compound is sensitive to oxygen but can be stored in a nitrogen atmosphere at 0 °C for several months:



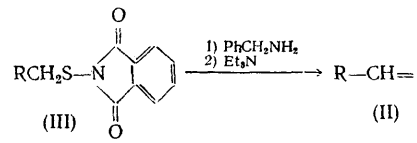
(I)

The attempt to synthesise *O*-phenyl thioformate by a similar procedure led to polymerisation products only.[19]

Acyl- and alkoxycarbonyl-thioformaldehydes (R−CO−CH = S, RO−CO−CH = S) represent a special variety of thiocarbonyl derivatives in which the electron-accepting carbonyl functional group is linked to the CH = S group. Such compounds have not been isolated in the monomeric state. However, their intermediate formation has been used for the synthesis of cyclic adducts.[20–22]

Bunte salts RCH_2SSO_3Na are used for the synthesis of R−CO−CH = S with R = Ph or PhNH[20] (see above), while the corresponding α-sulphonyl disulphide $4\text{-}BrC_6H_4COCH_2SSCH.(SO_2Tol)COC_6H_4Br\text{-}4$ has been used to obtain the thial with R = $4\text{-}BrC_6H_4$[21] (see below). Ph−CO−CH = S can also be obtained by the photolysis of diphenacyl sulphide.[22]

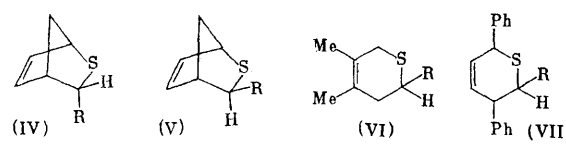
The first information about methoxycarbonylthioformaldehyde (IIa) can be found in the communication by Harpp and Back.[23] In a study of the reaction of *N*-(methoxycarbonylmethylthio)-phthalimide (IIIa) with benzylamine at room temperature, the thioxoamide $PhCH_2NHCOCSNHCH_2Ph$ was isolated. It was then assumed that methoxycarbonylthioformaldehyde (IIa) is an intermediate in this reaction:



(III) (II)

R = MeO−CO (a), EtO−CO (b).

The reactions of compounds (IIIa, b) with triethylamine in the presence of conjugated dienes lead to the corresponding alkoxycarbonylthioformaldehydes (IIa, b) *in situ*.[24] The *endo*-adducts (IV) and the *exo*-adducts (V) of cyclopentadiene and ethoxycarbonylthioformaldehyde (IIb) dissociate at 111 °C, which makes it possible to achieve the transfer of the TA (IIb) to other conjugated dienes. Thus, when a "kinetic mixture" of compounds (IV) and (V) with 2,3-dimethylbuta-1,3-diene was heated in toluene under nitrogen in a sealed tube at 120 °C for 21 h, the individual adduct (VI) was obtained in 82% yield. In the case of *trans,trans*-1,4-diphenylbuta-1,3-diene, which reacts with maleic anhydride 114 times more slowly than 2,3-dimethylbuta-1,3-diene,[25] refluxing of a mixture of the isomers (IV) and (V) in xylene readily affords the adduct (VII) (mixture of stereoisomers). Thus the thermal dissociation of the adducts (IV) and (V) can be used preparatively as the source of ethoxycarbonylthioformaldehyde (IIb):



(IV) (V) (VI) (VII)

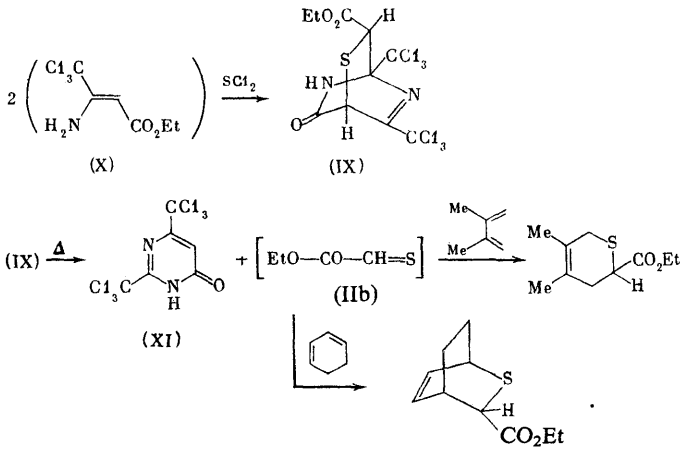
R = EtO—CO.

Bunte salts[20] and α-sulphonyl disulphides[21] are excellent substrates for the synthesis of alkoxycarbonylthioformaldehydes (II) and the acyl derivatives.

The 1,2-elimination of HCl; from ethoxycarbonylmethanesulphenyl chloride ($EtO{-}CO{-}CH_2SCl$) (VIII) when it is treated with triethylamine leads to ethoxycarbonylthioformaldehyde (IIb).[26] It too is trapped by various conjugated dienes. The yield of the products of [2 + 4]cycloaddition is then satisfactory. However, the interaction of the TA (IIb) with cyclohexa-1,3-diene is accompanied by the formation of other reaction products, probably as a result of the competing attack by the sulphenyl chloride (VIII) on the diene.[26]

A derivative of diazathiabicyclooctene (IX) has been recommended as a new precursor of alkoxycarbonylthioformaldehydes (II).[27] Compound (IX) was obtained in 34% yield by the reaction of ethyl 3-amino-4,4,4-trichlorocrotonate (X) with SCl_2. Heating of a solution of compound (IX) in chlorobenzene at 80 °C induces a retro-Diels-Alder reaction and the formation, together with the product (XI), of ethoxycarbonlthioformaldehyde (IIb), which has been successfully trapped with cyclohexa-1,3-diene or 2,3-dimethyl-

buta-1,3-diene (the yields of the adducts were 85% and 48% respectively):



This method of generating and trapping ethoxycarbonylthioformaldehyde (IIb) supplements effectively the recently developed elegant methods of synthesis of thioformyl compounds.[20–22]

The synthesis of n-butoxycarbonylthioformaldehyde from n-butylglyoxal and P_4S_{10} as well as its reactions with dienes have been briefly reported.[26]

IV. αβ-Unstaturated and aromatic thioaldehydes

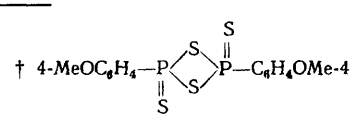
The methods of synthesis of αβ-unsaturated and aromatic TA are extremely varied. At the present time they can be subdivided into 12 general methods.

1. Thionation of aldehydes

The methods for the direct conversion of the carbonyl group ($>C=O$) into the thiocarbonyl group ($>C=S$)[11] in order to synthesise TA are rarely used. In the synthesis of 3-thioformylindolizines (XII) by the appropriate treatment of the corresponding formyl derivatives, the use of tetraphosphorus decasulphide is by no means as convenient as the employment of other thionating agents[28] (Table 1, Nos. 1–3). P_4S_{10} has been used to synthesise dimethylaminothioacroleine (XIII),[29] but no experimental data have been published.

The interaction of 2-pyrrolidinobenzaldehyde with Lawson's Reagent† in boiling toluene leads initially to the corresponding TA (XIV).[30]

The reactions of boron sulphide with benzaldehyde and its 3-methyl and 3-nitro-derivatives have also been investigated.[31] The 3-nitro-derivatives do not react with P_2S_3, while in the two remaining cases cyclic trimers of the corresponding TA—substituted 1,3,5-trithianes—were isolated. Such trimerisation is apparently promoted by thionation catalysts (HCl, I_2).

† 

2. Thionation of oximes and hydrazones

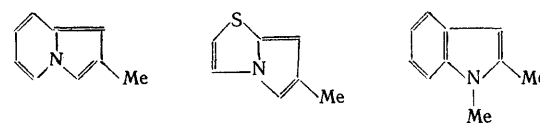
Refluxing of the oxime (XV) or the hydrazone (XVI) of 6-formylpurine in thioacetic acid or its anhydride leads to *N*-acetyl-6-thioformylpurine (XVII)[32] (Table 1, No. 4).

3. Hydrothiolysis of iminium salts

Iminium salts have been used successfully for the synthesis of thioformyl compounds (Table 1, Nos. 5–15).

The first stable thioaldehyde—3-ethyl-4′-methoxycarbonyl-5′-(2-methoxycarbonylpropionyl)-3′, 4-dimethyl-5-thioformyldipyrrolylmethane (XVIII)—was obtained by Woodward et al.[2] by the reaction of *N*-ethylformiminium bromide (XIX) with hydrogen sulphide in the presence of sodium methoxide in a benzene–methanol mixture. Slightly later, the enaminothial (XXI) was synthesised in a satisfactory yield by the reaction of a 1-ethyl-2-(2-*N*-methyl-*N*-phenylaminoethenyl)benzothiazolium salt (XX) with sodium hydrogen sulphide in methanol.[3]

A brief communication appeared in 1966[33] in which the problem of the synthesis of stable TA from 2-methylindolizine (XXII), 6-methylpryolo[2,1-*b*]thiazole (XXIII), and 1,2-dimethylindole (XXIV) was posed for the first time. It was correctly suggested that coupling of the thioformyl group to a nitrogen atom in a heterocycle can lead to the mesomeric stabilisation of the corresponding TA, for the synthesis of which a new version of the Vilsmeier–Haack reaction was used:[33]



(XXII) (XXIII) (XXIV)

Treatment of the initial compounds (XXII)–(XXIV) in dimethylformamide (DMF) with phosphoryl chloride leads to the Vilsmeier salts (XXV)–(XXVII) respectively, whose solvolysis *in situ* by aqueous sodium hydrogen sulphide affords the orange or red TA (XIIb), (XXVIIIa), and (XXIX).

Later the thioformylindolizines (XII) and (XXX)[28] and thioformylpyrrolo-[2,1-*b*]thiazoles (XXVIII) and (XXXI)[34] were synthesised by the same procedure and investigated in detail. The electrophilic substitution reactions in indolizines occur preferentially at the 3-position or, if the latter is occupied, to the 1-position. 3-Thioformyl-substituted compounds (XIIa, b, d–g) have been obtained in excellent yields from indolizine, 2-methylindolizine, and 1,2-, 2,6-, 2,7-, and 2,8-dimethylindolizines. 2-t-Butylindolizine gives rise to 5% of 1-thioformylindolizine (XXXa) together with the 3-formyl-substituted derivative (XIIc). The attempts to obtain the 1,3-dithioformyl derivative (XIIh)[28] led only to a polymer. Under these conditions, the two thioformyl groups were probably mutually destabilised as a result of cross-coupling.

A modified Vilsmeier reaction made it possible to synthesise a large series of thioformyl-substituted 5- and 7-pyrrolo[2,1-*b*]thiazoles (XXVIII) and (XXXI).[34] A 4:1 mixture of the 5-thioformyl derivative (XXVIIIe) and the 7-thioformyl derivative (XXXIe) has been obtained from 3,6-dimethylpyrrolo[2,1-*b*]thiazole. 6-t-Butyl-3-methylpyrrolo[2,1-*b*]thiazole also affords a mixture from which the 5-thioformyl derivative (XXVIIId) and the 7-thioformyl derivative (XXXId) were isolated by preparative thin-layer chromatography (TLC). The structure of the 5-thioformyl derivative (XXVIIId) was reliably confirmed by X-ray diffraction.[34]

Table 1. αβ-Unsaturated, aromatic, and sterically stabilised thioaldehydes.

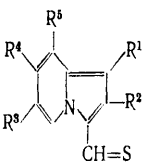
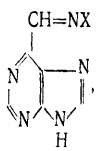
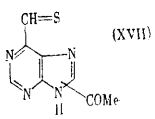
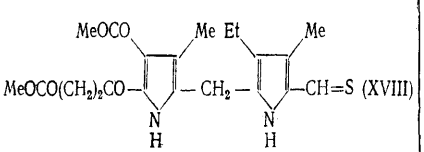
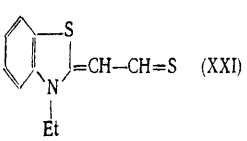
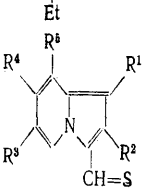
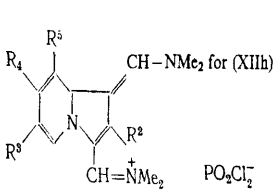
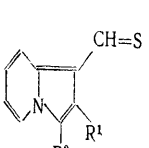
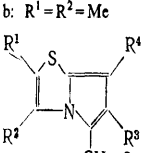
No.	Reagents	R–CH=S	M.p., °C	Yield, %	Refs.
1	R–CH=O, P_4S_{10}	 (XII)			
		c = $R^1=R^3=R^4=R^5=H$, $R^2=Me$	88–89	59	[28]
		d = $R^3=R^4=R^5=H$, $R^1=R^2=Me$	168–169	76	[28]
2	R–CH=O, P_4S_{10}	$Me_2NCH=CH–CH=S$ (XIII)	61–63	—	[29]
3	R–CH=O, Lawson reagent	2-[$N(CH_2)_4$]–C_6H_4–CH=S (XIV)	—	—	[30]
4	 MeCOSH or $(MeCO)_2S$	 (XVII)			
	(XV): X=OH		182–184	28	[32]
	(XVI): X=NH_2		—	34	[32]
5	R–CH=$\overset{+}{N}$HEt Br^-, H_2S (XIX)	 (XVIII)	145–146	—	[2]
6	R=CH–CH=$\overset{+}{N}$(Me)Ph X^-, NaSH (XX)	 (XXI)	—	—	[3]
7	R–CH=$\overset{+}{N}Me_2PO_2Cl_2^-$, NaSH (XXV)	 (XII)			
		a: $R^1=R^2=R^3=R^4=R^5=H$	56.5–58	77	[28]
		b: $R^1=R^3=R^4=R^5=H$, $R^2=Me$	88–89	86	[28]
		c: $R^1=R^3=R^4=R^5=H$, $R^2=t$-Bu	139–141	90	[28]
		d: $R^3=R^4=R^5=H$, $R^1=R^2=Me$	168–169	81	[28]
		e: $R^1=R^4=R_5=H$, $R^2=R^3=Me$	150–152	86	[28]
		f: $R^1=R^3=R^5=H$, $R^2=R^4=Me$	140–142	83	[28]
		g: $R^1=R^3=R^4=H$, $R^2=R^5=Me$	167–170 (decomp.)	82	[28]
	 for (XIIh)	h: $R^3=R^4=R^5=H$, $R^2=Me$, $R^1=CH=S$	197–200 (polymer)	96	[28]
8	R–CH=$\overset{+}{N}Me_2$ $PO_2Cl_2^-$, NaSH (XXV′)	 (XXX)			
		a: $R^2=H$, $R^1=t$-Bu	129–131	5	[28]
		b: $R^1=R^2=Me$	158.5–159	76	[28]
9	R–CH=$\overset{+}{N}Me_2$ $PO_2Cl_2^-$, NaSH (XXVI)	 (XXVIII)			

Table 1 (contd)

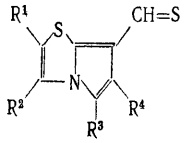
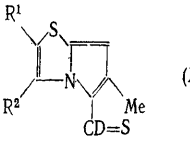
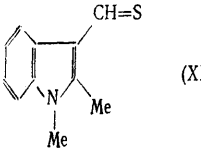
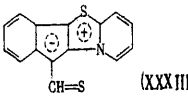
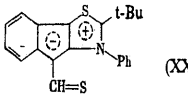
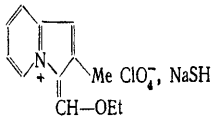
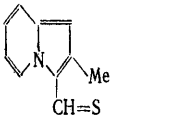
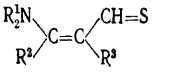
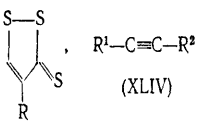
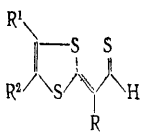
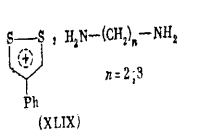
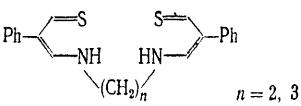
No.	Reagents	R—CH=S	M.p., °C	Yield, %	Refs.
		a: $R^1=R^2=R^4=H$, $R^3=Me$	101—103	89	[34]
		b: $R^2=R^4=H$, $R^1=R^3=Me$	127—128	89	[34]
		c: $R^1=R^2=H$, $R^3=R^4=Me$	165—165.5	71	[34]
		d: $R^1=R^4=H$, $R^2=Me$, $R^3=t$-Bu	117—118	12	[34]
		e: $R^1=R^4=H$, $R^2=R^3=Me$	152—154	49	[34]
		f: $R^4=H$, $R^1=R^2=R^3=Me$	169—170	77	[34]
10	R—CH=$\overset{+}{N}$Me$_2$ $PO_2Cl_2^-$, NaSH (XXVI′)	 (XXXI)			
		a: $R^1=R^2=H$, $R^3=R^4=Me$	162.5—164.5	65	[34]
		b: $R^1=H$, $R^2=R^3=R^4=Me$	195—199	92	[34]
		c: $R^1=R^2=R^3=R^4=Me$	224—226 (decomp.)	75	[34]
		d: $R^1=R^3=H$, $R^2=Me$, $R^4=t$-Bu	156—158	17	[34]
		e: $R^1=R^3=H$, $R^2=R^4=Me$	161—162	4.5	[34]
11	R—CD=$\overset{+}{N}$Me$_2$ $PO_2Cl_2^-$, NaSH	 (XXXII)			
		a: $R^1=R^2=H$	102—104	78	[34]
		b: $R^1=R^2=Me$	168—170	83	[34]
12	R—CH=$\overset{+}{N}$Me$_2$ $PO_2Cl_2^-$, NaSH (XXVII)	 (XXIXa)	160 (decomp.)	86	[33]
13	R—CH=$\overset{+}{N}$Me$_2$ ClO_4^-, NaSH (XXXIVa, b)	 (XXXIIIa)	>215 (decomp.)	44	[35]
		 (XXXIIIb)	>215 (decomp.)	43	[35]
14	 (XXXV)	 (XIIb)	88—89	33	[28,33]
15	R—CH=$\overset{+}{N}$Me$_2$$PO_2Cl_2^-$, NaSH (XXXVII)	 (XXXVI)			
		a: $R_2^1=(CH_2)_2O(CH_2)_2$, $R^2=R^3=Ph$	170—171	61	[36]
		b: $R_2^1=(CH_2)_4$, $R^2=R^3=Ph$	163.5—164	33	[36]
		c: $R_2^1=(CH_2)_2O(CH_2)_2$, $R^2=Ph$, $R^3=H$	139—140	27	[36]
		d: $R_2^1=(CH_2)_2O(CH_2)_2$; R^2, $R^3=(CH_2)_3$	116—117	50	[36]
		e: $R_2^1=$cyclo-C_6H_{11}, $R^2=R^3=Ph$	136.5	23	[36]

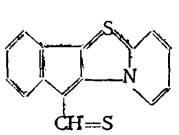
Table 1 (contd)

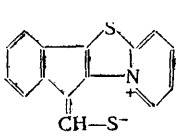
No.	Reagents	R–CH=S	M.p., °C	Yield, %	Refs.
16	 (XLV)	 (XLVI)			
		a: R=H, $R^1=R^2$=COOMe	88	70; 75	[40, 42]
		b: R=Me, $R^1=R^2$=COOMe	123–126	75	[42]
		c: R=Ph, $R^1=R^2$=COOMe	152–154	85; 70	[40, 42]
		d: R=Ph, $R^1=R^2$=COOEt	130–134	75	[42]
		e: R=Ph, R^1=H, R^2=COOMe	124	50	[42]
		f: R=Me, R^1=H, R^2=COPh	156 decomp.–274	40	[42]
		g: R=R^1=H, R^2=COPh	152 decomp.–198	70	[42]
		h: R=H, $R^1=R^2$=COPh	143	74; 70	[40, 42]
		i: R=Ph, $R^1=R^2$=COPh	—	63; 71	[39, 40]
17	 (XLIX)	 (La, b) $n = 2, 3$	—	60–80	[43]
18	PhCO–C(Ph)=CHCl, Na_2S	PhCO–CH(Ph)–CH=S ⇅ PhCO–C(Ph)=CH–SH (LI)	84–86	30	[44]
19	$PhCOCH_2SCH_2$–$C(CH_3)_3$ (LXXIV)	$(CH_3)_3C$–CH=S (LXXIII)	—	~50	[65]
20	R–Li, EtO–CH=S (LXXVI)	$(Me_3Si)_3C$–CH=S (LXXV)	129–131	16	[17]
21	R–Li, EtO–CH=S (LXXVIII)	2,4,6-(t-Bu)$_3C_6H_2$–CH=S (LXXVII)	146–147	56	[16]
	R–CH=NNH_2, S_2Cl_2 (LXXIX)	»	—	40	[16]

The deuteriated TA (XXXIIa, b) were synthesised from the corresponding pyrrolo[2,1-*b*]thiazoles using [$^2H_7$]dimethylformamide and phosphoryl chloride in 1,2-dichloroethane for studies by NMR and IR spectroscopy.[34]

The synthesis of stable thioformyl derivatives of 10*H*-indeno-[2,1-*d*]-pyrido-[2,1-*b*]thiazole (XXXIIIa, b) has also been reported.[35] Instead of DMF, dimethylthioformamide was used, which made it possible to increase the yield of the salts (XXXIVa) and (XXXIVb) from 63 and 40% to 93 and 87% respectively. This can be explained by the different formylating capacities of the ion-pair reaction intermediate $Me_2\overset{+}{N}CH-XPOCl_2Cl^-$, where X = S or O.[35]

The neutral structure (A) of the thioaldehyde (XXXIIIa), formally containing a tetracovalent endocyclic sulphur atom, is undoubtedly stabilised by the formation of the resonance zwitter-ion (B).[35]


(A), (XXXIIIa)

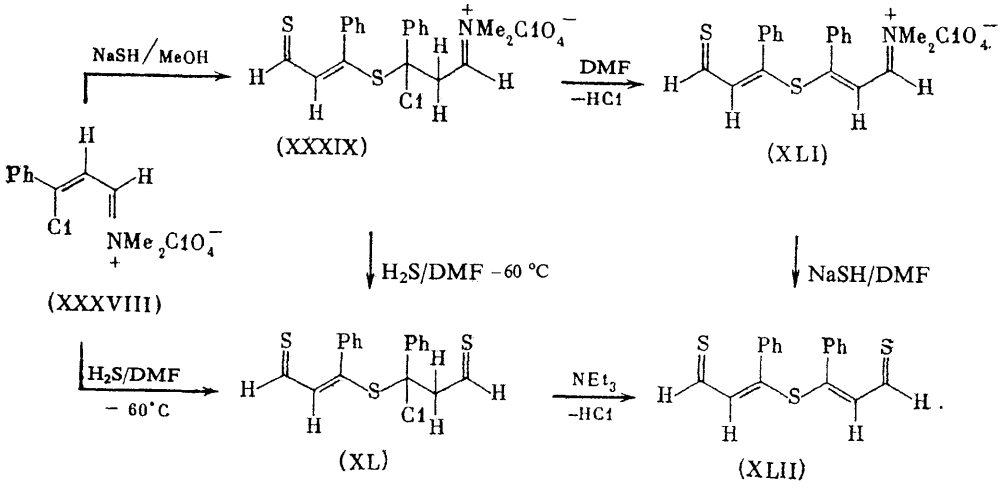

(B), (XXXIIIa)

A method of synthesis of thioformylindolizines (XII) from ethoxymethyleneindolizinium salts (XXXV) has been proposed.[28,33] It is based on the condensation of 3*H*-indolizinium perchlorates with triethyl orthoformate and subsequent treatment of the resulting salts (XXXV) with sodium hydrogen sulphide.

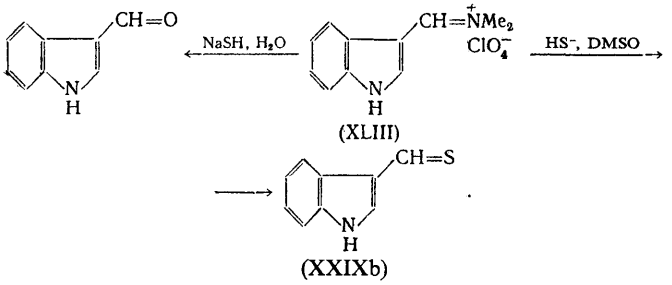
A single-stage method of synthesis of aliphatic and alicyclic enaminothioaldehydes (XXXVI), involving the successive treatment of the enamines (XXXVII) with DMF, $POCl_3$, and NaSH, has been described recently.[36] The thials (XXXVI) are orange or red crystalline substances which are stable for several months even at room temperature.

New synthetic possibilities for the hydrothiolysis of salts of the type (XXXVIII) have been demonstrated.[37] Depending on the character of the ion-pair states of the reactant and temperature, the hydrothiolysis of 3-chloro-*NN*-dimethyl-3-phenylprop-2-en-1-yliminium perchlorates (XXXVIII) leads to the asymmetric sulphides (XXXIX) or (XL). Their dehydrohalogenation products

are 1,7-bishetero-substituted dipropenyl sulphides (XLI) and (XLII) respectively:

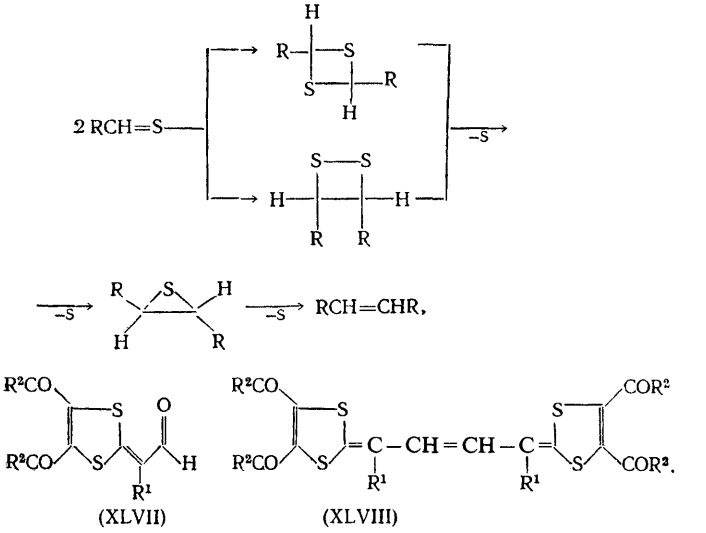


Under the conditions of the synthesis of 3-thioformyl derivatives of indole and indolizine by treating the corresponding methyleneiminium salts with an aqueous solution of sodium hydrogen sulphide,[33] *N*-[(3-indolyl)methyl]-*NN*-dimethyliminium perchlorate (XLIII) hydrolyses to 3-formylindole.[38] The hydrothiolysis of the salt (XLIII) can be readily achieved by treatment with anhydrous NaSH or hydrogen sulphide in dimethyl sulphoxide at 20 °C and leads to the formation of 3-thioformylindole (XXIXb) in solution:



4. Alkynylation of 1,2-dithiole-3-thiones

[2 + 3]Cycloaddition of acetylenedicarboxylic acid esters (XLIV, $R^1 = R^2$ = COOMe or COOEt) or dibenzoylacetylene (XLIV, $R^1 = R^2$ = COPh) as well as other activated acetylenes to 5-unsubstituted 1,2-dithiole-3-thiones (XLV) leads to 2-thioformylmethylene-1,3-dithioles (XLVI)[39–42] (Table 1, No. 16). These substances almost always contain an admixture of the isostructural aldehyde (XLVII). A long reaction time (24 h) as well as refluxing of the TA (XLVI) in benzene lead mainly to the alkenes (XLVIII)—the products of the bimolecular elimination of thial sulphur in accordance with the scheme[40]



5. Aminolysis of 1,2-dithiolium salts

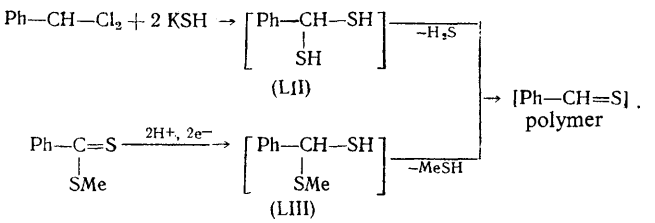
Treatment of 1,2-dithiolium salts (XLIX) at 25 °C with an equivalent amount of ethylenediamine in ethanol or of trimethylenediamine in benzene leads to the stable TA (La, b)[43] (Table 1, No. 17). This reaction opened a convenient synthetic route to 14-, 15-, and 16-membered tetraazamacrocycles.[43]

6. Hydrothiolysis of 1-chloro-2-benzoylstyrene

The hydrothiolysis of alkenyl chlorides is a widely used approach to the synthesis of thiocarbonyl compounds.[11] 2-Oxo-1,2-diphenyl-1-thioformylethane (LI), which exists in the stable alkenethiol tautomeric form[44] (Table 1, No. 18), has been obtained in this way.

7. The cleavage of *gem*-dithiols and their derivatives

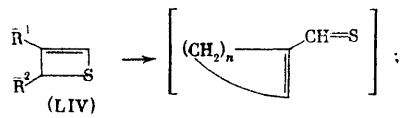
gem-Dithiols and their S-derivatives can be cleaved at one of the C–S bonds with formation of the thiocarbonyl group.[45] Thus the *gem*-dithiol (LII), obtained from benzylidene dichloride and potassium hydrogen sulphide, is readily converted into thiobenzaldehyde.[45] The primary product (LIII) of the reduction of methyl dithiobenzoate splits off methanethiol and is also converted into thiobenzaldehyde, which immediately polymerises.[45]



Certain 1,3,5-trithianes are readily cleaved on heating to the initial TA.[6,9,11,46] This can be used for the "storage" of the corresponding TA as trimers in order to investigate them subsequently.

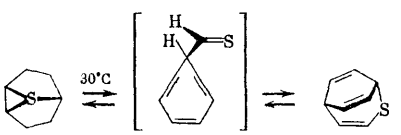
8. Rearrangement of cyclic sulphides

The spontaneous decomposition of certain 3,4-disubstituted thiets (LIV) begins with ring opening and the formation of αβ-unsaturated TA (LV), which rapidly polymerise.[47,48] When compounds (LV, n = 4, 5) were allowed to interact with 2,4-dinitrophenylhydrazine, the hydrazones of 2-thioformylcyclohexene and 2-thioformylcycloheptene were isolated.[47]



$R^1 = R^2 = (CH_2)_4$.
$R^1 = R^2 = (CH_2)_5$

1-Thioformylcycloheptatriene (LVI) is an active intermediate in thermal isomerisation via the mechanism[49]



9. Thermolysis of Unsaturated Sulphides

The synthesis of two extremely reactive compounds—thioacrolein and thiobenzaldehyde—has been achieved by the flash thermolysis of diallyl sulphide and allyl benzyl sulphide respectively.[50–53] According to IR spectroscopic data, thioacrolein begins to change slowly already at 77 K, while thiobenzaldehyde persists up to 110 K.[50]

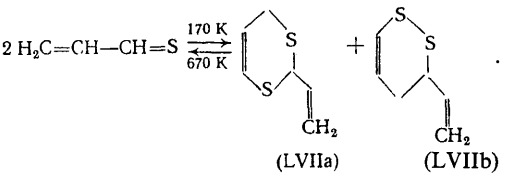
$$H_2C{=}CHCH_2{-}S{-}CH_2CH{=}CH_2 \xrightarrow{\Delta} [CH_2{=}CH{-}CH{=}S],$$

$$PhCH_2{-}S{-}CH_2CH{=}CH_2 \xrightarrow{\Delta} [Ph{-}CH{=}S].$$

Thioacrolein was identified in the thermolysis products of diallyl sulphide (550 °C, 10–50 mmHg) by microwave spectroscopy.[51] Under normal conditions, this thial persists for 1–2 min.

The use of photoelectron spectroscopy (interpretation of "molecular fingerprints") during thermolysis made it possible to determine the optimum temperature at which thioacrolein is formed from diallyl sulphide (660 K).[52,53]

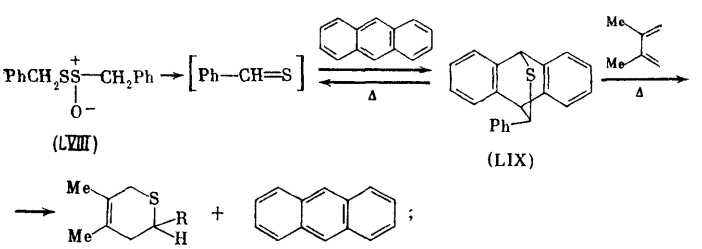
The photoelectron spectrum of monomeric thioacrolein was obtained in a study of the thermolysis products of the Diels–Alder dimers (LVIIa, b). This thermal reaction made thioacrolein available for preparative purposes and further spectroscopic studies.[52,53]



10. The cleavage of disulphides and their derivatives

New precursors of TA have been discovered in recent years.[20,21,54] In particular, these proved to be alkyl thiosulphinates, whose thermolysis has become a general and convenient method of synthesis of TA.[54,55] Thus, when *S*-benzyl phenylmethanethiosulphinate (LVIII) is heated in toluene at 100 °C, thiobenzaldehyde is formed. The blue colour which its presence imparts to the reaction mixture [UV spectrum: λ_{max} = 580–590 and 610 nm (shoulder), which corresponds to the spectrum at 77 K of thiobenzaldehyde obtained by the vacuum flash pyrolysis of allyl benzyl sulphide[50]] vanishes after 15 min at 20 °C.[54]

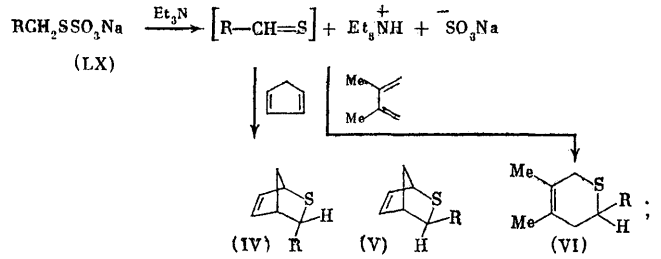
The thermolysis of the thiosulphinates (LVIII) is usually carried out in the presence of dienes of anthracene, which are TA "trapping agents".[54,55] The adduct with anthracene (LIX) (97% yield) can itself serve as a source of thiobenzaldehyde. When it is heated in the presence of 2,3-dimethylbutadiene in a sealed tube, the 2*H*-dihydrothiane (VI) and anthracene are formed.



(VI), R = Ph.
92%

The readily available Bunte salts (LX) are very convenient for the synthesis of TA with electron-accepting substituents.[20] They readily undergo 1,2-elimination on treatment with triethylamine and calcium chloride. The corresponding cyclic adducts (IV)–(VI) were obtained from them in the presence of conjugated dienes. Under these conditions, sodium *S*-4-nitrobenzyl thiosulphate (LXe) gives rise to the adduct (IV)–(VI) in high yields. On the other hand, the unsubstituted benzyl derivative (LXd) does not afford such adducts at all. This example demonstrates the significant role of the CH acidity of the methylene group in compound (LX) and shows that the conjugation of the thioformyl functional group with the benzene

ring cannot by itself ensure the 1,2-elimination process.[20]

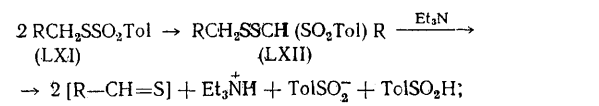


R = Et–CO (a), (Sect.III), Ph–CO (b), (Sect.III), PhNH–CO (c) (Sect.III), Ph (d), 4-$NO_2C_6H_4$ (e).

In methanol at 20 °C, thials react with cyclopentadiene to form the adducts (IV) and (V) in high yields (66–86%), while the reaction with 2,3-dimethylbuta-1,3-diene produces adducts in a lower yield. In a less polar system (benzene–ethanol), the yield of the adducts (VI) rises to 55–65%. The competitive attack by nucleophiles (for example, SO_3^{2-}) on the TA is probably lessened under these conditions.

The ability of the adducts (IV)–(VI) to dissociate on heating makes them valuable sources of reactive TA.[20]

Toluene-*p*-thiosulphonates (LXI) are readily converted into α-sulphonyl disulphides (LXII) which are cleaved with formation of TA on treatment with triethylamine similarly to the Bunte salts:[21]

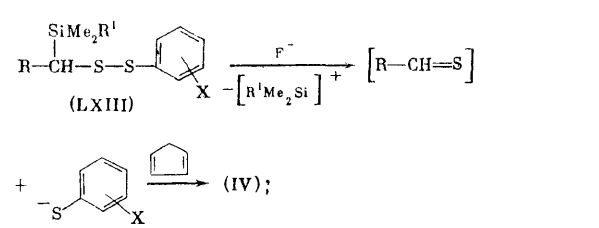


R = EtO–CO (a) (Sect.III), 4-BrC_6H_4–CO (b) (Sect.III), Ph (c), 4-$NO_2C_6H_4$ (d); Tol = 4-MeC_6H_4.

The disulphides (LXIIa, b, d) react with triethylamine at 20 °C and with a solution of cyclopentadiene in benzene to form the corresponding adducts (IV) and (V), the *endo*-isomer (IV) predominating. Among the starting compounds, the benzyl derivative (LXIIc) is least reactive. Nevertheless, it forms the adducts (IVc) and (Vc) in acetonitrile.

This new TA generating reaction has been called a fragmentation–elimination process via a concerted mechanism.[21]

An elegant and general method of synthesis of thioformyl compounds from aryl[α-(dimethylorganylsilyl)organylmethyl] disulphides (LXIII) has been proposed recently.[56] On treatment with the F^- anion, the disulphides are readily cleaved to the corresponding TA and the arenethiolate anion.



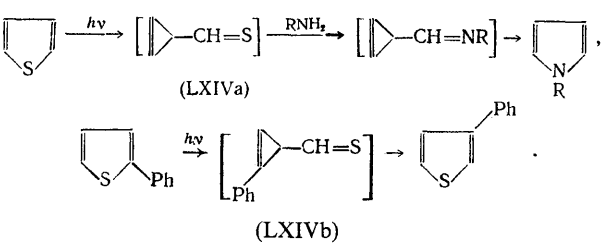
The effectiveness of the cleavage is determined by the stability of the arenethiolate leaving group. 2,4,6-Trichlorophenyl disulphides (LXIII, X = 2,4,6-trichloro-group) are extremely unstable. The 2-nitro-4-chloro-derivatives (LXIII, X = 2-NO_2 or 4-Cl) are extremely reactive, while the unsubstituted disulphides (LXIII, X absent) are cleaved only on heating.

The rate of fragmentation-elimination is also influenced by the reactivity of the source of the fluoride ion. In the presence of 18-crown-6, CsF or KF generate TA slowly at 20 °C, while tetrabutylammonium fluoride ($NBu_4^+F^-$) in tetrahydrofuran acts rapidly in the temperature range from 0 °C to –78 °C.

Thiobenzaldehyde adds to cyclopentadiene, forming a mixture of the cyclic *exo*- and *endo*-adducts (V) and (IV) in proportions of 1 : 7. The predominance of the *endo*-isomer can be due to the kinetic factor, but Dreiding models show that the *endo*-isomers are sterically less hindered and should therefore be more stable.[56]

11. Photochemical methods

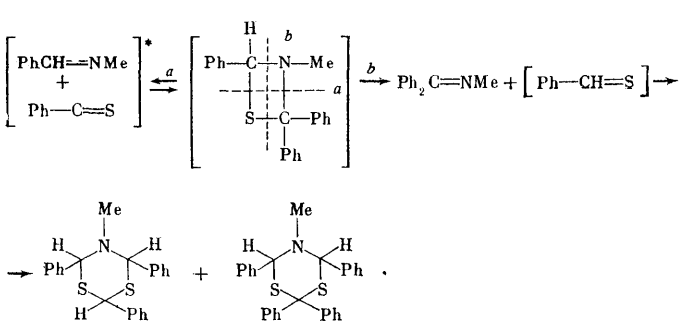
Certain types of conjugated TA are generated in photochemical reactions and play an important role in them.[8,57,58] Thus 3-thioformylcyclopropene (LXIVa) is an intermediate in the photolytic conversion of thiophen into *N*-alkylpyrroles in the presence of amines.[57] The formation of 1-thioformyl-2-phenylcyclopropene (LXIVb) has been explained by the rearrangement of 2-phenylthiophen to 3-phenylthiophen under the influence of UV irradiation.[58]



(LXIVa)

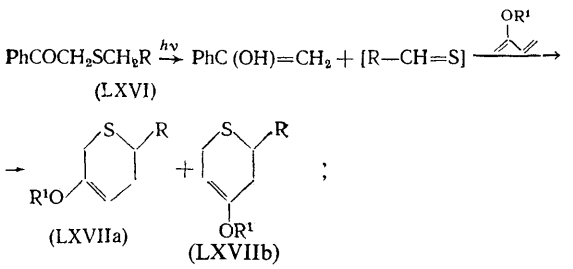
(LXIVb)

The formation of a polymer in the photolysis of ω-benzylthioacetophenones is apparently due to the intermediate generation of the monomeric thiobenzaldehyde.[8] The same TA is probably an intermediate in the formation of substituted 1,3,5-dithiazines (LXVa, b) and benzophenone methylimine from photoexcited thiobenzophenone and benzaldehyde *N*-methylimine.[8]



(LXVa) (LXVb)

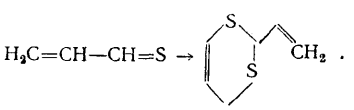
A simple method of synthesis of dienophilic TA by irradiating a mixture of organyl phenacyl sulphide (LXVI) with a diene at 0 °C has been developed recently.[59,60]



(LXVI) (LXVIIa) (LXVIIb)

R=H, Ph, Me—CO, Ph—CO, CN, AlkO—CO, Ph_2PO, $PhSO_2$, EtO—CO—CH=CH; $R^1=SiMe_2$—t-Bu.

The use of the most reactive dienes (for example, Danishevskii's diene)‡ makes it possible to "trap" the "exotic" thioformylsulphone ($PhSO_2$—CH=S) and thioformylphosphine oxide (Ph_2PO—CH=S), whose oxygen analogues are unknown.[60] In the case of the αβ-unsaturated TA (EtO—CO—CH=CH—CH=S), the yield of the adduct (LXVIIa) is low (10%), although the products of the self-condensation of this thial have not been detected. Under analogous conditions, thioacrolein cannot be trapped by the usual dienes, since it is stabilised as the dimer—2-vinyl-1,3-dithiene:[59]

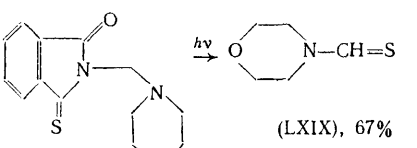


An excess of the diene and carefully purified reagents are necessary for the synthesis of the adducts (LXVII) in order to reduce to a minimum the catalytic thial self-condensation.[60] The yields of the adducts of TA with electron-donating substituents depend significantly on the structure of the diene, the nature of the substituent R in the TA, and the reaction conditions.

The regiospecificities of the cyloaddition of the compounds R—CH=S containing electron-accepting or electron-donating substituents R are not the same. In the presence of electron-accepting substituents, TA react like carbon dienophiles. Otherwise they behave similarly to carbonyl dienophiles. This difference agrees with quantum-chemical calculations.[60]

By virtue of the different regioselectivities of the reactions of dienes with TA having electron-donating or electron-accepting substituents, a large series of dihydrothiopyrans have become available.[61]

The photolytic cleavage of *N*-(*N*-morpholinomethyl)thiophthalimide (LXVIII) to the *N*-thioformylamine (LXIX),[62] which belongs to the class of the simplest thioformamides, proceeds in an unusual manner. The initial stage of this process is apparently the elimination of a proton from the methylene bridge.

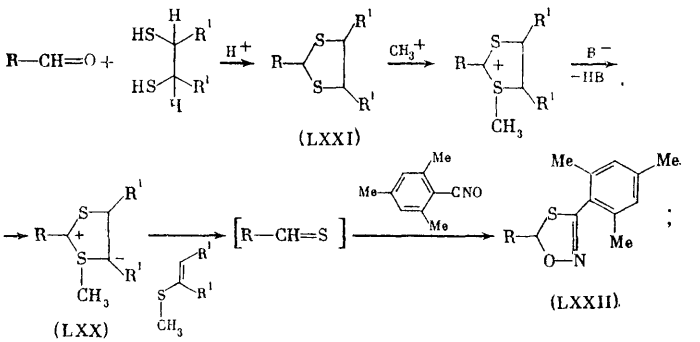


(LXVIII) (LXIX), 67%

‡$CH_2=CH(OSiMe_3)$—CH=CH—OMe.

12. Fragmentation of S-ylides

A novel method of synthesis of TA, based on the fragmentation of S-ylides of type (LXX), generated from an aldehyde (the oxygen analogue of the target TA) via the 1,3-dithiolan (LXXI), was proposed in 1985.[63] It proceeds in accordance with the scheme



(LXXI) (LXX) (LXXII)

R = Ph, H_2C=CH.....

The TA obtained react with mesitonitrile *N*-oxide to form stable 1,4,2-oxathiazoles (LXXII). In the absence of a "trapping agent", polymers or trimers are formed. In order to obtain thioacrolein, it is sufficient to treat its precursor—1,3-dithiolan (LXXI, R=CH=CH_2, R^1 = COOMe)—with lithium diisopropylamide. Thus 1,3-dithiolans are convenient reagents for the single-stage synthesis of highly reactive TA.[63,64]

This method harmoniously supplements the photochemical[59,60] or thermochemical[50–53] approaches to the synthesis of TA. It provides greater synthetic possibilities than does the 1,2-elimination induced by a base[20,21] or the cleavage of aryl [α-(dimethylorganylsilyl)-organylmethyl] disulphides.[56]

V. Sterically stabilised thioaldehydes

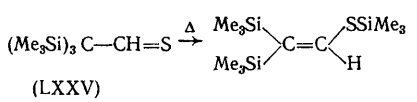
For more than 100 years, the attempts to obtain monomeric aliphatic TA were unsuccessful.[6,11] It was not until 1983 that it was possible to synthesise the first long-lived aliphatic TA—2,2-dimethylpropanethial (LXXIII).[65] The starting material for its synthesis was neopentyl phenacyl sulphide (LXXIV), whose photolysis in benzene in the presence of 5% of 2,3-dimethylbutadiene leads to the polymer [t-BuCH—S—]$_n$ in 60% yield. When this polymer is heated *in vacuo* (≥ 250 °C), 2,2-dimethylpropanethial (LXXIII) is formed (Table 1, No. 19).

The lifetime of this TA in chloroform, benzene, methylene chloride, or ether at 20 °C reaches 16 h. The relative stability of the TA (LXXIII) is probably determined not only by the bulky t-butyl group but also by the purity of the starting materials, which rules out the catalytic self-reactions of the thial. Indeed, its lifetime in a chloroform—ethanol mixture (15 min) falls to 5 min after the addition of trieythylamine and to several seconds in the presence of traces of HCl. The monomeric trimethylpropanethial (LXXIII) and its solution are extremely stable in air.

The first stable aliphatic Si-functional TA—tris(trimethylsilyl)-ethanethial (LXXV)—has been described recently.[17] Its synthesis is based on the reaction of tris(trimethylsilyl)methyllithium (LXXVI) with *O*-ethyl thioformate in tetrahydrofuran at –78 °C (10 min) and further at 20 °C (1.5 h) (Table 1, No. 20).

The thial (LXXV) is a pink-red crystalline compound which can be stored for a long time in the refrigator without changes and is

stable in air at 20 °C for about a week. This compound can be purified by column chromatography on silica gel or by freezing out from pentane at −78 °C. At ~80 °C, the TA (LXXV) rearranges quantitatively to 1,1-bis(trimethylsilyl)-2-trimethylsilylthioethene:



(LXXV)

The first stable *exo*-substituted thiobenzaldehyde—2,4,6-tris-t-butylthiobenzaldehyde (LXXVII)—was obtained by the reaction of 2,4,6-tri(t-butyl)phenyllithium (LXXVIII) with *O*-ethyl thioformate in tetrahydrofuran followed by chromatographic purification.[16] Another route to the synthesis of the TA (LXXVII) is based on the reaction of the hydrazone (LXXIX) with sulphur dichloride in the presence of triethylamine[16] (Table 1, No. 21).

The thial (LXXVII) is a strikingly stable purple crystalline compound which can be preserved for about a year at 20 °C or for two weeks on refluxing in benzene without access by air. The unsubstituted thiobenzaldehyde polymerises already at −160 °C.[50]

VI. Physical properties of compounds with the thioaldehyde group

According to microwave specroscopic data, the C=S bond length in the monomeric thioformaldehyde is 1.6108 Å.[66] This is longer than the C=O bond length in formaldehyde (1.2083 Å)[66] and is consistent with the predicted interatomic distance in the unperturbed thiocarbonyl group (1.607 Å).[11] The calculated dipole moment of thioformaldehyde is 1.6474(14) D.[67] Since μ for gaseous $CH_2=O$ is 2.27 D,[68] this shows that the polarity of the C=S bond is smaller than that of the C=O bond.

It has been established by microwave spectroscopy that the thioacrolein molecule is planar and has a dipole moment of 2.61 D.[51]

The photoelectron spectra of thioacrolein and acrolein are almost the same with ionisation peaks at 8.87 and 10.2 eV respectively.[52]

It is remarkable that the mass spectra of heterocyclic TA, namely 1,2-dimethyl-3-thioformylindole (XXIXa), 2-methyl-3-thioformylindolizine (XIIb), and 6-methyl-5-thioformylpyrrolo[2,1-*b*]thiazole (XXVIIIa), are characterised by an intense $(M-45)^+$ peak corresponding to the loss of the thioformyl group.[33]

The position of the absorption band of the thiocarbonyl group in the IR spectra (1100−1270 cm^{-1}) has now been reliably established as a result of the successful development of the chemistry of thioketones.[11]. The C=S bond stretching vibrations in the spectra of TA are in the same region. Thus the band at 1063 cm^{-1} corresponds to the absorption of the thiocarbonyl group in the IR spectrum of thioformaldehyde in an inert gas matrix at 14 K.[69] The absorption bands of the C=S group in the spectra of sterically stabilised TA, i.e. $Me_3C-CH=S$ (LXXIII) and $(Me_3Si)_3C-CH=S$ (LXXV), are at 1085 and 1120 cm^{-1} respectively.[17,65] The IR spectra of the stable heterocyclic TA (XXIXa), (XII), and (XXVIII) contain an intense band in the range 950−985 cm^{-1}.[33] The study of the solvent effect led to its assignment to the C=S bond vibration. In the spectrum of the TA (XXIXa), this band shifts from 978 cm^{-1} in cyclohexane to 956 cm^{-1} in 1,1,2,2-tetrabromoethane.[33] In the spectrum of the enaminothioaldehyde (XIII), the band at 1260 cm^{-1} corresponds to the ν(C=S) vibration.[29]

The electronic spectra of TA are characterised as a rule by three absorption regions due to the $n \rightarrow \pi^*$ transition in the visible part of the spectrum and the $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions in the UV region. The electronic spectra of stable heterocyclic TA—thioformylindolizines (XII)[28] and thioformylpyrrolo[2,1-*b*]thiazoles (XXVIII) and (XXXI)[34]—have been studied in detail. Thus the spectra of 3-thioformylindolizines (XII) contain four groups of intense maxima in the ranges 420−460, 300−325, 250−275, and 205−230 nm ($\lg\varepsilon > 3.7$). Three intense absorption regions can be observed in the spectra of 1-thioformylindolizines (XXX): 420−460, 260−280, and 210−240 nm. The difference between the overall forms of the spectra makes it possible to recognise readily 1- and 3-thioformylindolizines.[28] The spectra of 3-thioformylindolizines (XII) are characterised by two broad low-intensity bands (~520 and ~550 nm) ($\lg\varepsilon$ = 1.9−2.2), which do not have a distinct minimum. These bands undergo a hypsochromic shift with increase in solvent polarity and belong to the $n \rightarrow \pi^*$ transition in the thiocarbonyl group. The cause of the multiplicity of the spectrum still remains obscure. The spectrum of 2-t-butyl-1-thioformylindolizine (XXXa) in cyclohexane has a very broad $n \rightarrow \pi^*$ band with λ_{max} = 534 nm ($\lg\varepsilon$ = 1.84) and a shoulder at ~570 nm, while in the spectrum of 2,3-dimethyl- 1-thioformylindolizine (XXXb) there is a similar band in the range from ~510 to 560 nm ($\lg\varepsilon \simeq 1.9$).[28]

The electronic spectra of thioformylpyrrolo[2,1-*b*]thiazoles (XXVIII) and (XXXI)[34] and of 3-thioformylindole (XXIXb)[38] have a similar line form and the nature of the bands is likewise similar.

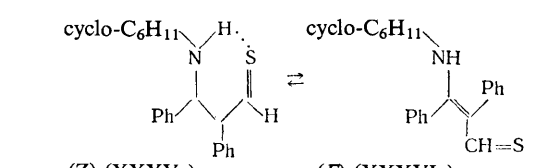
The electronic spectra of the sterically stabilised TA are characterised by the following parameters [the compound, λ_{max} (nm) (ε) the solvent, and the literature reference are quoted in succession]: $(CH_3)_3C-CH=S$, 508(16) (MeCN);[65] $(Me_3Si)_3C-CH=S$, 518(15), 272(9940), 212(4320) (C_6H_{12}); 503(14), 277(8720), 211(5330) (MeCN);[17] 2,4,6-t-$Bu_3C_6H_{12}-CH=S$, 564(19), 338(1850) (C_6H_{12}); 552(19), 340(1690) (EtOH).[16]

The spectra of the labile thioacrolein and thiobenzaldehyde have been recorded at 77 K under specially selected conditions.[50] The calculated values of λ_{max} agree very well with the experimental data.

	λ_{max} (found)			λ_{max} (calc.)		
	$n\rightarrow\pi^*$	$\pi\rightarrow\pi^*$	$n\rightarrow\sigma^*$	$n\rightarrow\pi^*$	$\pi\rightarrow\pi^*$	$n\rightarrow\sigma^*$
$CH_2=CH-CH=S$	580	276	—	570	265	—
$C_6H_5-CH=S$	575	320	228	567	302, 296	231, 226

In the ^1H NMR spectra of thioaldehydes, the signal of the thioformyl proton is in a low field within a fairly wide range [δ(p.p.m.) ranges from 9 to 13].[17,28,29,33,34,36,38–40,42,65] It is believed that 2,4,6-tri(t-butyl)thiobenzaldehyde (LXXVII) contains the "purest" thioformyl group whose proton signal is at δ = 13.02 p.p.m.[16]

According to ^1H NMR spectroscopic data, the enaminothial (XIII) exists to the extent of 95% as the rotational *S-trans*-isomer with a barrier to the unhindered rotation about the C−N bond of 17.1 kcal mol^{-1} at the coalescence temperature of 330 K.[29]



(Z)-(XXXVe) (*E*)-(XXXVIe)

δ, p.p.m. 15.24 (NH) 5.41 (NH)

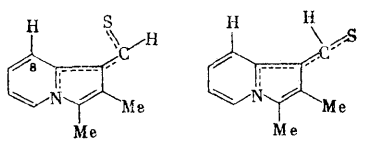
9.82 (CH=S) 9.95 (CH=S)

The thioaldehydes (XXXVIa–d) and (*Z*)-isomers and their structure corresponds to that of the initial enamines. The cyclohexylamino-substituted TA (XXXVIe) contains ~10% of the (*E*)-isomer.[36]

The ^{1}H NMR spectra of the thioformylindolizines (XII) and (XXX) have been investigated in detail.[28] The 1- and 3-thioformyl groups exert a strong diamagnetic anisotropic deshielding effect on the H(8) and H(5) atoms respectively located on the opposite side. The H(5) chemical shifts in the spectra of 3-thioformylindolizines (XII) are in the range δ = 11.1–11.6 p.p.m. In 2,3-dimethyl-1-thioformylindolizine (XXXb), the rotation about the ring–CH=S bond is hindered. This can be explained by the appreciable contribution of the dipolar mesomeric form (B):[28]

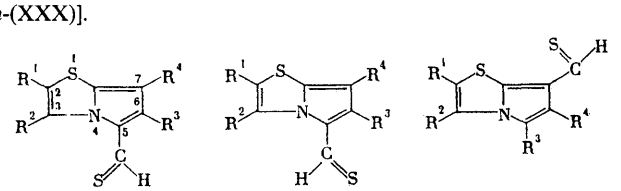
$$\underset{\text{(A)}}{\text{R—CH=S}} \leftrightarrow \underset{\text{(B)}}{\overset{+}{\text{R}}\text{=CH—S}^-}$$

Pronounced deshielding of H(8) and the singlet signal of the thioformyl proton show that below the coalescence temperature, the TA (XXXb) exists exclusively in the *syn*-configuration, which is more stable than the *anti*-form. This is determined by the intramolecular electrostatic attraction between the charges on the sulphur atom and the pyridine ring, which corresponds to a minimum in the potential energy of the molecule.[28]



syn-(XXXb) *anti*-(XXXb)

The temperature dependence of the ^{1}H NMR spectra shows that the rotation about the heterocyclic-CH=S bond is hindered in thioformylpyrrolo[2,1-*b*]thiazoles (XXVIII) and (XXXI).[34] These data agree with the existence of the 5-thioformyl derivatives (XXVIII) ether in the *syn*-configuration [compounds (XXVIIIa–d)] or in the *anti*-configuration [compounds (XXVIIIe, f)], while the 7-thioformyl derivatives exist only in the *syn*-configuration [*syn*-(XXX)].



syn-(XXVIII) *anti*-(XXVIII) *syn*-(XXX)

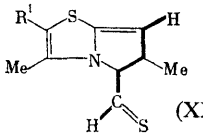
syn-(XXVIII)

	R¹	R²	R³	R⁴
a	H	H	Me	H
b	Me	H	Me	H
c	H	H	Me	Me
d	H	Me	t-Bu	H

anti-(XXVIII)

	R¹	R²	R³	R⁴
e	H	Me	Me	H
f	Me	Me	Me	H

The higher stability of the 5- and 7-*syn*-thioformyl derivatives relative to their *anti*-isomers is a consequence of the intramolecular electrostatic attraction of the partial charges on the sulphur atom of the thioformyl group and on the thiazole ring. Compounds (XXVIIIe, f) exist preferentially in the *anti*-form owing to the steric effect of the 3-methyl substituent, which repels the thioformyl sulphur atom from the plane of the ring. In compounds (XXVIIId), the effect of the t-butyl group is superimposed on that of the 3-methyl group, which forces the thioformyl group into the *syn*-configuration. The presence of the long-range spin–spin H(7)–CH=S interaction [the spin–spin coupling constant (SSCC) is 0.8 Hz] in the thioaldehydes (XXVIIIe, f) constitutes additional demonstration of their existence in the *anti*-form. In these TA, the H(7)–CH=S protons are disposed in the *W*-configuration (*W*), which is most favourable for the effective interaction through the conjugated system.[34]



(XXVIII), R^1 = H (e) or Me (f)

(*W*)

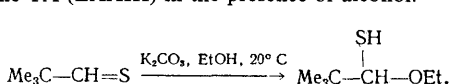
The ^{13}C NMR spectroscopic data for thioaldehydes are extremely limited. However, the existing information shows that the carbon nucleus of the ^{13}C=S moiety of the thioformyl group resonates in the region characteristic of thioketones.[11,16,17,70]

VII. Chemical properties of thioformyl compounds

The high reactivity of thioaldehydes can be inferred even from their extremely high tendency to undergo trimerisation, oligomerisation, and polymerisation. Not only the structure but also the conditions of the synthesis of TA determine the yield of particular products. Thus the synthesis of thioformaldehyde from formaldehyde and hydrogen sulphide in the presence of HCl leads mainly to the formation of the cyclic trimer (1,3,5-trithiane), while in an alkaline medium readily fusible polymers have been obtained.[71] The synthesis of thiobenzaldehyde from benzaldehyde and H_2S in a highly acid medium leads mainly to the more stable β-isomer; a weakly acid medium and a low reaction temperature afford not only greater amounts of the α-isomer but also a greater amount of the polymer with a molecular weight of ~1000.[71]

It has been convincingly demonstrated[72] that the self-transformations of the monomeric TA are catalytic processes. The addition of protic or Lewis acids induces the instantaneous trimerisation and polymerisation of 2,2-dimethylpropanethial (LXXIII) in all solvents. The authors explain by this observation the failure of many investigators to detect monomeric TA in the acid-catalysed thionation of aldehydes.

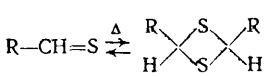
The decomposition of TA is also promoted by basic catalysts (triethylamine, K_2CO_3). Small amounts of the thioacetal (LXXX) and the isomeric 1,3,5-trithianes are formed under these conditions from the TA (LXXIII) in the presence of alcohol.[72]



(LXXIII) (LXXX)

In pure ether and chloroform, the TA (LXXIII) exists for a long time in the monomeric state but hydroxylated solvents induce its rapid trimerisation.[72]

Like non-enolisable thioketones, TA undergo reversible "head to tail" thermal dimerisation.[73]



R=Alk, Ar.

Thioacrolein is stabilised as the dimer (1,3-dithietan)[59] (see Section IV); dithianes can lose their thial sulphur and can be converted into symmetrically substituted ethylenes.[40] However, evidence for the formation of a dimeric product from 2,2-dimethylpropanethial (LXXIII) has not been obtained.[72]

TA are reactive in various reactions with nucleophiles. The aminolysis of the intermediate thioformaldehyde is an important step in the reactions of methanesulphenyl halides with secondary amines.[7]

$$[H{-}CH{=}S] \xrightarrow{R_2NH} (R_2N)_2CH_2 + H_2S.$$

Benzoylthioformaldehyde and morpholine, formed on decomposition of the sulphenamide (LXXXI), immediately react to form the *gem*-aminothiol (LXXXII).[74]

$$Ph{-}CO{-}CH_2{-}S{-}N(CH_2)_4 \rightarrow \underset{(LXXXI)}{Ph{-}CO{-}CH{=}S} +$$

$$+ HN(CH_2)_4 \rightarrow Ph{-}CO{-}\underset{\underset{N(CH_2)_4}{|}}{\overset{\overset{SH}{|}}{CH}} \quad .$$

(LXXXII)

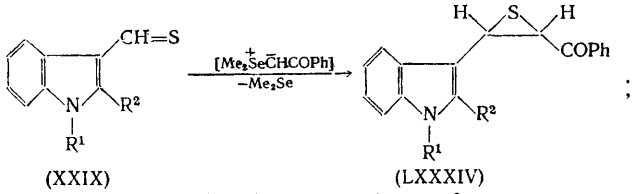
The *gem*-aminothiols (LXXXIII) are readily formed from thioformylimines and ammonia.[74]

$$R{-}\underset{\underset{NH}{\|}}{C}{-}CH{=}S \xrightarrow{NH_3} R{-}\underset{\underset{NH}{\|}}{C}{-}\underset{\underset{NH_2}{|}}{\overset{\overset{SH}{|}}{CH}}$$

(LXXXIII)

Like thioketones, thioaldehydes give rise to hydrazones and semicarbazones.[32,38]

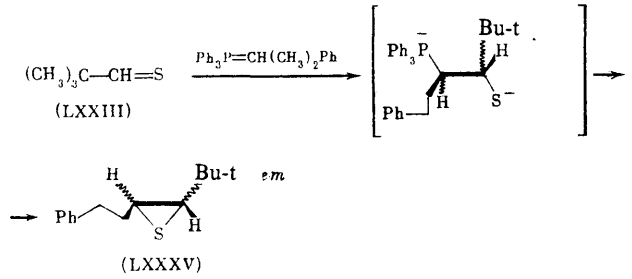
Ylides behave as nucleophiles in reactions with thiocarbonyl compounds.[11] The interaction of 3-thioformylindoles (XXIX) with dimethylselenonium benzoylmethylide takes place readily in solution in DMF at 0 °C and leads to 3-benzoyl-2-indolythiirans (LXXXIV).[75]



(XXIX) (LXXXIV)

$R^1 = R^2 = Me$ (a); $R^1 = R^2 = H$ (b); $R^1 = H$, $R^2 = Me$ (c).

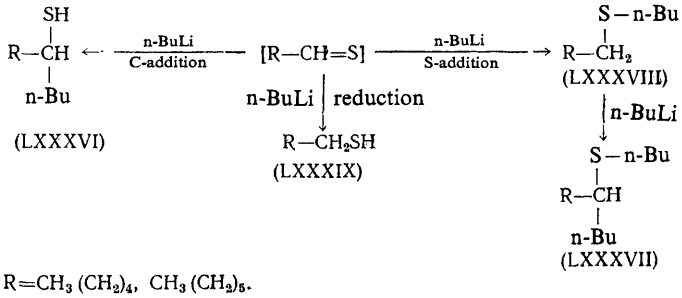
2,2-Dimethylpropanethial (LXXIII) reacts with (3-phenylpropylidene)triphenylphosphorane to form the thiiran (LXXXV).[72]



(LXXXV)

The reactions of thioketones with organometallic compounds proceed via two competing pathways—the usual nucleophilic and/or thiophilic addition.[11]

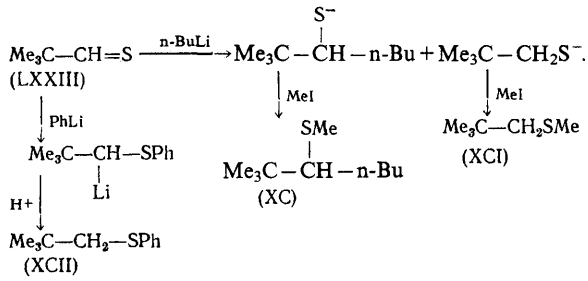
In their study of the interaction of TA with n-butyllithium, Wilson and co-workers observed four types of reactions: C-addition, S-addition, double addition, and reduction.[76] The ratios of the products depend on the structure of the substrate, the solvent, and temperature. For example, $CH_3(CH_2)_4{-}CH{=}S$ reacts with a fourfold excess of n-BuLi in ether at 25 °C to form 73% of the thiol (LXXXVI), 19% of the sulphide (LXXXVII), and insignificant amounts (3 and 4%) of compounds (LXXXVIII) and (LXXXIX). At 0 °C, the yield of compound (LXXXVI) falls to 17%, while in tetrahydrofuran it falls to 2%.



(LXXXVI) (LXXXIX) (LXXXVII)

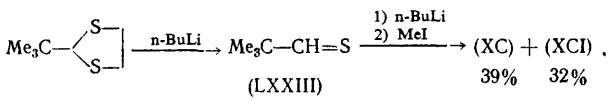
$R = CH_3(CH_2)_4$, $CH_3(CH_2)_5$.

2,2-Dimethylpropanethial (LXXIII) reacts in ether with n-BuLi to form an adduct via the carbon atom and a reduction product.[72] The formation of compounds (XC) (70%) and (XCI) (17%) after the addition of methyl iodide to the reaction mixture is convincing proof of the operation of the reaction pathways illustrated in the scheme.



(LXXIII) (XC) (XCI) (XCII)

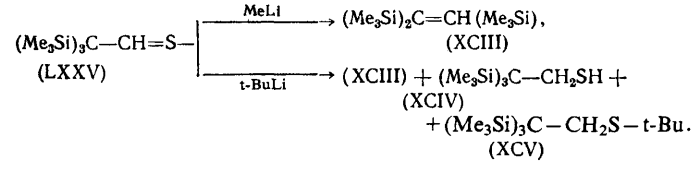
The reaction of 2-t-butyl-1,3-dithiolan with n-BuLi has been achieved[72] by Wilson's method.[76] The formation of the products (XC) and (XCI) in both cases indicates the involvement of the same TA (LXXIII) in the reactions.



(LXXIII) 39% 32%

The TA (LXXIII) reacts with phenyllithium via a thiophilic mechanism with formation of neopentyl phenyl sulphide (XCII) (30%).[65]

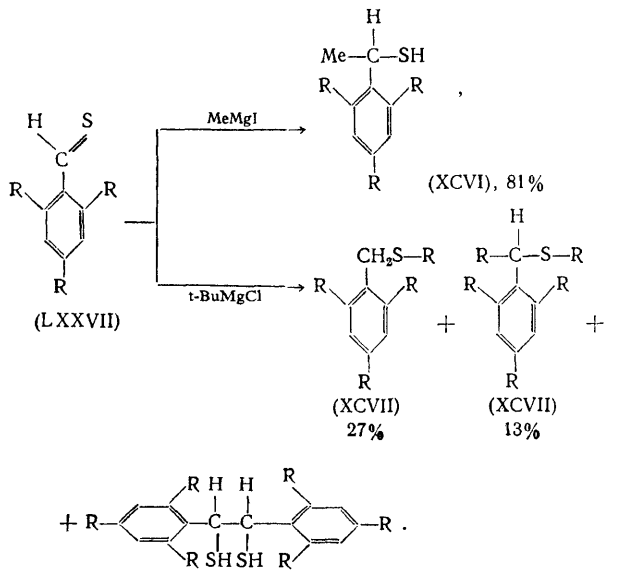
Treatment of tris(trimethylsilyl)ethanethial (LXXV) with methyl- or t-butyl-lithium leads to the alkene (XCIII) in 79 and 34% yields respectively.[17] The thiol (XCIV) (35%) and the sulphide (XCV) (10%) are also formed in the latter case.



(LXXV) (XCIII) (XCIV) (XCV)

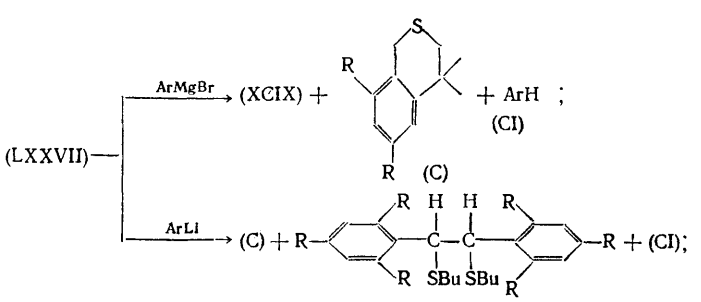
The TA (LXXV) react with a Grignard reagent similarly but at a much lower rate.[17]

Interesting results have been obtained in the study of the reactions of the stable (2,4,6-tri-t-butyl)thiobenzaldehyde (LXXVII) with Grignard and organolithium reagents.[77] The interaction of the thial (LXXVII) with methylmagnesium iodide affords the thiol (XCVI), while the reaction with t-butylmagnesium chloride gives rise to three products: the sulphides (XCVII) and (XCVIII) and the α-dithiol (XCIX).



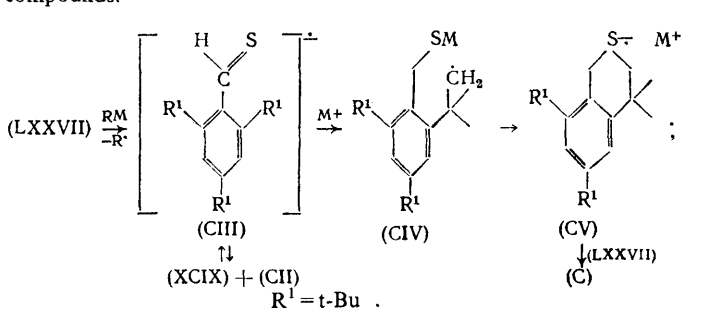
R = t-Bu (XCIX), 31%

In the reactions with the very bulky 2,4,6-tri-t-butyl-substituted phenylmagnesium bromide or phenyllithium, the adducts formed via the carbon or sulphur atom were not detected.[77]



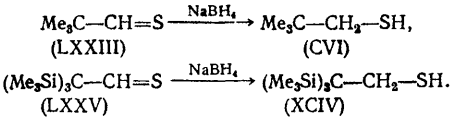
Ar = 2,4,6-(t-Bu)$_3$C$_6$H$_2$; R = t-Bu.

In order to account for the course of the reactions investigated, the authors resorted to the one-electron transfer mechanism[77] used at one time for the reactions of thioketones with organometallic compounds.[11]



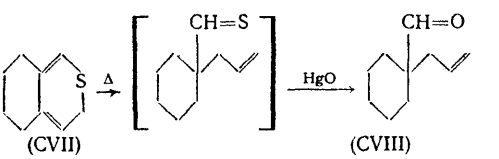
The key intermediate in the proposed scheme is the radical-anion (CIII). Its transformation via the pathway (CIII) → (CIV) → (CV) leads to compound (C), while its dimerisation affords the products (XCIX) and (CII). One should note especially that this is the first example of the dimerisation of thioketyl radicals and the first observation of the generation of a radical-anion from a TA.[77]

Like thioketones, thioaldehydes are readily reduced by the usual reductants to the corresponding thiols. Thus, treatment of 2,2-dimethylpropanethial (LXXIII) with sodium tetrahydroborate gives rise to the neopentanethiol (CVI);[65,72] tris(trimethylsilyl)-ethanethial (LXXV) is transformed quantitatively into the thiol (XCIV).[17] The reactions of TA with alkyl(aryl)lithium reagents or Grignard reagents are accompanied by reduction.[17,65,72,77]

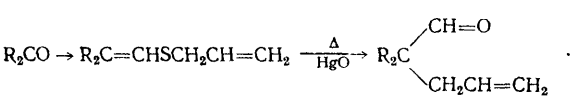


The tendency of TA to oxidise in the presence of atmospheric oxygen has been noted.[39–42] Even the extremely stable t-butyl-substituted thiobenzaldehyde (LXXVII) is converted into the corresponding aldehyde on treatment with oxygen.[16]

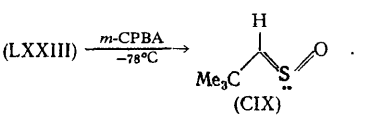
The oxidation of TA *in situ* is of interest for the determination of the reaction mechanism and for preparative purposes. Thus, whereas simple heating of the sulphide (CVII) at 160–180 °C leads to polymeric products, in the presence of red mercury oxide the aldehyde (CVIII) has been obtained in 82% yield.[78]



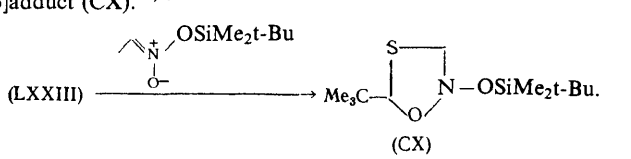
This procedure expands significantly the applicability of the thio-Claisen rearrangement and permits its employment for the synthesis of unsaturated aldehydes from carbonyl compounds.[78]



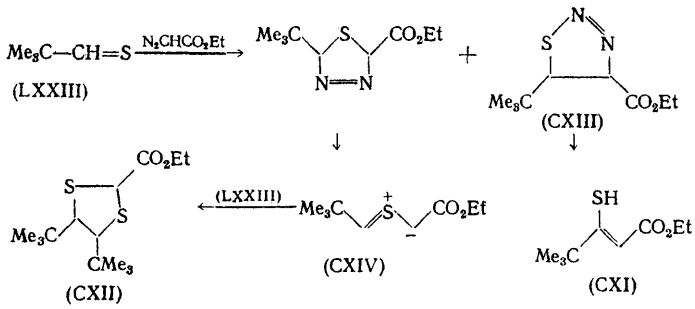
The oxidation of the TA (LXXIII) with *m*-chloroperbenzoic acid (*m*-CPBA) at a low temperature leads to the sulphine (CIX).[65,72]



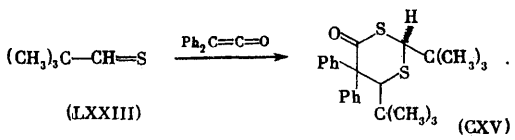
A distinctive feature of thiocarbonyl compounds is their ability to enter into 1,3-dipolar cycloaddition reactions with formation of valuable heterocyclic compounds.[11] In TA, this property is particularly marked and it has been used successfully to trap TA *in situ*.[22,72] Thus, 2,2-dimethylpropanethial (LXXIII) reacts instantaneously with the nitronate ester and affords the cyclic [2 + 3]adduct (CX).[65,72]



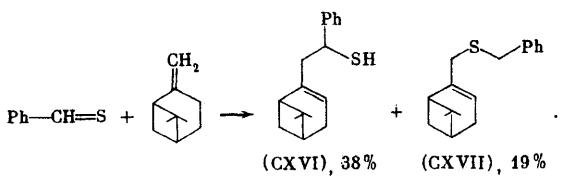
Thiocarbonyl compounds react with diazoalkanes to form the regioisomeric cyclic [2+3]adducts.[11] After the interaction of 2,2-dimethylpropanethial (LXXIII) with ethyl diazoacetate, the thiol (CXI) and an inseparable mixture of the diastereoisomers of compound (CXII) were obtained in equal amounts. The formation of compound (CXI) has been explained by the S–N heterolysis of the thiadiazoline (CXIII) formed initially and subsequent hydride transfer. The dithiolan (CXII) is formed via the thiocarbonyl ylide (CXIV).[65]



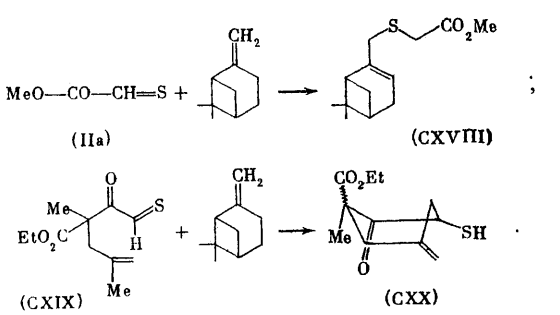
The reaction of the TA (LXXIII) with diphenylketen affords a mixture of 2:1 cyclic adducts (CXV) in a moderate yield. The reaction with dimethylketen or 1,1-diphenylallene do not occur.[72]



Thiobenzaldehyde is capable of participating as a 2π-component in the reaction involving addition to the double bond of β-pinene.[55] The formation of two adducts (CXVI) and (CXVII) is due to the different modes of addition.



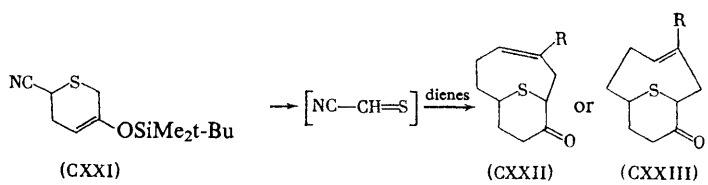
The photochemically generated TA (IIa) reacts with β-pinene at 20 °C to form the sulphide (CXVIII), while the TA (CXIX) affords the substituted cyclohexanone (CXX).[79]



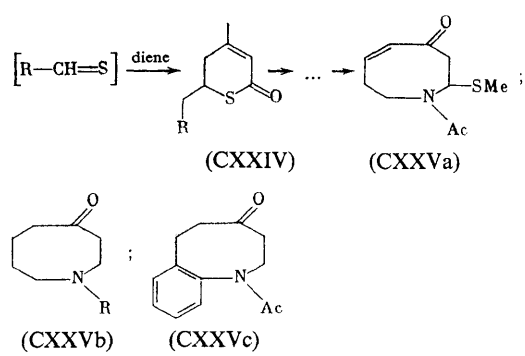
The reactions involving the "ene-inclusion" of TA are evidently promising for the synthesis of cyclic structures under mild conditions. The reactions of TA having electron donor or electron acceptor substituents, generated in different ways, with a wide variety of dienes were examined in detail in Sections III–V. Here it is useful to note studies specially devoted to the cycloaddition reactions of TA.

The characteristic features of the behaviour of thiobenzaldehyde, thioacetaldehyde, and certain other TA in reactions with 2,3-dimethylbutadiene (2,3-DMBD), anthracene, and 9,10-dimethylanthracene have been investigated in detail.[55] It has been found that benzene and toluene are the most suitable solvents, while DMF reduce the yield of the adduct. Appreciable attention has been devoted to the regiochemistry of the cycloaddition reactions and to its relation with the nature of the substituent in TA.[22,61] The dihydrothiopyrans obtained from TA in accordance with Diels–Alder principle can play an important role in the synthesis of natural products, especially of the juvenile hormone, erythronolides, analogues of zygosporin, etc.[61]

The adduct of cyanothioformaldehyde with 2-(t-butyldimethylsiloxy)buta-1,3-diene (CXXI) served as the starting compound for the recently developed synthesis of sulphur-containing bridged cyclodecenones (CXXII) and (CXXIII), which are otherwise difficult to obtain.[80]

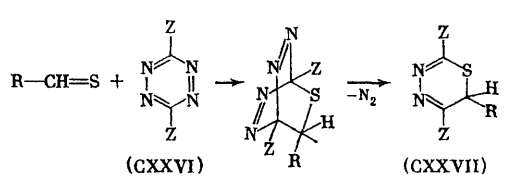


Several methods of synthesis of azocine derivatives (CXXV) have been developed from nitrogen-containing cyclic adducts (CXXIV).[81]



R = $NHCO_2t$-Bu, CH_2NHCO_2t-Bu, $CH_2N(Me)CO_2t$-Bu.

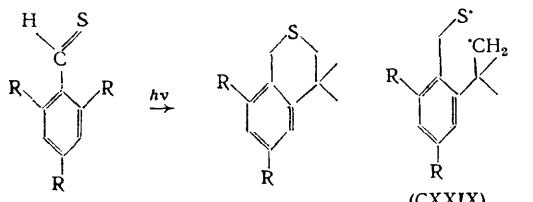
TA with electron-dontaing substituents—thioformates, thioformamides, and thiobenzaldehyde—behave as heterodienophiles in the reaction with tetrazine (CXXVI).[82] The thiadiazones (CXXVII), obtained as a result of the [4+2]cycloaddition, can lose the sulphur atom and can be converted into pharmacologically interesting pyrazoles.



R = OEt, OPr, $N(CH_3)_2$, $N(CH_2)_4O$, $N(CH_2)_5$, Ph.

The unusual properties of the excited thiocarbonyl functional group have been responsible for the development of the photochemistry of thiocarbonyl compounds.[11] The irradiation of a

benzene solution of (2,4,6-tri-t-butyl)thiobenzaldehyde (LXXVII) solution by light from a mercury or sodium lamp ($\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ excitation respectively) leads to the benzothiolan derivative (CX) in 91 or 96% yield respectively.[83] The photochemical formation of the heterocycle (CX) is in this instance unexpected, since the known photochemical reactions of aromatic thioketone containing δ-hydrogen atoms afford cyclopentanethiol derivatives.[11] The occurrence of δ-cyclisation via $n \rightarrow \pi^*$ excitation is also of special interest; in aromatic thioketones, this process takes place via the $S_2(\pi \rightarrow \pi^*)$ state.[11]

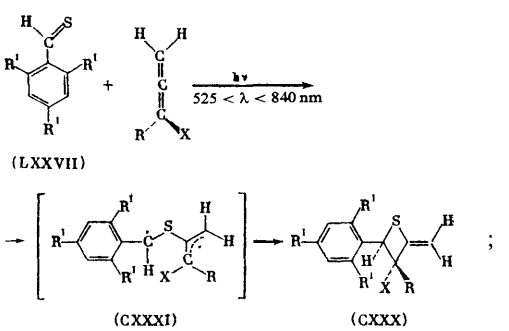


(LXXVII) (C) (CXXIX)

R = t-Bu.

A choice between the possible mechanisms of this reaction—the concerted [2+2]reaction or radical cyclisation via the biradical (CXXIX)—has not so far been made.[83]

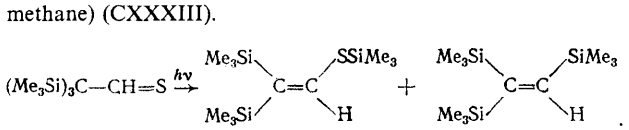
The photochemical reaction of the TA (LXXVII) with unsaturated cumulated systems has been investigated.[84] Irradiation of the TA (LXXVII) jointly with alkoxy-, alkylthio-, or phenylallenes led to a single stereoisomer, namely the thietan (CXXX), via the intermediate biradical (CXXXI).[84]



(LXXVII) (CXXXI) (CXXX)

R = t-Bu.

The photolysis of tris(trimethylsilyl)ethanethial (LXXV) affords two compounds—the substituted sulphide (CXXXII) and the substituted ethene (XCIII).[17] Irradiation of the corresponding aldehyde under analogous conditions led to tris(trimethylsilylmethane) (CXXXIII).

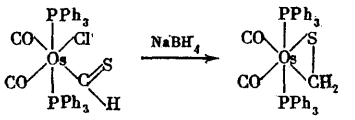


(LXXV) (CXXXII), 66% (XCIII), 33%

$(Me_3Si)_3C-CH=O \xrightarrow{h\nu} (Me_3Si)_3CH.$ (CXXXIII)

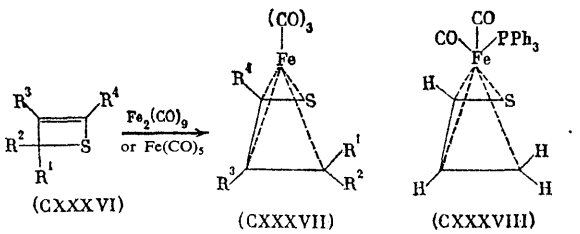
The formation of compound (CXXXII) from the TA (LXXV) via the 1,2-shift of the $SiMe_3$ group from the α-position to the thiocarbonyl carbon atom with the accompanying desulphurisation constitutes a new type of photochemical reaction of thiocarbonyl compounds.[17]

The ability of thioformyl compounds to form complexes with transition metals has been used successfully to detect short-lived TA. The first stable crystalline complex (CXXXIV) of thioformaldehyde has been obtained by the reaction of the unstable thioformyl derivative (CXXXV) with sodium tetrahydroborate.[85]



(CXXXV) (CXXXVI)

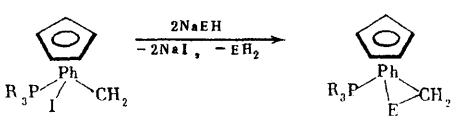
Complexes of the unstable thioacrolein (CXXXVII) have been obtained as red or orange crystals or oils by heating the thiets (CXXXVI) with iron nonacarbonyl or by treating them with iron pentacarbonyl and irradiating.[86] The structure of the complexes (CXXXVII) was established by the X-ray diffraction of the triphenylphosphine derivative (CXXXVIII) formed from compound (CXXXVII) by substituting one of the carbonyl groups by the PPh_3 ligand. The ^1H NMR spectra of the complexes (CXXXVII) have been compared with the spectrum of the molybdenum complex of acrolein.[86]



(CXXXVI) (CXXXVII) (CXXXVIII)

Rhodium complexes of thioformaldehyde and its chalcogen analogues have been obtained recently.[87] The first data are already available on selenoformaldehyde,[88] while telluroformaldehyde is so far unknown.

Compound (CXXXIX) reacts at room temperature in tetrahydrofuran with sodium hydrogen sulphide to form the thioformaldehyde complex (CXLa) in 50% yield. Treatment with NaSeH or NaTeH afforded similarly the complexes of selenoformaldehyde (CXLb) and telluroformaldehyde (CXLc).[87]



(CXXXIX) (CXL)

E = S (a), Se (b), Te (c).

- - - o0o - - -

The fluorine-containing aliphatic TA (CXLI) are formed in the reactions of trialkyl phosphorothionates with ω-hydroperfluoroaldehydes (CXLII) on heating the reactants at 80 °C for 3 h.[89] The ^1H NMR spectrum of the reaction mixture shows a signal at δ = 10.35 p.p.m., which refers to the proton of the monomeric form of the TA (CXLIa), whose content is about 10%. The TA (CXLI) persist in solution at 20 °C for a long time. They react with 2,3-DMBD and isoprene to form the corresponding cyclic adducts.

$$H(CF_2)_nCH=O + (RO)_3P=S \rightarrow [H(CF_2)_nCH=S] + (RO)_3P=O,$$

(CXLII) (CXLI)

n = 4 (a), 6 (b).

A selective route to the synthesis of the unstable thiopropynal (CXLIII) involving the vacuum pyrolysis of dipropargyl sulphide has been found.[90]

$$CH{\equiv}CCH_2SCH_2C{\equiv}CH \xrightarrow[-CH_2{=}C{=}CH_2]{750-950\,^{\circ}C,\ 10^{-3}\ torr} CH{\equiv}C{-}CH{=}S.$$

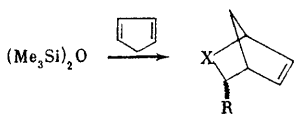
(CXLIII)

The ionisation potential of the TA (CXLIII) is 8.92 ± 0.05 eV and agrees well with the ionisation potentials of other thiocarbonyl compounds.[90] The C=S bond stretching vibration frequency in the IR spectrum of the TA (CXLIII) recorded in an argon matrix at 12 K is about 1100 cm^{-1}.[91]

A new simple method for the direct conversion of aldehydes into thio- and seleno-aldehydes with the aid of bis(trimethylsilyl)sulphide or selenide (CXLIV) in the presence of a catalytic amount n-butyllithium has been proposed.[92]

$$R{-}CH{=}O + (Me_3Si)_2X \xrightarrow[THF]{n\text{-}BuLi} \left[R{-}CH{=}S\right] +$$

(CXLIV)



X = S, Se
R = Ph, 2-thienyl, n-Pr, t-Bu.

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