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THIOFORMYL COMPOUNDS. SYNTHESIS, STRUCTURE AND PROPERTIES

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Available data concerning the synthesis of thioformyl compounds such as thioaldehydes, *O*-alkyl thioformates, alkyl dithioformates, thioformamides, thioformyl halides and thioformylphosphine oxides, have been summarized and systematized in the present review. The importance of thioformyl compounds as intermediates, synthons and reagents in fine organic synthesis is discussed.

Key words: thioaldehydes, *O*-alkyl thioformates, alkyl dithioformates, thioformamides, thioformyl halides, thioformylphosphine oxides

CONTENTS

1. INTRODUCTION

Since the beginning of the last century the long known aldehydes have been widely used in the synthesis of acetals, oximes, hydrazones, carboxylic acids, amines, alcohols, diols, etc. as well as in the manufacture of polymers, drugs, perfumery items, dyes, pesticides, explosives, etc.[1] However, their thio analogs, such as thioaldehydes, as well as other thioformyl compounds, thio- and dithioformic acid derivatives (alkyl thio- and alkyl dithioformates, thioformamides, thioformyl halides, thioformylphosphine oxides, etc., which contain a heteroatom–thioformyl bond) have long been neglected. This was due to the historically established opinion that thioformyl compounds are highly unstable and, consequently, that great care is needed for their synthesis and investigation.

The first information concerning stable thioaldehydes[2,3] initiated the development of the chemistry of compounds of this type, and allowed the synthesis of a number of thermodynamically stable thioaldehydes which are stabilized by electronic and steric factors. The elaboration of new technologies and chemical methods has revived interest in the generation of thioformaldehyde and its *C*-alkyl, -alkenyl, -aryl, -acyl, -alkoxycarbonyl and -cyano derivatives. Apart from the thioformamides ($R^1R^2N-CH=S$), many other heterofunctional thioformyl compounds such as RO–CH=S, RS–CH=S, Hal–CH=S, $R_2P(=O)-CH=S$ are known now. The investigation of these compounds was facilitated by the possibility to "conserve" them as adducts with appropriate dienes. The life span of unstable thioformyl compounds depending on temperature and medium, and the spectroscopic and mass spectrometric characteristics of these compounds as well as their synthetic potential and importance as intermediates and synthons in organic synthesis have been established. Thus, 5-thioformyldipyrrylmethane has been used as a key compound in a total synthesis of chlorophyll.[2] By the use of thioaldehydes mercaptoazetidinone derivatives, the penicillins, have been transformed to biosynthetically important peptides;[4,5] thioformyl derivatives of heterocyclic bases are employed in the manufacture of photosensitive materials.[3]

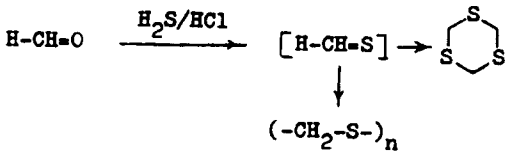
In the course of its development the chemistry of thioaldehydes has been given much consideration.[6-14] The present review summarizes available data concerning the synthesis, structure and properties of both thioaldehydes and thioformyl substituted compounds.

2. SYNTHESIS OF THIOFORMYL COMPOUNDS

2.1. Thioformaldehyde and Thioacetaldehyde

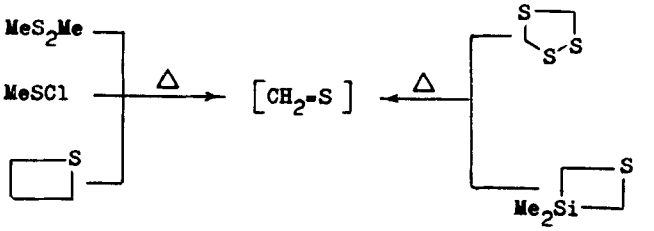
Thioformaldehyde, the simplest thioaldehyde, is an extremely unstable compound. Its half-life is ~6 min at a pressure of 0.01–0.5 Pa.[11] One of the previous (1868) synthetic routes to thioformaldehyde is based on the nowadays classical reaction of formaldehyde with hydrogen sulfide in the presence of an acid catalyst.[6]

1,3,5-Trithiane (trithioformaldehyde) and polymethylene sulfides, the products of thioformaldehyde conversion, isolated depending on the reaction conditions, served as indirect evidence for the initial formation of thioformaldehyde. Later on the development of effective synthetic routes to thioformaldehyde in combination with modern physico-chemical methods of investigation established unambiguously the existence of monomeric thioformaldehyde.[7,8,10] The use of flash-vacuum thermolysis with its short



Scheme 1

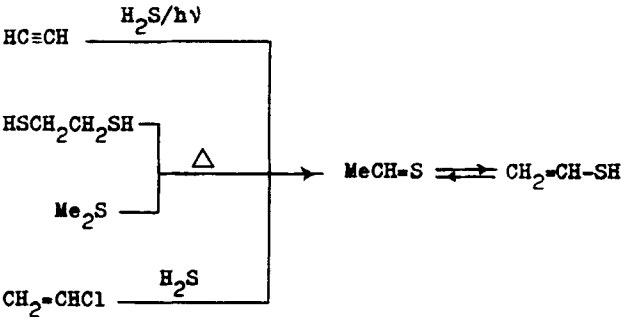
reaction time at reduced pressure, and analysis of the pyrolysis products in the gas phase present the most impressive achievements in this field. Monomeric thioformaldehyde was obtained by thermolysis of different sulfur compounds such as dimethyl sulfide, methanesulfenyl chloride, thietane, 1,2,4-trithiolane,[10,15] and 3,3-dimethyl-3-silathietane.[16]

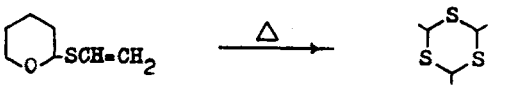


Scheme 2

It is rather interesting that thioformaldehyde has been observed in space.[10] The existence of these highly reactive molecules for a long time under the conditions of interstellar vacuum and cold is due to the large intermolecular distances. This accounts for the stability of individual molecules of thioformaldehyde which normally are very prone to oligo- and polymerization.

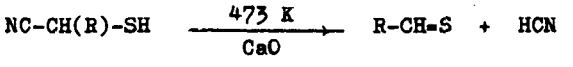
Thioacetaldehyde, the nearest thioformaldehyde analog, is also very unstable. It can be generated in a number of ways such as photochemical addition of hydrogen sulfide to acetylene,[10] thermolysis of 1,2-ethanedithiol[10] and dimethyl sulfide,[17] as well as reaction of vinyl chloride with excess hydrogen sulfide.[17] Thioacetaldehyde can exist in a tautomeric ethenethiol form. In the thermal decomposition of 2-(vinylthio)tetrahydropyran isomeric α- and β-trithioacetaldehydes were isolated.[18]





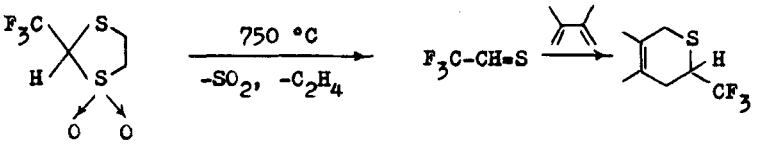
Scheme 3

Mild thermolysis of thiocyanohydrins (Scheme 4) which are a kind of reactive thioaldehyde "carriers", looks rather promising for the preparation of thioacetaldehyde and thioformaldehyde.[19]



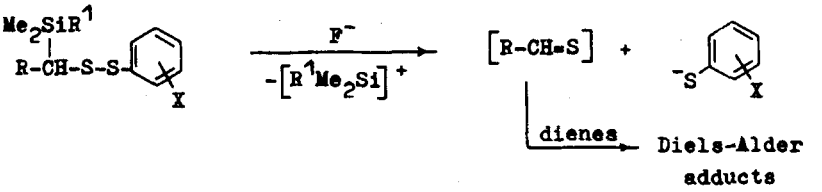
Scheme 4

Recently the highly reactive trifluorothioacetaldehyde was synthesized by thermolysis of 2-(trifluoromethyl)-1,3-dithiolane 1,1-dioxide (Scheme 5).[20] The structure of this compound was proven by spectroscopy and by preparation of Diels-Alder adducts such as that with 2,3-dimethyl-1,3-butadiene. In the solid state at −196 °C this dark-pink thioaldehyde is converted in several minutes to a colorless plastic mass.



Scheme 5

An elegant general route to thioformyl compounds from [α-(dimethylorganylsilyl)-organylmethyl] (aryl) disulfides (Scheme 6) has been suggested.[21] Under the action of fluoride anions ready elimination takes place to give the corresponding thioaldehyde and arenethiolate anion.



Scheme 6

The course of this elimination is determined by the stability of the arenethiolate leaving group. 2,4,6-Trichlorophenyl disulfides (X = 2,4,6-Cl_3) are very unstable. 2-Nitro and

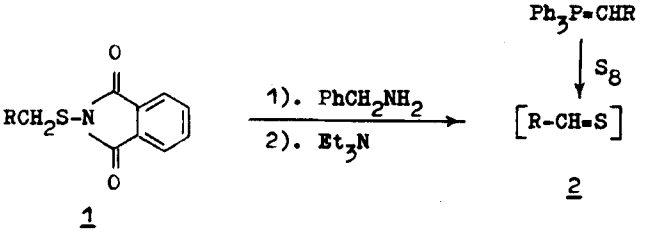
4-chloro derivatives (X = 2-NO_2 or 4-Cl) are rather reactive whereas unsubstituted disulfides (X = H) undergo cleavage only when heated. The fragmentation-elimination rate is also affected by the activity of the fluoride ion source. In the presence of 18-crown ether at 20 °C CsF or KF generate thioaldehydes very slowly while tetrabutylammonium fluoride ($Bu_4N^+F^-$) in tetrahydrofuran acts fast in the temperature range from 0 to −78 °C.

2.2. Acyl-, Alkoxycarbonyl-, and Cyanothioformaldehydes

Acyl- and alkoxycarbonyl thioformaldehydes (R—CO—CH=S, RO—CO—CH=S) are a special variety of thiocarbonyl derivatives in which the CH=S group is attached to the electron-acceptor carbonyl group. No compounds of this type have been isolated in their monomeric form. However, their intermediate formation is employed for the synthesis of cycloadducts.[22-24]

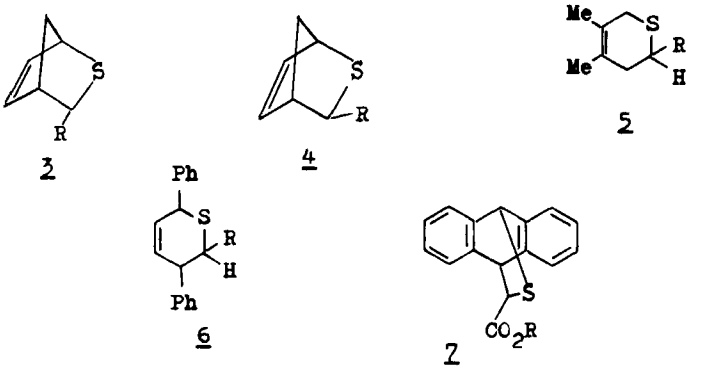
For the synthesis of R—CO—CH=S where R = Ph, PhNH use is made of the Bunte salts RCH_2SSO_3Na[22] (see 2.4.), whereas for the preparation of thials with R = 4-BrC_6H_4 the corresponding α-sulfonyl disulfide 4-$BrC_6H_4COCH_2SSCH(SO_2Tol)COC_6H_4Br$-4 has been used[23] (see 2.4.). Ph—CO—CH=S can also be obtained by photolysis of diphenacyl sulfide.[24]

The first data concerning methoxycarbonylthioformaldehyde were reported in.[25] In a study of the reaction of *N*-(methoxycarbonylmethylthio)phthalimide **1** with benzylamine at room temperature the thioxoamide $PhCH_2NHCOCSNHCH_2Ph$ was isolated. Methoxycarbonylthioformaldehyde **2a** was assumed to be the reaction intermediate.



1 2

R = MeO-CO (a), EtO-CO (b), t-BuO-CO (c), Ph_2HCO-CO (d)



3 4 5 6 7

Scheme 7

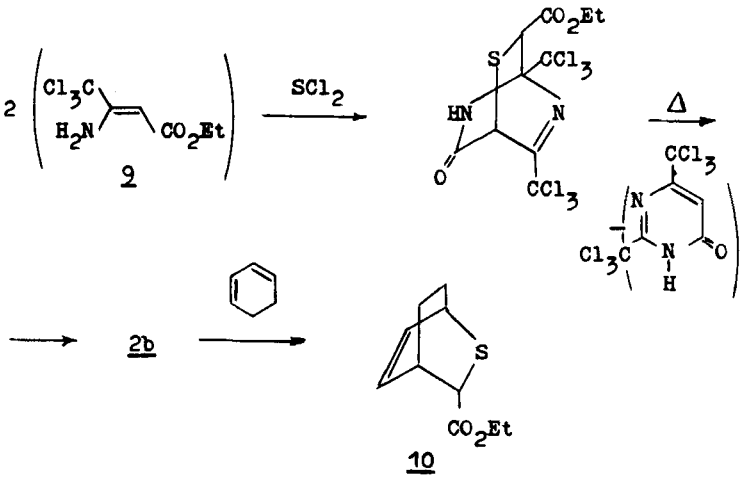
Reaction of the phthalimide derivatives **1a, b, c, d** with triethylamine in the presence of conjugated dienes leads *in situ* to the corresponding alkoxycarbonylthioformaldehydes **2a, b, c, d**.[26,27] The *endo*- (**3**) and the *exo*-adduct **4**, respectively, of cyclopentadiene and ethoxycarbonylthioformaldehyde **2b** dissociate at 111 °C which allows thioaldehyde **2b** transfer to other conjugated dienes. Thus, a single adduct **5** was obtained in 82% yield on heating a "kinetic mixture" of **3** and **4** with 2,3-dimethyl-1,3-butadiene in toluene under nitrogen in a sealed tube at 120 °C over 21 h. When use is made of *trans,trans*-1,4-diphenyl-1,3-butadiene which reacts with maleic anhydride with 1/114 the rate of 2,3-dimethyl-1,3-butadiene,[28] boiling of a mixture of **3** and **4** in xylene gives readily the adduct **6** (a mixture of stereoisomers). Thus, the thermal dissociation of the adducts **3** and **4** may be of preparative use as a source of ethoxycarbonylthioformaldehyde **2b**. The retro-Diels-Alder reaction of the anthracene adduct **7** is employed for the preparation of the thioaldehyde **2b**.[27]

Bunte salts[22] and α-sulfonyl disulfides[23] are excellent sources for the generation of alkoxycarbonylthioformaldehydes **2** and acyl derivatives.

1,2-Elimination of hydrogen chloride from ethoxycarbonylmethanesulfenyl chloride $EtO-CO-CH_2SCl$ upon treatment with triethylamine leads to ethoxycarbonylthioformaldehyde **2b**[29] which can be trapped with various conjugated dienes. The yield of the [2 + 4]-cycloaddition products is rather high in this case. However, the reaction of **2b** with 1,3-cyclohexadiene involves the formation of other products, possibly due to a competing attack of the sulfenyl chloride on the diene.[29]

Another convenient method for the generation of the alkoxy derivatives **2** is based on the reaction of the corresponding phosphonium ylides with elemental sulfur in boiling toluene.[30]

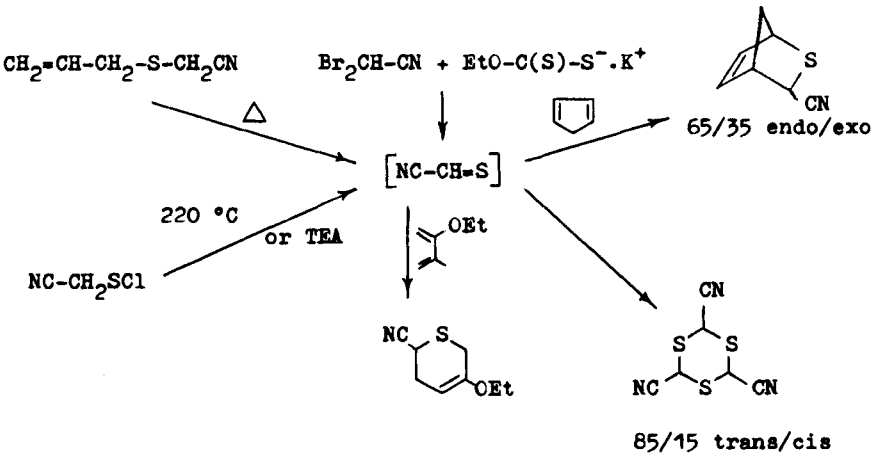
As a new precursor of ethoxycarbonylthioformaldehyde **2b** it was recommended to use the diazathiabicyclooctene derivative **8**,[31] obtained in 34% yield by the reaction of ethyl 3-amino-4,4,4-trichlorocrotonate **9** with SCl_2. Heating a solution of **8** in chlorobenzene at 80 °C induces a retro-Diels-Alder reaction which forms the thial **2b**, trapped previously as the cycloadducts **5** or **10** (in yields of 48 and 85%, respectively).



Scheme 8

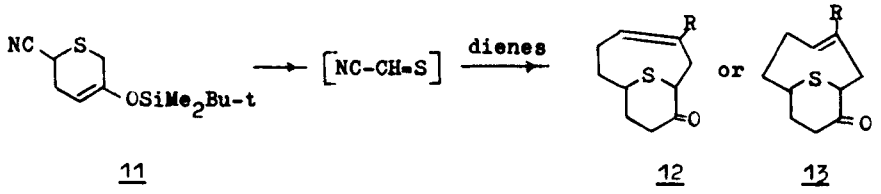
There is some information[29] concerning the synthesis of *n*-butoxycarbonylthioformaldehyde **2c** from *n*-butyl glyoxalate and tetraphosphorus decasulfide and its subsequent reactions with dienes.

Cyanothioformaldehyde was first prepared by treatment of dibromoacetonitrile with potassium *O*-ethyl dithiocarbonate and characterized as the cycloadduct with 2-ethoxy-1,3-butadiene.[32] The generation of monomeric thioformyl cyanide was performed by flash-vacuum thermolysis (10^{-5} mbar, 800 °C) of allyl cyanomethyl sulfide.[33] The lifetime of this thioformyl compound determined by microwave spectroscopy is 4.5 sec under 10^{-2} mbar, which is much shorter than that of formyl cyanide, 29 min under the same conditions. Thioformyl cyanide has also been prepared by dehydrochlorination of cyanomethanesulfenyl chloride with triethylamine in benzene at −30 °C or with potassium carbonate at 200 °C.[33] In the presence of 1,3-cyclopentadiene the corresponding adduct could be isolated.



Scheme 9

The adduct of cyanothioformaldehyde with 2-(*t*-butyldimethylsiloxy)-1,3-butadiene **11** provides the starting material for the recently developed synthesis of the otherwise difficultly accessible sulfur-containing bridge cyclodecenones **12** and **13**.[34]



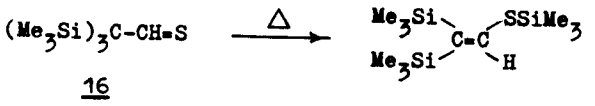
11 12 13

Scheme 10

2.3. Sterically Stabilized Thioaldehydes (see Table 1, Nos. 1–3)

For over 100 years all attempts to obtain monomeric aliphatic thioaldehydes were unsuccessful.[6,11] Only as late as 1983 the first relatively stable aliphatic thioaldehyde 2,2-dimethylpropanethial **14**, could be prepared[35] with phenacyl neopentyl sulfide **15** as starting material. The photolysis of the latter in benzene in the presence of 5% 2,3-dimethylbutadiene leads to the polymer [*t*-BuCH–S–]$_n$ in 60% yield. When heated in vacuum (> 250 °C) this polymer forms the thial **14**, the lifetime of which in chloroform, benzene, methylene chloride or ether at 20 °C reaches 16 h. The relative stability of **14**, due to its bulky *t*-butyl group, decreases in the presence of acid or base. Thus its lifetime in a chloroform/ethanol mixture (15 min) is reduced to 5 min when triethylamine is added and to a few seconds in the presence of traces of HCl. Monomeric dimethylpropanethial **14** and its solutions are rather stable in air.

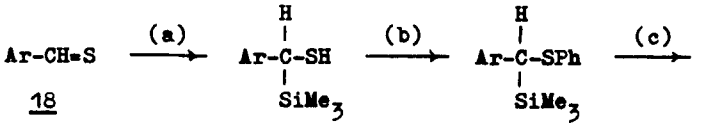
Recently the first stable aliphatic Si-functional thioaldehyde, tris-(trimethylsilyl)-ethanethial **16**, was reported.[36] It is synthesized by reaction of tris(trimethylsilyl)methyllithium **17** with *O*-ethyl thioformate in THF carried out first at −78 °C (10 min) and then at 20 °C (1.5 h). The thial **16** is a pinky-red crystalline compound which can be kept in a refrigerator for a long time without changing its properties and is stable for a week when stored at 20 °C in air. This compound can be purified by column chromatography on silica gel or by freezing from pentane at −78 °C. At 80 °C **16** undergoes quantitative rearrangement to 1,1-bis-(trimethylsilyl)-2-[(trimethylsilyl)thio]ethene.

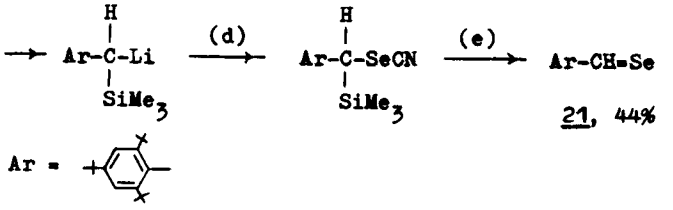


Scheme 11

2,4,6-(Tris-*t*-butyl)thiobenzaldehyde **18**, the first stable substituted thiobenzaldehyde, was obtained by reaction of 2,4,6-tris-*t*-butylphenyllithium with *O*-ethyl thioformate in THF, followed by GLC purification.[37] An alternative synthesis of **18** is based on the reaction of hydrazone **20** with sulfur dichloride in the presence of triethylamine.[37] The thial **18** is a remarkably stable crystalline compound of purple color, which remains unchanged over a year when stored at 20 °C or for two weeks in boiling benzene protected from air oxygen. Unsubstituted thiobenzaldehyde polymerizes already at −160 °C.[38]

It was possible to synthesize from **18** its selenium analog, 2,4,6-(tris-*t*-butyl)seleno-benzaldehyde **21**, the first stable selenoaldehyde (Scheme 12).[39]





(a) Me_3SiLi, THF-HMPA, -78 °C, 85%; (b) (i) n-BuLi, THF, -78 °C; (ii) PhI cat. $Pd(Ph_3P)_4$, PhH refl., 3 h, 98%; (c) lithium naphthalenide, -78 °C, 3.5 h; (d) (i) CuCN, 0 °C, 80 min; (ii) $(SeCN)_2$, -78 to 0 °C, 20 h, 57%; (e) n-Bu_4NF, -25 °C, CH_2Cl_2

Scheme 12

The selenoaldehyde **21**, a light-blue crystalline compound, can be kept at −15 °C for a long time; in the solid state it is stable at room temperature in air for about 7 days. In solution, however, **21** is sensitive to air oxygen and converts to the corresponding aldehyde in the temperature range −40 °C to −50 °C.

2.4. α,β-Unsaturated and Aromatic Thioaldehydes

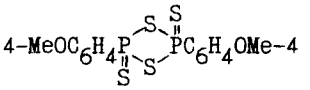
The synthetic routes to α,β-unsaturated and aromatic thioaldehydes are very diverse. At present they can be subdivided in twelve general methods.

2.4.1. Thionation of aldehydes (Table 1, Nos. 4–11) Until recently the direct transformation of a carbonyl (C=O) to a thiocarbonyl (C=S) group[11] has only been employed for the synthesis of thioaldehydes on rare occasions. For the preparation of the 3-thioformylindolizines **22** from the corresponding formyl derivatives use was made of tetraphosphorus decasulfide.[40] This led to the dimethylaminothioacrolein **23**[41] (no experimental data were reported).

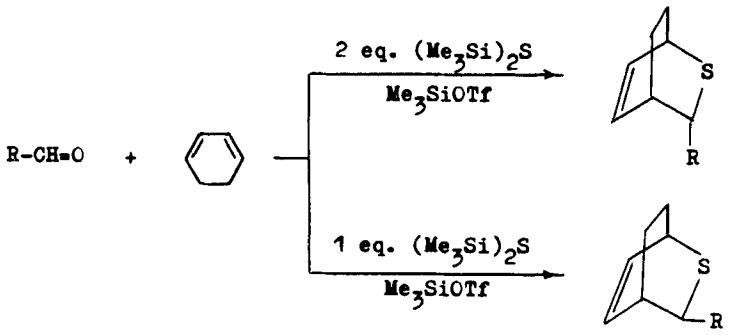
Reaction of 2-pyrrolidinobenzaldehyde with Lawesson's reagent† in boiling toluene gives first the corresponding thioaldehyde **24**.[42]

The reactions of boron sulfide with benzaldehyde and its 3-methyl and 3-nitro derivatives have been studied.[43] The latter do not react with B_2S_2, whereas in two other cases it was possible to isolate substituted 1,3,5-trithianes, the corresponding cyclic trimers of the thioaldehydes. This trimerization seems to be facilitated by thionation catalysts (HCl, I_2).

Recently a number of efficient methods for the mild thionation of aldehydes have been developed. Direct conversion of the −CH=O group to the −CH=S (−CH=Se) group is possible with bis(trimethylsilyl) sulfide $(Me_3Si)_2S$ or selenide $(Me_3Si)_2Se$, respectively, in the presence of catalysts such as *n*-butyllithium (in THF, 10–55 °C, 5–8 h[44]), $CoCl_2 \cdot 6H_2O$ (in acetonitrile[45]) or trimethylsilyl trifluoromethanesulfonate $CF_3SO_3SiMe_3$.[46]

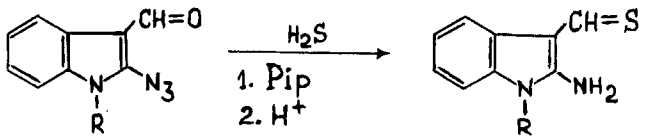
† 

Acetals undergo sulfuration in a similar way.[46] Varying the molar ratio of reagents allows the synthesis of thioaldehyde *endo*- and *exo*-diene adducts to be carried out under sterically strictly controlled conditions.[47]



Scheme 13

A non-traditional approach to a new class of stable enamine thioaldehydes derived from pyrazole and indole has been found.[48] In the first step the heterocyclic *o*-azido aldehydes **25** or **26** are reduced with hydrogen sulfide in the presence of piperidine to form the corresponding amino aldehydes. The latter, after addition of concentrated hydrochloric acid and of hydrogen sulfide, are converted to the 3-amino-4-thioformylpyrazoles **27** and the 2-amino-3-thioformylindoles **28**, respectively, (yellow and orange crystals), for example:



26 28

Scheme 14

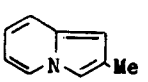
The fluoro substituted aliphatic thioaldehydes **29** are formed in the reaction of ω-H-perfluoro aldehydes **30** with trialkyl thionophosphates (80 °C, 3 h).[49] According to ^{1}H NMR data the content of monomeric **29** in the reaction mixture is ~ 10% and partial copolymerization of the aldehydes **30** with **29** is assumed. The thioaldehydes **29** remain unchanged in solution at 20 °C over 7 days. With 2,3-dimethyl-1,3-butadiene and isoprene the latter form the corresponding cycloadducts.

2.4.2. Thionation of oximes and hydrazones (Table 1, No. 12) Boiling of 6-purinecarbaldehyde oxime **31** or hydrazone **32** in thioacetic acid or its anhydride leads to *N*-acetyl-6-purinethiocarbaldehyde **33**.[50]

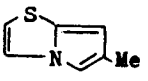
2.4.3. Hydrothiolysis of iminium salts (Table 1, Nos. 13–25) Iminium salts can effectively be used for the synthesis of thioformyl compounds. The first stable thioaldehyde, 3,4-

dimethyl-3-ethyl-4′-methoxycarbonyl-5-thioformyl-5′-(2-methoxycarbonylpropionyl)-dipyrrylmethane **34**, was obtained by Woodward[2] by reaction of *N*-ethylformiminium bromide **35** with hydrogen sulfide in the presence of sodium methoxide in a benzene/methanol mixture. Slightly later, 3-ethyl-2-(thioformylmethylene)-1,3-benzothiazole **37** was synthesized in good yield by reaction of the salt **36** with sodium hydrosulfide in methanol.[3]

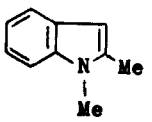
In 1966 first attempts were made to synthesize stable thioaldehydes from 2-methylindolizine **38**, 6-methylpyrrolo[2,1-*b*]thiazole **39** and 1,2-dimethylindole **40**.[51] It was



38



39



40

suggested that the thioformyl group-nitrogen atom conjugation could lead to mesomeric stabilization of the corresponding thioaldehydes. A new version of the Vilsmeier-Haak reaction was used for this synthesis.[51] According to this procedure, the Vilsmeier salts **41–43**, formed by reaction of the starting materials **38–40** with phosphoryl chloride in DMF, are treated *in situ* with aqueous sodium hydrosulfide to afford the orange or red thioaldehydes **22b**, **44a**, and **45**.

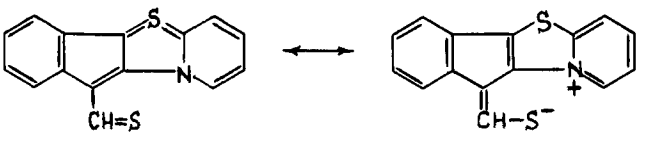
Later a large series of thioformylindolizines **22** and **46**[40] and of thioformylpyrrolo-[2,1-*b*]thiazoles **44** and **47**[52] were prepared in the same manner and studied in more detail. The thioformyl derivatives **22a, b, d–h** were obtained in high yield from indolizine, 2-methylindolizine, and from 1,2-, 2,6-, 2,7- and 2,8-dimethylindolizines. Along with the 3-formyl derivative **22**, 2-*t*-butylindolizine forms 1-thioformylindolizine **46a** (5% yield). All attempts to obtain the 1,3-dithioformyl derivative **22i**[40] led to polymers. It is likely that the two thioformyl groups are mutually destabilized due to cross-conjugation.

The modified Vilsmeier reaction allowed the synthesis of a large series of 5- and 7-pyrrolo[2,1-*b*]thiazolethiocarbaldehydes **44** and **47**.[52] From 3,6-dimethylpyrrolo[2,1-*b*]thiazole a 4 : 1 mixture of the 5- (**44e**) and 7-thioformyl derivatives **47e** was obtained. 3-Methyl-6-*t*-butylpyrrolo[2,1-*b*]thiazole also forms a mixture from which the 5- (**44d**) and 7-thioformyl derivatives **47d** can be isolated by preparative thin-layer chromatography. The structure of the 5-thiocarbaldehyde **44d** was proven by X-ray diffraction.[52]

For NMR and IR studies, the deuterated thioaldehydes **48a, b** were synthesized from the corresponding pyrrolo[2,1-*b*]thiazoles by use of [$^2H_7$]-DMF and phosphoryl chloride in 1,2-dichloroethane.[52]

A synthesis of the stable 10*H*-indeno[2,1-*d*]pyrido[2,1-*b*]thiazole thioformyl derivatives **49a, b** has been reported.[53] In this case *N*,*N*-dimethylthioformamide was used instead of DMF, which increased the yield of the starting salts **50a** and **50b** from 63 and 40% to 93 and 87%, respectively. This is due to different formylating abilities of the ion-pair intermediates $Me_2\overset{+}{N}CH{-}XPOCl_2Cl^-$ with X = S and O, respectively[53].

The neutral structure **A** of the thioaldehyde **49a**, which formally contains a tetracovalent endocyclic sulfur atom, is stabilized by resonance with the zwitterion **B**.[53]



49a (A) (B)

Scheme 15

A synthetic route to thioformylindolizine **22b** from the ethoxymethyleneindolizinium salt **51** has been devised.[40,51] This method is based on the condensation of 3*H*-indolizinium perchlorate with triethyl orthoformate, followed by NaHS treatment of the salt **51** formed.

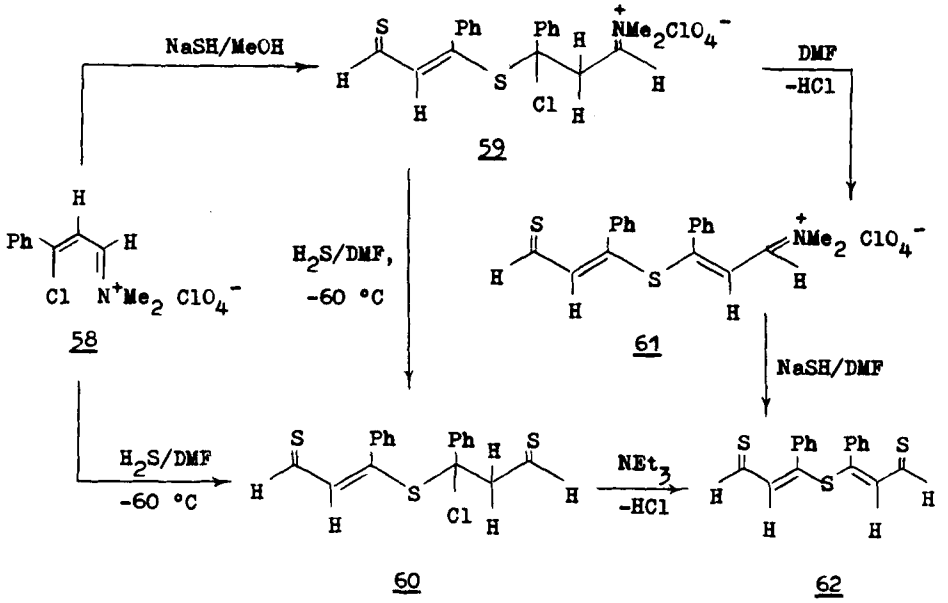
Recently a synthetic route to aliphatic and alicyclic enamino thioaldehydes **52**, which involves successive treatment of enamino imines with $POCl_3$ in DMF and NaSH in a single preparative stage involving the salts **53** has been reported.[54] The thials **52** are orange or red crystalline substances, stable over several months at room temperature.

A synthesis of the stable 2-alkoxycarbonyl enamino thioaldehydes **54** by solvolysis of the Vilsmeier salts of the new type **55** with aqueous or methanolic sodium hydrosulfide has been developed.[55] At the same time a procedure for the preparation of the 2-cyano enamino thioaldehydes **56** and the simple enamino thioaldehydes **52** from the corresponding Vilsmeier salts **57** and **53**, respectively, and freshly prepared methanolic (instead of aqueous) sodium hydrosulfide has been further improved.

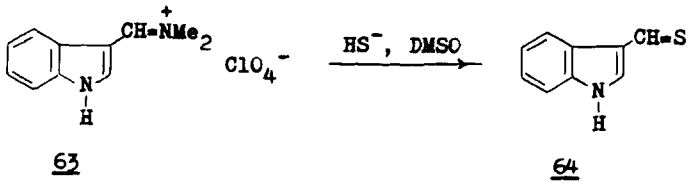
Electron-donating substituents in the β-position are known to stabilize α,β-unsaturated thioaldehydes.[41,56-58] The introduction of an electron-withdrawing group in the α-position of a thioaldehyde also increases its stability. For example, compared to 2-alkoxycarbonyl- (**54**) and 2-cyano- (**56**) enamino thioaldehydes the simple enamino thioaldehydes **52** are less stable upon storage at room temperature. The 2-alkoxycarbonyl enamino thioaldehydes **54** are the most stable of the three thioaldehyde types.[55]

New synthetic possibilities involving the hydrothiolysis of chloropropeneiminium salts **58** have been demonstrated.[59] Depending on the reagents' ion-pair status and on the temperature the hydrothiolysis of perchlorate **58** leads to the unsymmetrical sulfides **59** and **60**. By subsequent dehydrohalogenation they form the thioformyl substituted dipropenyl sulfides **61** and **62**, respectively.

Under the conditions of the synthesis of 3-thioformyl substituted indoles and indolizines by treatment of the corresponding methineimmonium salts with aqueous sodium hydrosulfide[51] *N*-[(3-indolyl)methine]-*N*,*N*-dimethylimmonium perchlorate **63** undergoes hydrolysis to 3-indolecarbaldehyde.[60] The hydrothiolysis of the salt **63** occurs readily under the action of anhydrous sodium hydrosulfide or hydrogen sulfide in dimethyl sulfoxide at 20 °C to the 3-indolethiocarbaldehyde **64**.[60,61]



Scheme 16



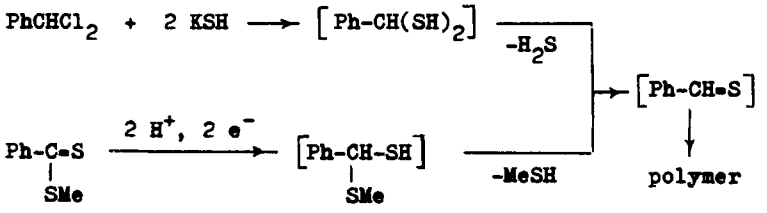
Scheme 17

2.4.4. Alkynylation of 1,2-dithiole-3-thiones (Table 1, No. 26) The [2+3]-cycloaddition of acetylenedicarboxylic acid esters **65**, $R^1 = R^2 =$ COOMe or COOEt, or dibenzoylacetylene **65**, $R^1 = R^2 =$ COPh, as well as other activated acetylenes to 5-unsubstituted 1,2-dithiole-3-thiones **66** leads to the 2-thioformylmethylene-1,3-dithioles **67**.[56,57,62,63] Very often these compounds are contaminated by small amounts of the corresponding aldehyde.

2.4.5. Aminolysis of 1,2-dithiolium salts (Table 1, No. 27) Treatment of the dithiolium salts **68** at 25 °C with an equivalent amount of either ethylenediamine in ethanol or trimethylenediamine in benzene furnishes the stable thioaldehydes **69**.[58] This reaction provides a simple synthetic route to 14-, 15-, and 16-membered tetraazamacrocycles.[58]

2.4.6. Hydrothiolysis of 1-chloro-2-benzoylstyrene (Table 1, No. 28) The hydrothiolysis of alkenyl chlorides presents a widely accepted approach to thiocarbonyl compounds.[11] In this way 1-thioformyl-1-phenyl-2-oxo-2-phenylethane **70**, existing as the stable alkenethiol tautomer, was obtained.[64]

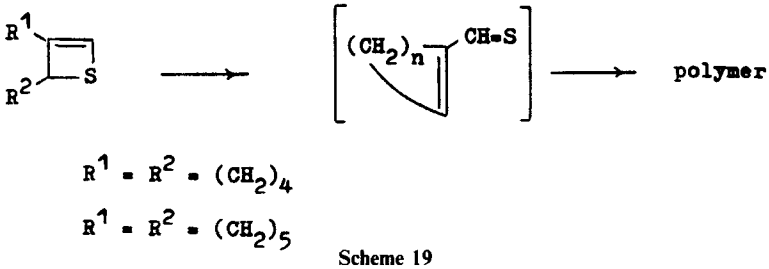
2.4.7. Cleavage of gem*-dithiols and their derivatives* *gem*-Dithiols and their *S*-derivatives can be cleaved at one of the C–S bonds to form corresponding thiocarbonyl compounds.[65] Thus, phenylmethanedithiol, obtained from benzal chloride and potassium hydrosulfide, as well as the product of the electrochemical reduction of methyl dithiobenzoate, are readily converted to thiobenzaldehyde (Scheme 18) which polymerizes instantly.[65]



Scheme 18

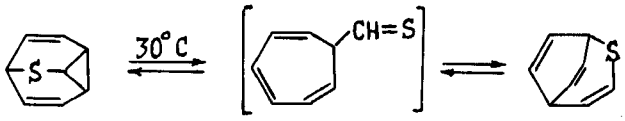
2.4.8. Thermal conversion of sulfides Some 1,3,5-trithianes undergo smooth elimination on heating to give the starting thioaldehydes.[6,9,11,66] Therefore one may keep as trimers the corresponding thioaldehydes intended for further examination.

Spontaneous decomposition of some 3,4-disubstituted thietes starts with ring opening and the formation of α,β-unsaturated cyclic thioaldehydes (Scheme 19) which undergo rapid polymerization.[67,68] Reaction of the starting thietes with 2,4-dinitrophenylhydrazine gave 2-formylcyclohexene and -cycloheptene hydrazone.[67]



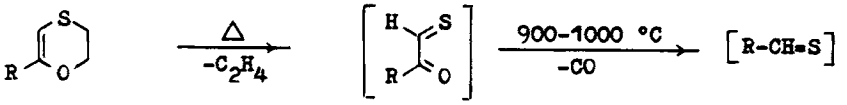
Scheme 19

1-Thioformylcycloheptatriene is an active intermediate in the thermal isomerization of a cyclic sulfide according to the following scheme:[69]



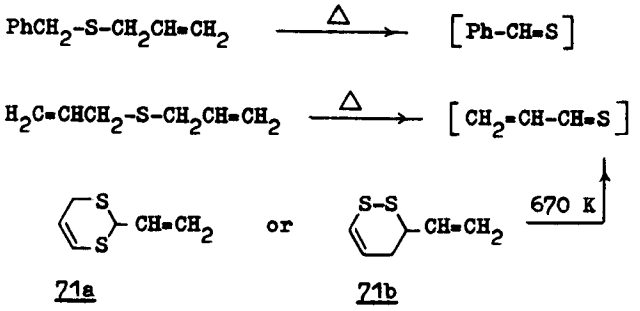
Scheme 20

Flash-vacuum thermolysis of 1,4-oxathiins at 750–850 °C gives α-oxo thioaldehydes which can be trapped with dienes. At higher temperature (900–1000 °C) they eliminate carbon monoxide to form simple thials.[70]



Scheme 21

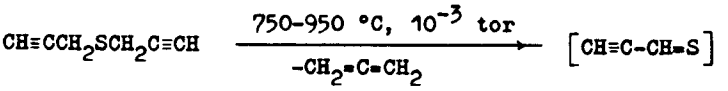
The synthesis of thiobenzaldehyde and thioacrolein has been performed by flash thermolysis of allyl benzyl sulfide and diallyl sulfide, respectively.[38,71-73] According to the IR spectra thioacrolein starts to change slowly as early as 77 K whereas thiobenzaldehyde remains intact up to 110 K.[38]



Scheme 22

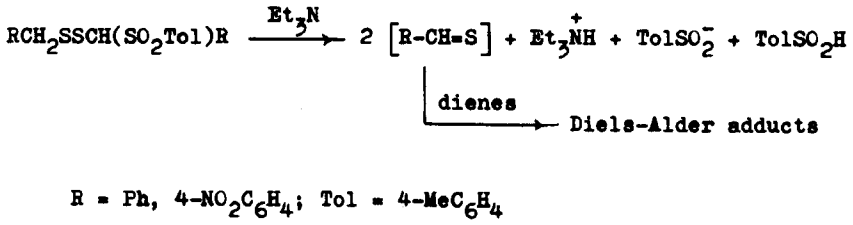
Thioacrolein was identified in the products of the thermolysis of diallyl sulfide (550 °C, 10–50 mm Hg) by microwave spectroscopy.[71] Under normal conditions this thial can be kept for 1–2 min. The use of PE spectroscopy ("molecular fingerprint" interpretation) during the thermolysis allows the optimal temperature for the formation of thioacrolein from diallyl sulfide (660 K) to be determined.[72,73] The PE spectrum of monomeric thioacrolein was obtained in a study of the thermolysis of the Diels-Alder adducts **71a, b**. This reaction furnished thioacrolein for preparative uses and further investigation.[72,73]

A selective synthetic route to unstable propynethial by vacuum pyrolysis of dipropargyl sulfide has been found.[74]



Scheme 23

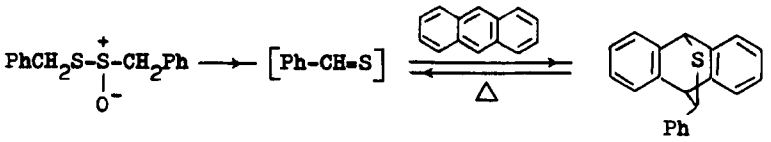
2.4.9. Cleavage of disulfides and their derivatives When treated with triethylamine, analogous to Bunte salts (cf. 2.2.)), α-sulfonyl disulfides suffer elimination to form thioaldehydes.[23] This reaction is a fragmentation-elimination process which follows a concerted mechanism:[23]



Scheme 24

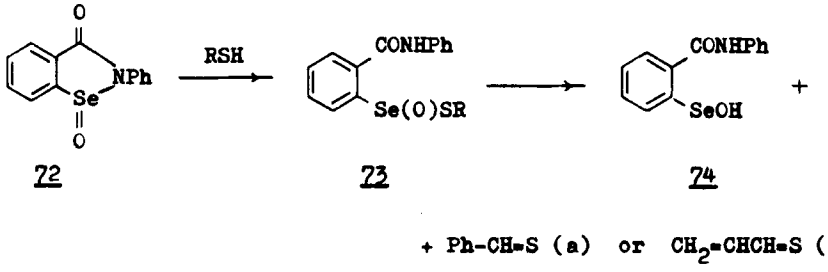
Thiobenzaldehyde is also generated by a general method of fluorine-induced cleavage of aryl (triorganylsilylmethyl) disulfides (Scheme 6).

During the last years new thioaldehyde precursors have been found.[22,23,75] Among these are a number of thiosulfinates whose thermolysis has provided a general and convenient method for thioaldehyde generation.[75,76] Thus, heating *S*-benzyl phenylmethanethiosulfinate in toluene at 100 °C leads to thiobenzaldehyde. The blue color of the reaction mixture, caused by the presence of the latter (UV spectrum: λ_{max} 580–590 and 610 nm (shoulder) which corresponds to the spectrum of thiobenzaldehyde at 77 K obtained by vacuum flash pyrolysis of allyl benzyl sulfide[38]) disappears in 15 min at 20 °C.[75] Normally the thermolysis of thiosulfinates is carried out in the presence of dienes or anthracene which are thioaldehyde "traps".[75,76] The adduct with anthracene (97% yield) can also serve as a source of thiobenzaldehyde.



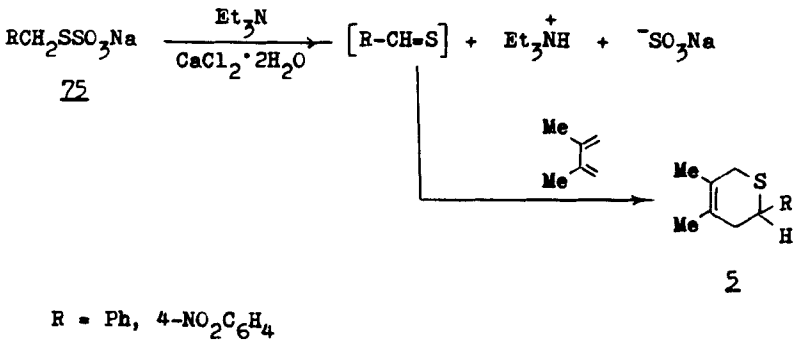
Scheme 25

The thioaldehyde formation in the reaction of 2-phenyl-1,2-benzisoselenoazol-3(2*H*)-one 1-oxide **72** with thiols has been examined.[77] In the reaction of the oxide **72** with α-toluenethiol in a 1:3 molar ratio in dichloromethane the formation of thiobenzaldehyde occurs. The latter is trapped with cyclopentadiene to give a 90% yield of the corresponding adduct. The reaction of 2-propene-1-thiol leads to thioacrolein dimer in 69% yield. Scheme 26 demonstrating these transformations involves the primary formation of thioseleninates **73** and elimination of the selenenic acid **74**:



Scheme 26

For the synthesis of arenethiocarbaldehydes convenient Bunte salts **75** are available.[22] They undergo readily 1,2-elimination when treated with triethylamine and calcium chloride. In the presence of conjugated dienes the corresponding cycloadducts **3–5** were obtained.



75 **5**

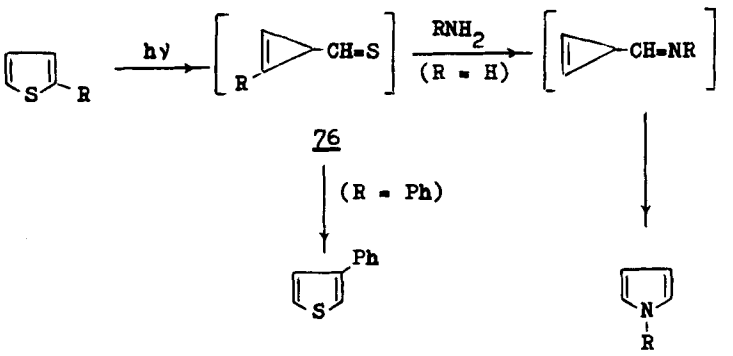
R = Ph, 4-$NO_2C_6H_4$

Scheme 27

These thials form with cyclopentadiene (methanol, 20 °C) the adducts **3** and **4** in high yield (66–88%) and add in low yield to the less active 2,3-dimethyl-1,3-butadiene. In a less polar system (benzene-ethanol) the yield of the adducts **5** is increased to 55–65%. Possibly this is due to suppression of the competing attack of nucleophiles (SO_3^{2-}, for example) on the thioaldehyde.

The ability of the adducts **3–5** to dissociate on heating makes them a valuable source of reactive thioaldehydes.[22]

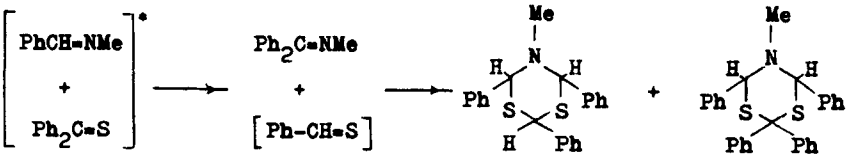
2.4.10. Photochemical methods Some types of conjugated thioaldehydes are generated by photochemical reactions in which they play key roles.[8,78,79] Thus, 3-thioformylcyclopropene **76a** is an intermediate of the photolytic conversion of thiophene to *N*-alkylpyrroles in the presence of amines.[78] The formation of phenylcyclopropenethiocarbaldehyde **76a** is explained by rearrangement of 2-phenylthiophene to 3-phenylthiophene under UV irradiation.



R = H (a), Ph (b)

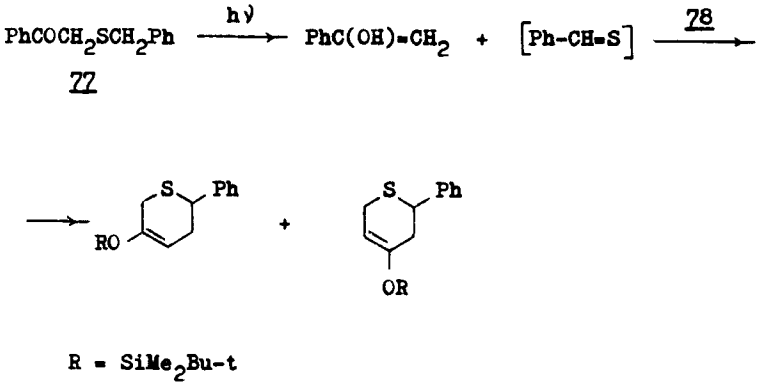
Scheme 28

The formation of polymers in the photolysis of ω-(benzylthio)acetophenone Ph–C(=O)–CH_2–S–CH_2Ph seems to be due to the intermediate generation of monomeric thiobenzaldehyde.[8] The same thioaldehyde appears to be an intermediate in the formation of substituted 1,3,5-dithiazine and benzophenone *N*-methylimine from photo-induced thiobenzophenone and benzaldehyde *N*-methylimine.[8]



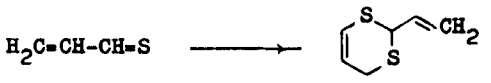
Scheme 29

Recently a simple method for the synthesis of dienophilic thioaldehydes by photolysis of phenacyl organyl sulfides **77** at 0 °C has been elaborated.[80,81] In this case the best diene turned out to be the Danishefsky diene CH_2=CH(OSiMe_3)CH=CHOMe **78**.



Scheme 30

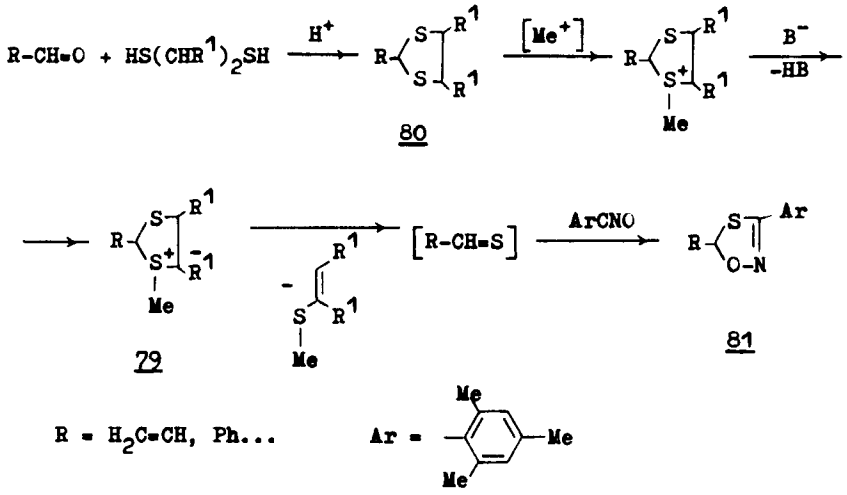
With the α,β-unsaturated thioaldehyde EtO–CO–CH=CH–CH=S the yield of the corresponding adduct is low (10%), although no autocondensation products of this thial have been found. Under analogous conditions thioacrolein cannot be trapped with normal dienes since it dimerizes to 2-vinyl-1,3-dithiene:[80]



Scheme 31

The synthesis of the adducts requires excess diene and carefully purified reactants to minimize catalytic thial autocondensation.[81]

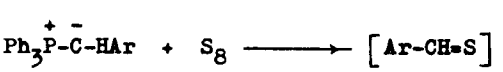
2.4.11. Fragmentation of S*-ylides* An original and simple thioaldehyde synthesis by fragmentation of *S*-ylides **79** generated from the aldehyde corresponding to the final thioaldehyde, via the 1,3-dithiolane **80** has been suggested.[82,83]



Scheme 32

The thioaldehyde thus obtained forms with mesitonitrile *N*-oxide stable 1,4,2-oxathiazoles **81**. In the absence of "traps" polymers or trimers are formed. The preparation of thioacrolein needs only $(i\text{-PrN})_2\text{Li}$ treatment of its precursor, the 1,3-dithiolane **80** (R = $CH{=}CH_2$, R^1 = COOMe).

The reaction of phosphonium ylides, arylmethylenetriphenylphosphoranes, with elemental sulfur in toluene forms aromatic thioaldehydes[30] (cf. also Section 2.2).

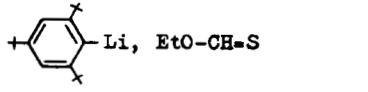
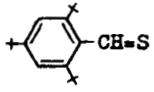
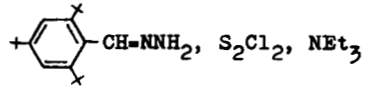
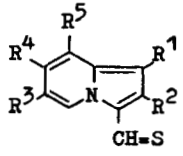


Scheme 33

2.5. Heterofunctional Thioformyl Derivatives RX—CH=S (X = O, S, N, P, Hal)

2.5.1. O-*Alkyl thioformates* *O*-Substituted thioformates AlkO—CH=S, which may be regarded as alkoxythioformaldehydes, are interesting not only as thiocarbonyl compounds in their own right, but as reagents for the introduction of thioaldehyde functions (cf. Scheme 39).[36,37] *O*-Ethyl thioformate was first prepared in 33% yield by hydrothiolysis of triethyl orthoformate.[84] Later on a new, simple and more effective synthetic route to *O*-alkyl thioformates (the *O*-methyl derivative, in particular) from the available dichloromethyl methyl ether has been suggested.[85] The reaction of the latter with potassium *O*-ethyl dithiocarbonate gives the *gem*-bis(*O*-ethyl dithiocarbonate) **82** which, when heated to 200–220 °C, forms *O*-methyl thioformate. This compound is sensitive to oxygen, but can be kept over several months under nitrogen at 0 °C.

Table 1. Sterically stabilized α,β-unsaturated and aromatic thioaldehydes

Run No. 1	Starting material 2	R–CH=S 3	m.p., °C 4	Yield % 5	Refs. 6
1	$PhCOCH_2SCH_2Bu\text{-}t$ **15**	*t*-Bu-CH=S **14**	–	50	35
2	$(Me_3Si)_3CLi$, EtO–CH=S **17**	$(Me_3Si)_3C$–CH=S **16**	129–131	16	36
3	 **19**	 **18**	146–147	56	37
	 **20**			40	37
4	R–CH=O, P_4S_{10}	 **22**			
		b: $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = Me$	88–89	59	40
		d: $R^3 = R^4 = R^5 = H$, $R^1 = R^2 = Me$	168–169	76	40
5	R–CH=O, P_4S_{10}	Me_2NCH=CH–CH=S **23**	61–63	–	41
6	R–CH=O, Lawesson reagent	2-$[N(CH_2)_4]$–C_6H_4–CH=S **24**	–	–	42

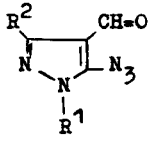
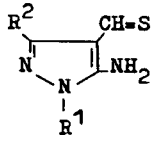
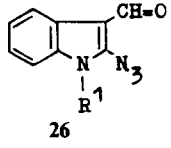
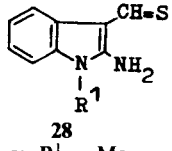
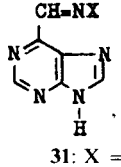
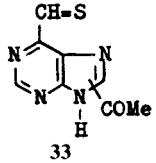
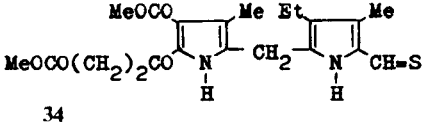
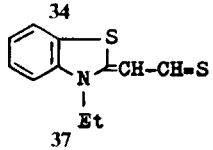
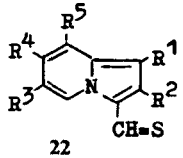
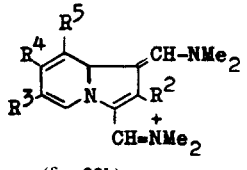
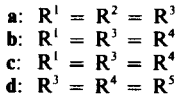
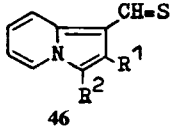
7	R–CH=O, $(Me_3Si)_2S$, cat. *n*-BuLi; $CoCl_2 \cdot 6H_2O$; Me_3SiOTf	R–CH=S **a**: R = Ph **b**: R = 2-thienyl **c**: R = *n*-Pr **d**: R = *t*-Bu **e**: R = furyl	– – – – –	96[a], 94[b] 97[a], 91[b] 80[a] 86[a] 88[b]	44, 45, 47 44, 45, 47 44 44 45, 47
			[a,b] Diels-Alder adducts with [a]CPD, [b]DMBD		
8	$RR^1C(OMe)_2$, $(Me_3Si)_2S$, Me_3SiOTf	$RR^1C{=}S$; R, R^1 = H, Alk, Ar	–	–	46
9	 1. H_2S/Pip 2. H_2S/H^+ **25**	 **27** **a**: R^1 = Me, R^2 = Ph **b**: R^1 = Ph, R^2 = Me **c**: R^1 = Ph, R^2 = *t*-Bu	 120–121 100–102 –	 40–60 	 48 48 48
10	 1. H_2S/Pip 2. H_2S/H^+ **26**	 **28** **a**: R^1 = Me **b**: R^1 = CH_2Ph **c**: R^1 = Ph	 – – –	 40–60 	 48 48 48
11	$H(CF_2)_n$–CH=O, $(AlkO)_3P{=}S$ **30** Alk = Me, Et	$H(CF_2)_n$–CH=S **29** n = 4, 6	–	50–60 (Diels-Alder adducts)	49
12	 , MeCOSH or $(MeCO)_2S$ **31**: X = OH **32**: X = NH_2	 **33**	182–184	 28 34	 50 50

Table 1. Continued

Run No. 1	Starting material 2	R–CH=S 3	m.p., °C 4	Yield % 5	Refs. 6
13	R–CH=$\overset{+}{N}$HEt Br^-, H_2S **35**		145–146	–	2
14	R=CH–CH=$\overset{+}{N}$(Me)Ph X^-, NaSH **36**	 **34**	–	–	3
15	R–CH=$\overset{+}{N}$$Me_2$ $PO_2Cl_2^-$, NaSH **41**	 **37**			
	 $PO_2Cl_2^-$ (for **22h**)	 **22**			
		a: $R^1 = R^2 = R^3 = R^4 = R^5 = H$	56.5–58	77	40
		b: $R^1 = R^3 = R^4 = R^5 = H$, R^2 = Me	88–89	86	40
		c: $R^1 = R^3 = R^4 = R^5 = H$, R^2 = *t*-Bu	139–141	90	40
		d: $R^3 = R^4 = R^5 = H$, $R^1 = R^2$ = Me	168–169	81	40
		e: $R^1 = R^4 = R^5 = H$, $R^2 = R^3$ = Me	160–162	86	40
		f: $R^1 = R^3 = R^5 = H$, $R^2 = R^4$ = Me	140–142	83	40
		g: $R^1 = R^3 = R^4 = H$, $R^2 = R^5$ = Me	167–170 (decomp.)	82	40
		h: $R^3 = R^4 = R^5 = H$, R^2 = Me, R^1 = CH=S	197–200 (polymer)	96	40
16	R–CH=$\overset{+}{N}$$Me_2$ $PO_2Cl_2^-$, NaSH **41'**	 **46**			
		a: $R^2 = H$, R^1 = *t*-Bu	129–131	5	40
		b: $R^1 = R^2$ = Me	158.5–159	76	40

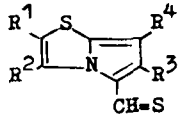
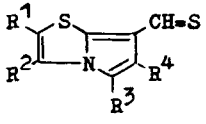
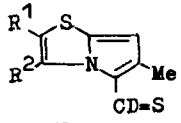
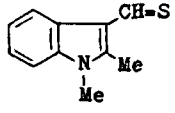
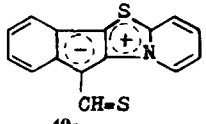
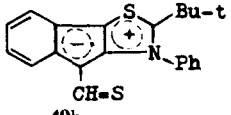
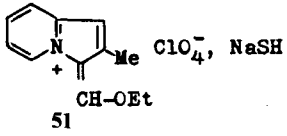
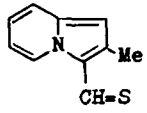
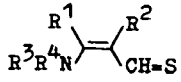
17	$R-CH=\overset{+}{N}Me_2\ PO_2Cl_2^-$, NaSH **42**	 **44**			
		a: $R^1 = R^2 = R^4 = H$, $R^3 = Me$	101–103	89	52
		b: $R^2 = R^4 = H$, $R^1 = R^3 = Me$	127–128	89	52
		c: $R^1 = R^2 = H$, $R^3 = R^4 = Me$	165–165.5	71	52
		d: $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = t$-Bu	117–118	12	52
		e: $R^1 = R^4 = H$, $R^2 = R^3 = Me$	152–154	49	52
		f: $R^4 = H$, $R^1 = R^2 = R^3 = Me$	169–170	77	52
18	$R-CH=\overset{+}{N}Me_2\ PO_2Cl_2^-$, NaSH **42′**	 **47**			
		a: $R^1 = R^2 = H$, $R^3 = R^4 = Me$	162.5–164.5	65	52
		b: $R^1 = H$, $R^2 = R^3 = R^4 = Me$	195–199	92	52
		c: $R^1 = R^2 = R^3 = R^4 = Me$	224–226 (decomp.)	75	52
		d: $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = t$-Bu	156–158	17	52
		e: $R^1 = R^3 = H$, $R^2 = R^4 = Me$	161–162	4.5	52
19	$R-CD=\overset{+}{N}Me_2\ PO_2Cl_2^-$, NaSH	 **48**			
		a: $R^1 = R^2 = H$	102–104	78	52
		b: $R^1 = R^2 = Me$	168–170	83	52
20	$R-CH=\overset{+}{N}Me_2\ PO_2Cl_2^-$, NaSH **43**	 **45**	160 (decomp.)	86	51

Table 1. Continued

Run No. 1	Starting material 2	R–CH=S 3	m.p., °C 4	Yield % 5	Refs. 6
21	R–CH=$\overset{+}{N}$Me$_2$ ClO_4^-, NaSH **50a,b**	 **49a**	> 215 (decomp.)	44	53
		 **49b**	> 215 (decomp.)	43	53
22	 **51**	 **22b**	88–89	33	40, 51
23	R–CH=$\overset{+}{N}$Me$_2$ $PO_2Cl_2^-$, NaSH **53**	 **52**			
		a: R^1 = Ph, R^2 = R^4 = H, R^3 = *c*-C_6H_{11}	108–109	41	55
		b: R^1 = Ph, R^2 = H; R^3, R^4 = $(CH_2)_5$	136–137	37	55
		c: R^1 = Ph, R^2 = H; R^3, R^4 = $(CH_2CH_2)_2O$	139–140	27	54
			138.5–139.5	42	55
		d: R^1, R^2 = $(CH_2)_3$; R^3, R^4 = $(CH_2CH_2)_2O$	116–117	50	54
			116–117	49	55
		e: R^1 = R^2 = Ph, R^3 = C_3H_7, R^4 = H	107.5–108.5	44	55
		f: R^1 = R^2 = Ph, R^3 = C_6H_{13}, R^4 = H	70	51	55
		g: R^1 = R^2 = Ph; R^3, R^4 = $(CH_2)_4$	163.5–164	33	54
			163.5–164	43	55
		h: R^1 = R^2 = Ph; R^3 = *c*-C_6H_{11}, R^4 = H	136.5	23	54
			136.5	87	55
		i: R^1 = R^2 = Ph; R^3, R^4 = $(CH_2CH_2)_2O$	170–171	61	54
			170–171	71	55
		j: R^1, R^2 = *o*-C6H4CH2; R3, R4 = (CH2)5	159–159.5	56	55

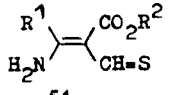
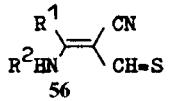
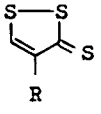
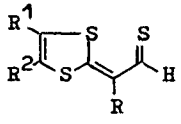
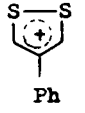
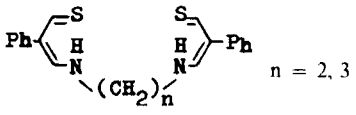
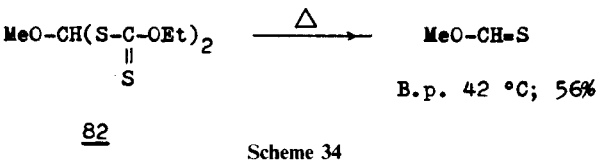
24	$R-CH=\overset{+}{N}Me_2$ **55** $PO_2Cl_2^-$, NaSH	 **54**			
		a: $R^1 = R^2 = Me$	110.5–111	83	55
		b: $R^1 = Et$, $R^2 = Me$	52.5–53	48	55
		c: $R^1 = Pr$, $R^2 = Et$	25–26	71	55
		d: $R^1 = Ph$, $R^2 = Et$	135.5–137	69	55
		e: $R^1 = p\text{-}MeC_6H_4$, $R^2 = Et$	90.5–92	83	55
		f: $R^1 = m\text{-}MeC_6H_4$, $R^2 = Et$	142–143	80	55
		g: $R^1 = 1\text{-}C_{10}H_7$, $R^2 = Et$	145.5–146.5	35	55
25	$R-CH=\overset{+}{N}Me_2$ **57** $PO_2Cl_2^-$, NaSH	 **56**			
		a: $R^1 = Me$, $R^2 = H$	137–138	60	55
		b: $R^1 = R^2 = Me$	79.5–80.5	61	55
		c: $R^1 = Me$, $R^2 = Et$	124.5–125	73	55
		d: $R^1 = Ph$, $R^2 = H$	120–121	53	55
		e: $R^1 = Ph$, $R^2 = Me$	131–132	81	55
		f: $R^1 = Ph$, $R^2 = Et$	90–91.5	70	55
		g: $R^1 = p\text{-}MeC_6H_4$, $R^2 = H$	155–156	83	55
		h: $R^1 = p\text{-}MeC_6H_4$, $R^2 = Me$	127–128	62	55
		i: $R^1 = m\text{-}MeC_6H_4$, $R^2 = H$	125.5–126.5	69	55
		j: $R^1 = m\text{-}MeC_6H_4$, $R^2 = Me$	123–124	75	55
		k: $R^1 = p\text{-}MeOC6H4$, R2 = H	184–185	88	55
		l: $R^1 = 2\text{-}C_{10}H7$, R2 = H	168.5–169.5	70	55
		m: $R^1 2\text{-}C_{10}H7$, R2 = Me	145–146	52	55

Table 1. Continued

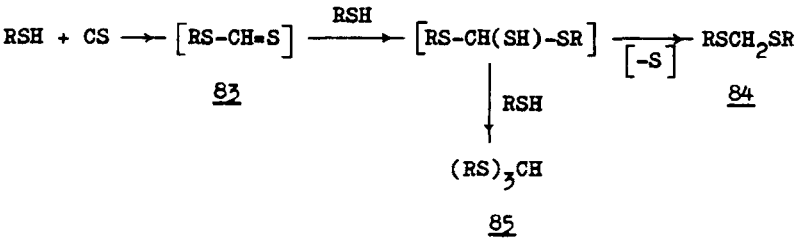
Run No. 1	Starting material 2	R–CH=S 3	m.p., °C 4	Yield % 5	Refs. 6
26	R^1–C≡C–R^2,  **65** **66**	 **67**			
		a: R = H, R^1 = R^2 = COOMe	88	70; 75	56, 57, 63
		b: R = Me, R^1 = R^2 = COOMe	123–126	75	57
		c: R = Ph, R^1 = R^2 = COOMe	152–154	85; 70	56, 57, 63
		d: R = Ph, R^1 = R^2 = COOEt	130–134	75	57
		e: R = Ph, R^1 = H, R^2 = COOMe	124	50	57
		f: R = Me, R^1 = H, R^2 = COPh	135 decomp.–274	40	57
		g: R = R^1 = H, R^2 = COPh	152 decomp.–198	70	57
		h: R = H, R^1 = R^2 = COPh	143	74; 70	56, 57
		i: R = Ph, R^1 = R^2 = COPh	–	63; 71	56, 62
27	 , H_2N–$(CH_2)_n$–NH_2 n = 2, 3 **68**	 n = 2, 3 **69**	–	60–80	58
28	PhCO–C(Ph)=CHCl, Na_2S	PhCO–CH(Ph)–CH=S ⇄ PhCO–C(Ph)=CH–SH **70**	84–86	30	64



Scheme 34

An attempt to synthesize *O*-phenyl thioformate in an analogous manner led only to polymerization.[85]

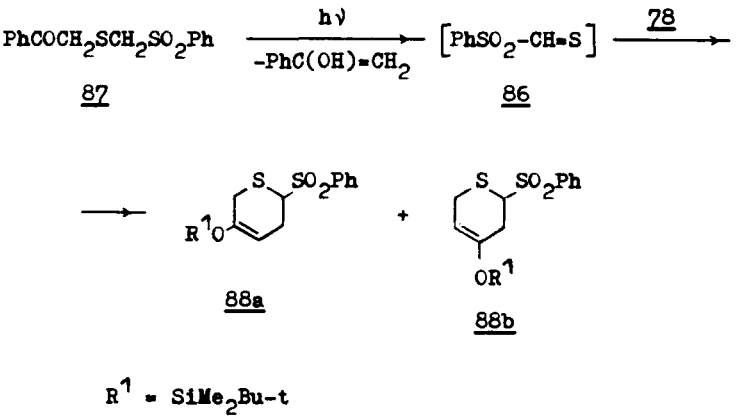
2.5.2. Dithioformates and their derivatives The dithioformates **83** are known as labile intermediates in the reaction of thiols with carbon monosulfide,[86,87] which follows the scheme:



Scheme 35

This reaction mainly leads to bis(alkylthio)methanes **84** and trialkyl orthotrithioformates **85a, b** in low yield. Though of limited synthetic value, Scheme 35 is essential from the viewpoint of general chemical transformations of carbon monosulfide.[87]

The exotic thioformyl sulfone **86** formed by photolysis of phenacyl phenylsulfonylmethyl sulfide **87** has been detected via the adducts **88a** and **88b** with the Danishefsky diene **78**, $[CH_2{=}CH{-}(OSiMe_3){-}CH{=}CH{-}OMe]$.[81]



Scheme 36

2.5.3. Thioformamide and N-*substituted thioformamides* The amino functional thioformyl derivatives differ from the known O-, S-, P- and Hal-functional derivatives by their relative thermodynamic stability. Thioformamide was obtained in 1815 by Gay-Lussac by reaction of hydrogen cyanide with hydrogen sulfide.[88]

$$H\text{-}CN + H_2S \longrightarrow [H\text{-}C(=NH)\text{-}SH] \longrightarrow \underset{\text{B.p. 32-34 °C}}{H_2N\text{-}CH=S}$$

Scheme 37

Further development of the chemistry of thioamides has led to additional synthetic routes to thioformamides. One of the general methods for the preparation of the latter involves the thionation of formamides according to the scheme below:

$$R^1R^2N\text{-}CH=O + Z \longrightarrow R^1R^2N\text{-}CH=S$$

$Z = P_4S_{10}$ (ref. 89), Lawesson reagent (see II.4.1.),

B_2S_3 (ref. 90), CS_2 (ref. 91)

Scheme 38

Imidoyl halides RN=CH–Hal and the corresponding immonium salts $R_2\overset{+}{N}$=CH–Hal Hal^- react with hydrogen sulfide in a similar way.[92,93]

A series of synthetic routes to thioformamides characterized by various types of substitution are based on the reaction of amines with carbon monosulfide,[86] with commercial *N*,*N*-dimethylthioformamide,[89] *O*-ethyl thioformate,[94] H_2S/HCN,[95] $CHCl_3$/NaOH[96] or formamide/P_4S_{10} mixtures:[89]

$$R^1R^2NH + Z \longrightarrow R^1R^2N\text{-}CH=S$$

$Z = CS$, $Me_2N\text{-}CH=S$, $EtO\text{-}CH=S$; $H_2S + HCN$; $H_2S + CHCl_3 + NaOH$;

$H_2N\text{-}CH=O + P_4S_{10}$

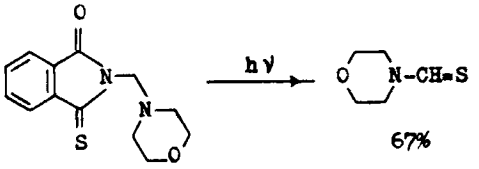
$R^1 = H$, $R^2 = Alk$; $R^1 = H$, $R^2 = Ar$; R^1, $R^2 = Alk$, cyclo-Alk,

e.t.c.

Scheme 39

In contrast to alternative methods for the preparation of thioformamides the reactions with CS occur in a neutral or nonpolar medium, need no heating and allow the mild introduction of thioformyl groups into chemically "sensitive" substrates.[86]

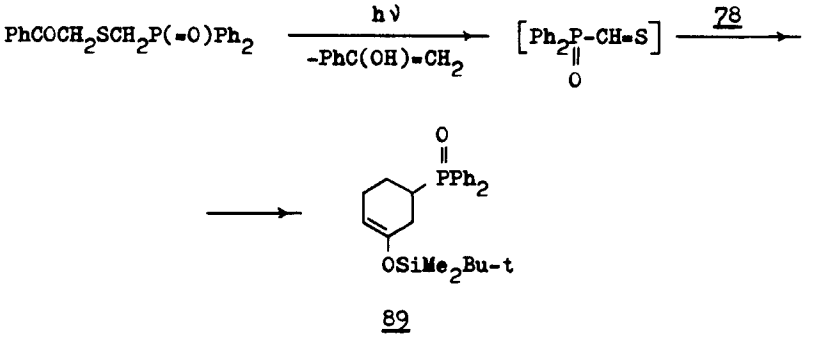
Photolytic cleavage of *N*-[(*N*-morpholinomethyl)thio]phthalimide to the corresponding *N*-thioformylamine proceeds in a peculiar manner.[97] The initial stage of this process seems to be proton elimination from the methylene bridge.



Scheme 40

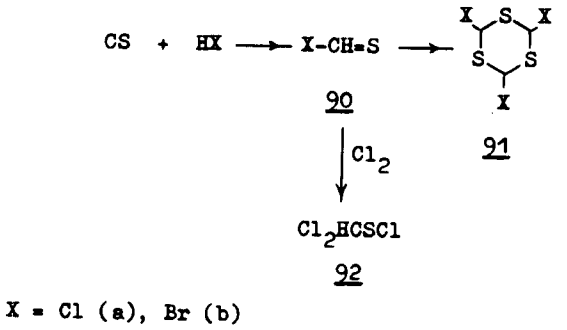
Thioformamides have found many uses in synthetic organic chemistry. They are employed in condensation *en route* to amidines,[98] enamines[99] or more highly functionalized thioformamides.[89]

2.5.4. Thioformylphosphine oxides Diphenylthioformylphosphine oxide, the first representative of this class of compounds, was synthesized by photolysis of phenacyl diphenylphosphoryl sulfide and detected as the adduct with the Danishefsky diene **89**[81] according to the following scheme:



Scheme 41

2.5.5. Thioformyl halides The thioformyl halides **90a, b** were first generated by addition of HCl or HBr to carbon monosulfide at low temperature (liquid nitrogen). Approaching room temperature, these compounds form trimers, the 1,3,5-trithianes **91**. In the presence of Cl_2 thioformyl chloride **90a** forms dichloromethanesulfenyl chloride **92**.[100]



Scheme 42

3. PHYSICAL PROPERTIES

According to microwave spectroscopy the length of the C=S bond in monomeric thioformaldehyde is 1.6108 Å.[101] This value is considerably higher than that for the C=O bond in formaldehyde (1.2083 Å)[101] and corresponds to the calculated interatomic distance in an unperturbed thiocarbonyl group (1.607 Å).[11] In *N*-methylbenzylthioformamide the C=S bond length determined by X-ray diffraction is slightly larger (1.660 Å).[102] The calculated dipole moment of thioformaldehyde is 1.6474(14) D,[103] whereas the dipole moment measured for gaseous CH_2=O is 2.27 D.[104] The dipole moment of thioformamide was calculated relying upon its microwave spectrum by use of the Stark effect and is equal to 4.01 D (μ H_2N–CH=O 3.37 D). The dipole moments for *N*-substituted thioformamides, *i.e.*, *N*-phenyl- and *N*,*N*-dimethylthioformamide, are 4.13 and 4.74 D, respectively, which is higher than the values for their carbonyl analogs, 3.35 and 3.86 D.[102] According to microwave spectroscopy the thioacrolein molecule is planar with a dipole moment of 2.61 D[71] (compared with μ 2.6, 3.11 D for acrolein[105]). Evidently, the dipole moment ratio for each given pair of thioaldehyde and corresponding aldehyde depends on their structure and is determined by the prevailing effect of polarization or polarizability.

The photoelectron spectra of thioacrolein and acrolein are nearly the same and show ionization peaks at 8.87 and 10.2 eV, respectively.[72] The ionization potential of thioformyl acetylene (8.92 $\pm$ 0.05 eV) is within the range common to other thiocarbonyl compounds.[74]

It is noteworthy that the mass spectra of the heterocyclic thioaldehydes 1,2-dimethyl-3-thioformylindole **45**, 2-methyl-3-thioformylindolizine **22a** and 6-methyl-5-thioformylpyrrolo[2,1-*b*]thiazole **44a** are characterized by an intense peak $[M-45]^+$ which corresponds to loss of the thioformyl group.[51]

The position of the thiocarbonyl absorption band in the IR spectra (1100–1270 cm^{-1}) is clearly defined due to successful development of the chemistry of thioketones.[11] The C=S bond stretching vibrations in the thioaldehyde spectra are found in the same region. Thus, in the IR spectrum of thioformaldehyde in an inert gas matrix at 14 K the band at 1063 cm^{-1} is assigned to the thiocarbonyl absorption.[106] The spectrum (77 K) of thioacetaldehyde shows a characteristic $\nu_{C=S}$ band 1068 cm^{-1}.[19] In the IR spectrum of propynethial (Scheme 23) recorded in an argon matrix at 12 K the $\nu_{C=S}$ frequency is $\sim$1100 cm^{-1}.[107] The C=S absorption band in the spectra of the sterically stabilized thioaldehydes Me_3C–CH=S and $(Me_3Si)_3C$–CH=S is present at 1085 and 1120 cm^{-1}, respectively.[35,36] In the IR spectra of the stable heterocyclic thioaldehydes **45**, **22**, and **44** there is a strong band in the 985–950 cm^{-1} region.[51] According to the solvent effects this band is due to the C=S vibration. In the spectrum of **45** this band is displaced from 978 cm^{-1} in cyclohexane to 956 cm^{-1} in 1,1,2,2-tetrabromoethane.[51] The 2-amino-3-thioformylindoles **28** and the 2-amino-4-thioformylpyrazoles **27** display strong absorption at 890–899 and 948–971 cm^{-1}, respectively.[48] In the spectrum of the enamino thioaldehyde **23** the $\nu_{C=S}$ vibration corresponds to the band at 1260 cm^{-1}.[41] The IR spectra of a large series of enamino thioaldehydes[55] provide ample information concerning the thiocarbonyl absorption. For the 2-alkoxycarbonyl enamino thioaldehydes **54** and the 2-cyano enamino thioaldehydes **56** the $\nu_{C=S}$ band occurs mainly in the 1252–1263 and 1230–1271 cm^{-1} region, respectively. The spectra

of other enamino thioaldehydes **52** are characterized by C=S vibration in the 1235–1263 cm^{-1} region.

The thioaldehyde electron spectra are characterized, as a rule, by three absorption regions due to the $n \rightarrow \pi^*$ transition in the visible portion of the spectrum, and $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions in the UV region. The electron spectra of the stable heterocyclic thioaldehydes, the thioformylindolizines **22**[40] and the -pyrrolo[2,1-*b*]thiazoles **44** and **47**[52] have been studied in detail. Thus, in the spectra of the 3-thioformylindolizines **22** there are four groups of intense maxima in the 460–420, 325–300, 275–250 and 230–205 nm regions ($\log \varepsilon > 3.7$). In the spectra of the 1-thioformylindolizines **46** three regions of strong absorption are observed: 460–420, 280–260 and 240–210 nm. The difference in the appearance of these spectra makes it possible to recognize readily 1- and 3-thioformylindolizines.[40] The spectra of the 3-thioformylindolizines **22** are characterized by two broad bands (~ 520 and ~ 550 nm) of low intensity ($\log \varepsilon$ 1.9–2.2), which have no distinct minimum. These bands shift hypsochromically with increasing solvent polarity and are related to the $n \rightarrow \pi^*$ transition in the thiocarbonyl group. The reason for the spectrum multiplicity is still unclear. In the spectrum of 2-*t*-butyl-1-thioformylindolizine **46a** in cyclohexane there is a very broad $n \rightarrow \pi^*$ band with $\lambda_{max} \sim 534$ nm ($\log \varepsilon$ 1.84) and a shoulder at $\sim 570\,cm^{-1}$ whereas the spectrum of 2,3-dimethyl-1-thioformylindolizine **46b** contains this band from ~ 510 to 560 nm ($\log \varepsilon \sim 1.9$).[40] An analogous line shape and nature of the bands are observed in the electron spectra of the thioformylpyrrolo[2,1-*b*]thiazoles **44** and **47**[52] and of 3-thioformylindole **64**.[60] The spectra of the 2-alkoxycarbonyl enamino thioaldehydes **54** contain three clearly defined maxima in the 215–219, 256–267 and 355–371 nm regions. The 2-cyano enamino thioaldehydes **56** show two maxima in the 247–266 and 365–381 nm regions. The spectra of other enamino thioaldehydes **52** also display two intense bands at 242–278 and 381–444 nm.[55] The electron spectra of sterically stabilized thioaldehydes are characterized by the following parameters [below compounds, λ_{max}, nm, (ε), solvent, reference are presented]: $Me_3C-CH=S$, 508 (16), MeCN, 35; $(Me_3Si)_3C-CH=S$, 518 (15), 272 (9940), 212 (4320), C_6H_{12}; 503 (14), 277 (8720), 211 (5330), MeCN, 36; 2,4,6-*t*-$Bu_3C_6H_2-CH=S$, 564 (19), 388 (1850), C_6H_{12}; 552 (19), 340 (1690), EtOH, 37. The spectra of the labile compounds thioacrolein and thiobenzaldehyde were run at 77 K under specially chosen conditions.[38] The calculated λ_{max} values are in good agreement with the experimental data.

	Found			Calculated		
	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \sigma^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \sigma^*$
$CH_2=CH-CH=S$	580	276	–	570	265	–
$C_6H_5CH=S$	575	320	228	567	302	231
					296	226

In the ^1H NMR spectra of thioaldehydes the thioformyl proton signal occurs downfield in a fairly wide range (δ from 9 to 13 ppm) (Table 2).

2,4,6-Tris-*t*-butylthiobenzaldehyde **18** is believed to have the "purest" thioformyl group with a proton signal at $\delta = 13.02$ ppm.[37] The signal of the selenoformyl proton

Table 2. ^{1}H NMR spectra of thioaldehydes (δ, ppm)

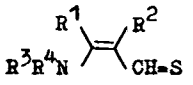
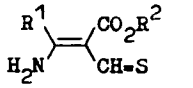
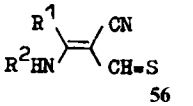
Run No. 1	Compound 2	CH=S Group (solvent) 3	Refs. 4
1	MeO–CH=S	9.52	85
2	Me_3C–CH=S **14**	11.67	35
3	$(Me_3Si)_3C$–CH=S **16**	11.45 ($CDCl_3$)	36
4	$H(CF_2)_4$–CH=S **29**	10.35	49
5	 **52**		
	a: R^1 = Ph, R^2 = R^4 = H, R^3 = *c*-C_6H_{11}	9.95d (0.05 H) ($CDCl_3$)	55
		9.70d (0.95 H)	55
	b: R^1 = Ph, R^2 = H; R^3, R^4 = $(CH_2)_5$	9.47d	55
	c: R^1 = Ph, R^2 = H; R^3, R^4 = $(CH_2CH_2)_2O$	9.73d	55
	d: R^1, R^2 = $(CH_2)_3$; R^3, R^4 = $(CH_2CH_2)_2O$	10.41s	55
	e: R^1 = R^2 = Ph, R^3 = Pr, R^4 = H	9.98 (0.03 H)	
		9.86 (0.97 H)	55
	f: R^1 = R^2 = Ph, R^3 = C_6H_{13}, R^4 = H	9.99 (0.05 H)	
		9.85 (0.95 H)	55
	g: R^1 = R^2 = Ph; R^3, R^4 = $(CH_2)_4$	9.86	55
	h: R^1 = R^2 = Ph, R^3 = *c*-C_6H_{11}, R^4 = H	9.96 (0.03 H)	
		9.82 (0.97 H)	54
		9.95 ($CDCl_3$)	54
		9.82	55
	i: R^1 = R^2 = Ph; R^3, R^4 = $(CH_2CH_2)_2O$	10.14 (0.9 H)	
		8.91 (0.1 H)	55
	j: R^1, R^2 = *o*-C6H4CH2; R3, R4 = (CH2)5	8.33	
6	 **54**		
	a: R^1 = R^2 = Me	10.97 ($CDCl_3$)	55
	b: R^1 = Et, R^2 = Me	10.97	55
	c: R^1 = Pr, R^2 = Et	10.94	55
	d: R^1 = Ph, R^2 = Et	10.87	55
	e: R^1 = *p*-MeC_6H_4, R^2 = Et	10.81	55
	f: R^1 = *m*-MeC_6H_4, R^2 = Et	10.55	55
	g: R^1 = 1-$C_{10}H_7$, R^2 = Et	10.93	55
7	 **56**		
	a: R^1 = Me, R^2 = H	10.48 ($CDCl_3$)	55
	b: R^1 = R^2 = Me	10.20	55
	c: R^1 = Me, R^2 = Et	10.19	55
	d: R^1 = Ph, R^2 = H	10.68	55
		10.40 (0.04 H)	55
	e: R^1 = Ph, R^2 = Me	10.38	55
		9.89 (0.01 H)	
	f: R^1 = Ph, R^2 = Et	10.37	55
		9.88 (0.01 H)	
	g: R^1 = *p*-MeC_6H_4, R^2 = H	10.59 (0.95 H)	55
		9.91 (0.05 H)	

Table 2. Continued

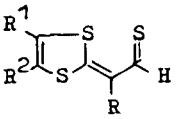
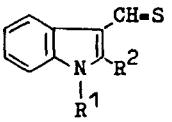
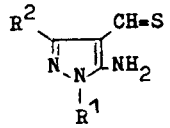
Run No. 1	Compound 2	CH=S Group (solvent) 3	Refs. 4
	h: R^1 = *p*-MeC_6H_4, R^2 = Me	10.35	55
	i: R^1 = *m*-MeC_6H_4, R^2 = H	10.66 10.34 (0.03 H)	55
	j: R^1 = *m*-MeC_6H_4, R^2 = Me	10.36 9.90 (0.04 H)	55
	k: R^1 = *p*-$MeOC_6H_4$, R^2 = H	10.63 10.39 (0.01 H)	55
	l: R^1 = 2-$C_{10}H_7$, R^2 = H	10.71 10.47 (0.03 H)	55
	m: R^1 = 2-$C_{10}H_7$, R^2 = Me	10.41 9.93 (0.02 H)	55
8			
	67		
	a: R = H, R^1 = R^2 = COOMe	11.65d ($CDCl_3$)	62
	b: R = Me, R^1 = R^2 = COOMe	9.65	62
	c: R = Ph, R^1 = R^2 = COOMe	10.85	57
	d: R = Ph, R^1 = R^2 = COOEt	10.92	57
	e: R = Ph, R^1 = H, R^2 = COOMe	10.84	57
	f: R = Me, R^1 = H, R^2 = COPh	10.90	57
	g: R = R^1 = H, R^2 = COPh	10.99d	57
	h: R = H, R^1 = R^2 = COPh	9.22d	62
	i: R = Ph, R^1 = R^2 = COPh	10.65	56, 62
9			
	45: R^1 = R^2 = Me	11.44 ($CDCl_3$)	51
	64: R^1 = R^2 = H	11.41 $(CD_3)_2SO$	60
	28a: R^1 = Me, R^2 = NH_2	10.36, 10.26	48
	28b: R^1 = CH_2Ph, R^2 = NH_2	10.51, 10.39	48
	28c: R^1 = Ph, R^2 = NH_2	10.62, 10.46	48
10			
	27		
	a: R^1 = Me, R^2 = Ph	10.90	48
	b: R^1 = Ph, R^2 = Me	10.75	48
	c: R^1 = Ph, R^2 = *t*-Bu	11.10	48

Table 2. Continued

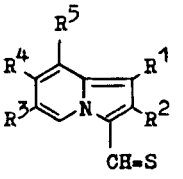
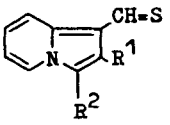
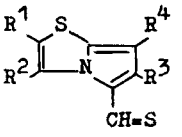
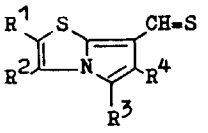
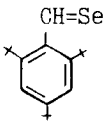
Run No. 1	Compound 2	CH=S Group (solvent) 3	Refs. 4
11	 **22**		
	a: $R^1 = R^2 = R^3 = R^4 = R^5 = H$	10.64 ($CDCl_3$)	40
	b: $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = Me$	10.55	40
	c: $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = t$-Bu	10.95	40
	d: $R^3 = R^4 = R^5 = H$, $R^1 = R^2 = Me$	10.40	40
	e: $R^1 = R^4 = R^5 = H$, $R^2 = R^3 = Me$	10.46	40
	f: $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = Me$	10.38	40
	g: $R^1 = R^3 = R^4 = H$, $R^2 = R^5 = Me$	10.53	40
12	 **46**		
	a: $R^2 = H$, $R^1 = t$-Bu	11.42 ($CDCl_3$)	40
	b: $R^1 = R^2 = Me$	10.72 ($CDCl_3$, -20 °C)	40
		10.91 (22 °C)	40
		10.95 (31.5 °C)	40
		11.00 (45 °C)	40
13	 **44**		
	a: $R^1 = R^2 = R^4 = H$, $R^3 = Me$	10.37 ($CDCl_3$)	52
		10.27 $(CD_3)_2SO$	52
	b: $R^2 = R^4 = H$, $R^1 = R^3 = Me$	10.28($CDCl_3$)	52
	c: $R^1 = R^2 = H$, $R^3 = R^4 = Me$	10.23 ($CDCl_3$)	52
		10.15 $(CD_3)_2SO$	52
	d: $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = t$-Bu	10.88 ($CDCl_3$)	52
	e: $R^1 = R^4 = H$, $R^2 = R^3 = Me$	11.06 ($CDCl_3$)	52
	f: $R^4 = H$, $R^1 = R^2 = R^3 = Me$	11.05 ($CDCl_3$)	52

Table 2. Continued

Run No. 1	Compound 2	CH=S Group (solvent) 3	Refs. 4
14			
	47		
	a: $R^1 = R^2 = H$, $R^3 = R^4 = Me$	10.62 ($CDCl_3$)	52
	b: $R^1 = H$, $R^2 = R^3 = R^4 = Me$	10.62 ($CDCl_3$)	52
	c: $R^1 = R^2 = R^3 = R^4 = Me$	10.55 ($CDCl_3$)	52
	d: $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = t$-Bu	11.11 ($CDCl_3$)	52
	e: $R^1 = R^3 = H$, $R^2 = R^4 = Me$	10.78 ($CDCl_3$)	52

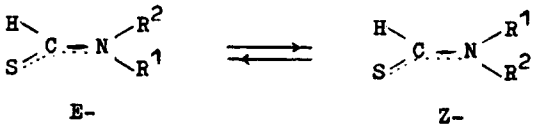
in the corresponding selenobenzaldehyde **21** is observed at $\delta = 17.38$ ppm which is indicative of a strong anisotropic effect of the C=Se bond.



Ref. 39

21

The *N*-unsymmetrically substituted thioformamides **93** exist as *E*- and *Z*-conformers the ratio of which has been determined by ^{1}H NMR.



E- **Z-**

93 93

Scheme 43

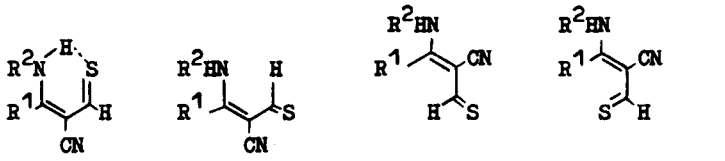
According to ^{1}H NMR data the enamino thial **23** exists mainly (95%) as an *s-trans*-rotamer with a barrier of rotation about the C–N bond of 17.1 kcal/mol with a coalescence temperature of 330 K.[41]

The enamino thioaldehydes **52**, **54**, and **56** are thioformaldehyde analogs. However, judging by their spectral characteristics, and especially their ^{1}H NMR spectra, these compounds and thioaldehydes are very much alike (Table 2).[55]

For the 2-cyano enamino thioaldehydes **56** two geometric isomers **A** and **C** and the corresponding rotamers **B** and **D** are possible.

Table 3. The ratio of thioformamide **93** isomers[102]

R^1	R^2	[Z]/[E]	Solvent
H	Me	6.9	C_6H_6
H	Et	8.1	DMSO
H	*i*-Pr	2.3	C_6H_6
H	*i*-Bu	2.5	C_6H_6
H	*t*-Bu	0.04	C_6H_6
H	CH_2Ph	5.2	C_6H_6
H	CHMePh	2.8	C_6H_6
H	CH_2CH_2OMe	3.01	neat
H	CH_2CH_2OEt	3.8	neat
H	$CH_2CH_2NMe_2$	13.3	DMSO
Me	CH_2Ph	0.64	neat
Me	CHMePh	0.37	neat
Me	CH_2CH_2OH	0.33	C_6H_6
Et	CH_2CH_2OH	0.64	C_6H_6
i-Pr	CH_2CH_2OH	0.32	C_6H_6
i-Pr	CH_2Ph	0.25	C_6H_6
t-Bu	CH_2CH_2OH	0.00	C_6H_6

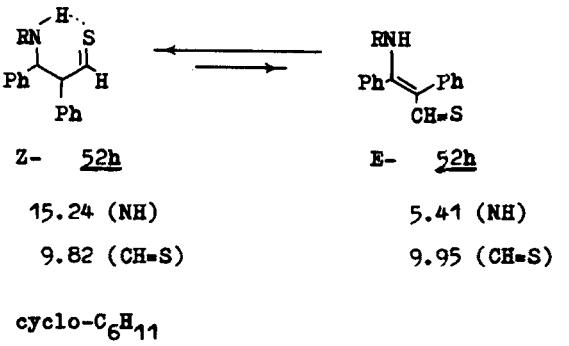


A **B** **C** **D**

Scheme 44

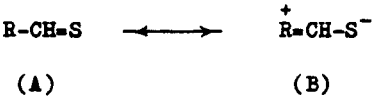
The signals of the thioformyl protons of compounds **56** in ^{1}H NMR spectra ($CDCl_3$) are recorded at $\delta \sim 10-10.5$ ppm. Weak signals at $\delta \sim 10$, < 0.05 H are assigned to the geometric isomers and their rotamers in compounds **56** with a monosubstituted amino group. Analysis of the ^{1}H NMR spectra has shown that the *s-trans*-isomers **B** and/or **C** are present in much smaller amounts than the *cis–cis* isomer **A** due to hindered rotation about the C(1)–C(2) bond. In these spectra there are no weak maxima showing the presence of the *trans-s-cis*-isomer **D**. The ^{1}H NMR spectra of the 2-alkoxycarbonyl enamino thioaldehydes **54** are similar to those of the thioaldehydes **56**.[55]

The thioaldehydes **52a, b, c, d** are *Z*-isomers and structurally similar to the starting enamines. The cyclohexylamino substituted thioaldehyde **52h** contains about 10% of the *E*-isomer.[54]



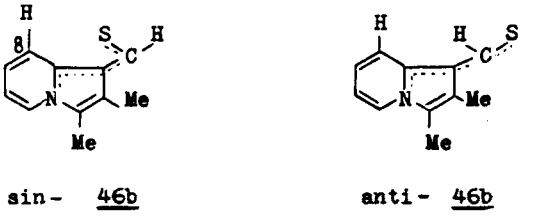
Scheme 45

The ^{1}H NMR spectra of the thioformyl indolizines **22** and **46** have been studied in detail.[40] The 1- and 3-thioformyl groups produce a strong diamagnetic anisotropic deshielding effect on the opposite 8-H and 5-H atoms, respectively. The 5-H chemical shifts in the spectra of the 3-thioformylindolizines **22** are in a δ range of 11.1–11.6 ppm. In 2,3-dimethyl-1-thioformylindolizine **46b** the rotation about the ring-CH=S bond is hindered. This is due to a significant contribution of the bipolar mesomeric form (**B**):[40]



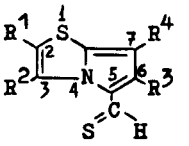
Scheme 46

The large 8-H deshielding and the thioformyl proton singlet signal indicate that below the coalescence temperature **46b** exists in a *syn*-configuration, more stable than the *anti*-form. This is due to the intramolecular electrostatic attraction between the sulfur atom and the pyridine ring charges which corresponds to a potential energy minimum of the molecule.[40]

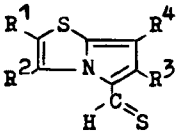


Scheme 47

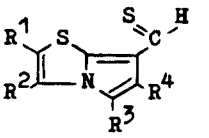
The temperature dependence of the ^{1}H NMR spectra provides evidence for a hindered rotation about the heterocycle-CH=S bond in the thioformylpyrrolo[2,1-*b*]thiazoles **44** and **47**.[52] These data are in agreement with the existence of the 5-thioformyl derivatives **44** either in the *syn*-configuration [compounds **44a–d**] or the *anti*-configuration [compounds **44e, f**], and of the 7-thioformyl derivatives only in the *syn*-configuration [*syn*-**47**].



sin-**44**



anti-**44**

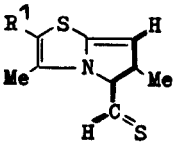


sin-**47**

	R^1	R^2	R^3	R^4
a	H	H	Me	H
b	Me	H	Me	H
c	H	H	Me	Me
d	H	Me	*t*-Bu	H
e	H	Me	Me	H
f	Me	Me	Me	H

Scheme 48

The higher stability of the 5- and 7-*syn*-thioformyl derivatives with respect to their *anti*-isomers is a consequence of the intramolecular electrostatic attraction of the partial charges on both the thioformyl sulfur atom and the thiazole ring. Compounds **44e, f** exist predominantly in the *anti*-form due to the steric effect of the 3-methyl substituent which repels the thioformyl sulfur atom out of the ring plane. In compound **44d** the influence of the *t*-butyl group overlaps with the effect of the 3-methyl group which lets the thioformyl group retain the *syn*-configuration. The existence of long-range spin–spin 7-H–CH=S interaction (SSCC 0.8 Hz) in the thioaldehydes **44e, f** furnishes additional support for the assumption that these compounds occur in the *anti*-form. In these thioaldehydes the 7-H and CH=S protons are arranged in a W configuration which is most favorable for effective interaction throughout the conjugated system:[52]



(W)

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

The character of the ^{1}H NMR spectra of the 2-amino-3-thioformylindoles **28** implies hindered rotation of the thioformyl group. The ratio of the two forms of **28** at 20 °C has been determined as 23 : 77.[48]

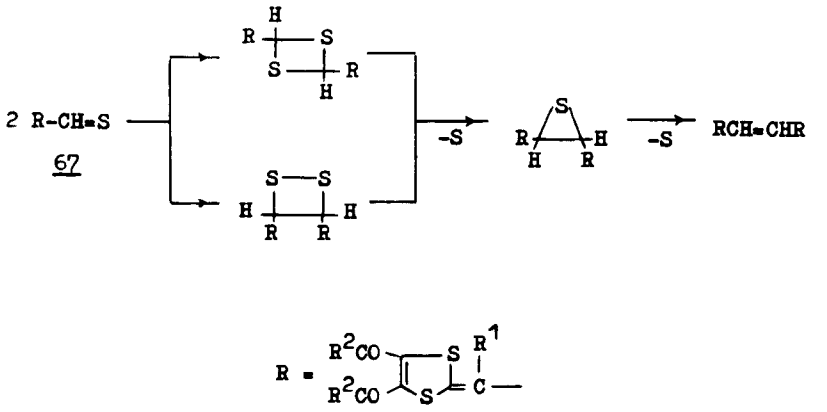
The rather scarce data on the ^{13}C NMR spectra of thioaldehydes show that the ^{13}C nucleus in the thioformyl group resonates in the region characteristic of thioketones (Table 4).

4. CHEMICAL TRANSFORMATIONS

The high reactivity of thioaldehydes is already evident from the fact that they are highly prone to tri-, oligo- and polymerization. The yield of these products is determined not only by the structure, but also by the conditions of thioaldehyde generation. Thus, the preparation of thioformaldehyde from formaldehyde and hydrogen sulfide in the presence of hydrogen chloride mainly leads to the formation of trimer (1,3,5-trithiane) whereas in alkaline medium high-melting polymers are obtained.[109] The synthesis of trimeric thiobenzaldehyde from benzaldehyde and hydrogen sulfide in a highly acidic medium affords mainly the more stable β-isomer; a weakly acid medium and low reaction temperature give larger proportions of not only the α-isomer but also a polymer of ~ 1000 M.[109]

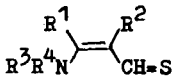
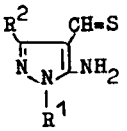
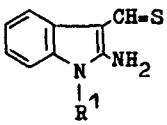
It has been convincingly shown[110] that the self-transformations of monomeric thioaldehydes constitute a catalytic process. The addition of protic and Lewis acids causes instant trimerization or polymerization of 2,2-dimethylpropanethial **14** in all solvents. This accounts for the fact that many investigators failed to detect monomeric thioaldehydes in the acid-catalyzed thionation of aldehydes. The transformations of thioaldehydes to 1,3,5-trithianes are also favored by basic catalysts such as triethylamine and K_2CO_3.[110] In pure ether and chloroform **14** exists for a long time in the monomeric state whereas hydroxyl-containing solvents induce fast trimerization.[110]

Like unenolized ketones, thioaldehydes can undergo reversible thermal dimerization of the "head-to-tail" type.[111] A prolonged reaction time (24 h) or refluxing of **67** in benzene lead chiefly to alkenes, the products of bimolecular abstraction of the thial sulfur according to Scheme 49:[56]

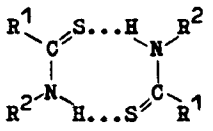


Scheme 49

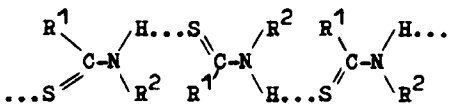
Table 4. ^{13}C NMR spectra of thioaldehydes (CH=S group)

Run No.	Compound	δ, ppm ($CDCl_3$)	Refs.
1	$Me_2NCH{=}CH{-}CH{=}S$	206.6 (−75 °C)	108
2	$(Me_3Si)_3C{-}CH{=}S$ **16**	248.2	36
3	2,4,6-(*t*-Bu)$_3C_6H_2{-}CH{=}S$ **18**	250.4	37
4			
	52		55
	a: R^1 = Ph, R^2 = R^4 = H, R^3 = *c*-C_6H_{11}	210.5	
	b: R^1 = Ph, R^2 = H; R^3, R^4 = $(CH_2)_5$	209.17	
	c: R^1 = Ph, R^2 = H; R^3, R^4 = $(CH_2CH_2)_2O$	212.28	
	d: R^1, R^2 = $(CH_2)_3$; R^3, R^4 = $(CH_2CH_2)_2O$	197.37	
	e: R^1 = R^2 = Ph, R^3 = Pr, R^4 = H	192.93	
	f: R^1 = R^2 = Ph, R^3 = C_6H_{13}, R^4 = H	192.85	
	g: R^1 = R^2 = Ph; R^3, R^4 = $(CH_2)_4$	209.04	
	h: R^1 = R^2 = Ph, R^3 = *c*-C_6H_{11}, R^4 = H	192.22	
	i: R^1 = R^2 = Ph; R^3, R^4 = $(CH_2CH_2)_2O$	213.59; 190.62	
	j: R^1, R^2 = *o*-C6H4CH2; R3, R4 = (CH2)5	210.34	
5			
	27		48
	a: R^1 = Me, R^2 = Ph	203.5	
	b: R^1 = Ph, R^2 = Me	202.0	
	c: R^1 = Ph, R^2 = *t*-Bu	202.8	
6			
	28		48
	a: R^1 = Me	189.3; 184.6	
	b: R^1 = CH_2Ph	189.5; 185.7	
	c: R^1 = Ph	191.9; 186.8	

Thioacrolein is stabilized as the dimer (1,3-dithietane) (cf. Section 2.4.10). However, there is no evidence for the formation of the corresponding dimer of 2,2-dimethylpropanethial **14**.[110] *N*-Monosubstituted thioformamides give rise to associates among which the cyclic **94** are more stable to dissociation than the chain associates **95**.[102]



94

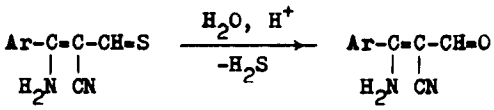


95

Scheme 50

Thioaldehydes are active in different reactions with nucleophilic reactants.

Hydrolysis of the enamino thioaldehydes **56** in ethanol at 60 °C in the presence of sulfuric acid gives mainly the corresponding aldehydes which, in turn, may be involved in further transformations.[55]

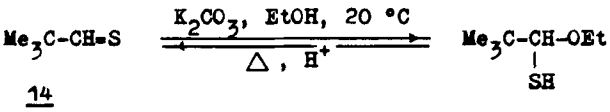


56

Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-$C_{10}H_7$

Scheme 51

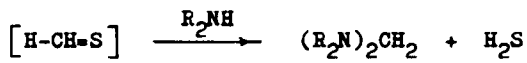
In the presence of *alcohol* and potassium carbonate 2,2-dimethylpropanethial **14** forms small amounts of thioacetal and isomeric 1,3,5-trithianes.[110]



14

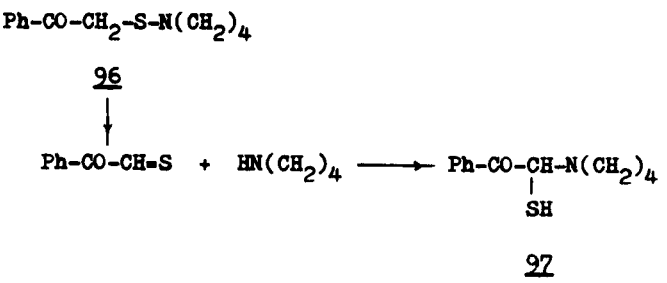
Scheme 52

Aminolysis of the intermediate thioformaldehyde is an essential step in the reaction of methanesulfenyl halides with secondary amines.[7]



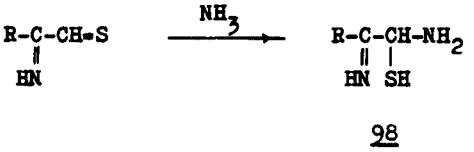
Scheme 53

Benzoylthioformaldehyde and morpholine formed upon decomposition of sulfenamide **96** are instantly involved in a reaction affording the *gem*-amino thiol **97**.[112]



Scheme 54

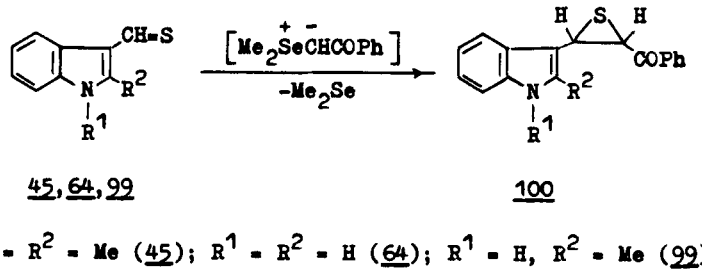
The *gem*-amino thiols **98** are readily formed from thioformylimines and ammonia.[112]



Scheme 55

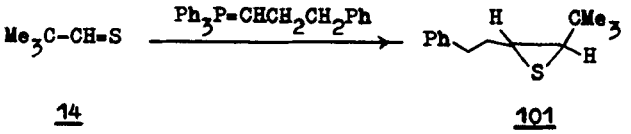
Like thioketones, thioaldehydes yield hydrazones and semicarbazones.[50,60]

Ylides in their reactions with thiocarbonyl compounds behave as nucleophiles.[11] The reaction of the 3-thioformylindoles **45**, **64**, and **99** with dimethylselenonium benzoylmethylide is readily carried out in DMF solution at 0 °C to lead to the 2-indolyl-3-benzoylthiiranes **100**.[113]



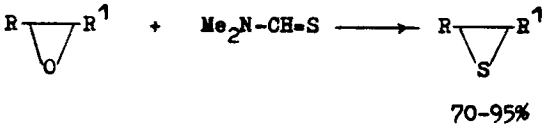
Scheme 56

2,2-Dimethylpropanethial **14** reacts with (3-phenylpropylidene)triphenylphosphorane to form the thiirane **101**.[110]



Scheme 57

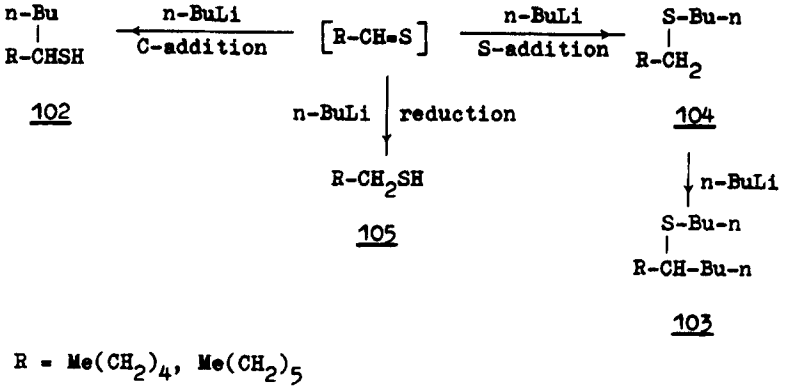
N,N-Dimethylthioformamide proved to be an effective reagent in the synthesis of thiiranes from oxiranes.[114]



Scheme 58

Thioketones react with *organometallic compounds* in two competing ways, *i.e.*, normal nucleophilic and/or thiophilic addition.[11]

In studying the reaction of thioaldehydes with *n*-butyllithium Wilson *et al.* observed four reaction types: *C*-addition, *S*-addition, double addition and reduction.[115] The ratio of products depends on the structure of substrate, solvent, and temperature. For example, the thioaldehyde $Me(CH_2)_4$–CH=S forms with a 4-fold excess of *n*-BuLi in ether at 25 °C the thiol **102** (73%), the sulfide **103** (19%) and small quantities of the sulfide **104** (3%) and the thiol **105** (4%). At room temperature the yield of **102** decreases to 17% and to 2% with THF as the solvent.

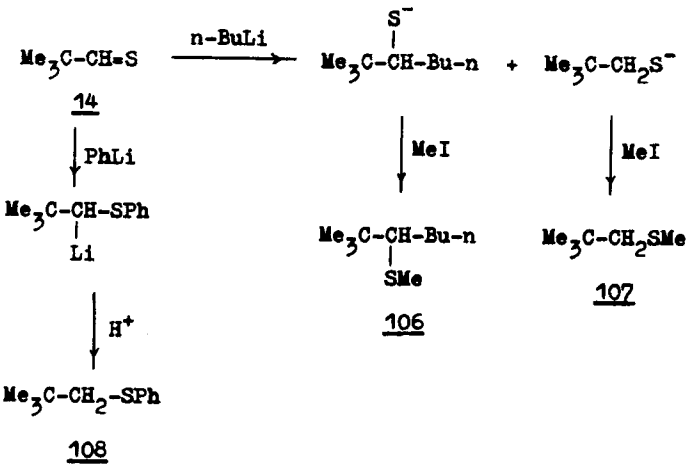


Scheme 59

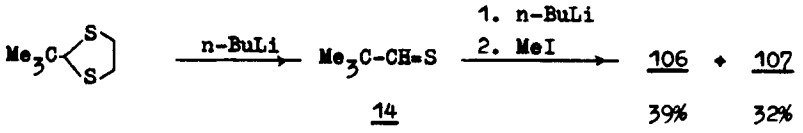
In ether 2,2-dimethylpropanethial **14** reacts with *n*-BuLi to give the product of addition at the carbon atom and the product of reduction.[110] The fact of the preparation of compounds **106** (70%) and **107** (17%) by addition of methyl iodide to the reaction mixture provides convincing evidence that the reaction routes shown in Scheme 60 take place.

The authors[110] have carried out the reaction of 2-*t*-Bu-1,3-dithiolane with *n*-BuLi by the Wilson method.[115] The formation of **106** and **107** in these two cases suggests that one and the same thioaldehyde **14** participates in the reaction.

Compound **14** reacts with phenyllithium by a thiophilic mechanism to form neopentyl phenyl sulfide **108** (30%).[35]

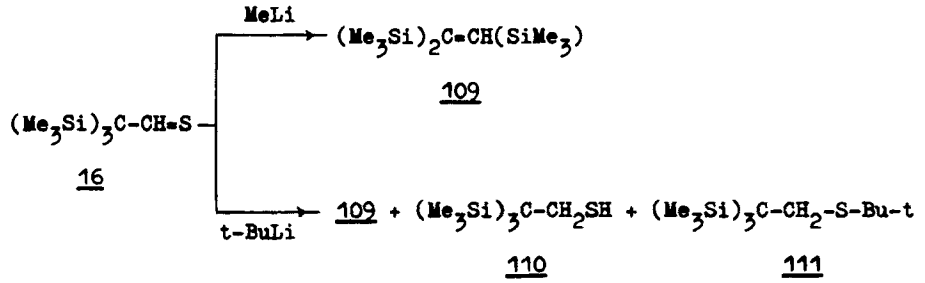


Scheme 60



Scheme 61

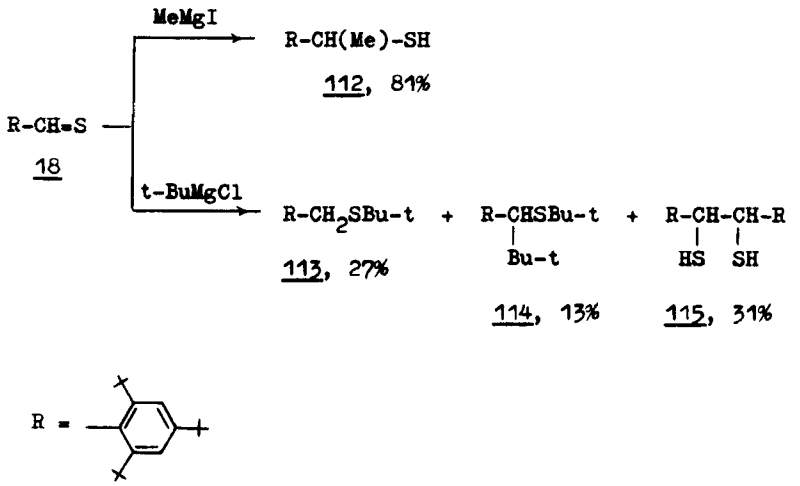
Treatment of the tris(trimethylsilyl)ethanethial **16** with methyl- or *t*-butyllithium leads to the alkene **109** in 79 and 34% yield, respectively.[36] In the latter case the thiol **110** (35%) and the sulfide **111** (10%) are also formed.



Scheme 62

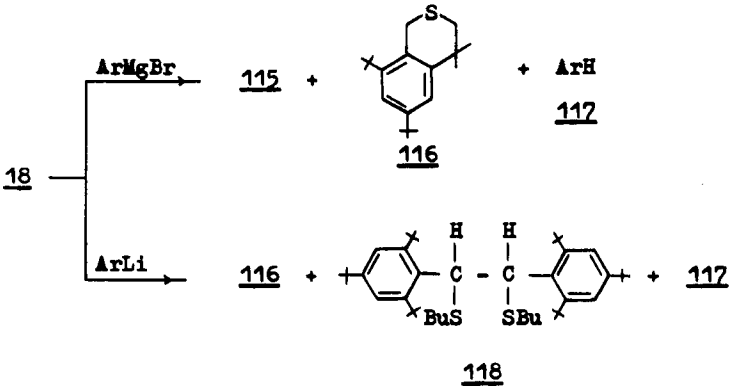
With Grignard reagents the reaction of **16** proceeds in a similar manner, but considerably more slowly.[36]

Some interesting results have been obtained in a study of the reaction of stable (2,4,6-tri-*t*-butyl)thiobenzaldehyde **18** with Grignard and organolithium reagents.[116] The reaction of **18** with methylmagnesium chloride leads to the thiol **112**, whereas that with *t*-butylmagnesium chloride gives three products, *i.e.*, the sulfides **113** and **114** and the α-dithiol **115**.



Scheme 63

In the corresponding reactions with the very bulky (2,4,6-tri-*t*-butyl)phenylmagnesium bromide or -phenyllithium no products of addition at carbon or sulfur have been observed.[116]

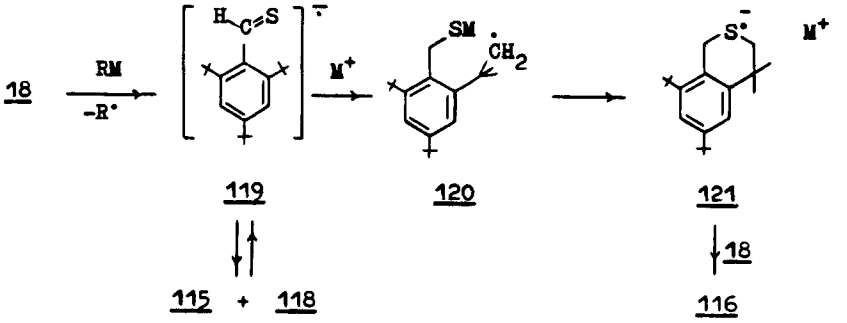


Scheme 64

The above reactions have been interpreted in terms of a one-electron transfer mechanism[116] encountered earlier in the reactions of thioketones with organometallic compounds.[11]

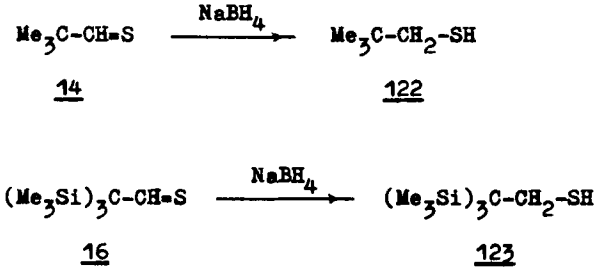
The key intermediate of the proposed Scheme 65 is the radical anion **119**. Its **119** → **120** → **121** transformation leads to compound **116**, whereas its dimerization gives the products **115** and **118**. It should be emphasized that this presents the first case

of dimerization of thioketyl radicals and the first observation of radical anion generation from thioaldehydes.[116]



Scheme 65

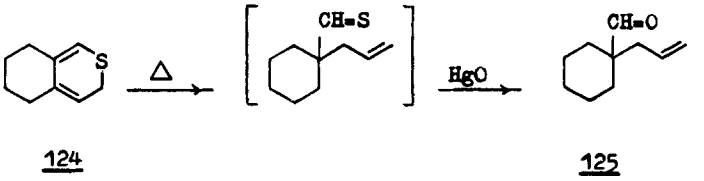
Like thioketones, thioaldehydes are readily *reduced* to the corresponding thiols by standard reducing agents. Thus, under the action of sodium borohydride on 2,2-dimethylpropanethial **14** neopentanethiol **122** was obtained;[35,110] tris(trimethylsilyl)-ethanethial **16** is quantitatively transformed to the thiol **123**.[36] Reduction takes place in the reaction of thioaldehydes with alkyl(aryl)lithium reagents or with Grignard reagents.[35,36,110,116]



Scheme 66

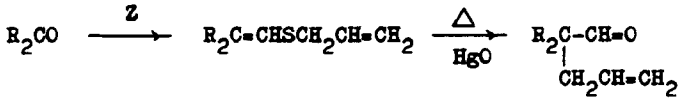
Thioaldehydes are prone to *oxidation* in the presence of air oxygen.[56,57,62,63] Even the very stable *t*-butyl-substituted thiobenzaldehyde **18** is converted to the corresponding aldehyde under the action of oxygen.[37]

Thioaldehyde oxidation *in situ* is of interest in a preparative respect and for elucidating the reaction mechanism. Thus, simple heating of the sulfide **124** at 160–180 °C leads to polymeric products, whereas in the presence of red mercury oxide the aldehyde **125** is obtained in 82% yield.[117]



Scheme 67

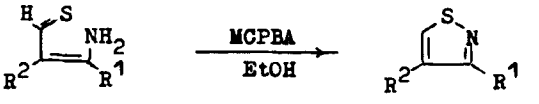
Such a procedure, involving the initial interaction of ketones with lithium di(ethoxy)allylthiomethylphosphonate, greatly extends the limits of the application of the thio Claisen rearrangement and allows the preparation of unsaturated aldehydes from thiocarbonyl compounds.[117]



Z = $(EtO)_2\overset{-}{P}OCHSCH_2CH{=}CH_2\ Li^+$

Scheme 68

The *N*-unsubstituted enamino thioaldehydes **54** and **56** are oxidized by MCPBA in ethanol solution at 65 °C to give the corresponding isothiazoles **126** in good yield.[55]

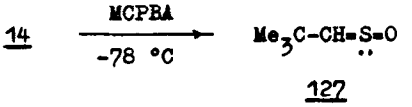


54, 56 **126**

Scheme 69

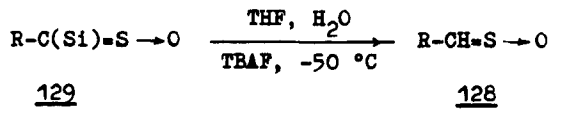
The use of iodine instead of MCPBA causes resinification, whilst the treatment with sulfur leads to only partial oxidation of **54** and **56**. The oxidation of the *N*-alkyl analogs of **54** and **56** affords only resinous products.[55]

The oxidation of **14** with *m*-chloroperbenzoic acid at low temperature leads to the sulfine **127**.[35,110]



Scheme 70

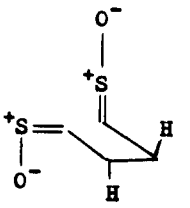
The aryl substituted sulfines **128** can be prepared by fluorodesilylation of the thioacylsilane *S*-oxides **129**.[118]



R = Ph, 4-MeC_6H_4, 3-ClC_6H_4, 2,4,6-$Me_3C_6H_2$, Me_3C

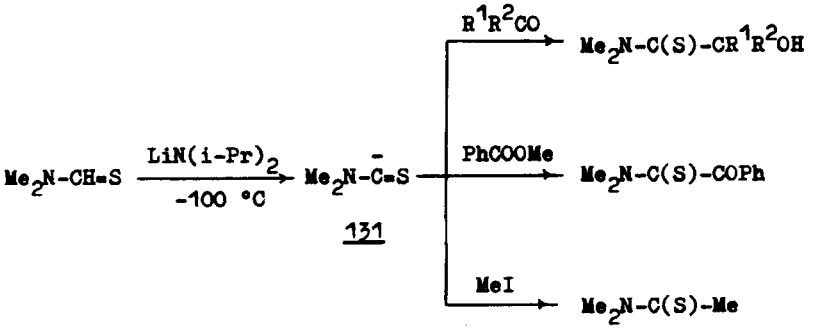
Scheme 71

The first bis(thial *S*-oxide), (*Z,Z*)-*d,l*-2,3-dimethyl-1,4-butandithial *S,S'*-dioxide **130**, a new biologically active organosulfur compound, has been isolated recently from onion extract.[119]



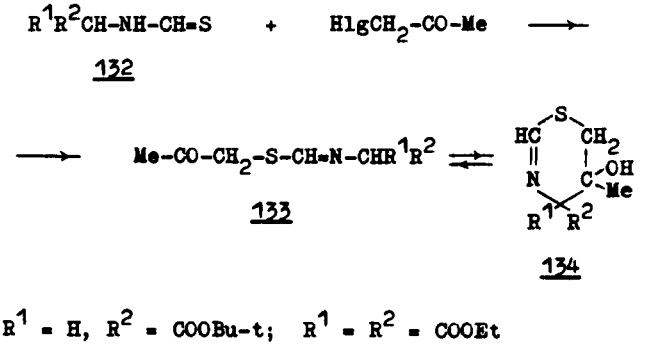
130

N,N-Dimethylthioformamide with lithium diisopropylamide forms nearly quantitatively the carbanion **131**, which is an excellent thioacylating agent of compounds of different classes.[120]



Scheme 72

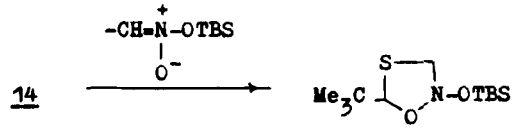
The ability of the *N*-thioformyl compounds **132** to react with halo acetones has been employed in the synthesis of the biologically essential *d,l*-7-amino-3-*d,l*-acetoxycephalosporanic acid (7-ADCA).[121,122]



Scheme 73

Compounds **133** and **134** have been suggested to interconvert readily.[121]

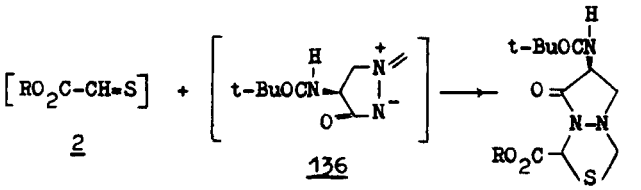
Thiocarbonyl compounds are noted for their ability to enter *1,3-dipolar cycloaddition* which leads to the formation of valuable heterocyclic compounds.[11] In thioaldehydes this property is especially pronounced and can be used for *in situ* trapping.[24,110] Thus, 2,2-dimethylpropanethial **14** instantly reacts with a nitronate ether to yield the [2+3]-cycloadduct **135**.[35,110]



135

Scheme 74

As a result of cycloaddition to the pyrazolidinium ylide **136**, the *in situ* generated thioformyl derivatives **2** form nuclear analogs of pyrazolidinone antibacterial preparations **137**.[27]

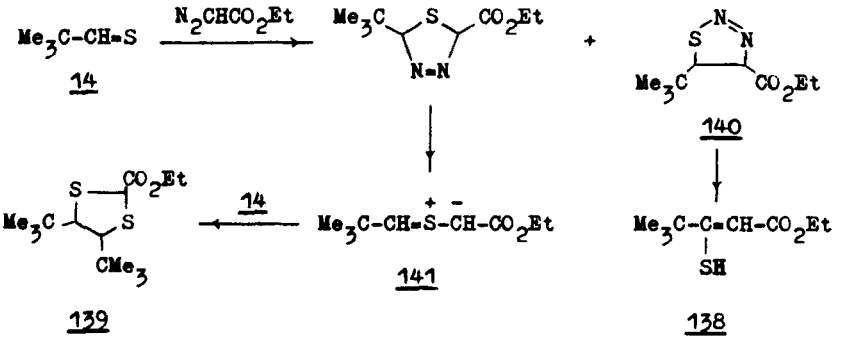


137

R = H, Me, Et, t-Bu, allyl, $HCPh_2$

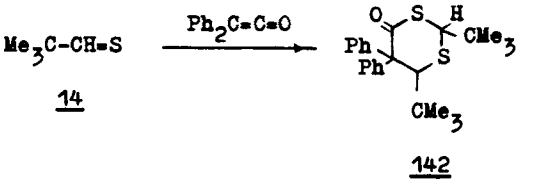
Scheme 75

Thiocarbonyl compounds form with diazoalkanes regioisomeric [2+3]-cycloadducts.[11] In the reaction of 2,2-dimethylpropanethial **14** with ethyl diazoacetate the thiol **138** and an unseparable mixture of diastereoisomers **139** have been isolated. The formation of **138** is explained by S–N-heterolysis of the previously formed thiadiazoline **140**, followed by hydride transfer. The formation of the dithiolane **139** involves the thiocarbonyl ylide **141**.[35]



Scheme 76

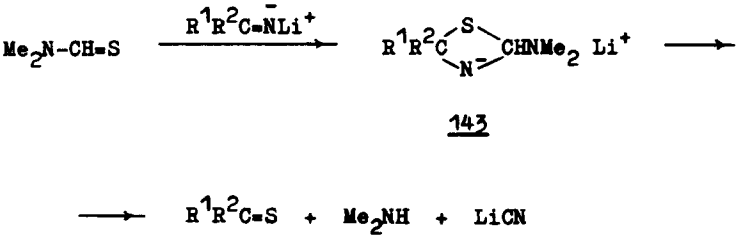
In the reaction with diphenylketene the thioaldehyde **14** gives a mixture of the 2:1 cycloadducts **142** in moderate yield. With dimethylketene no reactions occur.[110]



14 **142**

Scheme 77

The reaction of *N,N*-dimethylthioformamide with ketimine anions is of a [2+2]-cycloaddition type *via* the four-membered cyclic intermediate **143** which is further transformed to a thioketone.[123]

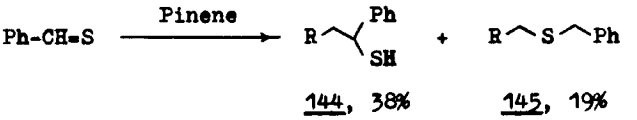


143

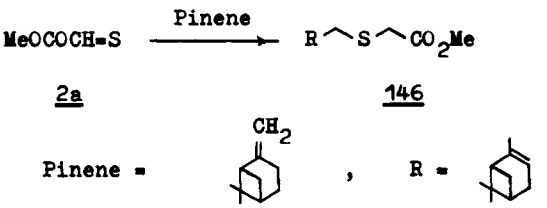
Scheme 78

Being a 2π-component, thiobenzaldehyde can be involved in the addition to the β-pinene double bond.[76] The formation of the two adducts **144** and **145** is governed by different orientation of the addition.

The photochemically generated thioaldehyde **2a** forms with β-pinene at 20 °C the sulfide **146**.[124]



144, 38% **145**, 19%



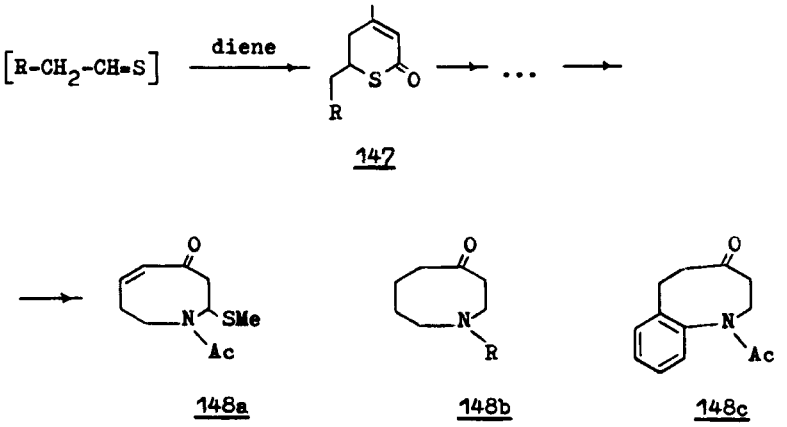
2a **146**

Scheme 79

It is evident that the ene reaction of thioaldehydes is very promising for the synthesis of cyclic structures under mild conditions.

The reactions of donor- or acceptor-substituted thioaldehydes, generated in various ways, with diverse dienes have been discussed in more detail in Sections 2.1–4. Therefore we find it reasonable to dwell upon work dedicated to cycloadditions of thioaldehydes.

The characteristic behavior of thiobenzaldehyde, thioacetaldehyde and some other thioaldehydes in their reactions with 2,3-dimethyl-1,3-butadiene, anthracene, and 9,10-dimethylanthracene have already been examined in detail.[76] It has been found that benzene and toluene are the most convenient solvents whereas DMF decreases the yield of adducts. Much attention has been given to the regiochemistry of cycloaddition and its relation to the nature of the substituent in the thioaldehyde.[24,125,126] Relying on calculations of the molecular orbital (MO) energy the regioselectivity in Diels-Alder reactions of some thioaldehydes has been forecasted.[127] The dihydrothiopyrans obtained from thioaldehydes by the Diels-Alder procedure may be essential in the synthesis of natural compounds, such as juvenile hormone, erythronolides, zygosporin analogs, etc.[125] Several synthetic routes to azocine derivatives **148** from the nitrogen-containing cycloadducts **147** have been elaborated.[128]



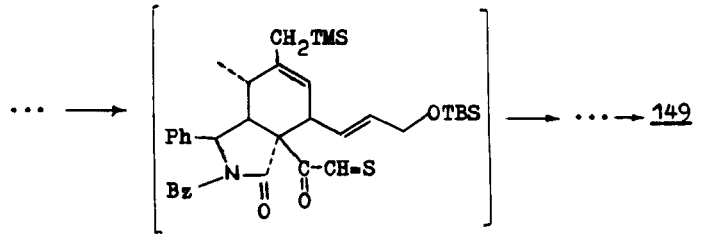
Scheme 80

In the complex synthesis of the S-bridged [11]cytochalazanes **149** one of the most important steps is the generation of an intermediate thioaldehyde **150** and its trapping by dienes.[129]

In the reaction with the tetrazine **151** donor-substituted thioaldehydes, *i.e.*, thioformates, thioformamides and thiobenzaldehyde behave as heterodienophiles.[130] The thiadiazines **152** formed as a result of [4+2]-cycloaddition may lose a sulfur atom and transform to pharmacologically interesting pyrazoles.

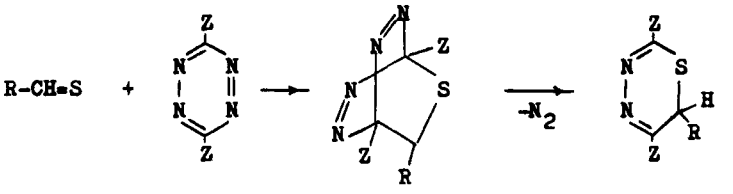
The characteristic properties of the excited thiocarbonyl function have given rise to the development of *the photochemistry* of thiocarbonyl compounds.[11]

Exposure of a benzene solution of (2,4,6-tri-*t*-butyl)thiobenzaldehyde **18** to irradiation with a mercury or sodium lamp ($\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ excitation) leads to the benzothiolane derivative **116** in 91 and 96% yield, respectively.[131]



150

Scheme 81

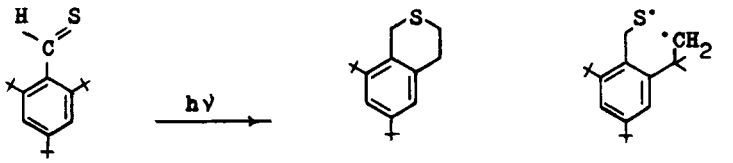


151 152

R = OEt, OPr, NMe_2, $N(CH_2)_4O$, $N(CH_2)_5$, Ph

Scheme 82

The photochemical formation of the heterocycle **116** is unexpected in this case since the known photoreactions of aromatic thioketones containing δ-hydrogen atoms give cyclopentanethiol derivatives.[11] The δ-cyclization involving $n \rightarrow \pi^*$ excitation is also of interest; in aromatic thioketones this process occurs *via* the S_2 ($\pi \rightarrow \pi^*$) state.[11]

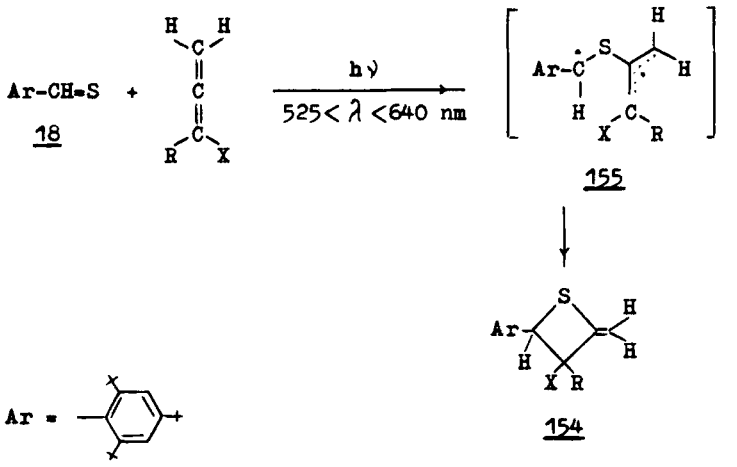


18 116 153

Scheme 83

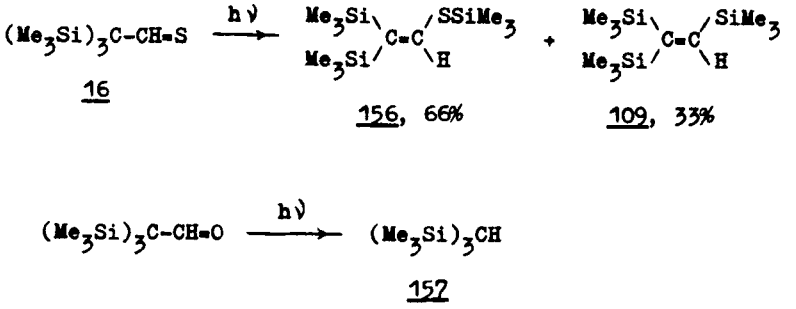
A choice between the possible mechanisms of this transformation, a concerted [2+2]-reaction or a radical cyclization *via* the biradical **153**, has not been made yet.[131]

The photochemical reaction of **18** with unsaturated cumulenes has been investigated.[132] Irradiation of **18** together with alkoxy-, alkylthio- or phenylallenes leads to the thietane **154** via the intermediate biradical **155**.[132]



Scheme 84

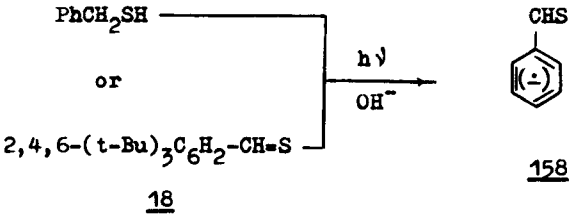
The radical anions of aldehydes have long been known and successfully studied by stituted sulfide **156** and the ethene **109**.[36] The corresponding aldehyde, when irradiated under analogous conditions, forms tris(trimethylsilylmethane) **157**.



Scheme 85

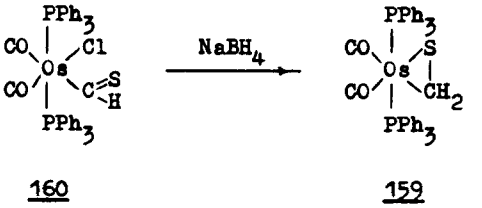
The formation of **156** from **16** by a 1,2-shift of the Me_3Si group from the α-position towards the thiocarbonyl carbon, accompanied by desulfurization, constitutes a new type of photoreaction of thiocarbonyl compounds.[36]

The radical anions of aldehydes have long been known and successfully studied by ESR spectroscopy,[133] whereas those of thioaldehydes remained unknown until recently. In 1988 the radical anion of thiobenzaldehyde **158** was obtained by photolysis of benzyl mercaptan or 2,4,6-tri-*t*-butylthiobenzaldehyde **18** in alkaline medium at room temperature.[134] The spectrum of **158** is analogous to that of benzaldehyde radical anions and typical of the spectra of radicals in which the unshared electron pair interacts with the sulfur atom.



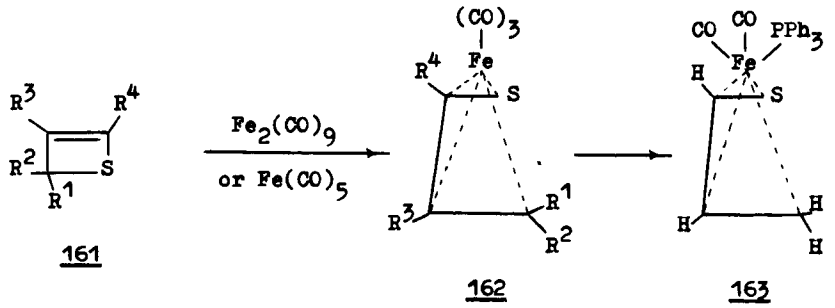
Scheme 86

The ability of thioformyl compounds to form *complexes* with transition metals is successfully employed for the trapping of thioaldehydes of short life span. The first stable crystalline thioformaldehyde complex **159** was obtained by reaction of the unstable thioformyl derivative **160** with sodium borohydride.[135]



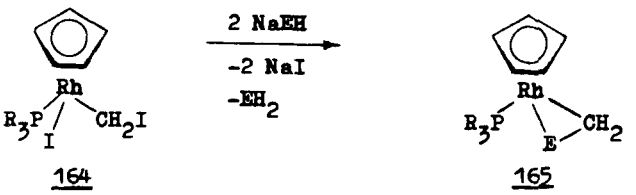
Scheme 87

Treatment of the thietes **161** either with iron nonacarbonyl upon heating or with iron pentacarbonyl upon irradiation gave the unstable thioacrolein complexes **162** as red or orange crystals or oils.[136] The structure of the complexes **162** was proven by X-ray diffraction of the triphenylphosphine derivative **163**, formed from **162** by replacement of a carbonyl group by the Ph_3P ligand. The ^1H NMR spectra of the complexes **162** were compared with that of the acrolein molybdenic complex.[136]



Scheme 88

Recently rhodium complexes of thioformaldehyde and its chalcogen analogs have been prepared.[137,138] Compound **164** reacts with sodium hydrosulfide at room temperature in THF to form the thioformaldehyde complex **165a** in 50% yield. Analogously, by action of NaSeH or NaTeH the seleno- and telluroformaldehyde complexes **165b** and **165c** have been prepared.[137]



164 165

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

Scheme 89

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