Some Recent Synthetic Routes to Thioketones and Thioaldehydes

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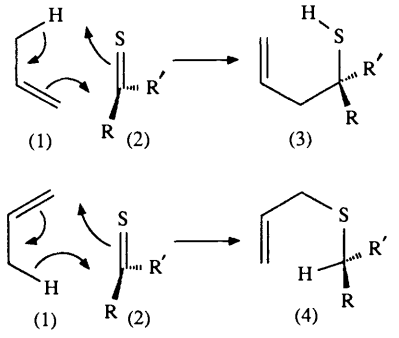
1 Introduction

The chemistry of thioketones and thioaldehydes has been widely studied and their reactions reviewed[1—3] because they offer useful routes for the incorporation of sulfur heteroatoms into the synthesis of heterocycles or natural products. They have high reactivities associated with the poor orbital overlap of the (C-2*p*, S-3*p*) π-bond. This has meant that only a few examples of stable, isolable thioketones have been made[4,5] and the even greater reactivity of thioaldehydes delayed the isolation of the first examples[6—8] to as recently as 1982. The tendency with thiocarbonyl compounds is for spontaneous oligomerization to occur unless there is electronic stabilization[1] (thioamides, thionoesters, and thionoacids are usually fairly stable) or steric stabilization (thioketones and thioaldehydes need bulky substituents if they are to be isolable).

Most of the studies on the reactivity of thiocarbonyl groups have been conducted on stable thioketones and these have shown general similarities between the chemistry of carbonyl and thiocarbonyl groups. A significant increase in reaction rate is observed, however, for thiocarbonyls because of the inherent instability of the C—S π-bond: for example, thiobenzophenone reacts about 2000 times faster[1] than benzophenone when treated with phenylhydrazine to give the hydrazone. Similarly, the reduction of thioketones to thiols with sodium borohydride is much faster[1] than the corresponding reduction of ketones to alcohols.

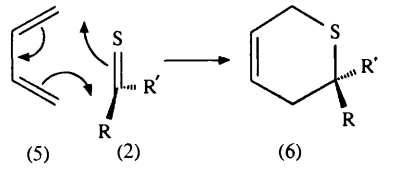
The most significant differences between thiocarbonyl and carbonyl chemistry are observed in reactions involving nucleophiles, olefins, and conjugated dienes. Thus, nucleophilic attack on carbonyl compounds is generally at the carbonyl carbon, but with thiocarbonyls it can occur either at carbon or sulfur. Examples of nucleophiles which attack thioketones at sulfur[1] include phenyl lithium (to give thioethers) and sodium bisulphite (to give thiosulfates).

With mono-olefins (1), thiocarbonyl compounds (2) can undergo 'ene'-type reactions (Scheme 1). For example thiobenzaldehyde reacts with (−)-β-pinene to give 'ene' reaction products.[9] Both C—C σ-bond formation, to give a thiol (3), and C—S σ-bond formation, to give a sulfide (4), can be observed.



Scheme 1 'Ene'-reaction of thiocarbonyl compounds.

Thiocarbonyl compounds undergo cycloaddition reactions much faster than carbonyl compounds. Thus the Diels–Alder [4 + 2] cycloaddition reaction (Scheme 2) between a conjugated diene (5) and a thioketone or thioaldehyde (2) gives stable cycloadducts (6) and, in particular, transient thiocarbonyls are routinely characterized as such cycloadducts.



Scheme 2 Diels–Alder reaction of a thiocarbonyl compound.

So despite their highly reactive nature, a wide range of literature is available on the reactions of both stable and transient thioketones and thioaldehydes and on their use in synthesis.[10] As the latter has become more widespread, so too has the variety of synthetic methods for the generation of thiocarbonyls become more extensive. This article concentrates on the plethora of synthetic approaches to thioketones and

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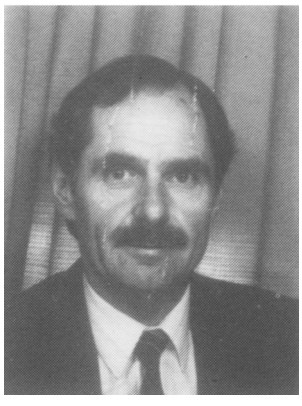
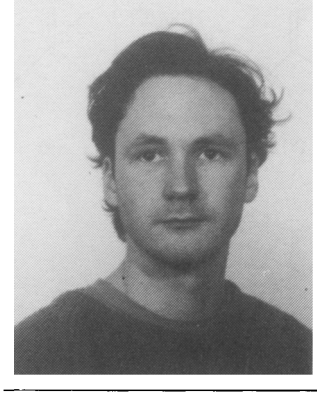


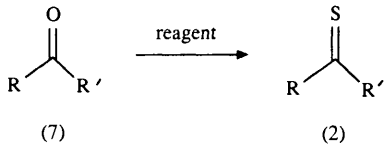
Dr. W. M. McGregor was born in Glasgow in 1965 and gained his Ph.D. on the study of thiocarbonyl compounds from the University of Glasgow in 1989. He has since been employed in a variety of postdoctoral positions and also as a research chemist with Scottish & Newcastle Breweries. His research interests include organosulfur chemistry, host–guest chemistry, and the design and synthesis of novel monomers. He is currently in Strasbourg studying complexes of calixarenes.



thioaldehydes, rather than on their reactivity which is reviewed extensively elsewhere.[1—3]

2 Methods for Converting Carbonyls into Thiocarbonyls

The availability of carbonyl compounds makes thionation of carbonyls (7) to give thiocarbonyls (2) a very desirable route (Scheme 3) and many methods of effecting this transformation are known. In the past thiocarbonyl transfer from thiophosgene and analogous compounds[11] has been used, but this method is often ineffective and is now rarely used. Many better methods and reagents are now known.



(7) (2)

Scheme 3 Thionation of carbonyl compound.

2.1 Hydrogen Sulfide/Acid

The use of hydrogen sulfide gas in the presence of an acid catalyst is a classical method for the generation of thiocarbonyl groups which has been used for over a century (it is much more commonly used than the related reagent H_2S_2/HCl). The acid catalyst is usually hydrogen chloride, which reversibly protonates the carbonyl group, facilitating substitution at carbon by H_2S, and subsequent elimination to give the thiocarbonyl. This reagent (H_2S/HCl) has also been used to convert ketals into thioketones.[12]

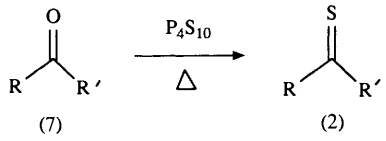
Despite the difficulties associated with the use of hydrogen sulfide gas this approach is still in use, partly because it gives good yields and clean products.

This method[13] is straightforward when the starting material is a ketone (7) (with R and R′ as alkyl or aryl) and gives good yields of pure thioketones (2), often isolated as cycloadducts. The synthesis of thioaldehydes with H_2S/HCl is less straightforward, but a successful route to thioaldehyde adducts has been devised (Scheme 4). Although no free thioaldehyde is generated by this method, the cycloadducts are identical to those derived from the appropriate thioaldehyde by other routes.

The silyated compound (8) is converted[14] (Scheme 4) into the reactive thioketone (9) which can be trapped *in situ* as the Diels–Alder cycloadduct (10) and then can be desilylated with tetrabutyl ammonium fluoride (TBAF) to give the thioaldehyde adduct (11). Use of an analogue of (8), but with a chiral silicon centre, gives asymmetric induction and allows (10) and (11) to be made enantioselectively.[14b]

2.2 Phosphorus-based Reagents

Many variants on inorganic reagents[15] containing phosphorus and sulfur have been reported, including $PCl_5/Al_2S_3/Na_2SO_4$, P_2S_5/NEt_3, $RPS(OR')_2$, $PSCl_n(NMe_2)_{3-n}$, but the one most commonly used to convert ketones (7) into thioketones (2) is phosphorus pentasulfide (in fact P_4S_{10}) (Scheme 5).



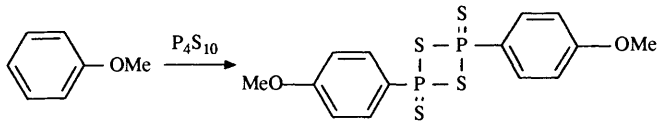
(7) (2)

Scheme 5 Thionation with phosphorus pentasulfide.

It was first used in the synthesis of Michler's thioketone in 1886 and since then has found extensive application in the synthesis of thioketones and related thiocarbonyl compounds. The main problem with this reagent is its insolubility in most organic solvents.

The best results have, however, been achieved using phosphorus pentasulfide as a homogeneous reagent (it is appreciably soluble in pyridine or diglyme) and many thionations have been successfully performed in pyridine[4,16,17] to give a variety of stable or transient thioketones containing alkyl, alkenyl, aryl, or ester substituents. The main advantages of this method are good yields, no organic by-products, and facile purification of the thionated products.

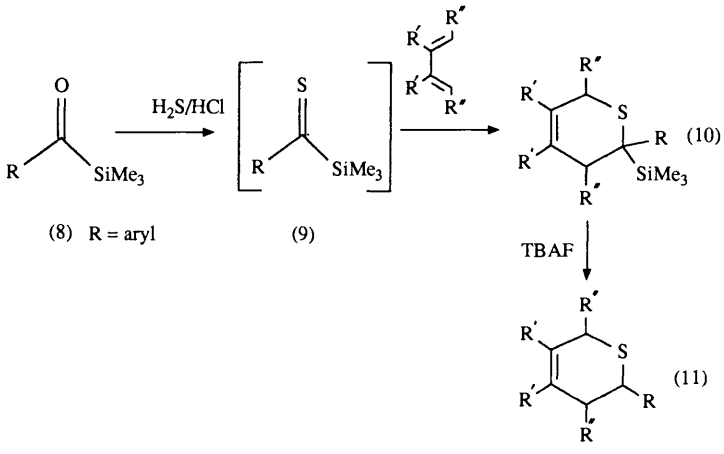
Another successful phosphorus-based reagent is 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-phosphetane-2,4-disulfide (13), known as Lawesson's reagent.[15] It is made (Scheme 6) by the action of phosphorus pentasulfide on anisole (12) and is considered to be an organic analogue of P_4S_{10}.



(12) (13)

Scheme 6 Synthesis of Lawesson's Reagent.

This reagent is soluble in, for example, benzene, toluene, or xylene and has been used in these solvents to convert ketones (7) into thioketones (2) in good yields.[15,18] The thioketones or thioketone derivatives, with alkyl or aryl substituents, made by this method usually require chromatographic purification to remove the anisole-related by-products.



(8) R = aryl (9)

Scheme 4 Synthesis of thioaldehyde adducts using H_2S/HCl.

2.3 Silicon- or Tin-based Reagents

Although, for example, SiS_2 can be used [19] to convert carbonyls into thiocarbonyls, more recently better silicon reagents have become available.

Ketones (7) can also be converted into transient alkyl- or aryl-substituted thioketones (2) with bis(trimethylsilyl)sulfide in acetonitrile (with catalytic amounts of $CoCl_3$ or $CF_3SO_3SiMe_3$) at room temperature, making mild conditions possible in thionation reactions.[20] This reagent (in the presence of catalytic amounts of butyl lithium) also converts aldehydes into transient thioaldehydes[20b] (R = alkyl, aryl). In both cases the transient thiocarbonyls are isolated as Diels–Alder cycloadducts in high yields.

A similar reagent is bis(tricyclohexylstannyl)sulfide which, in the presence of catalytic amounts of boron trichloride, converts ketones into thioketones in high yield[20c] (only stable thioketones have been reported).

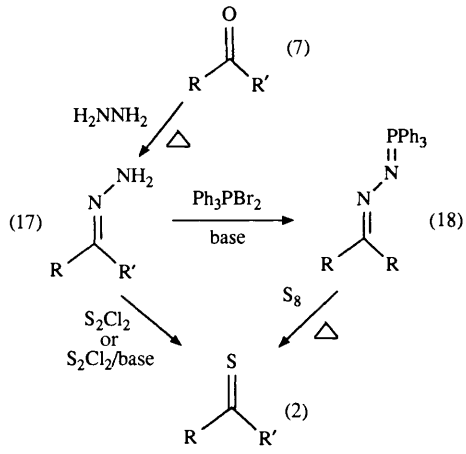
2.4 *Via* Dithiolanes

Ketones are readily converted into 1,3-dithiolanes by reaction with ethane-1,2-dithiol using a suitable catalyst such as $BF_3.OEt_2$. Parent or *S*-substituted 1,3-dithiolanes are useful precursors of thioketones, giving either a stable or transient thioketone when treated with a base (Scheme 7). This type of chemistry cannot be applied to the synthesis of thioaldehydes because treatment with base of a dithiolane (or derivative) formed from an aldehyde preferentially gives an 'umpolung' reaction by removal of the hydrogen α to both sulfur atoms.

Simple 1,3-dithiolanes (14) do dissociate (Scheme 7) on treatment with base to give thioketones (2) but it is possible to use a more reactive analogue, such as the *S,S*-dioxide (15a), methyl sulfonium (15b) or even the silyl derivative (15c). Good yields of thioketones[21] (or derivatives) are obtained from (14), (15a), (15b), and (15c) on treatment with a base, and from (15a) by thermolysis.

2.5 *Via* Hydrazones

Some stable thioketones (with R and R′ = alkyl or aryl) have been made *via* hydrazones (17) by reaction with sulfur dichloride[22] (Scheme 8). Notably, the first stable thioaldehydes[6a] (2) were also made from hydrazones (17) (R = hindered aryl, R′ = H) by reaction with sulfur dichloride and triethylamine. Similarly, conversion of a hydrazone (17) into the phosphorazone (18) then heating with elemental sulfur also gave stable thioketones[23] (2) (R and R′ = alkyl).

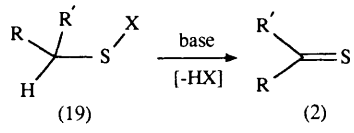


Scheme 8 Conversion of hydrazones into thiocarbonyls.

3 Thiocarbonyl Compounds from Non-carbonyl Precursors

3.1 Elimination of HX

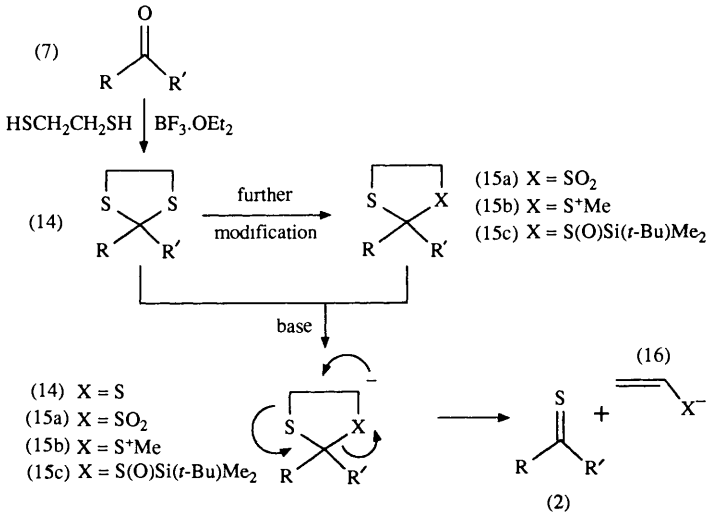
A large variety of transient thioaldehydes[24] (2) (R = H, ester, amide, aryl, phenacyl, cyano; R′ = H) have been made by base-induced elimination of HX (Scheme 9) from suitable sulfides (19) and reacted *in situ*, usually in Diels–Alder cycloadditions. Yields are often good with few by-products. Some thioketones[25] have also been made by such base-induced eliminations (R = R′ = ester, aryl) giving either a stable thioketone or a Diels–Alder adduct of a transient thioketone.



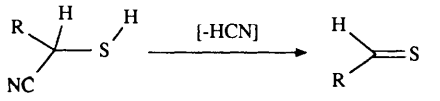
X = Cl, $SO_3^-Na^+$, SO_2Ar, phthalimido

Scheme 9 Elimination of HX from sulfides.

Additionally, the thioaldehyde (21a) and thioformaldehyde (21b) have been recently made[26] by gas-phase dehydrocyanation (Scheme 10) of (20a) and (20b). These very reactive species (21a) and (21b) have been detected by photoelectron spectroscopy.



Scheme 7 Base-mediated decomposition of 1,3-dithiolanes.



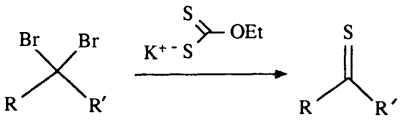
(20a) R = Me
(20b) R = H

(21a) R = Me
(21b) R = H

Scheme 10 Dehydrocyanation of cyanothiols.

3.2 Using Xanthates

Geminal dibromides (22a) and (22b) are converted by treatment with two equivalents of potassium *O*-ethyl xanthate (Scheme 11) into transient thioketones[27] or thioaldehydes[21c] (2), trapped *in situ* as Diels–Alder cycloadducts. The mechanism is likely to involve displacement of bromide by xanthate. The second equivalent of xanthate then causes elimination to the thioketone. Yields vary from poor to good and since there is often a variety of by-products purification is usually necessary.



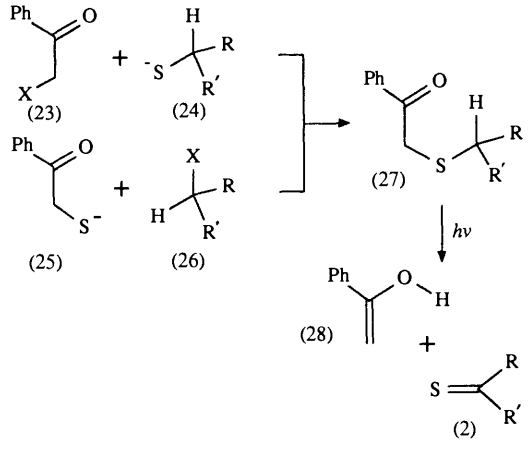
(22a) R = R′ = acyl, ester, phthalimido
(22b) R = H ; R′ = cyano

(2)

Scheme 11 Conversion of geminal dibromides into thiocarbonyls.

3.3 Photolysis of Thioacetophenones

A good photochemical approach to thioaldehydes and thioketones is by photolytic Norrish type-II cleavage of ω-substituted thioacetophenones (27) (Scheme 12), themselves easily made by reaction of a thiolate, (24) or (25), with a halide, (23) or (26).

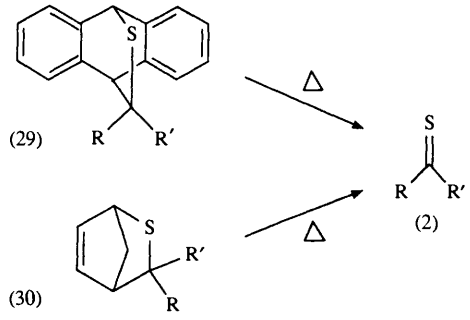


Scheme 12 Photolytic cleavage of thioacetophenones.

The first description of photolysis of a phenacyl sulfide (27) was in 1966 and was soon shown to result in thiocarbonyl compounds (2).[28] This approach[29] has subsequently been used to produce a stable thioketone (benzophenone), and transient thioaldehydes (R = H, R′ = alkyl, aryl, phenacyl, ester, cyano), usually trapped *in situ* as Diels–Alder cycloadducts. Problems can occur when R and/or R′ contain phenacyl groups. The substituents then contain the same chromophore as the photolabile part of (27) and yields are reduced dramatically.

3.4 Pyrolytic Methods

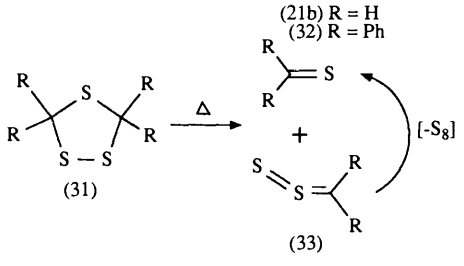
Pyrolysis is usually used only in the case of transient thioketones and thioaldehydes, as a thermally labile adduct is a convenient way of storing such transient species. The most common pyrolytic method of generating thioketones and thioaldehydes is by the retro-Diels–Alder reaction (Scheme 13).



Scheme 13 Generation of thiocarbonyls by the retro-Diels–Alder reaction.

The anthracene adducts (29) and the cyclopentadiene adducts (30) of thioketones[17] and thioaldehydes,[9,24,29] and other bridged cycloadducts,[30], (R = H. R′ = alkyl, aryl, cyano, ester, phenacyl; R = R′ = ester) decompose thermally (Scheme 13) to give thiocarbonyl compounds (2). The ring strain associated with bridged cycloadducts makes retro-Diels–Alder reactions feasible and both (29) and (30) dissociate reversibly on heating to liberate the thiocarbonyl (2) which can be reacted *in situ* with another substrate, *e.g.* with a substituted butadiene.

A more unusual reaction[31a] is the thermolysis of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (31) which decomposes above its melting point (124 °C) to give a mixture of thiobenzophenone (32) and the ylid (33), which spontaneously decomposes to (32) and elemental sulfur (Scheme 14). The intermediacy of (33) has been proven by intercepting it by cycloaddition. Earlier reactions[9] of this type gave thioformaldehyde (21b) by thermolysis at 840 K.

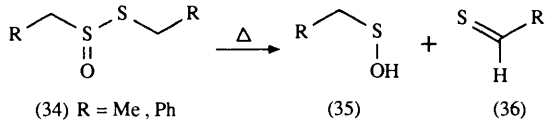


Scheme 14 Thermolysis of 1,2,4-trithiolanes.

Thiosulfinates (34) decompose thermally[9] (Scheme 15) to give sulfinic acids (35) and thioaldehydes (36) (R = alkyl, aryl), trapped *in situ* as Diels–Alder cycloadducts.

Flash vacuum pyrolysis (FVP) is a very clean and efficient way of generating (in the gas phase) transient species for spectroscopic or chemical investigations at low temperatures. It generally involves using temperatures in excess of 400 °C and pressures of less than 10^{-4} mbar for the vacuum pyrolysis, and isolation of the free thiocarbonyl compound in a liquid nitrogen trap or argon matrix.

Many pyrolytic routes to thioformaldehyde[32a] have been described and it has been generated by FVP[31] from (31) (Scheme 14) and from thioformaldehyde dimer. Interest in FVP gene-



(34) R = Me, Ph

(35)

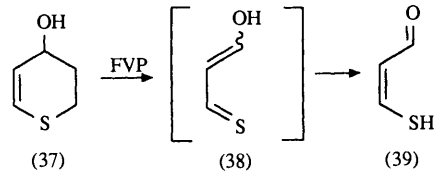
(36)

Scheme 15 Thermolysis of thiosulfinates.

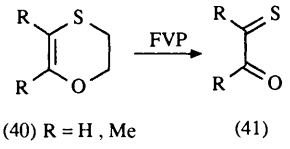
ration of thioformaldehyde and related species, and their photoelectron spectra, is associated with the discovery of these species in interstellar space, and the photoelectron spectra of such thioaldehydes generated by FVP are routinely compared with microwave spectra from radiotelescopes.[32b]

FVP has been used to generate thioaldehydes[24b] from the adducts (37) and (40) and the subsequent reactions of the species, isolated at liquid nitrogen temperatures, have been investigated.

For example, FVP of (37) also gives a thioaldehyde[33] (38), which spontaneously tautomerizes to (39) (Scheme 16). Similarly, (40) with FVP gives the thioketones (41) isolated at low temperature (Scheme 17), and subsequently reacted with conjugated dienes to give Diels–Alder cycloadducts.[33]



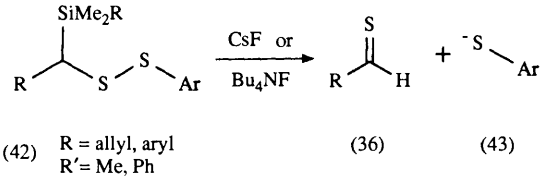
Scheme 16 Flash vacuum pyrolysis of (37).



Scheme 17 Flash vacuum pyrolysis of (40).

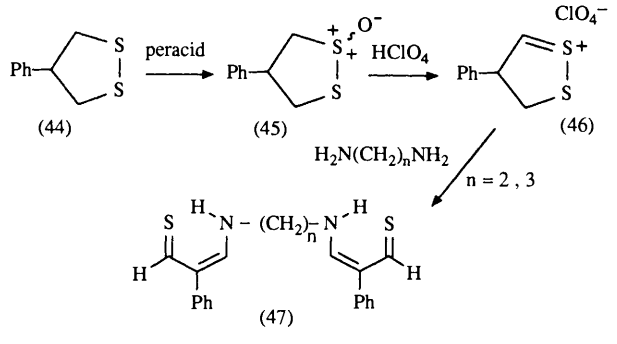
3.5 Miscellaneous Methods

Fluorine-induced elimination of α-silyl disulfides (42) gives transient thioaldehydes (36), trapped *in situ* with conjugated dienes, under very mild conditions and with high yields[24c] (Scheme 18).



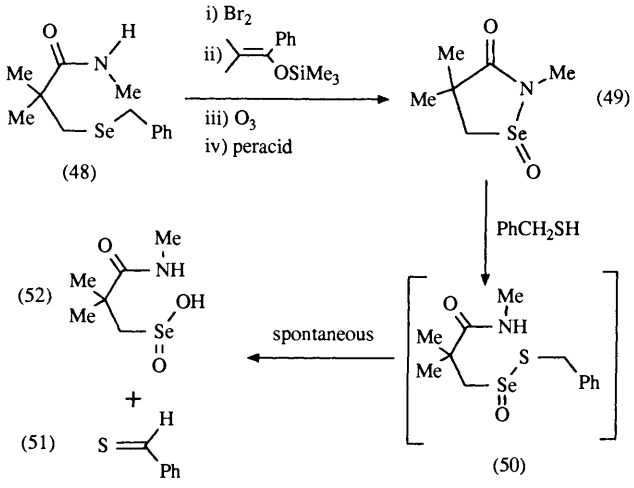
Scheme 18 Elimination of α-silyl disulfides.

An unusual synthesis (Scheme 19) of stable thioaldehydes (47) involves converting the disulfide (44) into the thiosulfinate (45) which can undergo elimination with perchloric acid to give the salt[34] (46). Reaction with an aliphatic diamine and spontaneous rearrangement gives the stable thioaldehyde[19] (47).



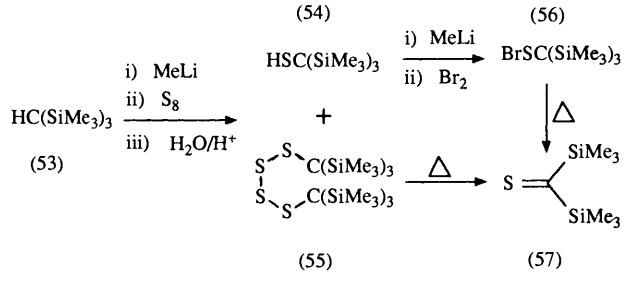
Scheme 19 Synthesis of a stable thioaldehyde.

Investigations into glutathione peroxidase (a mammalian selenoenzyme) used the model compound (49) which when treated with benzyl thiol gives the thioselenoxide (50) (Scheme 20). Spontaneous *syn*-elimination of (50) then gives[35] the unstable species thiobenzaldehyde (51) which was trapped *in situ* with cyclopentadiene in high yield.



Scheme 20 Elimination of thioselinate.

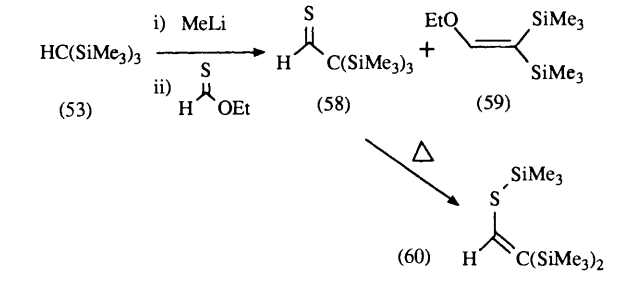
An involved route to the thioketone (57) from tris(trimethylsilyl)methane (53) is shown in Scheme 21. Treatment of (53) with methyl lithium gives tris(trimethylsilyl)methyl lithium which reacts with elemental sulfur and is subsequently quenched with aqueous acid to give a mixture of (54) and (55). The thiol (54) can be converted into the sulfenyl bromide (56). Pyrolysis of the tetrasulfide (55) or of the sulfenyl bromide (56) gives the stable thioketone[5] (57).



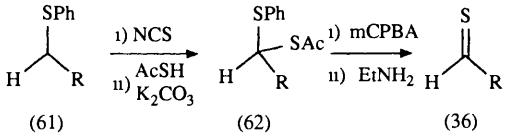
Scheme 21 Synthesis of a silylated thioketone.

A related synthesis (Scheme 22) gives the stable thioaldehyde[6b] tris(trimethylsilyl)ethanethial (60) in 16% yield by treating tris(trimethylsilyl)methane (53) with methyl lithium, then with *O*-ethylthioformate to give (58) in low overall yield. Interestingly, even when heated to 80 °C, (58) cannot oligomerize (for steric reasons) but instead isomerizes to give (60) quantitatively.

Treatment of the sulfide (61) with *N*-chlorosuccinimide (NCS) (Scheme 23) then with thioacetic acid and base gives the dithioacetal (62). Oxidation of (62) with *m*-chloroperoxybenzoic



Scheme 22 Synthesis of a silylated thioaldehyde.



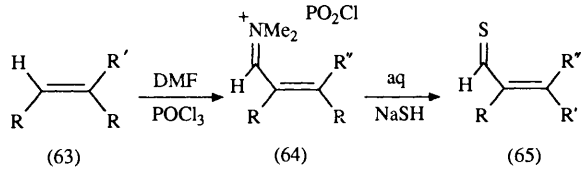
(61) (62) (36)

R = alkyl, aryl, ester, carboxyalkyl, carboxyaryl

Scheme 23 Thioaldehydes from dithioacetals

acid (*m*CPBA) and treatment with triethylamine gives the thioaldehyde[29b] (36) The unstable thioaldehydes (36) were trapped *in situ* as their Diels–Alder cycloadducts

An adaptation of the Vilsmeier–Haack aldehyde synthesis involves treatment of the enamines (63) with *N,N*-dimethyl formamide and phosphoryl chloride (Scheme 24), and gives the Vilsmeier salt (64), which can then be treated with aqueous NaSH to give the stable thioaldehydes[7] (65)

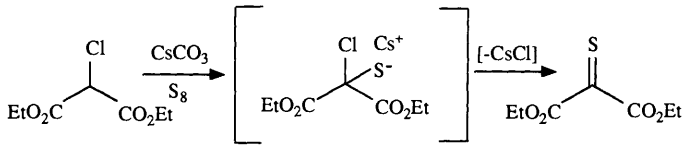


(63) (64) (65)

R = ester, R′ = alkyl, aryl, R″ = NH_2
R = R′ = Ph, R″ = morpholino

Scheme 24 Vilsmeier-type synthesis of thioaldehydes

An unusual approach[36] to the preparation of the thioketone (68) involves treatment of diethyl 2-chloromalonate (66) with caesium carbonate and elemental sulfur (Scheme 25) to give the intermediate salt (67) This spontaneously decomposes to give the highly reactive thioketone (68), which was trapped *in situ* by Diels–Alder cycloaddition in very high yield



(66) (67) (68)

Scheme 25 Elimination of a caesium salt

4 Overview

The synthesis of thioaldehydes and thioketones has been extensively investigated Both stable and transient thioaldehydes and thioketones can be made by a wide variety of routes, and good yields of the thiocarbonyl or thiocarbonyl reaction products can be obtained Transient examples can be trapped at low temperatures or generated and reacted *in situ* A range of methodology is available for converting different functional groups into thiocarbonyl groups and this offers considerable scope for introduction of a sulfur heteroatom into the synthesis of natural products or other materials

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