FUNCTIONALIZED DITHIOESTERS: AN OVERVIEW

2.1 Introduction

Functionalized dithiocarboxylates are versatile multifunctional synthons in organic synthesis. The work presented in this thesis utilizes the chemistry of \( \beta \)-oxodithiocarboxylates for the synthesis of various heterocycles. This overview attempts to present the general reactivity patterns of \( \beta \)-oxodithiocarboxylates with a particular emphasis to the work carried out in our laboratory during the recent years.

2.2 Dithiocarboxylic Acids and Esters: Synthesis

Dithiocarboxylic acids and their esters can be obtained by a variety of synthetic procedures. Some general methods for their synthesis are described here. Mayer and Scheithauer have reported that thioacyl halides undergo facile reaction with thiols in the presence of base to afford alkyl or aryl dithiocarboxylates in good yields. Bisthioacetylthioanhydrides also react with thiols to give corresponding dithiocarboxylates. Addition of thiols to thioacetylphenylthiophosphonylsulfides and thioketenes also result in the formation of respective dithiocarboxylates.

Thuillier has reported that \( \alpha,\beta \)-unsaturated iminodithioesters undergo conjugate addition with organometallic reagents and subsequent sulfhydrolysis of the intermediate ketene-N,S-acetal obtained with hydrogen sulfide furnish dithiocarboxylates having branched alkyl chains (Scheme 1).
Schuijl and co-workers have shown that terminal alkynes can also be used in the synthesis of dithioesters. For example propyne 4 on treatment with butyl lithium and then with elemental sulfur furnish the corresponding lithium alkyne thiolate 5 which on subsequent addition of two equivalents of thiol gives the dithioester 6 (Scheme 2).

Dithiocarboxylic acids can also be obtained by the addition of organolithium reagents to carbon disulfide. For example α-hydroxynaphthyl lithium 7 on addition to carbon disulfide gave dithiocarboxylic acid 8 (Scheme 3).
Several functional groups can be transformed into dithiocarboxylic acids or dithioesters by sulfurization. Aldehydes can be transformed into corresponding dithiocarboxylic acids by treatment with hydrogen sulfide or ammonium polysulfide.\textsuperscript{12} Thioiminoesters in pyridine or ether on treatment with hydrogen sulfide gave dithioesters in good yield. Thioiminoesters are obtained by the simple addition of thiols to nitriles.\textsuperscript{13} Long chain carboxylic acids also have been converted to dithiocarboxylates.\textsuperscript{14} The carboxylic acids first transformed into dilithioketeneacetals \textsuperscript{9} which on reaction with carbon disulfide followed by alkylation with methyl iodide and decarboxylation gave the dithiocarboxylates \textsuperscript{11}. The synthesis of methyl dithiononanoate by this method has been depicted in (Scheme 4).
Carbanions derived from malonic acid,\(^{15}\) phenols, naphthols, hydroxy quinolines,\(^{16}\) aldehyde,\(^{17}\) ketones,\(^{18}\) nitromethane,\(^{19}\) pyrroles, indoles, quinolines and their derivatives also react with carbon disulfide to afford respective dithiocarboxylic acids.

2.2.1 Synthesis of \(\beta\)-Oxodithiocarboxylic acids and Esters

Among functionalized dithiocarboxylic acids, \(\beta\)-oxodithiocarboxylic acids and their esters are valuable 1,3-bielectrophilic three carbon synthons with potential applications in the synthesis of heterocycles. They are usually prepared by the thiocarbonylation of active methylene ketones. Recent studies in our laboratory have shown that they can also be derived from \(\alpha\)-oxoketenedithioacetals.

\(\beta\)-Oxodithiocarboxylic acids are synthesized by the reaction of enolizable ketones with carbon disulfide in the presence of a strong base. Aliphatic and cyclic ketones react with carbon disulfide in the presence of sodium \(t\)-pentoxide to afford corresponding \(\beta\)-oxodithiocarboxylic acids (Scheme 5).\(^ {21}\)

![Scheme 5](image)

\(\beta\)-Oxodithioesters can be synthesised from substituted acetophenones by the addition of carbon disulfide in the presence of potassium \(t\)-butoxide followed by alkylation (Scheme 6).\(^ {22}\)
Scheme 6

Active methylene compounds, on treatment with dimethyl trithiocarbonate in the presence of sodium hydride as a base in DMF, gave β-oxodithioesters 20 in good yields (Scheme 7). Dithioesters of sulfones and sulfoxides can also be prepared by this method.

Scheme 7

Earlier studies from our laboratory have shown that when ethylacetoacetate reacts with dimethyl trithiocarbonate in the presence of sodium hydride in benzene, carbethoxy substituted dithioacetate 23 is formed which indicates that the intermediate dithioester 22 undergoes a base induced deacylation (Scheme 8).
Oliva and co-workers have reported that doubly activated active methylene ketones such as 2,4-pentanedione on treatment with dimethyl trithiocarbonate in the presence of sodium acetate in DMF, methylthiothiocarbonylation takes place effectively leading to the formation of 25 in good yield (Scheme 9).

2.2.1.1 Synthesis of β-Oxodithiocarboxylates from α-Oxoketenedithioacetals

α-Oxoketenedithioacetals 26 can be prepared in good yields from active methylene ketones on their reaction with carbon disulfide followed by alkylation. Therefore their
conversion to β-oxodithioesters would provide an alternative and convenient access to these intermediates.

A convenient method for the transformation of α-oxoketenedithioacetals to β-oxodithioesters has been recently reported from our laboratory.\(^{27}\) For example when \(\text{H}_2\text{S}\) was bubbled through a refluxing mixture of an aroyl ketenedithioacetal and \(\text{BF}_3\) etherate the respective aroyldithioesters \(27\) were obtained in good yields (Scheme 10).

\[
\begin{align*}
\text{Scheme 10} \\
\text{The ketenedithioacetals prepared from cyclic and aliphatic ketones also gave corresponding β-oxodithioesters on treatment with hydrogen sulfide in the presence of a Lewis acid.} \\
\text{Sodium methylsulfenylmethylide is a highly versatile reagent as a base as well as a nucleophile. Demethylation reactions of substituted aromatic compounds induced by the attack of dimethyl anion are known.}\(^{28}\) Similarly a selective demethylation reaction of dimethyl ketenedithioacetals with dimethyl sodium should result in the formation of β-oxodithioesters. Aroyl ketenedithioacetals \(26\) on treatment with methylsulfenylmethylide in DMSO gave respective β-oxodithioesters in good yields (Scheme 11).\(^{29}\)
\end{align*}
\]
α-Oxoketenedithioacetals derived from cyclic and aliphatic ketones also gave the respective β-oxodithiocarboxylates in good yields on treatment with dimsyl sodium. A probable mechanism for this demethylation reaction involves the nucleophilic attack of the dimsyl anion on one of the methylthio groups of the α-oxoketenedithioacetals resulting in the demethylation. The enethiolate anion formed on protonation affords the dithiocarboxylates.

2-Ylidene-1,3-dithiolanes are known to undergo base induced ring opening to afford respective vinyl dithiocarboxylates.30 Thus the dithiolane 28 on treatment with LDA in THF in the presence of HMPA affords the dithioester 30 (Scheme 12).

\[ \text{R}^1 \text{SLi} \xrightarrow{\text{aq. HCl}} \text{R}^1 \text{S}^2 \text{R} \]

Scheme 12

We have recently shown that this protocol can also be used for the preparations of vinyl β-oxodithiocarboxylates. Thus, when 2-arylmethylidene-1,3-dithiolanes were treated with methy sulfenylmethylide prepared from DMSO and sodium hydride the respective vinyl benzyldithioacetates 32 were formed in excellent yields (Scheme 13).29

\[ \text{O} \xrightarrow{\oplus \ominus} \text{NaH}_2 \text{C} \xrightarrow{\text{DMSO, 70°C}} \text{S} \xrightarrow{\ominus \oplus} \text{CH}_3 \]

Scheme 13
This transformation also has been found to be general and efficient for a wide variety of aliphatic and cyclic α-oxoketenedithioacetals as well.

Another valuable method for the synthesis of vinyl dithioesters involves the Wittig reaction of (triphenylphosphonium)methylarenecarbodithioate iodides 33 with aldehydes. The phosphonium iodides 33 were prepared from piperidinium salts of arene dithiocarboxylic acids (Scheme 14).

![Scheme 14](image)

2.2.2 Synthesis of α,β-Unsaturated Dithiocarboxylates

Though α,β-unsaturated dithioesters are versatile intermediates in organic synthesis there are only a few practical methods in the literature for their synthesis. A summary of general and important methods for their synthesis are given here with an emphasis to the recent results from our laboratory. Thiolate anions obtained by the addition of vinyl cuprate to carbon disulfide on alkylation lead to the formation of α-ethylenic dithioesters 39 (Scheme 15).

![Scheme 15](image)
Hartke and co-workers have shown that α,β-unsaturated amides can be transformed to α,β-unsaturated dithioesters through a sequence of reactions. The amide 39 on treatment with triethyl oxonium tetrafluoroborate afford the ethoxy substituted iminium salt 40. It could be transformed into thionoester 41 by treatment with hydrogen sulfide at low temperature. Subsequent treatment with piperidine leads to the formation of the thioamide 42. The thioamide on alkylation followed by sulfohydrolysis at low temperature afford the dithiocinnamate 44 (Scheme 16).
The addition of Grignard reagent 46 to phenyl isothiocyanate results in the formation of an intermediate N-phenylthiocarboxyimide 47, which on treatment with hydrogen sulfide affords the γ,δ-unsaturated dithioesters 48. This can be isomerized to the corresponding α,β-unsaturated dithioester 49 in the presence of triethylamine (Scheme 17).[^35]

\[
\text{PhNCS} + \text{46} \xrightarrow{\text{THF, -10 °C}} \text{47} + \text{Et}_3\text{N}
\]

\[\text{48} \xrightarrow{\text{H}_2\text{S}, \text{CH}_3\text{CN}} \xrightarrow{\text{Et}_3\text{N}} \text{49}\]

**Scheme 17**

Gosselin *et. al.* have reported that pyrolysis of the bridged dithioester 50 gave methyl propenedithioate 51 (Scheme 18).[^36] The unstable dithioate could be trapped in a CFCl₃ or CDCl₃ matrix at -196 °C. At higher temperature it undergoes a facile dimerisation involving a [4+2] cycloaddition.

[^35]: Gosselin, J. *et. al.*
[^36]: The unstable dithioate could be trapped in a CFCl₃ or CDCl₃ matrix at -196 °C. At higher temperature it undergoes a facile dimerisation involving a [4+2] cycloaddition.
α,β-Unsaturated dithioesters are also obtained by the Petersons reaction of trimethyl silyl dithioacetate with aldehydes (Scheme 19).37

\[
\begin{align*}
\text{R}^1\text{H} & \quad \text{Me}_3\text{Si} & \quad \text{S} & \quad \text{SR}^2 \\
52 & \quad 53 & \quad 54 \\
\text{LDA/THF} & \quad -60 \text{C} \\
\end{align*}
\]

Scheme 19

α-Ethylenic dithioesters could be synthesised from β-hydroxydithioesters also. β-Hydroxydithioesters are obtained by the addition of thioenolate anion derived from methyl dithioacetate 55 to carbonyl compounds. The elimination of water from β-hydroxydithioesters under different conditions lead to the formation of corresponding α,β-unsaturated dithioesters 58 (Scheme 20).38

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{S} & \quad \text{SCH}_3 \\
55 & \quad 56 & \quad 57 \\
\text{NaH} \\
\end{align*}
\]

Scheme 20

The carbanions generated from aliphatic dithiocarboxylic acids 59 on treatment with butyl lithium add to aldehydes or ketones to give aldols 60 which on subsequent alkylation and dehydration afford corresponding α,β-unsaturated dithioesters 58 (Scheme 21).39
\[
\text{BuLi (2 equiv.)}
\]

\[
\text{H}_3\text{C} \quad \text{SH} \quad + \quad \text{R}^1\text{R}^2\text{O} \quad \xrightarrow{\text{BuLi (2 equiv.)}} \quad \text{R}^1\text{R}^2\text{S}\text{Li}
\]

\[
\text{59} \quad 60
\]

\[
\text{Mel} \quad \text{OH} \quad \text{S} \quad \text{SMe} \quad \xrightarrow{-\text{H}_2\text{O}} \quad \text{R}^1\text{R}^2\text{S}\text{SMe}
\]

\[
\text{57} \quad 58
\]

**Scheme 21**

β-Hydroxydithioesters 62 were also obtained by the selective addition of organometallic reagents to α-substituted methyl acetodithioacetates 61. Their dehydration by treatment with \( p \)-toluenesulfonic acid or methyl sulfonyl chloride afforded α,β-unsaturated dithioesters 63 (Scheme 22).

\[
\text{OH} \quad \text{S} \quad \text{SCH}_3 \quad \xrightarrow{1 \cdot 2 \text{RM, Et}_2\text{O}} \quad \text{OH} \quad \text{S} \quad \text{SCH}_3
\]

\[
\text{61} \quad 62
\]

\[
\text{R}^3\text{TsOH or MeSO}_2\text{Cl}} \quad \xrightarrow{2 \cdot \text{H}_2\text{O}} \quad \text{R}^1\text{R}^2\text{S}\text{SCH}_3
\]

\[
\text{63}
\]

**Scheme 22**
β-Aminosubstituted-α,β-unsaturated dithiocarboxylates can be synthesized from 3-thiooxo-1,2-dithiole 64. When 64 was treated with morpholine in chloroform the intermediate dithiolate 66 was formed which on subsequent alkylation gave 3-morpholinodithioacrylate 67 (Scheme 23).41

\[ \text{Scheme 23} \]

Alternatively initial alkylation of the dithiole-3-thione 64 by methyl iodide followed by reaction with aniline gave the β-phenylaminodithioacrylate 69 (Scheme 24).41

\[ \text{Scheme 24} \]
In our laboratory a facile method for the preparation of $\alpha,\beta$-unsaturated dithioesters from ketenedithioacetals has been developed recently. $\alpha$-Oxoketenedithioacetals 26 on selective reduction using sodium borohydride gave the carbinol acetals 70, which on treatment with Lawesson's reagent gave the corresponding dithioesters 71 (Scheme 25).

This method can be extended for the synthesis of $\beta$-disubstituted $\alpha,\beta$-unsaturated dithiocarboxylates as well. The ketenedithioacetal 26 derived from substituted acetophenones on treatment with methyl Grignard gave the resulting intermediate carbinol acetals 72 which was subjected to the reaction with Lawesson's reagent to afford the dithioesters 73 in good yields (Scheme 26).
Ketenedithioacetal derived from aliphatic ketones also follow the same reaction pathway. For example acyketenedithioacetals on the addition of methyl Grignard and subsequent treatment with Lawesson's reagent gave methyl-3-methyl-2-butenedithioate.  

2.2.3 Synthesis of α-Oxodithiocarboxylates

There are only a few methods available for the preparation of α-oxodithiocarboxylates. Some of the frequently used methods for their synthesis are described here. Methyl benzoyldithiocarboxylates are obtained by the reaction of benzaldehyde with carbon disulfide in the presence of potassium cyanide and subsequent alkylation with diazomethane (Scheme 27).
α-Oxodithioesters were also obtained from aryl methyl ketones. Methyl ketones on treatment with pyridine and iodine leads to the intermediate pyridinium salts which react with sulfur in the presence of triethyl amine to afford corresponding α-oxodithioester 76 on subsequent alkylation (Scheme 28).44

\[
\begin{align*}
R-\text{CH}_3 & \quad \text{I}_2
\end{align*}
\]

Scheme 28

Alexander and co-workers have also accomplished the conversion of aryl methyl ketones to corresponding α-oxodithiocarboxylates.45 Substituted acetophenones are treated with ethyldisulfide in the presence of a base, such as sodium t-butoxide, and subsequent alkylation with methyl iodide give the α-oxodithiocarboxylates 76 (Scheme 29).

\[
\begin{align*}
R-\text{CH}_3 & \quad \text{Et-S-S-Et} \quad \text{t-BuONa, DMF} \quad \text{Mel}
\end{align*}
\]

Scheme 29
2.3 Dithiocarboxylic acids and Esters: Reactions

Dithiocarboxylic acids and esters are valuable precursors for the synthesis of several heterocyclic compounds. Lithium or sodium enethiolates can easily be obtained from dithiocarboxylic esters. Enethiolates have some advantages over enolates derived from enolizable ketones. They have good thermal stability and do not undergo equilibrium with the proton donors. Formation of enethiolate is highly stereospecific and cis isomers is formed exclusively (Scheme 30).

\[ R_1S \overset{\text{LDA/THF}}{\rightarrow} R_1\overset{\text{S}}{\text{L}} \]

Scheme 30

\( \delta \)-Ketodithioesters are obtained by the Michael addition of lithium enethiolate to \( \alpha,\beta \)-unsaturated carbonyl compounds. The Michael addition takes place stereospecifically under kinetically controlled conditions (Scheme 31).

\[ R^3C\overset{\text{R}^1}{\text{S}} + R^1\overset{\text{R}^4}{\text{S}}Li \rightarrow R^3\overset{\text{R}^1}{\text{S}} \]

Scheme 31

Ketenedithioacetals are synthesised by the base catalysed alkylation of dithioesters. Sulfones and sulfoxides are valuable intermediates in organic synthesis. They are obtained by the oxidation of dithioesters. Aliphatic sulfines are obtained by the oxidation of aliphatic
dithioester with \( m \)-chloroperbenzoic acid in methylene chloride and it undergoes rearrangement to corresponding dithioperoxy ester at room temperature (Scheme 32).\(^{49}\)

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{S} \quad \text{SCH}_3 \\
\text{m-CPBA}
\end{array} \quad \begin{array}{c}
\text{H}_3\text{C} \quad \text{S} \quad \text{SCH}_3 \\
\text{CH}_2\text{Cl}_2 \\
\rightarrow
\end{array} \quad \begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \quad \text{S} \quad \text{S} \quad \text{CH}_3 \\
\rightarrow
\end{array}
\]

Scheme 32

Thiolesters are obtained by the oxidation of dithiocarboxylates with selenic anhydride (Scheme 33).\(^{50}\)

\[
\begin{array}{c}
\text{R} \quad \text{S} \quad \text{S} \quad \text{R} \\
\text{55} \quad \text{Ph-SeO}_2\text{O} \rightarrow \text{R} \quad \text{S} \quad \text{S} \quad \text{R} \\
\text{87} + \text{PhSeSePh}
\end{array}
\]

Scheme 33

2.3.1 Reactions of \( \beta \)-oxodithioesters

\( \beta \)-Oxodithioesters are potential multifunctional synthons useful in the synthesis of heterocyclic compounds. They are also useful precursors for the synthesis of \( \beta \)oxothioamides and functionalized ketene-N,S-acetals. \( \beta \)-Oxodithiocarboxylates on treatment with trimethyl silyl sulfide in the presence of \( N \)-chlorosuccinimide and imidazole leads to the formation of substituted 3-thioxo-1,2-dithioles (Scheme 34).\(^{51}\)

\[
\begin{array}{c}
\text{O} \quad \text{S} \quad \text{SMe} \\
\text{27} \quad \text{NCS, Imidazole} \quad \text{(TMS)}_2\text{S, CH}_2\text{Cl}_2 \\
\rightarrow
\end{array}
\]

Scheme 34
β-Phenylamino substituted α,β-unsaturated dithioester 91 derived by the selective addition of aniline to one of the carbonyl groups of methyldithiocarboxylate 90 undergo thermal cyclization to afford 92 (Scheme 35). 52

\[
\text{O} \quad \text{Me} \quad \text{Me} \quad \text{O} \quad \text{Me} \quad \text{Me}
\]

\[
\text{PhNH}_2 \quad \text{MeOH}
\]

\[
\text{O} \quad \text{S} \quad \text{SMe} \quad \text{Me}\]

\[
\text{Ph}
\]

\[
\text{Me} \quad \text{Me}
\]

\[
\text{N} \quad \text{Ph}
\]

\[
\text{O} \quad \text{SH}
\]

\[
\text{Me} \quad \text{Me} \quad \text{Ph}
\]

\[
\text{O} \quad \text{S} \quad \text{SMe} \quad \text{Me}
\]

\[
\text{PhOPh} \quad \Delta
\]

\[
\text{O}
\]

\[
\text{SH}
\]

\[
\text{Me}
\]

\[
\text{Ph}
\]

\[
\text{O} \quad \text{S} \quad \text{SMe} \quad \text{Me}
\]

\[
\text{Ph}
\]

\[
\text{O} \quad \text{S} \quad \text{SMe} \quad \text{Me}
\]

\[
\text{Ph}
\]

\[
\text{Me}
\]

Scheme 35

Substituted 2H-thiopyran-2-thiones 95 and 97 were obtained by the reaction of β-oxodithiocarboxylic acid 94 with α-acetylinic ketones 93 and β-chlorovinyl aldehydes 96 respectively (Scheme 36 and Scheme 37). 53

\[
\text{O} \quad \text{R}^2
\]

\[
\text{Ph}
\]

\[
\text{O} \quad \text{R}^1
\]

\[
\text{HS} \quad \text{S}
\]

\[
\text{R}^1 = \text{aryl, alkyl; R}^2 = \text{aryl or alkyl}
\]

Scheme 36
Scheme 37

Methyloacetidithioacetate 98 has been shown to react with dithiolium salt 99 to afford 3-acetyl substituted 2H-thiopyran-2-one derivatives 100 (Scheme 38)."
The dithiocarboxylate 102 obtained from cyclohexanone on treatment with Vilsmeier reagent prepared from POCl₃ and DMF to afford 2-chloro-3-(1-chloro-1-methylthio) methylene cyclohex-ene-carbaldehyde 103 (Scheme 40), which has formed as a result of multiple iminoalkylations.

![Scheme 40](image)

Carbethoxy dithioacetate 23 on treatment with chloromethylene iminium salt prepared from POCl₃ and DMF gave 2H-thiopyran-2-one derivative 104 (Scheme 41).

![Scheme 41](image)

β-Oxodithioesters on alkylation using α-haloesters, bromocrotonate and α-halonitriles lead to the formation of several heterocyclic compounds.

The reactions of β-oxodithioesters with dicyclohexyl carbodiimide have been studied recently in our laboratory. The reaction was aimed at the activation of the thiocarbonyl group for selective displacement with other nucleophiles. However, it has been found that after the initial addition of the adduct undergo cyclization involving intramolecular displacement of the methylthio group. For example when methyl aryl dithioacetates are
treated with two equivalents of DCC in the presence of DMAP in CH₂Cl₂, 4-arylmethylidene-3-cyclohexylimino-1,3-thiazetidines 106 are formed (Scheme 42).

Scheme 42

The brief discussion given above on the preparation and reactions of dithiocarboxylates indicates that even though they are compounds which can be prepared easily from readily available starting compounds, their applications in the synthesis of functionalized heterocyclic compounds and in other synthetic transformations have not been explored in much detail.
2.4. References

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