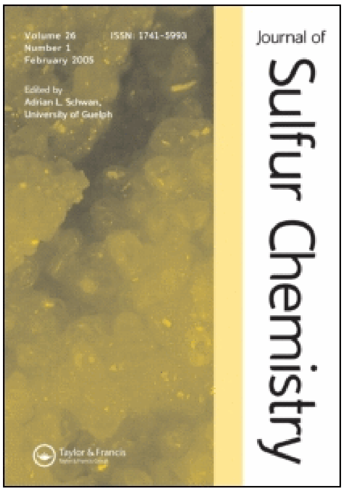

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Reactions of Carbon Disulfide with *C*-nucleophiles

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REACTIONS OF CARBON DISULFIDE WITH *C*-NUCLEOPHILES

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The aim of this review is to present reactions of carbon disulfide with C-nucleophiles which form carbon–carbon bonds. Compounds with an activated methyl or methylene group react, in the presence of a base, as carbanions with the electrophile carbon disulfide to give dithiocarboxylates which can be converted to ketene dithioacetals on treatment with excess alkylation reagent. Acidification affords dithiocarboxylic acids. Bases of low nucleophilicity because of steric hindrance and sodium hydride, respectively, are often used for the deprotonation steps.

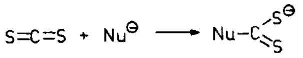
Key words: Dithiocarboxylation, dithioesters, ketene dithioacetals.

CONTENTS

1. INTRODUCTION

A variety of reactions of carbon disulfide in which its carbon atom functions as an active electrophile are known. Syntheses involving carbon disulfide are much more versatile than those of carbon dioxide. Whereas carbon dioxide reacts with such strong nucleophiles such as hydroxide ion, organometallic compounds, and phenoxide ion, carbon disulfide exhibits a much more varied reactivity. Several factors can probably account for this difference. One is the greater length of the C–S bond (182 pm) than that of the C–O bond (143 pm), which results in greater steric accessibility of the carbon atom for compound or complex formation with carbon disulfide. Another factor is that the difference between the dissociation energies of the C=S and the C–S bond (188.3 kJ mol^{-1}) is less than between C=O and C–O (305.4 kJ mol^{-1}). In addition, the stretching force constants of bonds with second-row elements are generally smaller than those of bonds with first-row elements. Thus, less energy is required for the same extent of bond stretching in carbon disulfide and therefore less energy to form the transition state for a given reaction.[1]

Furthermore the organic-chemical properties of carbon disulfide compared with those of carbon dioxide and of carbonyl sulfide are first of all characterized by the lower tendency of the primary products formed with nucleophiles to regenerate carbon disulfide under different temperature and solvolysis conditions.

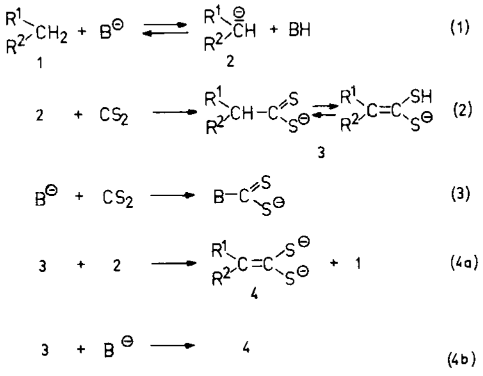


$$S{=}C{=}S + Nu^{\ominus} \longrightarrow Nu{-}C\begin{matrix}S^{\ominus}\\ S\end{matrix}$$

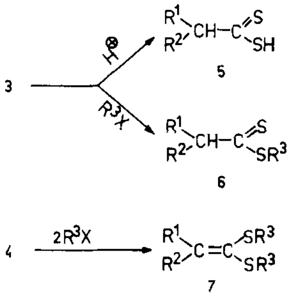
SCHEME 1

Alkylation, acylation, oxidation and condensation reactions as well as numerous secondary reactions are characteristic for these primary products.[2,3,4]

Compounds with an activated methyl or methylene group react, in the presence of a base, as carbanions with the electrophile carbon disulfide to give dithiocarboxylates. Salt formation of dithiocarboxylic acids with electron-withdrawing substitutents R^1 and R^2 is possible in two steps so that the remaining H-atom with an additional mole of base can be abstracted to leave a 1-alkene-1,1-dithiolate (Scheme 2). Subsequent alkylation leads to dithiocarboxylic esters **6** and ketene dithioacetals **7**, respectively. Acidification gives the dithiocarboxylic acids **5** (Scheme 3).



SCHEME 2



SCHEME 3

Reactions of CH-acidic compounds with carbon disulfide depend above all on two factors. On one hand it must be possible to generate a carbanion with the help of a base, on the other hand it is advantageous to use a solvent where the reaction can be carried out in a homogeneous phase in order to avoid long reaction times. Solvents containing hydroxyl groups can also react with carbon disulfide. With alkali metal alkoxides as bases and alcohols as solvents an equilibrium is established [eqn. (1)]. Upon addition of carbon disulfide part of it reacts with the carbanion according to eqn. (2), however, another part reacts with the alkoxide according to eqn. (3). According to eqn. (4a) some of the starting material is regenerated. The reaction [eqn. (4b)] is only possible if the alkoxide does not react with carbon disulfide according to eqn. (3).

An especially useful variant of the reaction of CH-acidic compounds with carbon disulfide in alcoholic solution has been reported.[5] Bases of low nucleophilicity because of steric hindrance and sodium hydride, respectively, are often used for the deprotonation steps.

a) Sodium or potassium *t*-pentoxide[6-12]

The use of *t*-pentoxides in benzene or *N*,*N*-dimethylformamide has been shown to be advantageous because in these cases the formation of the *O*-alkyl dithiocarbonic ester salt from the alkoxide and carbon disulfide is largely suppressed.

b) Sodium or potassium *t*-butoxide[6a,13-20]

t-Butoxides (in Et_2O, benzene, *N*,*N*-dimethylformamide, or benzene/*N*,*N*-dimethylformamide) are equally efficient bases. A potassium *t*-butoxide/tetrahydrofuran/CS_2/alkyl halide combination has been developed as a particularly useful procedure[21] for the generation of α-oxo ketene dithioacetals.

c) Lithium 2,6-di-*t*-butyl-4-methylphenoxide[22,23]

Although lithium 2,6-di-*t*-butyl-4-methylphenoxide does not add to carbon disulfide, this base effects the transformation under equilibrium conditions and is not effective for carbon acids weaker than saturated ketones.

d) Lithium diisopropylamide alone or in combination with lithium bis[trimethylsilyl]amide[24-26]

Utilization of lithium dialkylamide bases generally requires sequential introduction of the reagents since they readily add to carbon disulfide to afford dithiocarbamates after alkylation. The use of strong amide bases opened the way for the synthesis of conjugated ketene dithioacetals from a variety of enolate anions such as α,β-enones, esters, and lactones as well as from nitriles and hydrazones.

e) Sodium hydride in the presence of *N*,*N*-dimethylacetamide[27,28] or in dimethyl sulfoxide[29-35]

This base affords low to moderate yields of α-oxo ketene dithioacetals from aliphatic ketones. With esters this system generates substantial amounts of Claisen condensation products.[27]

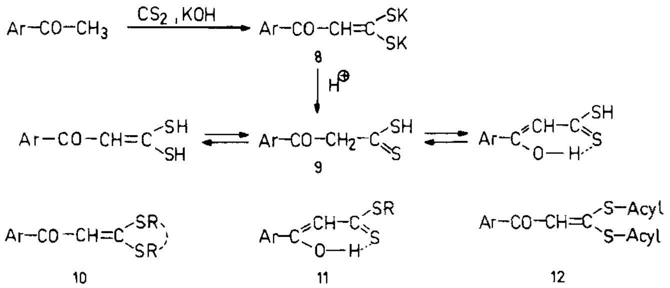
Good yields of α-oxo ketene dithioacetals are obtained with sodium hydride and carbon disulfide from aryl or hetaryl ketones and active methylene compounds.

Sandström and Wennerbeck[36a] have found a modification, which consists of reaction between the methylene compound and sodium hydride in benzene, followed by addition of carbon disulfide and sufficient *N*,*N*-dimethylformamide to allow the second step of the reaction to proceed, to be particularly useful.

2. REACTIONS WITH KETONES AND KETIMINES

2.1. *Dithiocarboxylation of Dialkyl and Alkyl Aryl Ketones*

The first synthesis of an α-oxo ketene dithioacetal has been known since 1910 when Kelber[37-39] heated acetophenone with potassium hydroxide and carbon disulfide and obtained the dipotassium salt **8** of a β-oxo dithioic acid **9** isolable as such in poor yield by neutralization with sulfuric acid. It exists mainly in the chelated enol form. The stability of such dithioic acids is dependent upon the substrate structure and those derived from active methylene compounds generally display considerable instability.[1,13] Dialkylation of β-oxo dithioic acids under basic conditions gives α-oxo ketene dithioacetals **10**, whereas monoalkylation leads to dithioesters **11**. The nature of the base and of the counterion appears to have an effect on the alkylation process.[40,41] Double *S*-acylation yields **12**.[42]



SCHEME 4

Thuillier and Vialle found that α-oxo ketene dithioacetals can be prepared directly from ketones in good yields by using sodium *t*-pentoxide as the base and two equivalents of an alkyl halide.[6b,c]

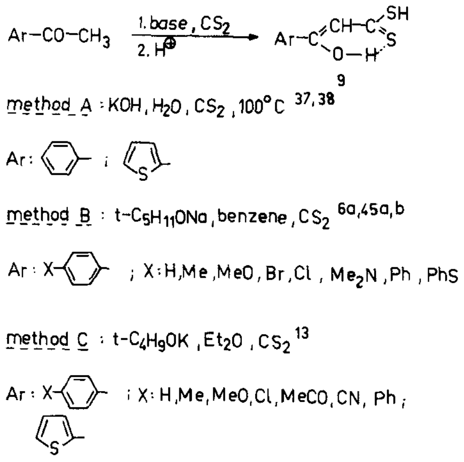
They and other workers[6a,13,43] were also able to obtain good yields of β-oxo dithioic acids from aliphatic and aromatic ketones and these dithioic acids were converted to α-oxo ketene dithioacetals by procedures similar to those of Kelber and co-workers.

Although many α-oxo ketene dithioacetals are readily prepared from ketone enolates in a one-pot process, the efficiency of these preparations is dependent upon the specific structural features of the enolate and the reaction conditions. The most direct and economical synthesis of α-oxo ketene dithioacetals seems to be the reaction of a methyl ketone (alkyl, cycloalkyl, aryl and hetaryl) with sodium hydride in benzene or toluene, carbon disulfide, and methyl iodide.[27,28] With these solvents it is essential to have present a small amount (ca. 5% v/v) of a polar cosolvent such as *N*,*N*-dimethylacetamide.

α-Oxo ketene dithioacetals are of special interest as versatile three-carbon synthons. They are highly functionalized α,β-unsaturated carbonyl substrates which can undergo a variety of transformations.[44]

The reactions of acetophenones and acetylheterocycles with carbon disulfide have been intensively investigated. In all cases, the dithiocarboxylate is the primary product.

β-Keto dithioic acids:

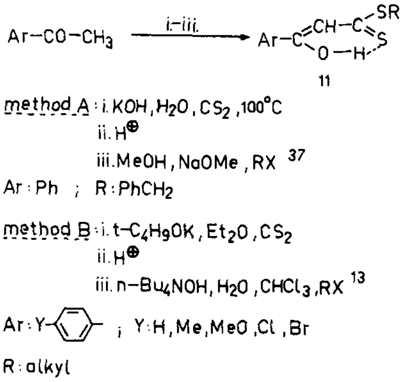


SCHEME 5

More recently, mention is made in the literature of the dithiocarboxylation of acetophenones[46,47,48] and of α- and β-acetylnapthalenes.[49]

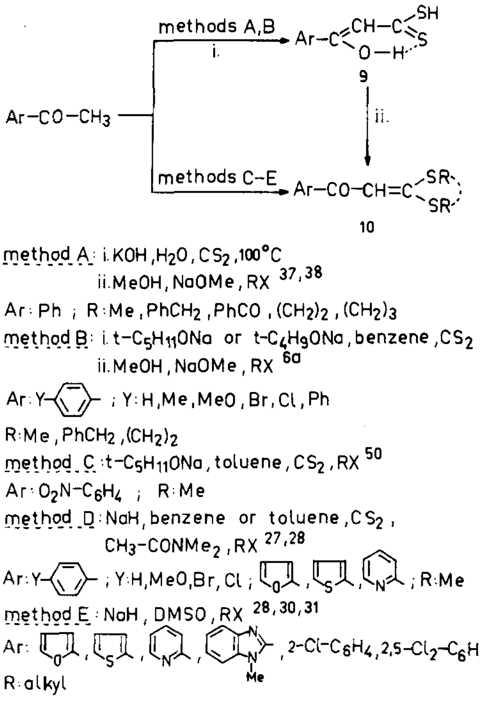
β-Keto dithio esters:

The dithioesters **11** are most conveniently prepared by the ion pair extraction technique (method B).[13]



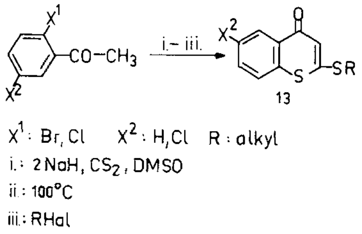
SCHEME 6

α-Oxo ketene dithioacetals:



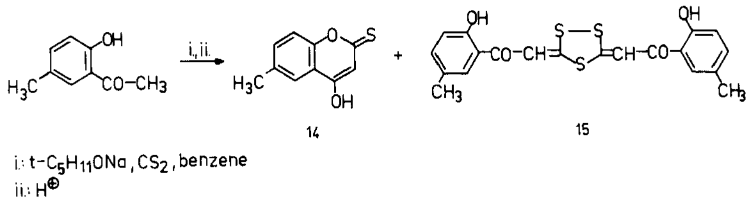
SCHEME 7

Methods C–E show that α-oxo ketene dithioacetals can be prepared directly from the appropriate ketones in good yields. 2-(Alkylthio)-4-oxo-4*H*-1-benzothiins **13** are formed when 2-chloro-(bromo)-acetophenones react with carbon disulfide at elevated temperatures.[31]



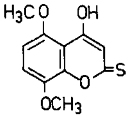
SCHEME 8

The interaction of 2-hydroxy-5-methylacetophenone, carbon disulfide and sodium *t*-pentoxide affords 4-hydroxy-6-methylchromen-2-thione **14** together with the trithiolane derivative **15**.[51]



SCHEME 9

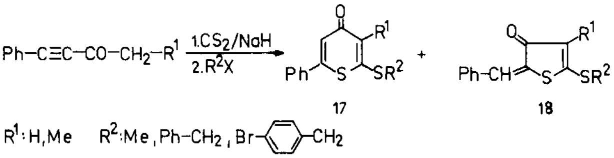
2,5-Dimethoxyacetophenone has been converted to **16** in high yield by reaction with carbon disulfide in the presence of potassium *t*-butoxide.[52]



16

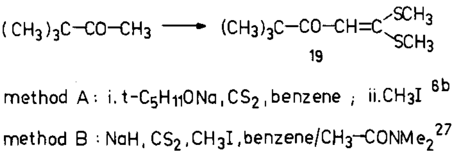
SCHEME 10

Dithiocarboxylation of acetylenic ketones in the basic system sodium hydride/*N*,*N*-dimethylformamide to a primarily formed, but not isolated, monosodium salt leads, by subsequent intramolecular cyclization and alkylation, to a mixture of 4*H*-thiopyran-4-ones **17** and 3(2*H*)-thiophenones **18**.[53]



SCHEME 11

Aliphatic ketones with only one CH-acidic group in the molecule, such as pinacolone, also give α-oxo ketene dithioacetals.



$$(CH_3)_3C{-}CO{-}CH_3 \longrightarrow (CH_3)_3C{-}CO{-}CH{=}C(SCH_3)_2$$

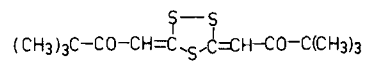
19

method A: i. t-C$_5$H$_{11}$ONa, CS$_2$, benzene ; ii. CH$_3$I [6b]

method B : NaH, CS$_2$, CH$_3$I, benzene/CH$_3$-CONMe$_2$ [27]

SCHEME 12

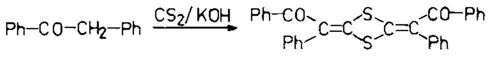
A trithiolane **20** is formed by oxidation of the β-keto dithio acid prepared in ether by reaction of pinacolone with sodium amide and carbon disulfide.[54]



20

SCHEME 13

In 1891 Meyer and Wege[55] reported the preparation of the desaurin **21** by heating of deoxybenzoin with powdered potassium hydroxide in carbon disulfide under reflux (see also[56]).



21

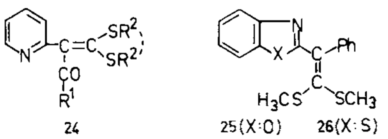
SCHEME 14

Analogs of **21** were subsequently prepared by treatment of compounds of the type $ArCOCH_2Ar'$ and $ArCOCH_2CH_3$ with carbon disulfide and a base.[39,57] Desaurins were also obtained by pyrolysis of the dibenzoyl derivatives or heavy-metal salts of dithioacids of type **5**;[39] pyrolysis of the free acids also gave the desaurins, but in very poor yields. Gompper and Töpfl[5] obtained desaurins directly from compounds of type **5** by treatment with acylating agents or with oxidizing agents (bromine, iodine or ammonium peroxysulfate). A modern procedure has been published.[58] Treatment of deoxybenzoin with sodium amide in benzene, followed by reaction with carbon disulfide, gave the red sodium salt of benzoylphenyldithioacetic acid **22**.[59] Subsequent methylation afforded **23**.[5] Shahak and Sasson[27] used sodium hydride in benzene/*N*,*N*-dimethylacetamide as base to generate **23**.

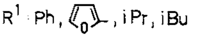
22 23

SCHEME 15

2-(Acylmethyl)-pyridines, -benzoxazole and -benzothiazole are active methylene componds for the synthesis of conjugated ketene dithioacetals **24**,[9] **25** and **26**,[60] respectively, with a $NaH/DMSO/CS_2/RX$ combination.



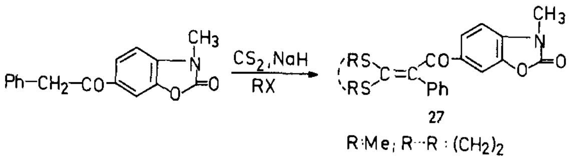
24 25(X:O) 26(X:S)



R^2 : Me ; R^2-R^2 : $(CH_2)_2$, $(CH_2)_3$

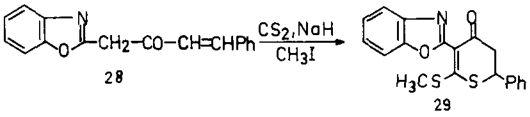
SCHEME 16

Good yields of α-oxo ketene dithioacetals **27** have been obtained with the same base system from 3-methyl-6-(phenylacetyl)-benzoxazolinone.[50]



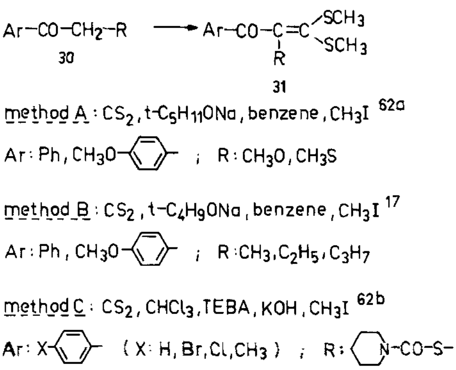
SCHEME 17

Reaction of 2-(cinnamoylmethyl)-benzoxazole **28** with carbon disulfide affords the 2,3-dihydrothiopyran-4-one **29** by intramolecular cyclization.[60]



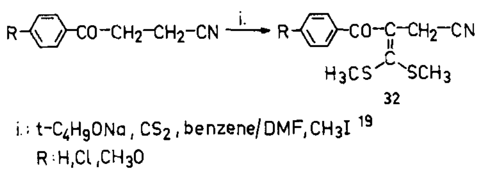
SCHEME 18

Conjugated ketene dithioacetals **31** have been prepared from the ketones **30**.[62a]



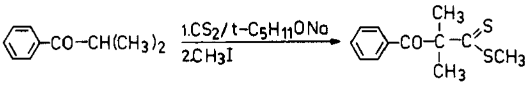
SCHEME 19

With 4-oxobutanenitriles the ketene dithioacetal formation proceeds at the α-methylene carbon atom.



SCHEME 20

The formation of the dithioester **33** in the reaction of isopropyl phenyl ketone with carbon disulfide has been reported.[63]



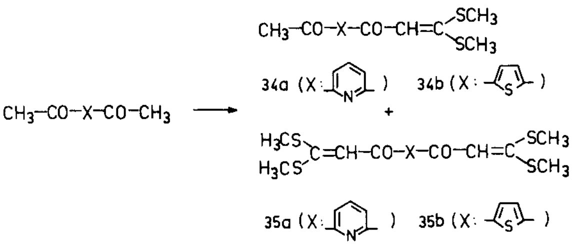
33

SCHEME 21

2.2. *Reactions with Diacetyl Compounds*

The preparation of bis(ketene dithioacetals) is readily achieved by use of the appropriate bis(methyl ketones). 2,6-Diacetylpyridine on reaction with the requisite amount of NaH/CS_2/MeI gave a product mixture which was solvent dependent. In toluene, the monoketene dithioacetal **34a**, the bis(ketene dithioacetal) **35a** and unreacted ketone were obtained. Increasing the amount of *N*,*N*-dimethylacetamide used in the reaction improved the yield of **35a**. When the reaction was carried out in dimethyl sulfoxide with sodium hydride as the base, the bis(ketene dithioacetal) **35a** was obtained exclusively. Monofunctionalization of 2,6-diacetylpyridine to give **34a** was possible by careful modification of the reaction conditions.

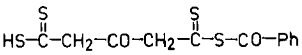
2,5-Diacetylthiophene has also been converted into its bis(ketene dithioacetal) **35b**. With toluene/*N*,*N*-dimethylacetamide as the solvent system, **35b** is always contaminated by the monoketene dithioacetal **34b**.[28]



SCHEME 22

2.3. *Reactions with Ketones with CH-Bonds on Both Sides of the Carbonyl Group*

Depending on the reaction conditions different products are obtained. The synthesis of thiopyrones is of preparative importance. The reaction of acetone with carbon disulfide/metallic sodium gave not only trithiocarbonate, but, after benzoylation, also a monobenzoyl derivative of the acetone-bis-(dithiocarboxylic acid) **36**.[64]

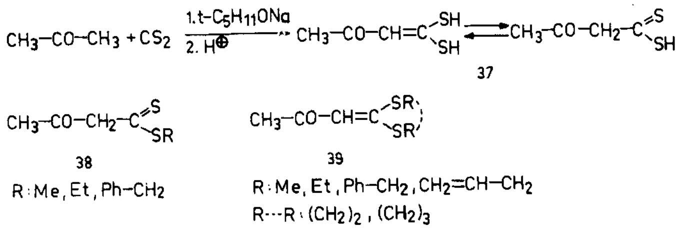


$$HS-\overset{S}{\overset{\|}{C}}-CH_2-CO-CH_2-\overset{S}{\overset{\|}{C}}-S-CO-Ph$$

36

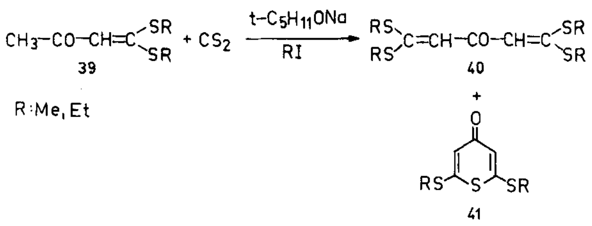
SCHEME 23

Mono-dithiocarboxylation of acetone in the presence of sodium *t*-pentoxide furnished the corresponding dithioacid **37**, and subsequent alkylation gave the dithioesters **38** and the dithioacetals **39**, respectively.[43]



SCHEME 24

Upon treatment of the ketene dithioacetals **39** with carbon disulfide/sodium *t*-pentoxide/alkyl iodide a mixture of bis(ketene dithioacetals) **40** and thiopyranones **41** is formed.

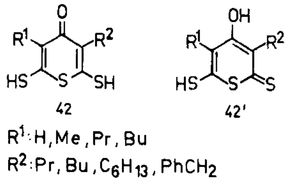


SCHEME 25

The direct formation of **40** (R = Me) from acetone has been described by Shahak and Sasson[27] upon use of $CS_2/CH_3I/NaH$/benzene/*N*,*N*-dimethylacetamide.

Analogous behavior has been observed in the dithiocarboxylation of other aliphatic ketones.[6b,26,27]

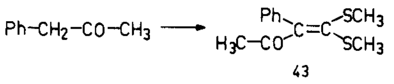
Apitzsch[65] reported that treatment of a ketone containing two adjacent methylene groups with potassium hydroxide and carbon disulfide afforded salts possessing the thiopyran-4-one structure. In a later investigation, Arishkevich and co-workers[66] obtained the 2,6-dimercaptothiopyranones **42** from ketones and KOH/CS_2 in poor yields. They possess the constitution **42′** in the solid state.[61]



SCHEME 26

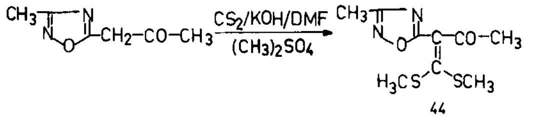
In the case of asymmetric ketones, carbon disulfide first attacks the carbon atom with the higher CH-acidity.[6b] Mono adducts are formed with benzyl- or hetarylmethyl methyl ketones, where the C=C bonds of the arene and the ketene dithioacetal moieties are conjugated.[15,67]

1,1-Bis-(methylthio)-2-acetyl-2-phenylethylene has been prepared by reaction of phenylacetone with $CS_2/NaH/CH_3I$ in benzene/DMF.[36a]



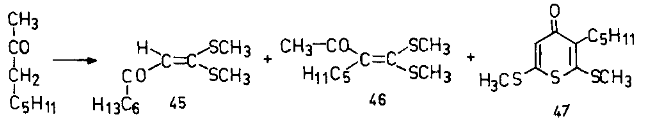
SCHEME 27

The methylene group in 5-acetonyl-3-methyl-1,2,4-oxadiazole is highly CH-acidic and reacts to yield the ketene dithioacetal **44**.[61]



SCHEME 28

Two isomeric adducts can be obtained with asymmetric ketones with two reactive methylene groups. In the case of dialkyl ketones the sterically less hindered product is preferred.[22] The ratio of products depends on the kind and amount of base employed.[23] Although carbon disulfide alkylation of thermodynamically or kinetically generated ketone enolate anions provides, in principle, a synthetic route to regiospecifically substituted α-oxo ketene dithioacetals, this strategy is limited by the interference of complex equilibria which are difficult to control.

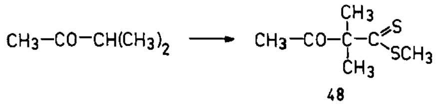


SCHEME 29

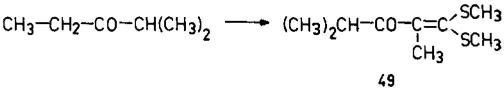
Kinetic deprotonation of 2-octanone with 1.1 equiv. of lithium hexamethyldisilazide (LHMDS) in THF, followed by sequential addition of carbon disulfide, lithium diisopropylamide (LDA), and iodomethane afforded the ketene dithioacetals **45** (29%) and **46** (22%) as well as the thiopyranone **47** (21%). Deprotonation of 2-octanone under thermodynamic conditions with 0.9 equiv. of LHMDS afforded a substantially different mixture of **45** (22%) and **46** (59%). Utilization of lithium 2,6-di-*t*-butyl-4-methylphenoxide afforded **46** (78%) as the major product and only little **45** (4%).

Thuillier and Vialle[6b] reported that reaction of methyl isopropyl ketone with sodium *t*-pentoxide, carbon disulfide, and iodomethane in benzene gave the dithioester **48**, formed by reaction of the more substituted enolate anion with carbon disulfide

(Scheme 30), while ethyl isopropyl ketone afforded the ketene dithioacetal **49** under similar conditions (Scheme 31).



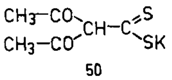
SCHEME 30



SCHEME 31

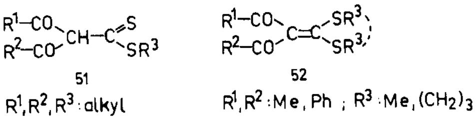
2.4. Reactions with Diketones

Dithiocarboxylation of 1,3-dicarbonyl compounds is also possible. The potassium salt of diacetyldithioacetic acid **50** has been prepared from acetylacetone by reaction with potassium hydroxide and carbon disulfide.[68]



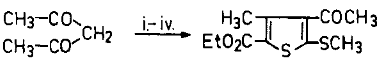
SCHEME 32

Under ion pair extraction conditions, tetrabutylammonium salts of acetylacetone, benzoylacetone, and dibenzoylmethane react with carbon disulfide to yield salts of dithioacids. Alkylation gave the dithioesters **51** and the ketene *S,S*-acetals **52**.[41] Ketene *S,S*-acetals **52** have also been prepared by the method of Sandström and Wennerbeck,[36a,69a] i.e., reactions between the 1,3-dicarbonyl compounds and sodium hydride in benzene/DMF (or HMPA). The reaction can also be carried out in DMSO/K_2CO_3 (or KOH).[69b,c]



SCHEME 33

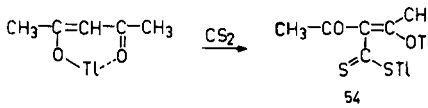
Clarke *et al.*[70] treated acetylacetone with carbon disulfide in the presence of potassium hydroxide and obtained the dianion, $Ac_2C{=}CS_2^{2-}$, which upon successive treatment with ethyl bromoacetate, iodomethane, and alkali, afforded the thiophene **53**.



i: CS_2, KOH/H_2O, DMF
ii: $BrCH_2CO_2Et$
iii: CH_3I
iv: KOH/ H_2O

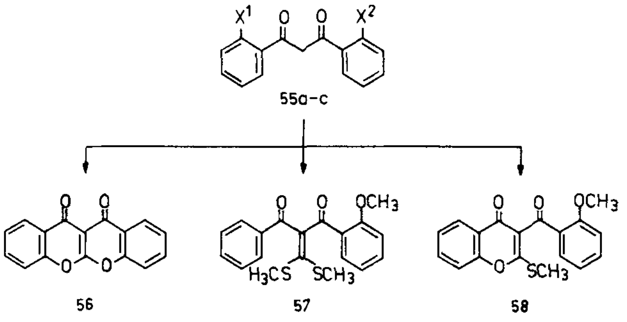
SCHEME 34

The thallium salt of acetylacetone reacts with carbon disulfide to give the dithallium salt **54**.[71]



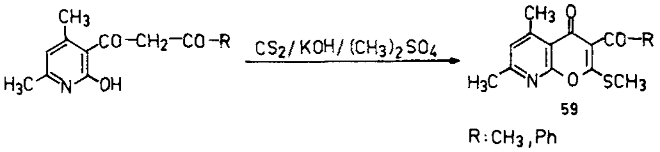
SCHEME 35

Reaction of bis-(2-hydroxybenzoyl)-methane **55a** ($X^1 = X^2 = OH$) with $CS_2/KOH/(CH_3)_2SO_4$ in DMSO produces **56**. With the same method and **55b** ($X^1 = H$; $X^2 = OCH_3$) the ketene *S,S*-acetal **57** is formed whereas **55c** ($X^1 = OH$; $X^2 = OCH_3$) gives 3-(2-methoxybenzoyl)-2-(methylthio)-chromone **58**.[72]



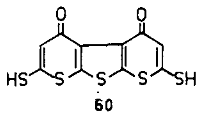
SCHEME 36

Pyridothiopyrones **59** can easily be prepared from hydroxypyridyl diketones.[73]



SCHEME 37

1,4-Diketones react with carbon disulfide in the same way as 1,3-diketones, however, heterocycles often result from secondary reactions. A four-fold dithiocarboxylation occurs with acetonylacetone. In this case the intermediate thioacid reacts further to give **60**.[66]

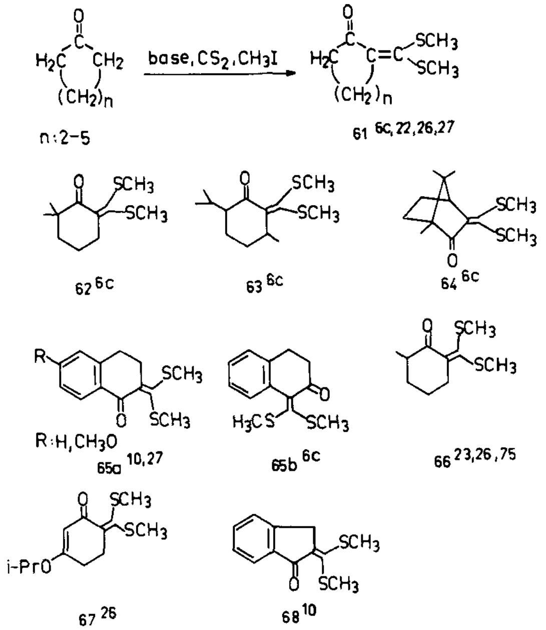


SCHEME 38

Dithiocarboxylation of a 1,5-diketone has also been described.[74]

2.5. Reactions with Cyclic Ketones

The cyclic α-oxo ketene dithioacetals **61–68** have been prepared from the appropriate cyclic ketones by treatment with carbon disulfide and a base, followed by alkylation.

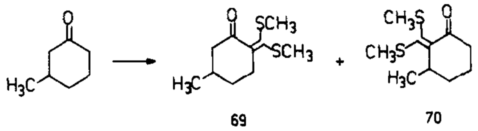


SCHEME 39

Dieter[26] has developed an efficient method for the synthesis of conjugated ketene dithioacetals. This method adapts known procedures by which carbanions are generated and added to carbon disulfide in the presence of alkylating agents and those involving alkylation of dithioic acid dianions and dithioester enolates. The conjugated ketene dithioacetals **61** ($n = 3$), **66** and **67** have been prepared with lithium diisopropylamide or lithium hexamethyldisilazide as the base.

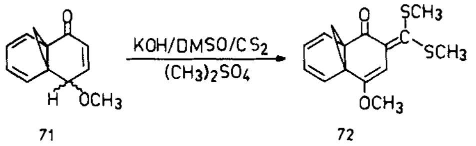
It is interesting to note that 2-methylcyclohexanone affords the α-oxo ketene dithioacetal **66** when treated with 2,6-di-*t*-butyl-4-methylphenoxide in THF under equilibrium conditions or with lithium diisopropylamide under kinetic conditions.

Two isomeric mono-adducts can be obtained when unsymmetric ketones contain two reactive methylene groups. The product of bis-(methylthio)methylenation at the alternative group is formed as the minor product **70**.[22]



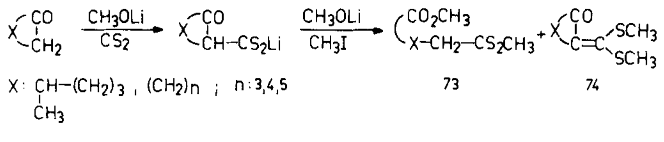
SCHEME 40

In the case of the tricyclic α,β-unsaturated ketone **71** the ketene *S*,*S*-acetal function is generated in the α-position.[33]



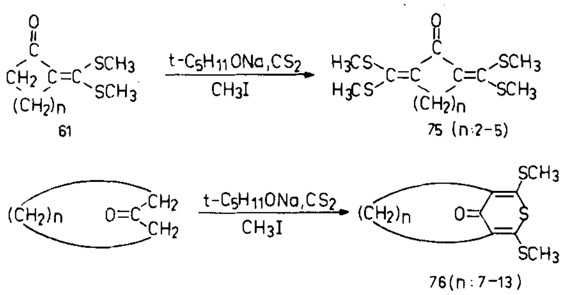
SCHEME 41

Methyl esters of 1,1-dithiodicarboxylic acids **73** and/or dimethyl ketene dithioacetals **74** are formed by reaction of cyclic ketones with lithium methoxide and carbon disulfide in THF, followed by treatment with methyl iodide.[76] The formation of **73** proceeds *via* dithiocarboxylation and carbonyl carbon–carbon bond cleavage *via* an inverse Dieckmann-type reaction.



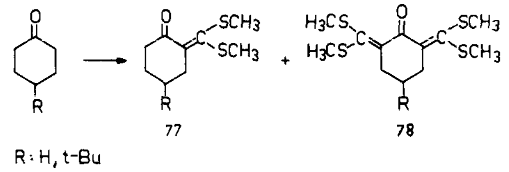
SCHEME 42

Cyclic ketones can also be bis-dithiocarboxylated. The bis-(ketene dithioacetals) **75** result if $n = 2$–5. Rings with $n = 7$–13 react with $CS_2/t\text{-}C_5H_{11}ONa/CH_3I$ to give the thiopyran-4-ones **76**.[6c,77]



SCHEME 43

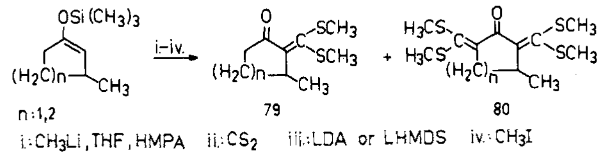
Using a combination of $CS_2/NaH/CH_3I$ in benzene/*N*,*N*-dimethylacetamide Shahak and Sasson[27] transformed cyclohexanone to 2,6-di[bis(methylthio)-methylene]-cyclohexanone **75** ($n = 3$, $R = CH_3$). Quiroga and co-workers[78] found that the ratio **77**:**78** depends on the nature of the solvents (Et_2O, THF, HMPT) and bases (lithium diisopropylamide, sodium hydride, lithium 2,6-di-*t*-butyl-4-methylphenoxide) used.



SCHEME 44

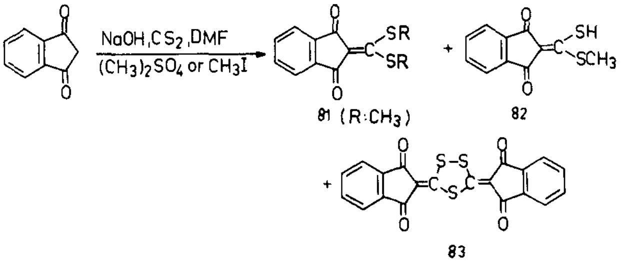
The formation of the bis-ketene dithioacetal **78** is favored in less polar solvents. It is not observed in the system LDA/HMPT.

Treatment of regiospecific enolates, generated from silyl enol ethers, of 3-methylcyclopentanone and 3-methylcyclohexane, respectively, sequentially with carbon disulfide, lithium diisopropylamide (LDA) or lithium hexamethyldisilazide (LHMDS), and methyl iodide afforded the regiospecifically substituted α-oxo ketene dithioacetals **79** and significant quantities of the bis-ketene dithioacetals **80**, depending on the base and reaction temperature employed.[23,75] This procedure could not be generalized to acyclic and 3-alkyl substituted bicyclic enolate anions.



SCHEME 45

Reaction of indan-1,3-dione with carbon disulfide, followed by methylation with dimethyl sulfate or methyl iodide in the presence of sodium hydroxide gives the ketene dithioacetal **81**, the dithioester **82** and the trithiolane **83** in varying yields, depending on the molar ratio of indan-1,3-dione to methylating agent.[79a]



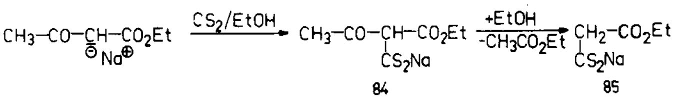
SCHEME 46

The ketene dithioacetals **81** (R = Me, EtOOC–CH$_2$, PhCOCH$_2$; R,R = –(CH$_2$)$_2$–, –(CH$_2$)$_3$–) have been prepared with CS$_2$/sodium *t*-pentoxide in DMF.[8] 2-(4,4-Dimethyl-2,5-dioxocyclohexylidene)-1,3-dithiolane has been obtained from dimedone, carbon disulfide, sodium hydride, and 1,2-dibromoethane in dry DMF.[79b] Alkylation with dibromomethane yields a dithiethanylidenecyclohexanedione.[79c]

2.6. *Reactions with Ketones with a Second Acceptor Group (Different from a Keto Group) in the Molecule*

The first report on the formation of a desaurin by reaction of an active methylene compound with carbon disulfide in the presence of a base is that of Norton and Oppenheim,[80] who obtained a yellow product from the reaction of ethyl acetoacetate with carbon disulfide and zinc or lead oxide. The structures of these compounds were later confirmed by Yates *et al.*[56,81]

The sodium salt of acetoacetic ester reacts with carbon disulfide in ethanol *via* the sodium salt of 2-ethoxycarbonyl-3-oxobutanedithioic acid **84** to afford, after alcoholysis, the sodium salt of ethoxycarbonyldithioacetic acid **85**.[82,83]

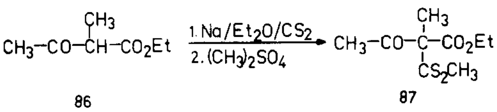


$$CH_3{-}CO{-}\underset{\ominus Na^{\oplus}}{CH}{-}CO_2Et \xrightarrow{CS_2/EtOH} CH_3{-}CO{-}\underset{CS_2Na}{CH}{-}CO_2Et \xrightarrow[-CH_3CO_2Et]{+EtOH} \underset{CS_2Na}{CH_2}{-}CO_2Et$$

84 85

SCHEME 47

The reaction of the active methyne compound **86** with carbon disulfide has been reported, too.[84]



$$CH_3{-}CO{-}\overset{CH_3}{CH}{-}CO_2Et \xrightarrow[2.\,(CH_3)_2SO_4]{1.\,Na/Et_2O/CS_2} CH_3{-}CO{-}\overset{CH_3}{\underset{CS_2CH_3}{C}}{-}CO_2Et$$

86 87

SCHEME 48

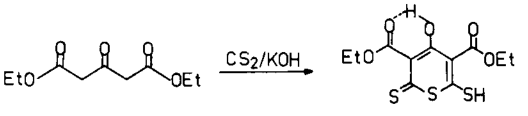
The ketene *S*,*S*-acetals **88** and **89** are formed in the reaction between methyl (or ethyl) acetoacetate or ethyl benzoylacetate and $CS_2/NaH/CH_3I$ in benzene/DMF[36a] or $CS_2/K_2CO_3/CH_3I$ in DMSO.[36b]

88 (R:Me,Et) 89

SCHEME 49

Concerning the reaction of additional acetoacetates and other β-keto esters in the presence of a base and subsequent alkylation cf.[85a–c]

Upon use of the ion pair extraction technique the tetrabutylammonium salts of ethyl and methyl acetoacetate, ethyl benzoylacetate and cyanoacetone react with carbon disulfide to give salts of dithioacids. Alkylation gave dithioesters and ketene dithioacetals.[86] The diethyl ester of acetone-α,α′-dicarboxylic acid, on treatment with carbon disulfide and potassium hydroxide, is converted to the thiopyrone derivative **42**.[65c,87]

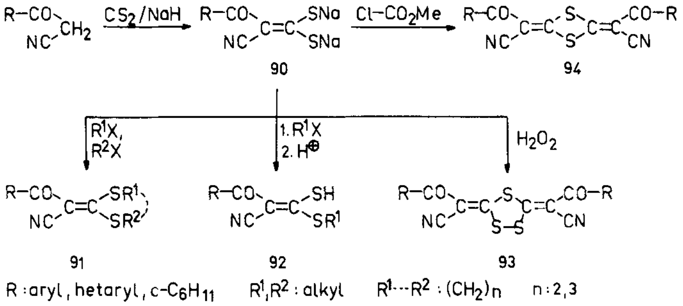


42 (R^1,R^2 : CO_2Et)

SCHEME 50

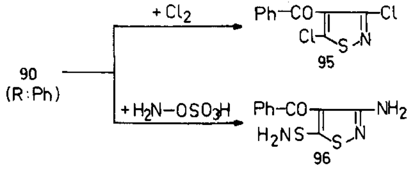
Acylacetonitriles react with carbon disulfide/sodium hydride in dimethyl sulfoxide[29,35] or benzene/*N*,*N*-dimethylformamide[36a] to give the disodium salts **90**. Treatment of **90** with alkylation reagents yields the open-chain or cyclic acylcyanoketene *S*,*S*-acetals **91**. Arylation is possible with 1-chloro-2,4-dinitrobenzene.

Addition of only one equivalent of alkyl halide to **90** and acidification of the reaction mixture leads to the monoalkylated compounds **92**.



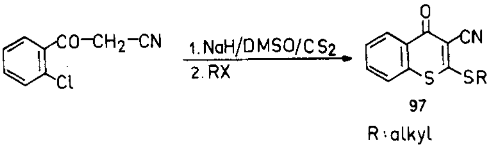
SCHEME 51

Compound **90** reacts with hydrogen peroxide to form the 1,2,4-trithiolane **93**, whereas treatment with methyl chloroformate yields the 1,3-dithietane **94**.[88] By chlorination of **90** isothiazole **95** is available. *S*-Amination of the disodium salt gives the isothiazole **96**.



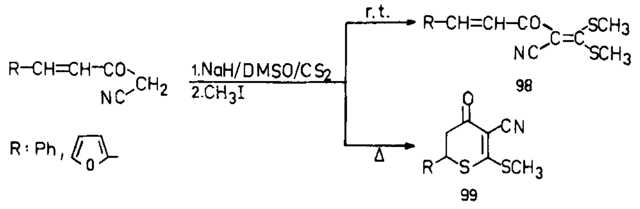
SCHEME 52

Rudorf[30] obtained the benzothiopyranones **97** by reaction of (2-chlorobenzoyl)-acetonitrile with CS_2/NaH and subsequent alkylation.



SCHEME 53

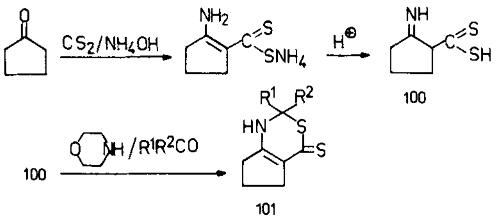
α,β-Unsaturated ketones undergo reaction with base and carbon disulfide at the α′-methylene group to yield **98**. Intramolecular cyclization can occur at elevated temperature to afford the 5,6- dihydrothiopyranones **99**.[34]



SCHEME 54

2.7. *Reactions with Ketones in the Presence of Ammonia or with Ketimines*

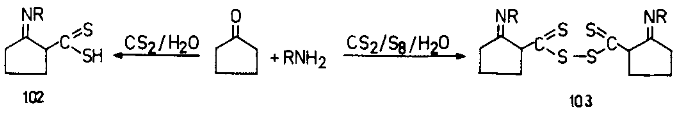
Takeshima *et al.*[89-96] found that cyclopentanone reacts with carbon disulfide in the presence of ammonia to give stable 2-iminocyclopentanedithiocarboxylic acid **100**. The morpholinium salt of **100** yields with ketones the corresponding thiazines **101**.



R^1,R^2 : Me,Et ; R^1 : Me , R^2 : i-Pr ; R^1---R^2 : $(CH_2)_n$; n : 4,5,6

SCHEME 55

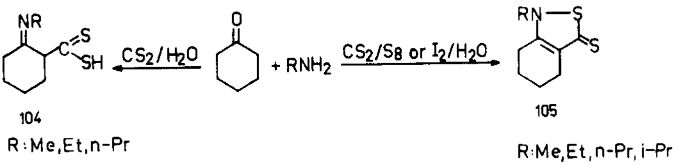
Only with methylamine the direct reaction between cyclopentanone, a primary amine, and carbon disulfide is successful; yields, however, are low.[97] The yields increase and also other primary amines can be used if the reaction is carried out in the presence of potassium fluoride.[90] A convenient synthesis of 2-(alkylimino)cyclopentanedithiocarboxylic acids **102** by reaction of cyclopentanone with carbon disulfide in excess aqueous amine has been described.[92] Reaction in the presence of sulfur gives the disulfides **103** (cf.[98]).



R : alkyl

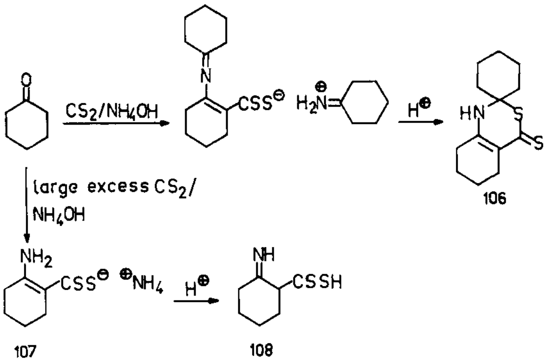
SCHEME 56

Under the same conditions cyclohexanone affords the 2-(alkylimino)cyclohexanedithiocarboxylic acids **104** in poor yields and in the presence of sulfur or iodine the isothiazole derivatives **105**.



SCHEME 57

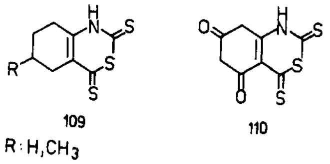
Prior to the synthesis of **100** it was reported that cyclohexanone in its reaction with CS_2/NH_4OH gives the thiazine **106**.[99]



SCHEME 58

The salt **107**, when briefly treated with acetic acid, gives 2-iminocyclohexanedithiocarboxylic acid **108**; prolonged treatment results in the formation of **106**.[100] 2-Methylcyclohexanone does not react with carbon disulfide/aqueous ammonia and 3-methylcyclohexanone gives only a small amount of 2-imino-4-methylcyclohexaneditiocarboxylic acid.

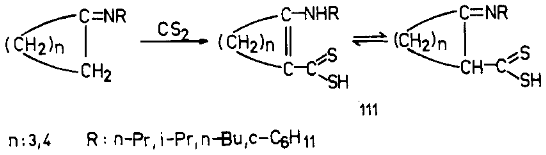
4-Methylcyclohexanone, under the same conditions, furnishes a compound to be regarded as a precursor of **106**, whereas cycloheptanone gives 2-iminocycloheptanedithiocarboxylic acid in 20% yield. The reaction of cyclohexanones or phloroglucinol with carbon disulfide in the presence of triethylamine and aqueous ammonia leads to the benzothiazinedithiones **109** and **110**.[101]



SCHEME 59

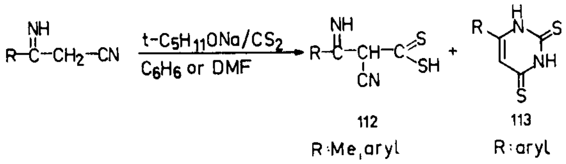
Concerning the reaction of acetone and methyl ethyl ketone with carbon disulfide and ammonia cf.[102]

Ketimines with at least one hydrogen atom attached to the β-carbon atom are sufficiently activated for the reaction with carbon disulfide to give the dithiocarboxylic acids **111**. Especially in the series of the cyclopentanoneimines the products are relatively stable.[90,103,104]



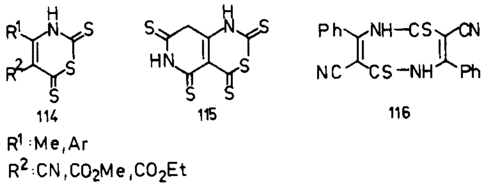
SCHEME 60

Concomitant action of carbon disulfide and sulfur on ketimines gives 1,2-dithiole-3-thiones and/or isothiazoline-5-thiones. This reaction can also be applied to ketimines derived from open-chain ketones.[104] Treatment of β-imino nitriles with carbon disulfide and sodium *t*-pentoxide gives the corresponding 2-cyano-3-iminodithiocarboxylic acids **112**, accompanied in some cases by pyrimidine-2,4-dithiones **113**.[105a,b]



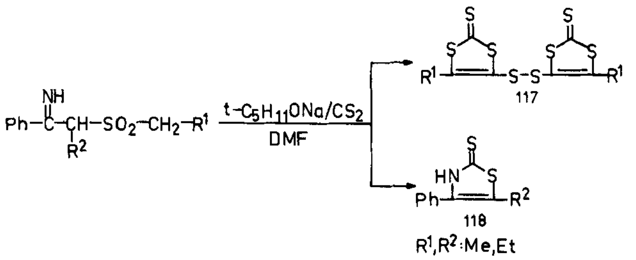
SCHEME 61

β-Imino-β-arylpropionitriles or β-imino esters, when treated with carbon disulfide in DMF at low temperature, afford the 1,3-thiazine-2,6-dithiones **114**. When excess sodium *t*-pentoxide is used in this reaction, β-iminobutyronitrile yields pyrido[4,3-*d*][1,3]-thiazine-2,4,5,7(1*H*,8*H*)-tetrathione **115**. β-Imino-β-phenylpropionitrile, under the same conditions, gives the 1,5-diazocine-2,6(1*H*,5*H*)-dithione **116**.



SCHEME 62

β-Imino sulfones react with carbon disulfide to give 1,3-thiazine-2,6-dithiones.[106] β-Imino sulfones bearing an α-alkyl group react differently from those without an α-substituent: in the former case the carbon disulfide attacks the α′-methylene group to give the disulfides **117**, together with the 1,3-thiazole-2(3*H*)-thiones **118**.[107]



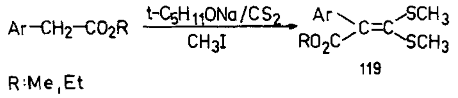
SCHEME 63

3. REACTIONS WITH ESTERS, LACTONES, NITRILES, AMIDES, THIOCARBONATES, THIOCARBAMATES, AND CARBOXYLIC ACIDS

The strong electron-withdrawing effect of the ester and/or cyano group facilitates the formation of carbanions. The base used must match the acidity of the active methylene compound. It is necessary to avoid ester condensation or a reaction between the base and carbon disulfide.

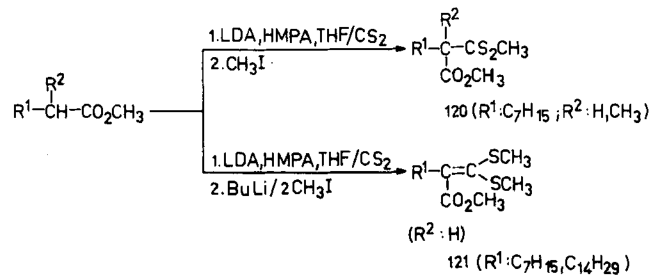
3.1. Reactions with Esters and Lactones

Simple esters require relatively strong bases. Arylacetic acid esters enter into dithiocarboxylations when sodium *t*-pentoxide is used as base.[108]



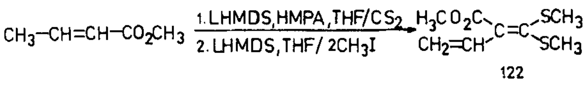
SCHEME 64

The combination CS_2/MeI/NaH was tried with esters such as ethyl acetate and diethyl succinate. Here competition with a Claisen condensation was observed and only very small yields of the corresponding ketene *S*,*S*-acetals could be isolated. However, in the case of ethyl phenylacetate 80% of the desired product was formed.[27] The use of strong amide bases opened the way for the synthesis of the dithioesters **120** and the ketene *S*,*S*-acetals **121** from aliphatic esters.[24]



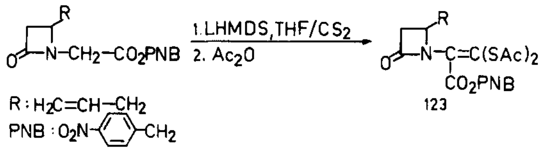
SCHEME 65

Good yields of the conjugated ketene dithioacetal **122** could be obtained from methyl crotonate when lithium hexamethyldisilazide (LHMDS) was employed as the base.[26]



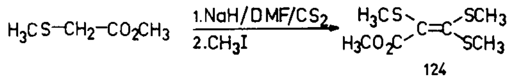
SCHEME 66

With the same base the synthesis of the 3,3-bis(acetylthio)acrylic acid ester **123** is possible.[109,114]



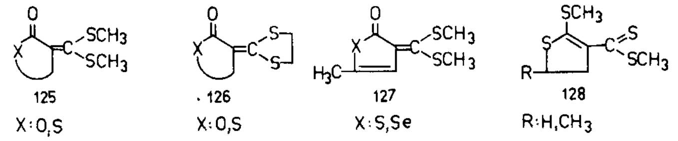
SCHEME 67

Methyl (methylthio)acetate reacts with NaH/CS_2/MeI to give methyl tris(methylthio)acrylate **124**.[110]



SCHEME 68

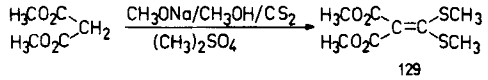
Lactones, thiolactones and dithiolactones possess an activated CH_2 group adjacent to their carbonyl or thiocarbonyl function. Conjugated ketene dithioacetals or dithiocarboxylates have been prepared in good yields with sodium *t*-pentoxide or sodium hydride as bases.[7,111-113]



SCHEME 69

Good yields of conjugated dithioacetals could be obtained from γ-butyrolactones when lithium hexamethyldisilazide was used as the base.[26]

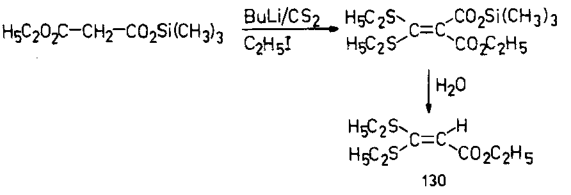
Malonic esters are acidic enough to give (with sodium alkoxides of primary alcohols) anions which are able to add carbon disulfide.[5]



SCHEME 70

Furthermore, malonic esters have been dithiocarboxylated with bases such as aqueous alkali,[115-119] potassium hydroxide in ether/dioxane or potassium hydroxide in dioxane,[12,120] *t*-butoxide or sodium amide in *N*,*N*-dimethylformamide or dimethyl sulfoxide,[12,121] metallic sodium in ether[83,122] as well as sodium hydride in benzene, tetrahydrofuran or dioxane.[123-127] Ester enolates, generated with lithium diisopropylamide (LDA) from methyl 2-(silyloxy)cyclopropanecarboxylates, and CS_2/CH_3I afford methyl dihydrothiophenecarboxylates. The mechanism of this ring enlargement of cyclopropanes is considered to be an anionic 1,3-sigmatropic rearrangement which even takes place at −78 °C.[128]

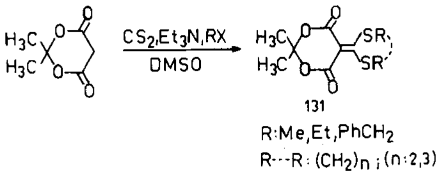
Reaction of ethyl trimethylsilyl malonate with CS_2/*n*-BuLi/EtI and subsequent hydrolysis/decarboxylation affords ethyl 3,3-bis(ethylthio)acrylate **130**.[129]



SCHEME 71

Like malonic esters also thiomalonic *O*,*O*-esters can be dithiocarboxylated.[130]

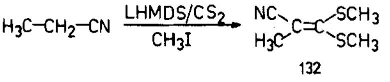
Condensation of Meldrum's acid with carbon disulfide in the presence of triethylamine, followed by alkylation, yields the (bisalkylthio)methylene derivatives **131**.[131a,b]



SCHEME 72

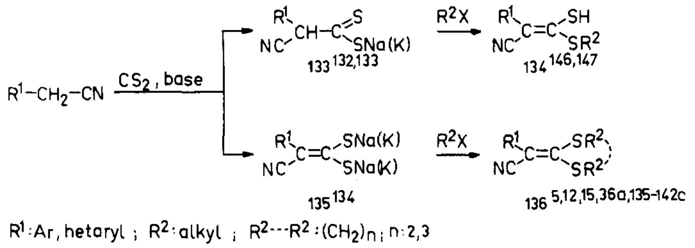
3.2. *Reactions with Nitriles*

The cyanoketene *S*,*S*-acetal **132** has been prepared from propionitrile and carbon disulfide by a one-step procedure utilizing lithium hexamethyldisilazide as the base.[26] A convenient synthesis of *β*,*β*-bis(alkylthio)acrylonitriles was found by Creemer *et al.*[144a] Acetonitrile reacts with CS_2, *n*-BuLi, and $(Me_2CH)_2NH$ to give $(LiS)_2C{=}CHCN$, and the latter can be alkylated. Dithiocarboxylation is also possible in benzene with sodium hydride as the base.[144b]



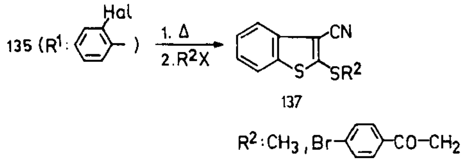
SCHEME 73

In the case of the reaction of aryl- or hetarylacetonitriles with carbon disulfide the use of various bases has been investigated such as sodium hydride in DMF/benzene or DMSO,[15,36a,132,133,139–142b] potassium *t*-butoxide in *t*-butanol[134] or THF,[142c] sodium amide in diethyl ether,[5,138,145] potassium hydroxide in methanol (ethanol)[68,143] or sodium ethoxide in ethanol.[147]



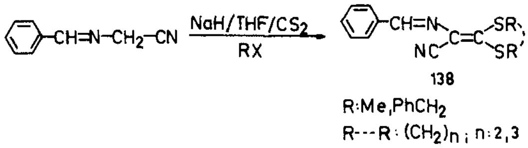
SCHEME 74

Starting from *o*-halobenzyl cyanides and carbon disulfide in the presence of sodium hydride the dithiolates **135** are formed. Alkylation with cooling gives *S*,*S*-acetals of the type **136**, while on heating the benzo[*b*]thiophenes **137** are obtained.[142a]



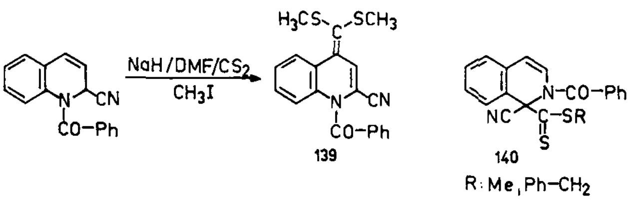
SCHEME 75

Dithiocarboxylation of (benzylideneamino)acetonitrile and subsequent alkylation yields the ketene *S*,*S*-acetals **138**.[148]



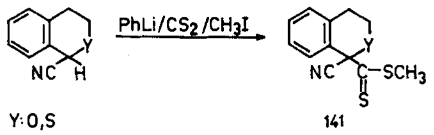
SCHEME 76

The ketene dithioacetal **139** is formed from *N*-benzoylquinolinecarbonitrile. The dithioesters **140** are obtained in an analogous manner.[149]



SCHEME 77

1-Cyanoisochroman and 1-cyanoisothiochroman can be dithiocarboxylated *via* their lithium salts to yield the dithioesters **141**.[150]

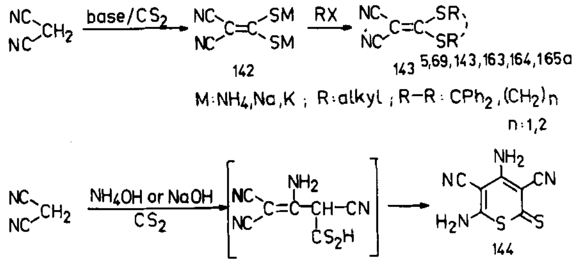


SCHEME 78

3.3. *Reactions with Malononitrile, Cyanoacetates, Ester Amides and Cyanoacetamides*

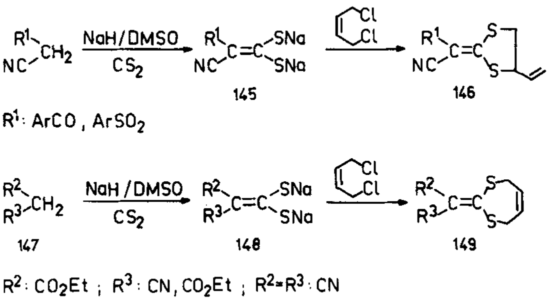
Malononitrile reacts with carbon disulfide in the presence of a base to the diammonium (liq. NH_3,[151,152]), disodium ($NaNH_2$/liq. NH_3;[65c,153] EtONa/EtOH or MeONa/MeOH;[5,12,121,154-159b,172] NaH/DMSO;[160,161] NaH/THF;[162] NaH/benzene/DMF[69a] or dipotassium salt (KOH/EtOH;[134,143] KOH/dioxane)[12] of a dithiocarboxylic acid **142**.

The ketene *S*,*S*-acetals **143** can easily be synthesized by alkylation of the dithiolates **142**. If the alkylation reaction is carried out with bifunctional alkylating agents, cyclic ketene dithioacetals are formed. In most cases **142** has not been isolated. Reaction of malononitrile with CS_2/NH_4OH gives **144** as the main product.[165b] The same product has been obtained from dimeric malononitrile.



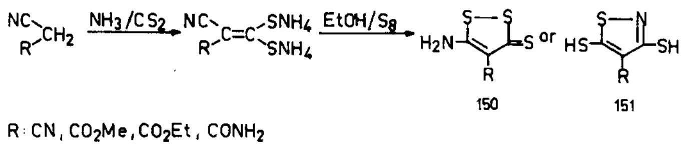
SCHEME 79

The dithiolates **145** react with (*Z*)-1,4-dichlorobut-2-ene to give the vinyldithiolanes **146**, whereas reaction of the dithiolates **148**, obtained from carbon disulfide and the malonic acid derivatives **147**, with the same dichlorobutene leads to the dihydrothiepins **149**.[161]



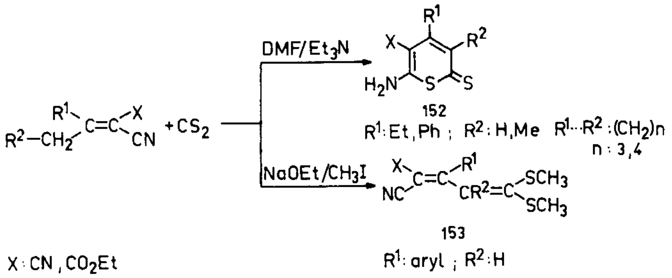
SCHEME 80

Nitriles with an active methylene group in the α-position react with carbon disulfide in the presence of elemental sulfur and with base catalysis to give the 5-amino-1,2-dithiole-3-thiones **150** and salts of the 3,5-dimercapto-1,2-thiazoles **151**, respectively.[166,167]



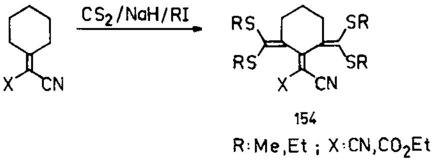
SCHEME 81

The dithiocarboxylic acids obtained by reaction of alkylidenemalononitriles with CS_2/NEt_3 are unstable both as free acids and as salts. They suffer intramolecular cycloadditions yielding **152**.[166,167]



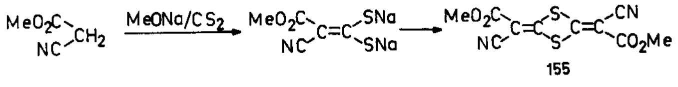
SCHEME 82

The reaction with CS_2/CH_3I/NaOEt on the other hand gives the push-pull butadienes **153**.[168,169] Cyclohexylidenemalonitrile or the corresponding methyl cyanoacetate react with CS_2/NaH/RX in THF to afford the compounds **154**.[170]



SCHEME 83

A general method for the preparation of desaurins involves base-catalyzed reaction of carbon disulfide with active methylene compounds to give dithiolate anions, which are subsequently converted thermally or by the presence of oxidizing (I_2, Br_2, $S_2O_8^{2-}$) or acylating reagents (oxalyl chloride, phthalyl chloride).[5,55,171] 2,4-Bis(cyanomethoxycarbonylmethyene)-1,3-dithietane **155** is obtained from cyanoacetic ester *via* the corresponding dithiolate anion.



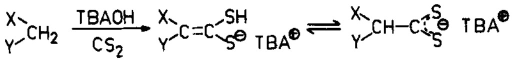
SCHEME 84

The cyano substituted dithiocarboxylic acids or the geminal dithiols generated by treatment of the salts with mineral acids are generally unstable and decompose with evolution of hydrogen sulfide. Enedithiols decompose to give stable 1,2-dithiole-3-thiones.[151,173]

Unstable dithioacid esters are also oxidized to the corresponding disulfides.[174]

The dithiolates **142** were found to be useful intermediates for the synthesis of heterocycles.[159a,175-177]

Under ion pair extraction conditions, the tetrabutylammonium salts of diethyl malonate, methyl cyanoacetate or malononitrile react with carbon disulfide to give salts of the dithioacids **156**.[40]

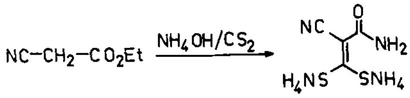


156

X=Y: CN, CO_2Et ; X: CN, Y: CO_2Me

SCHEME 85

Cyanoacetates are sufficiently acidic to give (with sodium alkoxides of primary alcohols) anions for addition of carbon disulfide. In order to avoid the disturbing influence of transesterifications it is necessary to use for the ester and the base the same alcoholic moiety.[5,12,83,121,143,154,155,158,164,172,173,179,181] The use of methanol (ethanol)/potassium hydroxide,[134,143,180] ether/dioxane or dioxane/potassium hydroxide,[12,182] sodium/ether[83] and sodium hydride/THF[162] has also been described. Bis(ammoniothio)-2-cyanoacrylamide **157** has been prepared by reaction of a mixture of ethyl cyanoacetate, carbon disulfide and aqueous ammonia.[164,165a,183]

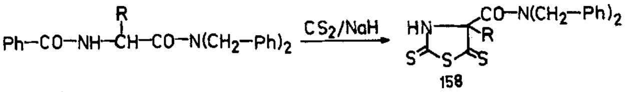


157

SCHEME 86

Like malonic esters or cyanoacetates, also malonic ester anilides,[184,185] and cyanoacetamides[5,36a,121,143,151,154,159,173,186,187] react with carbon disulfide in the presence of a base.

The reaction of *N*-benzoyl-*N'*,*N'*-dibenzylamides of various amino acids with carbon disulfide/sodium hydride leads to the thiazolidine-2,5-dithiones **158**.[178]



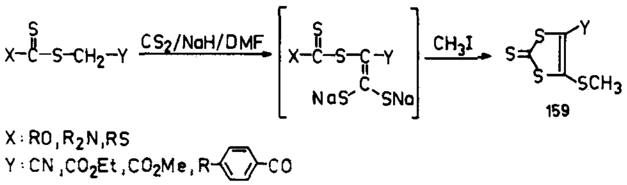
158

R: H, Me, i-Bu, $PhCH_2$

SCHEME 87

3.4. *Reactions with Thiocarbonates and Thiocarbamates*

Dithiocarboxylation of dithio- and trithiocarbonic acid derivatives gives, after methylation, the 1,3-dithiole-2-thiones **159**.[188a-f]

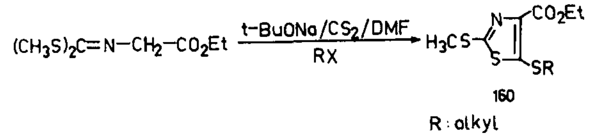


SCHEME 88

With phase transfer catalysis in some cases ketene *S*,*S*-acetals are obtained.[188f]

O-Ethyl *S*-cyanomethyl dithiocarbonate (X = EtO, Y = CN) reacts with carbon disulfide under phase transfer conditions to form 1,3-dithiole-2-thiones in good yields.[189]

A novel synthesis of thiazoles **160** from a cyclocondensation reaction between *S*,*S*-dimethyl *N*-(ethoxycarbonylmethyl)iminodithiocarbonate, carbon disulfide and alkylation of the intermediate thiazole-5-thiolate was reported recently.[190,191a]

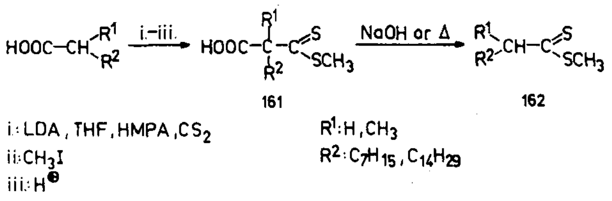


SCHEME 89

Dithiocarbamic acid esters with a CH-acidic methylene group adjacent to nitrogen react in the system DMF/sodium *t*-butoxide with carbon disulfide to yield 1,3-thiazoline-2-thiones. Thiocarbamic acid esters give 1,3-thiazolin-2-ones.[191b]

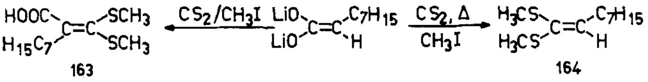
3.5. *Reaction with Carboxylic Acids*

A direct pathway to dithioesters and ketene dithioacetals from aliphatic carboxylic acids was reported by Konen *et al.*[24] The addition of carbon disulfide to the dianions of alkylcarboxylic acids proceeds smoothly and rapidly, producing a dithiocarboxylate salt which is subsequently alkylated to give a methyl 2-carboxydithio ester **161** which can easily be decarboxylated (with NaOH or by heating) to **162**.



SCHEME 90

Carboxylate dianions can also be converted to 2-carboxyketene dithioacetals **163**. Heating of the carbon disulfide adduct results in decarboxylation to a dithiolate dianion which affords ketene dithioacetals **164** upon alkylation.

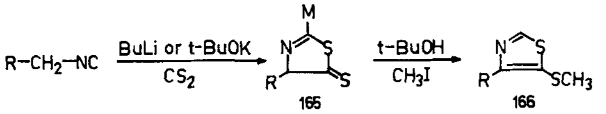


SCHEME 91

Attempted preparation of 2-carboxyketene dithioacetals by alkaline hydrolysis of the corresponding 2-carbalkoxy derivatives has been reported by several authors to result in decarboxylation or in mixtures of 2-carboxyketene dithioactals and decarboxylated analogs.[24,43,82,185]

4. REACTIONS WITH ISONITRILES

α-Metallated isonitriles possessing a nucleophilic C-atom and an electrophilic center react with carbon disulfide to give the cyclic adducts **165** which, on proton transfer by *t*-butanol and methylation, yield the 5-(methylthio)thiazoles **166**.[192]

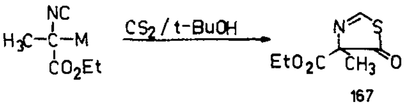


M: Li,K

R: H, Ph, CO_2Et

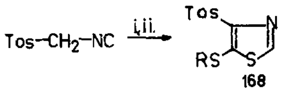
SCHEME 92

With α-metallated secondary isonitriles the reaction leads to the thiazoline **167**.



SCHEME 93

Base-induced reaction of tosylmethyl isocyanide (TosMIC) with carbon disulfide gives the thiazoles **168** in high yield as the only product.[193]



i: NaOH/$Bu_4N^{\oplus}Br^{\ominus}$, $CHCl_3$, CS_2

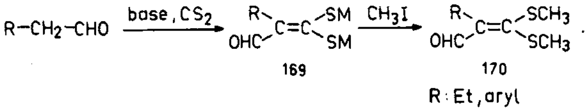
ii: RX

R: Me, Et, Bu, $PhCH_2$, $CH_2{=}CH{-}CH_2$, PhCO, CH_3CO

SCHEME 94

5. REACTIONS WITH ALDEHYDES AND HYDRAZONES

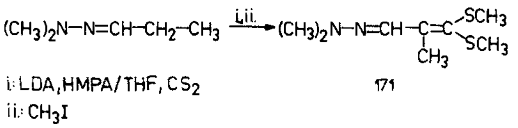
Phenylacetaldehydes have been converted to α-formylketene dithioacetals **170** in moderate yields with sodium hydride in dimethyl sulfoxide.[194] *n*-Butyraldehyde afforded low yields with NaH/DMSO or the sodium *t*-pentoxide/$Et_2O/CS_2/CH_3I$ combination, but could be converted into an α-formylketene dithioacetal in 45% yield with a KH/THF/CS_2/CH_3I combination.[194,195a] The reaction of CS_2 with ethyl formylacetate sodium salt and subsequent alkylation is described in a Japanese patent.[195b]



SCHEME 95

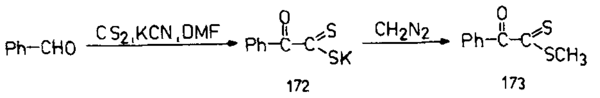
Alkylation of the primarily formed dithiolates **169** first with methyl iodide and then with an α-CH-acidic halo compound yields ketene *S,S*-acetals which undergo cyclization upon base treatment to afford thiophenes.[196]

The conjugated ketene dithioacetal **171** has been prepared from a hydrazone with lithium diisopropylamide (LDA) as the base.[26]



SCHEME 96

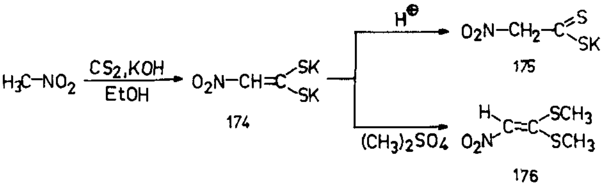
The phenyldithioglyoxalic acid **172** has been prepared by reaction of benzaldehyde with carbon disulfide in the presence of potassium cyanide.[197] The dithioacid was characterized after esterification to **173** with diazomethane.



SCHEME 97

6. REACTIONS WITH ALIPHATIC NITRO COMPOUNDS

Reaction of nitromethane with carbon disulfide in the presence of alcoholic potassium hydroxide leads to the resonance stabilized dianion **174**.[198,199]



SCHEME 98

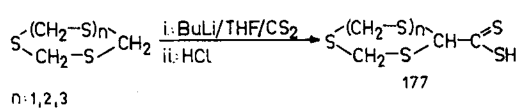
Acidification of **174** gives the monopotassium salt **175**. The salt **175** and the free nitrodithioacetic acid could not be isolated in a pure state. Treatment of **174** with one equivalent of an alkylating reagent gives rise to an explosive oil, probably an ester of nitrodithioacetic acid, on the other hand the nitroketene dithioacetal **176** is formed by methylation with dimethyl sulfate.[198,200]

1-Nitro-2,2-bis(methylthio)ethylene **176** is an extremely interesting synthon and used as a two-carbon fragment for the synthesis of heterocyclic compounds with nitro or amino substituents.[201] The dithiocarboxylation of nitroethane, 1-nitropropane and 2-nitropropane has been described;[199,202] however, it has also been mentioned that higher nitroalkanes do not react with carbon disulfide to yield well-defined products.[200]

The condensation of carbon disulfide with the anion of nitroacetonitrile and subsequent alkylation give only very low yields of ketene dithioacetals.[203]

7. REACTIONS WITH SULFIDES, SULFOXIDES AND SULFONES

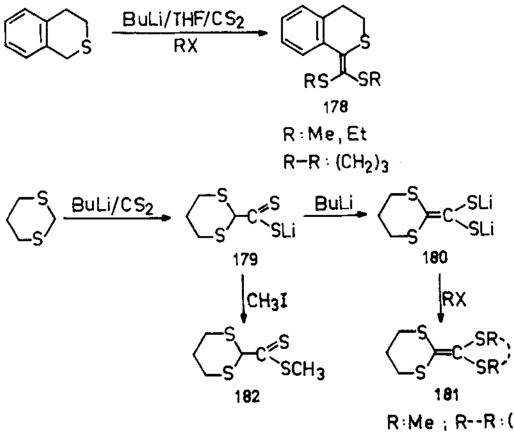
Cyclic sulfides are sufficiently CH-acidic for metalation with butyllithium at −30 °C. The resulting carbanions react at room temperature with carbon disulfide to give lithium dithiocarboxylates which are red colored in solution. Acidification with HCl leads to the orange dithiocarboxylic acids **177**.[204,205]



SCHEME 99

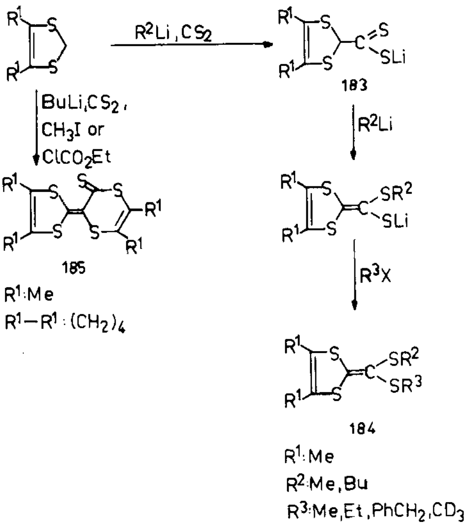
Sulfur-stabilized carbanions react with carbon disulfide to form alkenes with three[206] or four thio substituents.[207a–c]

Dilithio-1,3-dithiane-2-carbodithioate **180** can be prepared from lithio-1,3-dithiane and carbon disulfide by immediate treatment with a second equivalent of *n*-BuLi. Failure to add *n*-BuLi results in a disproportionation reaction of **179** to yield **180** and an extremely unstable dithioacid which rapidly decomposes. The dianion **180** can be alkylated without prior isolation. Alkylation of the monoanion **179** can be achieved if the reaction with the alkylating agent is sufficiently rapid to avoid disproportionation.[207a]



SCHEME 100

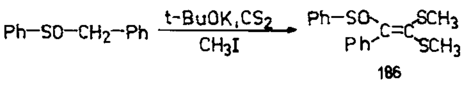
4,5-Dimethyl-1,3-dithiole can be lithiated and then treated with carbon disulfide to produce the dithiocarboxylate **183**. Further reactions with alkyllithium gives the dithioester enolates which can be alkylated to yield the 2-[bis(alkylthio)methylene]-1,3-dithioles **184**.[208a] The reaction of 4,5-disubstituted 2-lithio-1,3-dithioles with carbon disulfide, followed by treatment with ethyl chloroformate or methyl iodide, produces the dithiolylidenedithiinthiones **185**.[208b]



SCHEME 101

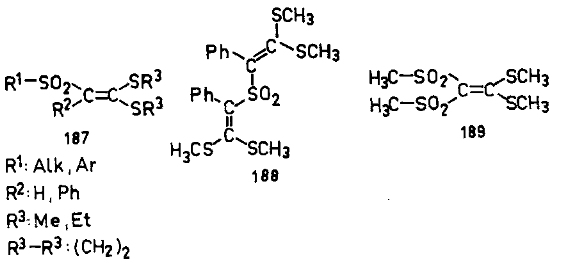
The reaction of trialkyl trithioorthoformates with carbon disulfide and subsequent methylation of the products leads to methyl tris-(alkylthio)-dithioacetates (pentathiomonoorthooxalates).[208c]

The base-induced reaction of methyl or methylene groups activated by sulfinyl or sulfonyl groups with carbon disulfide, followed by alkylation of the intermediate dithiolate anion, has been used for the preparation of dithioacetals. Application of this reaction sequence to benzyl phenyl sulfoxide gave **186**.[209]



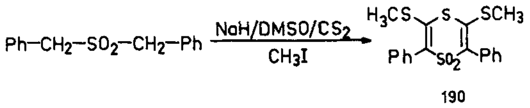
SCHEME 102

This reaction has also been investigated as a synthetic route to structures of the types **187–189**, starting with the appropriate sulfone or disulfone.[209-211]



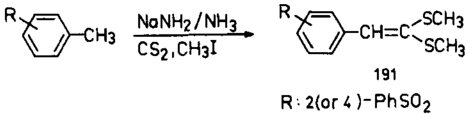
SCHEME 103

The dithiocarboxylation of dibenzyl sulfone with 2 equiv. carbon disulfide in the presence of 4 equiv. sodium hydride and subsequent methylation yields the 1,4-dithiin 1,1-dioxide **190**.[210]



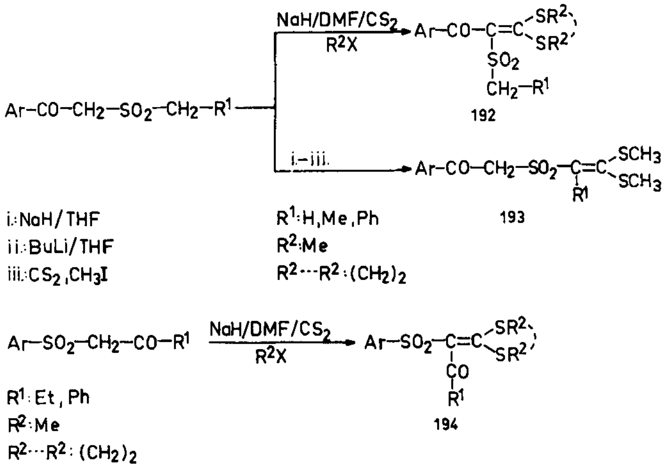
SCHEME 104

Even *o*-tolyl (or *p*-tolyl) phenyl sulfone can easily be dithiocarboxylated at the methyl group.[212]



SCHEME 105

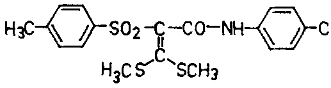
α-Sulfonyl ketones have been dithiocarboxylated with NaH in DMF or NaH/THF and BuLi/THF.[213] Depending on the reaction conditions different addition compounds can be obtained with carbon disulfide.



SCHEME 106

Alkyl- and arylsulfonylacetanilides react with carbon disulfide in the presence of aqueous sodium hydroxide and dimethyl sulfate in DMF to give ketene *S*,*S*-acetals, *e.g.* **195**.[214a] In a similar way (alkylsulfonyl)acetates are dithiocarboxylated.[214b]

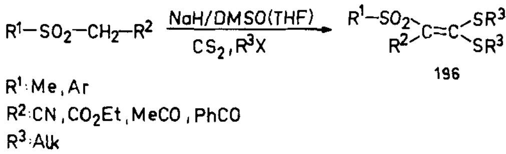
Concerning the dithiocarboxylation of arylsulfonylacetamides see [215].



195

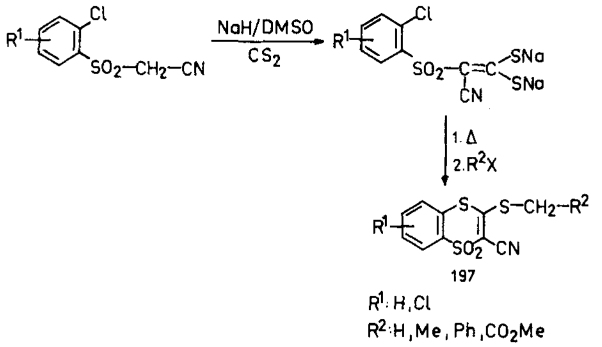
SCHEME 107

The sulfonylketenethioacetal derivatives **196** have been synthesized by reaction of sulfonyl carbanions with carbon disulfide in the presence of sodium hydride in DMSO or THF, followed by treatment with an alkyl halide.[216-219a] In some cases 1,3-dithioles are formed.[219b]



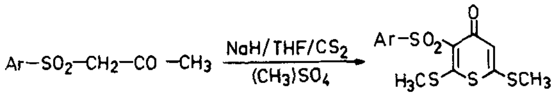
SCHEME 108

(2-Chlorophenylsulfonyl)acetonitriles undergo reaction with sodium hydride and carbon disulfide to form dithiolates. Intramolecular cyclization can occur at elevated temperature to afford the 1,4-benzodithiin 1,1-dioxides **197**.[219a]



SCHEME 109

The thiopyrones **198** can be prepared by treatment of arylsulfonylacetones with CS_2/NaH in boiling THF.[217]



198

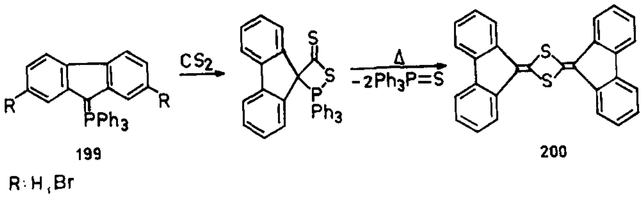
SCHEME 110

8. REACTIONS WITH *P*-, *N*-, OR *S*-YLIDES, THEIR SALTS AND PHOSPHONATE CARBANIONS

Phosphonium, pyridinium and sulfonium ylides being nucleophiles attack the carbon atom of carbon disulfide. As a rule the primarily formed adducts are subject to further rearrangement and addition reactions.

8.1. Reactions with P-Ylides

The result of the reaction of ylides with carbon disulfide depends on the phosphorane used and the reaction conditions. The intermediates can be formulated as betaines which rearrange to more stable products. Schönberg *et al.*[220] report that fluorenylidenetriphenylphosphoranes react with carbon disulfide to give the 2,4-difluorenylidene-1,3-dithietanes **200**.

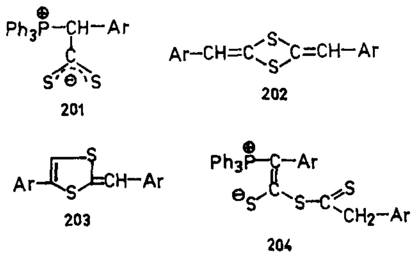


SCHEME 111

Since compounds **199** have no hydrogen atoms attached to the ylide carbon atom, their overall reaction with carbon disulfide is necessarily restricted to dimerization of the intermediate thioketene system to give 1,3-dithietan derivatives.

The addition of diphenylmethylenetriphenylphosphorane to carbon disulfide yields polymeric diphenylthioketene.[221]

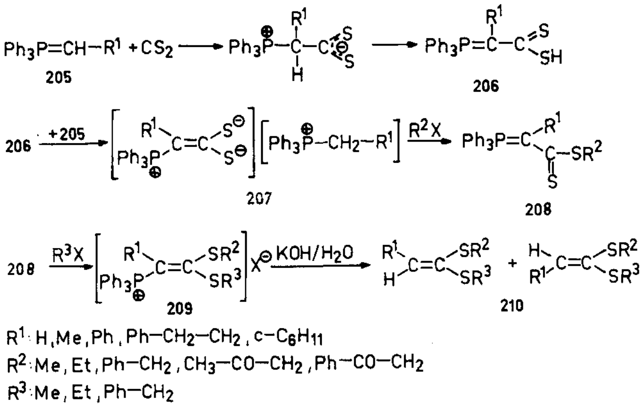
The reaction of benzylidenetriphenylphosphorane and some of its *p*-benzylidene substituted derivatives with carbon disulfide gives rise to the formation of one or more of the compounds **201**–**204** depending upon the experimental conditions.[222,223]



SCHEME 112

The alkylidenetriphenylphosphoranes **205** react with carbon disulfide in the molar ratio 2:1 to yield the phosphonium salts **207**, which by reaction with halo compounds furnish the 2-(triphenylphosphoranylidene)alkanedithioates **208**.[224,225a; cf.225b] The compounds

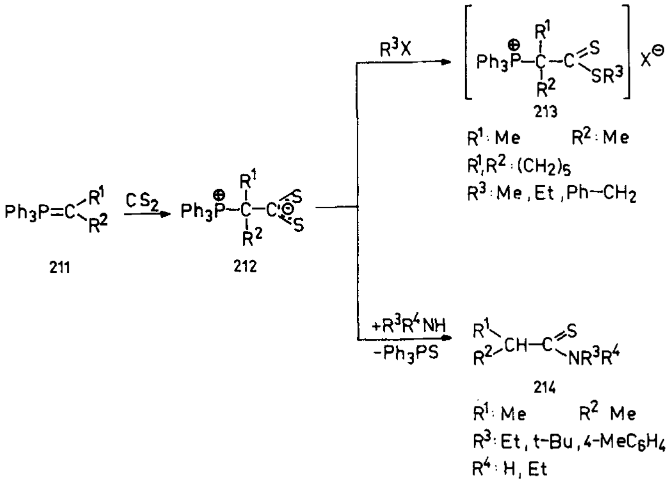
208 do not undergo Wittig reactions, but react with halo compounds to give the phosphonium halides **209**. The reaction of the salts **207** with ω,ω′-dihalo compounds leads to cyclic ketene *S*,*S*-acetals. Alkaline hydrolysis of **209** gives the ketene *S*,*S*-acetals **210**.



SCHEME 113

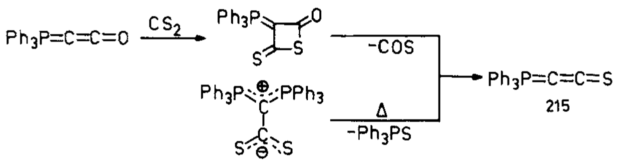
Cyanomethylenetriphenylphosphorane **205** (R^1 = CN) gives a 98% yield of the dithiocarboxylic acid **206**.[226]

The phosphonium ylides **211** react with carbon disulfide to yield the betaines **212** which react with halo compounds to form the phosphonium salts **213**.[225a]



SCHEME 114

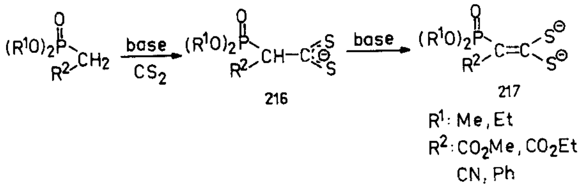
Amines as trapping reagents for the potentially occurring thioketenes react with **212** to afford the thioamides **214**.[227] In the absence of an appropriate trapping reagent the zwitterionic adduct **212** reacts to form a 1,2,4-trithiolane with thermal or, when coordinated to transition metals, photochemical activation.[228,229] A four-membered ring is postulated as an intermediate in the conversion of a triphenylphosphoranylideneketene by carbon disulfide to triphenylphosphoranylidenethioketene **215**.[230] It has also been synthesized by thermal cleavage of the [(dithiocarboxy) (triphenylphosphoranylidene)-methyl]-triphenylphosphonium inner salt.[231]



SCHEME 115

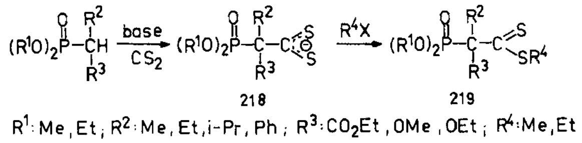
8.2. Reactions with Phosphonate Carbanions

α-Monosubstituted phosphonate carbanions react with carbon disulfide *via* the primary adducts **216** to give the 1,1-alkenedithiolates **217** which can be characterized by alkylation, oxidation, protonation and phosgenation.[232,233]



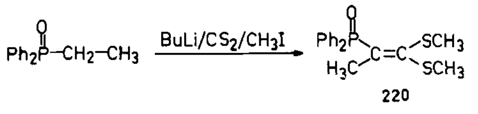
SCHEME 116

α,α-Disubstituted phosphonate carbanions add to carbon disulfide to furnish the salts **218**, which on alkylation yield the phosphono substituted dithioesters **219**.[232]



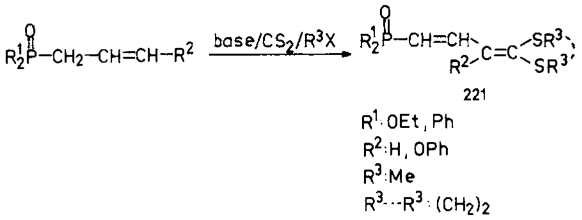
SCHEME 117

The bases used for this deprotonation are NaH,[232] *n*-BuLi,[232] lithium diisopropylamide[234] or *n*-BuLi/lithium bis[trimethylsilyl]amide.[234] Dithiocarboxylation of carbanions of diphenylphosphane oxides is also possible.[234]



SCHEME 118

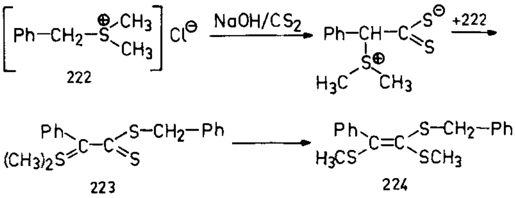
Vinylketene *S,S*-acetals **221** are obtained with the combination BuLi/LiN[Si(CH_3)$_3$]$_2$/CS_2/R^3X.[235]



SCHEME 119

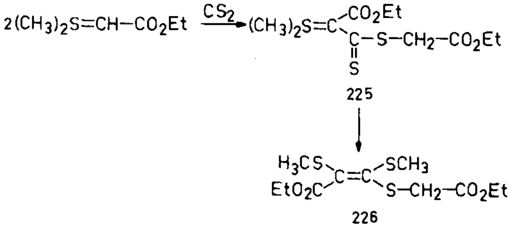
8.3. *Reactions with S-Ylides*

Treatment of an aqueous solution of benzyldimethylsulfonium chloride **222** and sodium hydroxide with carbon disulfide affords an ylide **223**, which rearranges completely and quantitatively to the styrene derivative **224** on standing at room temperature for several days.[236]



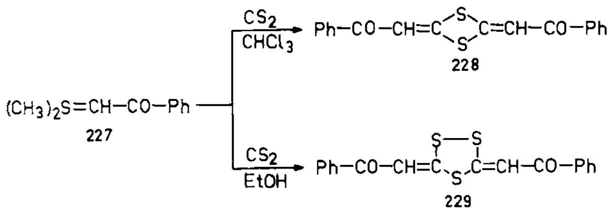
SCHEME 120

Ethyl (dimethylsulfuranylidene)acetate reacted vigorously with carbon disulfide at −20 °C without solvent to yield **225**. Rearrangement of **225** gave a *cis-trans* mixture of **226**.[236]



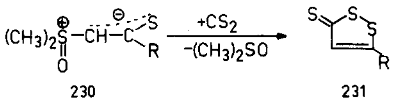
SCHEME 121

Reaction of (dimethylsulfuranylidene)acetophenone **227** with carbon disulfide in aprotic solvents does not take the same course as with the benzylides. When **227** was treated with carbon disulfide in chloroform the 1,3-dithietane **228** was isolated. Reaction in ethanol gave the 1,2,4-trithiole **229**.[236]



SCHEME 122

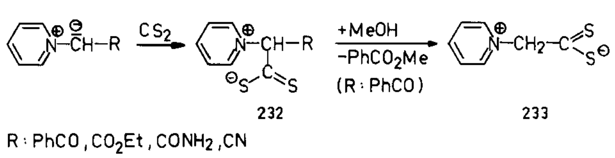
The addition of sulfoxonium ylides to carbon disulfide affords cyclic products. Condensation of the dimethyl-oxo-(2-thionoalkylidene)-sulfuranes **230** with carbon disulfide gives the 3-thiono-1,2-dithiolanes **231**[237] whereas dimethyl-[2-(2-methylaminoaryl)-2-oxoethylidene]-oxosulfurane gives 2-mercapto-1-methyl-4-oxo-1,4-dihydroquinolines.[238]



SCHEME 123

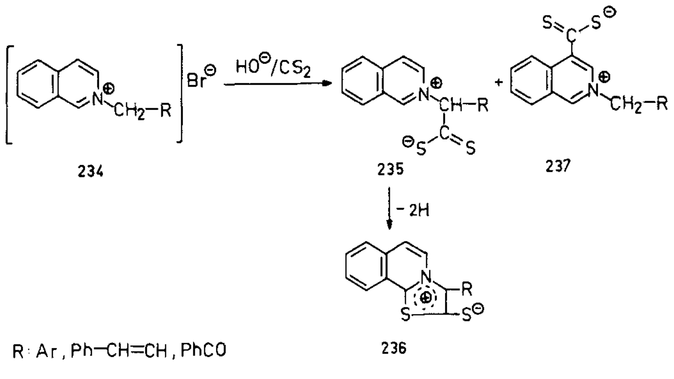
8.4. *Reactions with N-Ylides*

With pyridinium ylides carbon disulfide condensation occurs with the carbanion to give the dithiocarboxy betaines **232**; in the presence of methanolic alkali, loss of the benzoyl substituent (R = PhCO) occurs with formation of dithioacetic acid pyridinium betaine **233**.[239]



SCHEME 124

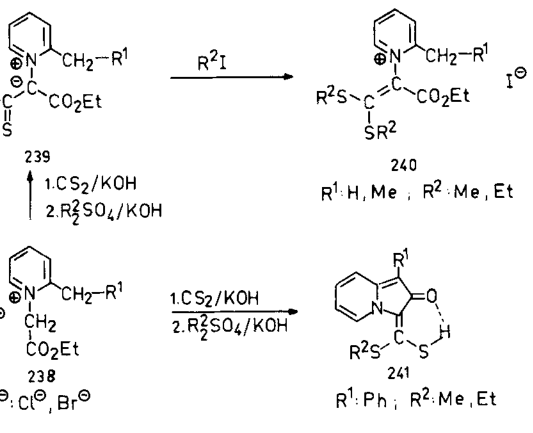
The compounds **232** and **233** can be converted to pyridiniodithioacetic ester salts or ylides. Ketene *S,S*-acetals and derivatives may also be obtained.[239–242b] Dithiocarboxylation also takes place with *N*-benzyl(phenacyl)isoquinolinium bromides in aqueous alkali/dioxane, but the dithiocarboxylic betaines **235** immediately cyclize to form the thiazolo[2,3-*a*]isoquinolinium-2-thiolates **236**.[243–246]



SCHEME 125

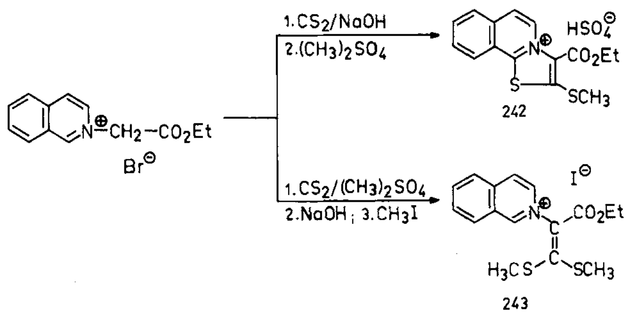
In addition to **236** the dithiocarboxylates **237** have also been isolated.[244]

The pyridinium iodides **240** are readily obtained from the 1-(ethoxycarbonylmethyl)-pyridinium halides **238** and $CS_2/KOH/R^2_2SO_4/R^2I$ *via* the corresponding ylides **239**. On the other hand, treatment of 2-benzyl-1-(ethoxycarbonylmethyl)pyridinium bromide **238** (R^1 = Ph) with carbon disulfide and then a dialkyl sulfate in the presence of potassium hydroxide afforded the 3-methylene-2,3-dihydroindolizin-2-ones **241**.[247]



SCHEME 126

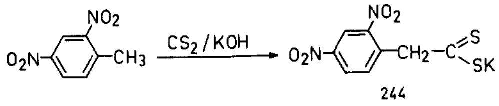
The reaction of 2-ethoxycarbonylmethylisoquinolinium bromide with carbon disulfide and sodium hydroxide afforded thiazolo[2,3-*a*]isoquinolinium sulfate **242** and an isoquinolinioketene dithioacetal **243**, respectively.[248,249]



SCHEME 127

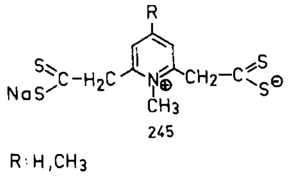
9. REACTIONS WITH ACTIVATED METHYL AND METHYLENE GROUPS BOUND TO AROMATIC AND HETEROCYCLIC SYSTEMS

Activated methyl groups bound to aromatic ring systems can be dithiocarboxylated. Treatment of 2,4-dinitrotoluene with carbon disulfide and methanolic potassium hydroxide yields the potassium salt of 2,4-dinitrophenyldithioacetic acid **244**.[68]



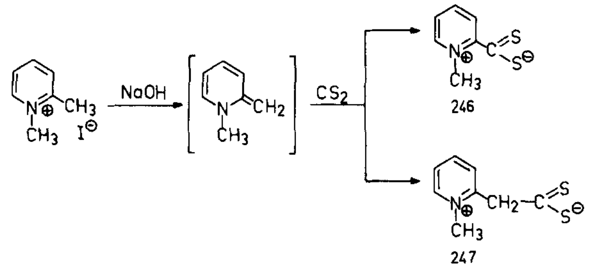
SCHEME 128

Although condensation of carbon disulfide with the methyl groups of 2,6-dimethylpyridine and 2-methylquinoline has been claimed to give salts of dithio acids[68], Foye *et al.*[250] found that neither 2-methylpyridine, 2,6-dimethylpyridine, nor 2,4,6-trimethylpyridine react with carbon disulfide in the presence of various concentrations of base. Conversion to the 1-methylpyridinium salts, however, generated more active methyl groups which did condense with carbon disulfide. The products from 2,6-dimethylpyridine and 2,4,6-trimethylpyridine were the sodium salts of the 2,6-bis(dithioacetic acid) zwitterion **245**.[250]



SCHEME 129

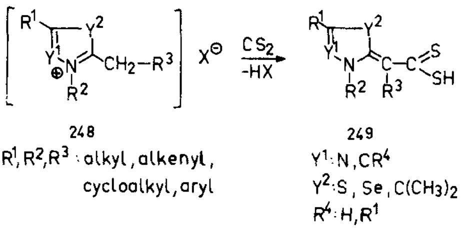
With 2-methylpyridine methiodide carbon disulfide condensation took place with elimination of the 2-methyl group to give the 1-methylpyridinio-2-dithiocarboxylic acid zwitterion **246**.[250] In another case, however, the same procedure resulted in the formation of the 1-methylpyridinio-2-dithioacetic acid zwitterion **247**.[251-253]



SCHEME 130

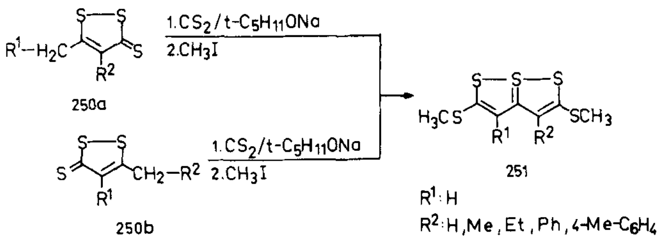
Analogous dithioacids and their esters can be prepared from 1-methylquinaldinium iodides, 1,4-dimethylpyridinium iodide, 1,2-dimethylbenzothiazolium iodide and 1,4,6-trimethylpyrimidinium iodide.[250,253,254]

The dithioacids **249** and their derivatives are produced by dithiocarboxylation of the compounds **248**.[255]



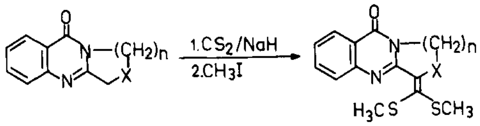
SCHEME 131

Carbon disulfide has been condensed with 1,2-dithiole-3-thiones with a methylene group in the 5-position.[256] In no case could the initially formed condensation product be isolated. In all cases the two isomeric 1,2-dithiole-3-thiones **250a** and **250b** gave the same 1,6,6aλ⁴-trithiapentalene **251**.



SCHEME 132

However, with 1,2-dibromoethane as alkylating agent, **250a** and **250b** gave two isomeric alkylated products.[257] By reaction with carbon disulfide in alkaline medium even 1,6,6aλ^4-trithiapentalenes with adjacent methylene groups yield dithiolates.[258] When fused quinazolones were treated with sodium hydride and carbon disulfide and then methylated the ketene *S*,*S*-acetals **252** were obtained.[259a,b]

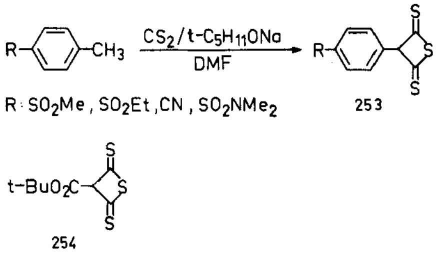


252

X: CH$_2$ n: 1,2
X: S n: 1-3

SCHEME 133

Alkyl *p*-tolyl sulfones, *p*-tolunitrile or *N*,*N*-dimethyl-*p*-toluenesulfonamide, when refluxed with a large excess of carbon disulfide in the presence of sodium 1,1-dimethylpropoxide in *N*,*N*-dimethylformamide, afforded the thietane-2,4-dithiones **253**.[260,cf.212] The reaction is strongly influenced by the substituents on the aromatic ring. Also, *t*-butyl acetate gave the 3-(*t*-butoxycarbonyl)thietane-2,4-dithione **254** in very poor yield.



R: SO$_2$Me, SO$_2$Et, CN, SO$_2$NMe$_2$

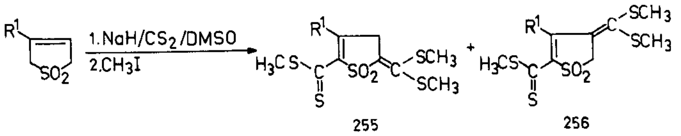
253

254

SCHEME 134

10. REACTIONS WITH CH-ACIDIC HETEROCYCLES

There are many heterocyclic compounds which possess activated methylene or methyne groups adjacent to carbonyl, thiocarbonyl or sulfonyl groups. Therefore, they can be converted into the corresponding dithiocarboxylated compounds. Sulfolanes react in the 2- and 5-position with CS$_2$/*n*-BuLi with subsequent alkylation to give ketene *S*,*S*-acetals. On the other hand dithiocarboxylation of Δ^3-sulfolenes in the presence of NaH/CH$_3$I leads to the dithioesters **255** and **256**.[261]

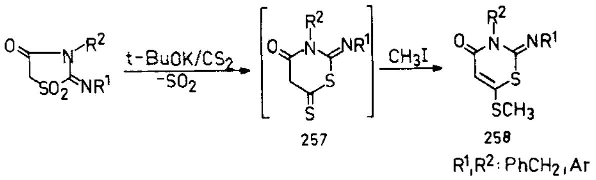


255 256

R^1: H, Me

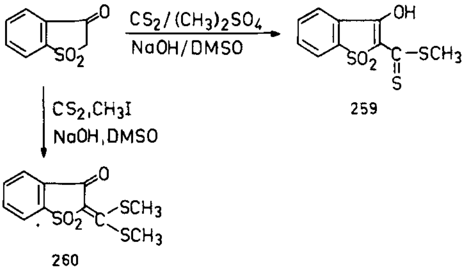
SCHEME 135

2-Imino-4-oxoperhydrothiazole 1,1-dioxides react with CS_2/t-BuOK/CH_3I and suffer ring expansion with elimination of SO_2. The supposed intermediates **257** were not isolated. Methylation gives the stable 2-imino-4-oxo-2,3-dihydro-4*H*-1,3-thiazines **258**.[262]



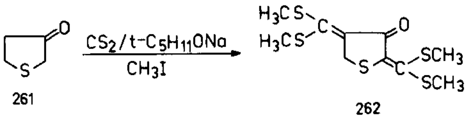
SCHEME 136

The formation of methyl dithiocarboxylates during synthetic investigations of sulfonylketene thioacetals has been mentioned.[217] 2,3-Dihydrobenzo[*b*]thiophen-3-one 1,1-dioxide, on treatment with sodium hydroxide and carbon disulfide in dimethyl sulfoxide, followed by esterification with dimethyl sulfate or methyl iodide, forms methyl 3-hydroxy-1,1-dioxobenzo[*b*]thiophene-2-dithiocarboxylate **259** and 2,3-dihydro-2-bis(methylthio)methylene-3-oxobenzo[*b*]thiophene 1,1-dioxide **260**.[263]



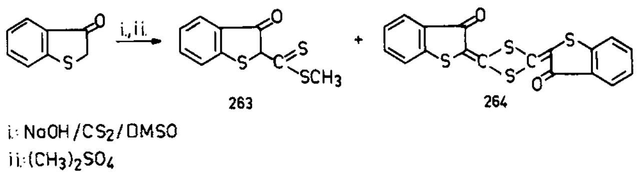
SCHEME 137

The cyclic ketone **261** can react with CS_2/t-$C_5H_{11}ONa/CH_3I$ to yield 2,4-bis[bis(methylthio)methylene]thiolan-3-one **262**.[264]



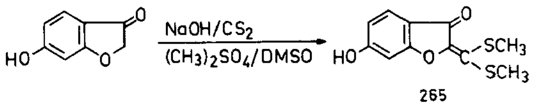
SCHEME 138

Reaction of benzothiophen-3(2*H*)-one with $CS_2/NaOH/Me_2SO_4$ gave a mixture of methyl 3-oxo-2,3-dihydrobenzothiophene-2-dithiocarboxylate **263** and the desaurin type compound **264**.[265]



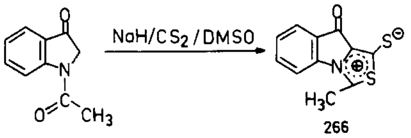
SCHEME 139

Dithiocarboxylation of 6-hydroxycoumaran-3-one, followed by treatment of the crude reaction mixture with dimethyl sulfate in the presence of NaOH gave the heterocyclic ketene thioacetal **265**.[266a,cf.266b]



SCHEME 140

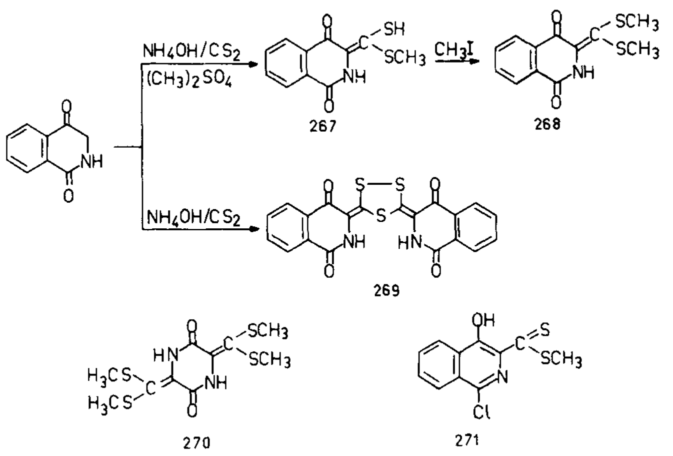
It has been found that carbon disulfide also reacts with the active methylene group of 1-acetyl-3-indolinone to give the mesoionic compound **266**.[267,273]



SCHEME 141

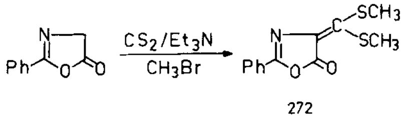
Concerning the dithiocarboxylation of 4,5-dihydro-2*H*-3-benzothiepin-1-one and its sulfone cf.[268]

Addition of carbon disulfide and dimethyl sulfate to 1,4-dioxo-1,2,3,4-tetrahydroisoquinoline in aqueous ammonia gave methyl 1,4-dioxo-1,2,3,4-tetrahydroisoquinoline-3-dithiocarboxylate **267** which was further methylated with methyl iodide to the ketene *S*,*S*-acetal **268**. Reaction in the absence of an alkylating reagent afforded the 1,2,4-trithiolane **269**. Treatment of 1,4-diacetylpiperazine-2,5-dione or 1-chloro-4-hydroxyisoquinoline with carbon disulfide gave **270** and **271**, respectively.[269]



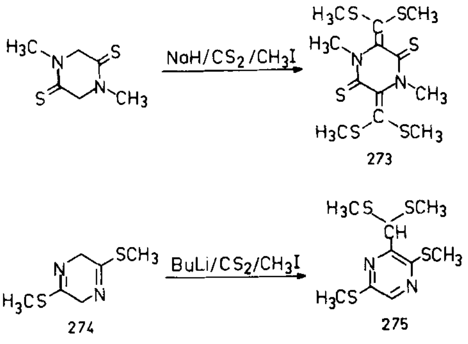
SCHEME 142

In a similar way, Kobayashi *et al.* reported the synthesis of 3-bis(methylthio)-methylenoxindole,[270] 9-methyl-4-bis(methylthio)methylene-1,3-dioxo-1,2,3,4-tetrahydro-β-carboline,[271] and 4-bis(methylthio)methylene-1,3-dioxo-1,2,3,4-tetrahydroisoquinolines.[272] Triethylamine mediated condensation of 2-phenyl-5-oxo-4,5-dihydro-1,3-oxazole with carbon disulfide and *S*-methylation afforded the ketene dithioacetal **272**.[274,cf.275]



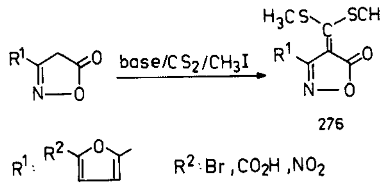
SCHEME 143

Dimethyldithiodiketopiperazine reacts with carbon disulfide and sodium hydride, followed by methyl iodide, to the difunctional ketene *S*,*S*-acetal **273**. The related reaction of the lithium salt of the dihydropyrazine **274** affords the pyrazine **275**.[276]



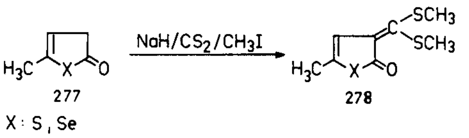
SCHEME 144

By treatment of a 5-oxo-4,5-dihydro-1,2-oxazole with carbon disulfide the ketene dithioacetal **276** has become available.[277]



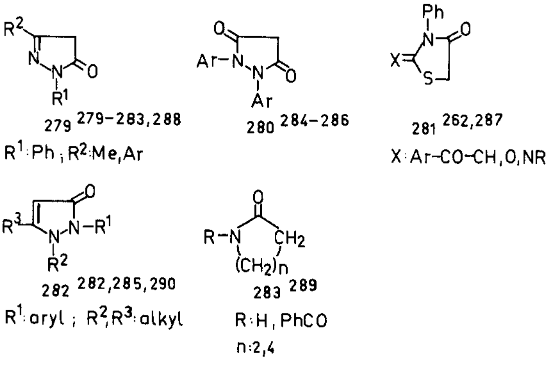
SCHEME 145

The thiolenone and the corresponding selenium compound **277** can be converted into the dithiocarboxylated compounds **278.**[278]



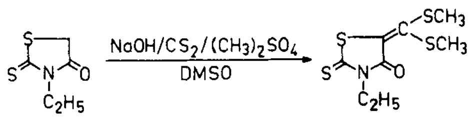
SCHEME 146

A wide variety of heterocyclic CH-acidic carbonyl compounds react with carbon disulfide. Thus, in some cases it has been possible to prepare the free dithiocarboxylic acids in the solid state and to characterize them as salts, anhydrides and esters.



SCHEME 147

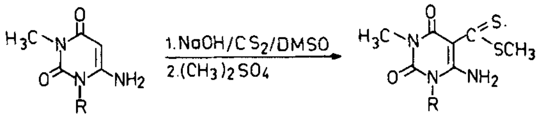
Edwards and Kendall[154] reported the synthesis of 2-thioxo-3-methyl-5-bis-(methylthio)methylenethiazol-4-(5*H*)-one by reaction of 3-methylrhodanine with carbon disulfide in the presence of metallic sodium as base in ether, followed by treatment with methyl iodide. The reaction of 3-ethylrhodanine with carbon disulfide in the presence of sodium hyroxide in dimethyl sulfoxide and subsequent alkylation gave the heterocyclic ketene thioacetal **284.**[291]



284

SCHEME 148

It has been reported that the reaction of 6-aminouracil with carbon disulfide was used to prepare methyl 6-aminouracil-5-dithiocarboxylate **285** in good yield.[292,293] 6-Arylaminouracils gave the corresponding pyrimido[4,5-*b*]quinoline-2,4-diones.[294]

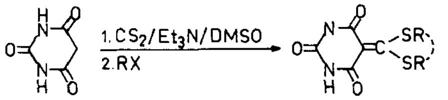


285

R: Me, Ph

SCHEME 149

Condensation of barbituric acid with carbon disulfide in the presence of triethylamine, followed by alkylation, yields the bis(alkylthio)methylene derivatives **286**.[12,131a]



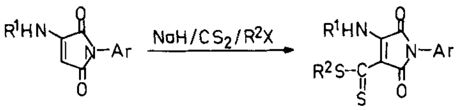
286

R: Me, Et

R···R: (CH2)2, (CH2)3

SCHEME 150

Aminomaleimides can be deprotonated with sodium hydride and then dithiocarboxylated with carbon disulfide.[295]



287

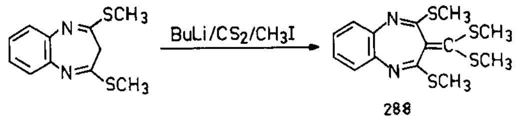
R1: 4-Me-C6H4, n-Bu

R2: Me, n-Bu, Ph-CH2

Ar: 4-Me-C6H4

SCHEME 151

2,4-Bis(methylthio)-1,5-benzodiazepine can be used as a starting material for the preparation of ketene *S*,*S*-acetals. Treatment of the lithium salt with carbon disulfide yields the dianion of a dithiocarboxylic acid, and this can be alkylated to form the diazaheptafulvenes **288**.[296]

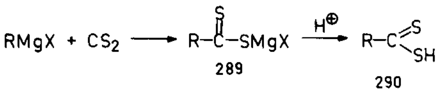


SCHEME 152

11. REACTIONS WITH ORGANOMETALLIC COMPOUNDS

11.1. Syntheses with Grignard Reagents

Organometallic compounds react as potential carbanions with carbon disulfide to give dithiocarboxylates. The reaction of carbon disulfide with Grignard reagents is a general method for the synthesis of dithiocarboxylic acids.



SCHEME 153

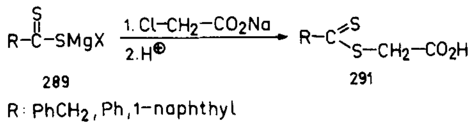
Thus a great number of aliphatic,[297-309] cycloaliphatic,[299,301,310-312] araliphatic,[298,306-309,313-318] aromatic,[297,300,302,304,310,319-337] and heteroaromatic dithiocarboxylic acids[304,306-310,321,332,338-347] as well as ferrocenedithiocarboxylic acid[348] have been prepared. As a rule, yields are low because of side reactions. By use of tetrahydrofuran or tetrahydrofuran/ether as solvents the notoriously low yields in the aliphatic series can be increased to about 50% without use of catalysts.[349-351]

In 1973, an improved procedure for the synthesis of dithioesters R^1CSSR^2 from Grignard compounds R^1MgX in tetrahydrofuran, carbon disulfide, and alkyl halides R^2Hal was described.[352] Methyl, aryl and heteroaryl Grignard compounds reacted sluggishly, while *t*-butyl- and cyclohexylmagnesium halides mainly gave other products, such as trithiocarbonates $(R^2S)_2C{=}S$. Use of catalytic amounts of a copper(I) halide considerably enhances the rate of the reaction of R^1MgX with carbon disulfide and also provides a route to the dithioesters $t\text{-}C_4H_9CSSR^2$ and $c\text{-}C_6H_{11}CSSR^2$.[353]

The yield of dithiobenzoic acid increases from 20% to 78% if the solvent THF is distilled from $LiAlH_4$ instead of from sodium.[349] Bis-Grignard reagents are reported to give bis-(dithiocarboxylic acids).[354]

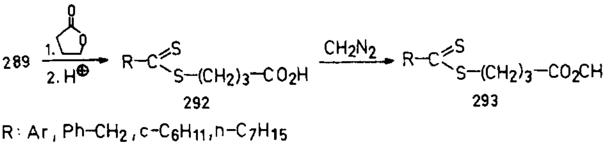
The magnesium salts **289** can be directly alkylated to the corresponding dithioesters. Methyl and ethyl esters of dithioacetic acid, phenyldithioacetic acid, dithiobenzoic acid, and dithio-α-naphthoic acid have been prepared in moderate yields.[355,356a,b]

The methyl, ethyl and butyl ester of dithio-*p*-toluic acid have been synthesized.[330] It is also possible to isolate the dithioacids as their sodium or potassium salts which, on reaction with chloroacetic acid and sodium carbonate, yield the corresponding carboxymethyl dithiocarboxylic esters **291**.[315,332]



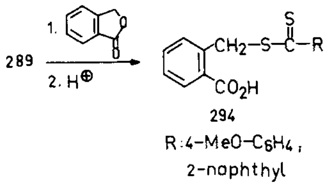
SCHEME 154

A study of the scope of the syntheses of selected aliphatic dithioacids by reported and modified Grignard methods showed that the yields of the dithioacids were poor and depended on the nature of the R group.[357] 3-Carboxypropyl dithioesters **292** have been prepared in a single step by reaction between a Grignard reagent, carbon disulfide, and γ-butyrolactone.



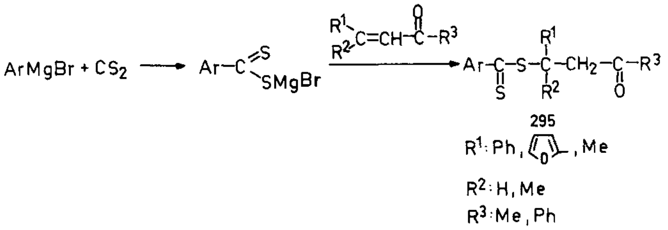
SCHEME 155

A similar reaction with phthalide gave the dithioesters **294**.



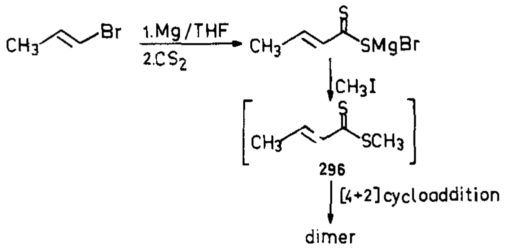
SCHEME 156

Dithioesters **295** have been prepared by Grignard reaction with carbon disulfide and α,β-unsaturated ketones.[358]



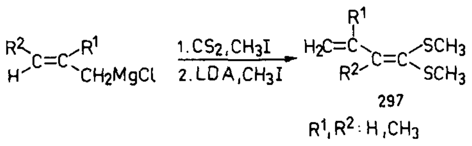
SCHEME 157

Methyl dithiocrotonate **296** (as a dimer) has been obtained in the following way:[359]



SCHEME 158

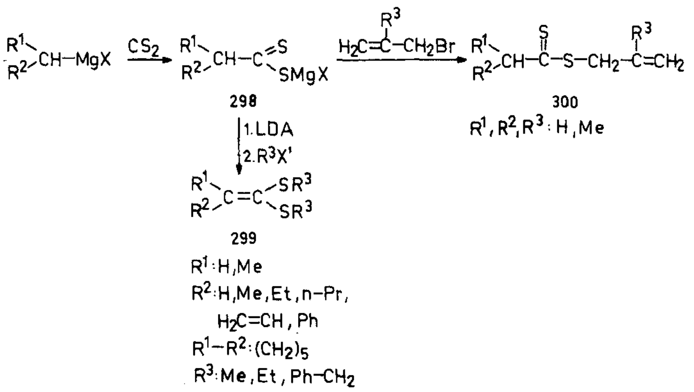
Allylic Grignard reagents react with carbon disulfide, followed by methylation, to give the corresponding conjugated ketene dithioacetals **297**.[360] An inversion of the allyl chain occurs.



SCHEME 159

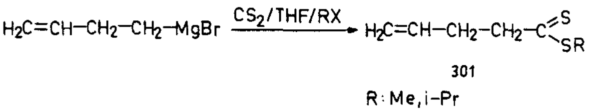
The dithiocarboxylate **298** reacts with lithium diisopropylamide (LDA) to give a dithiolate, the alkylation of which leads to the ketene dithioacetal **299**.[361,362]

The 2-alkenyl alkanedithioates **300** can easily be obtained by alkylation of **298**.[351]



SCHEME 160

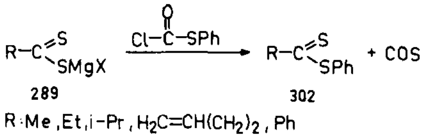
Addition of carbon disulfide to homoallyl Grignard reagents and alkylation of the resulting dithioates with iodomethane or 2-iodopropane (in the presence of HMPA) furnishes the dithioesters **301**.[363]



SCHEME 161

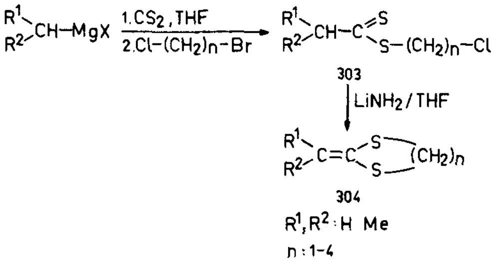
Methyl α- and β-dithiocyclogeranates were prepared by Gosselin.[364]

The otherwise difficultly accessible phenyl dithiocarboxylates **302** are prepared in good yield by reaction of S-phenyl carbonochloridothioate with the halomagnesium dithiocarboxylates **289**.[365]



SCHEME 162

Chloroalkyl alkanedithioates **303** can be synthesized from the corresponding Grignard reagents with carbon disulfide and appropriate chlorobromoalkanes. Compounds **303** cyclize on treatment with lithium amide to give the 2-alkylidene-1,3-dithiacycloalkanes **304**.[366]

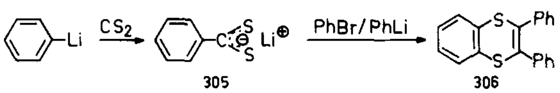


SCHEME 163

11.2. Syntheses with Other Alkyl- and Arylmetallic Compounds

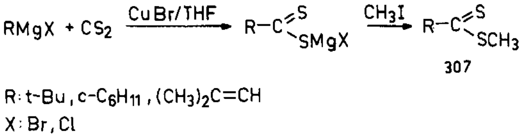
Organolithium and organosodium compounds have been used for the preparation of lithium dithio-α-naphthoate and sodium (lithium) diphenyldithioacetate, respectively.[367–370]

Concerning the reaction of lithium dithiobenzoate **305** (prepared by reaction of phenyllithium with carbon disulfide) with bromobenzene/phenyllithium to give 2,3-diphenyl-1,4-benzodithiin **306**, cf.[371]



SCHEME 164

Since in many cases aryl- and heteroaryllithium compounds are more easily prepared than the Grignard reagents the possibility of synthesizing dithioesters $RCSSCH_3$ from the lithium compounds, carbon disulfide and methyl iodide has been studied. Copper(I) halides catalyse the formation of carbodithioates RCSSLi in the reaction of aryl- or heteroaryllithium reagents with carbon disulfide. Subsequent addition of methyl iodide gives the dithioesters $RCSSCH_3$ in high yields. Appreciable amounts of the methyl sulfides $RSCH_3$ and tars are obtained when the reaction with carbon disulfide is carried out in the absence of copper(I) salts, especially in the case of more basic organoalkali metal compounds.[372] Methyl dithiocarboxylates **307** have been prepared in high yields by treatment of organocopper(I) compounds with carbon disulfide and methyl iodide.[353,373]

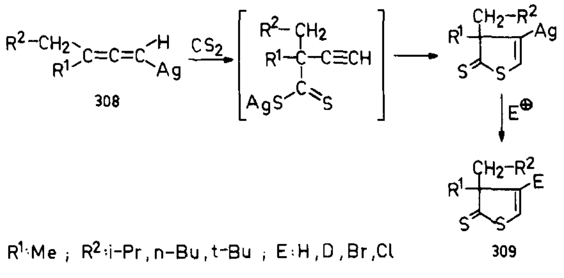


SCHEME 165

The participation of the organocopper(I) compounds in the reaction was established by synthesis of these dithioesters in high yields from the preformed cuprate compounds, obtained from the Grignard reagent and copper(I) bromide.

Alkylcopper compounds in the presence of triphenylphosphine or 1,2-bis[diphenylphosphino]ethane undergo insertion reactions with carbon disulfide to form the corresponding dithiocarboxylate complexes which react with methyl iodide to give virtually pure methyl dithiocarboxylates.[374]

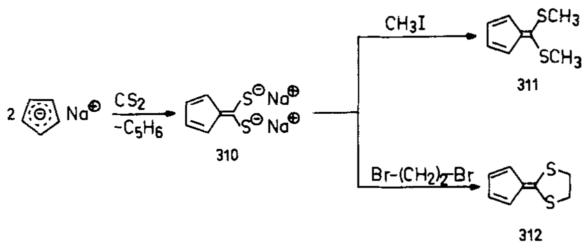
Allenylsilver(I) compounds **308** react with carbon disulfide to give silver 2-ethynylalkane dithioates, which are then converted to the β,γ-unsaturated γ-dithiolactones **309** by cyclization.[375,376,cf.377]



SCHEME 166

Diethylzinc slowly reacts with carbon disulfide to give the zinc salt of dithiopropanoic acid.[378]

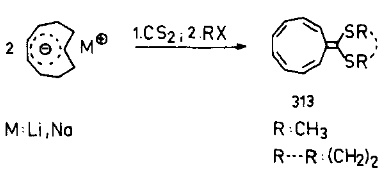
Salts of stable carbanions (stabilized by resonance in the carbon skeleton) readily react with carbon disulfide. The dianion **310** can be obtained from sodium cyclopentadienide and carbon disulfide.[379]



SCHEME 167

Reactions with 1*H*-indene[380,381] or fluorene have also been described.[12,382]

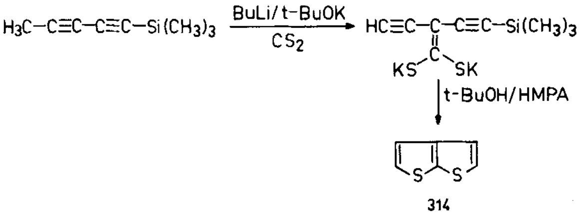
Starting from lithium or sodium *cis,cis,cis,trans*-cyclononatetraenide reaction with carbon disulfide and subsequent alkylation gives the nonafulvenes **313**.[381,383,384]



SCHEME 168

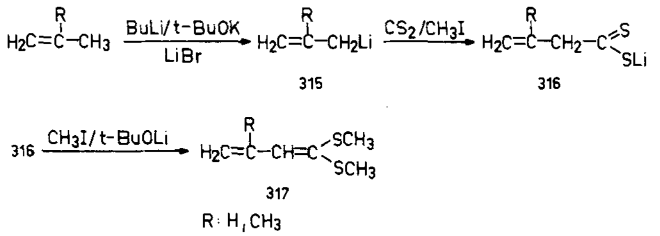
When the lithium salt of mesitylacetylene was treated with carbon disulfide at 20 °C and subsequently with methyl iodide, the corresponding α,β-acetylenic dithioester could be isolated.[385a]

Metallation of the acetylenes MeC≡CR (R = C≡C−SiMe$_3$, C≡CMe, C≡C−SMe, C≡C−N(alkyl)$_2$, S−C≡CSiMe$_3$, S−C≡C−Me) with *n*-BuLi · *t*-BuOK, followed by succesive addition of carbon disulfide, *t*-butyl alcohol, and hexamethylphosphoric triamide gives thieno[2,3-*b*]thiophene, thieno-1,4-dithiin, and some of their derivatives in fair yields.[385b] A propargyl anion is an intermediate in the reaction of 1-(trimethylsilyl)-1,3-pentadiyne with carbon disulfide. Cyclization of an intermediate 1,1-dithiolate gives **314**.



SCHEME 169

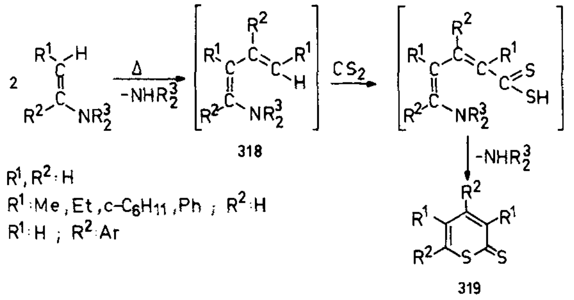
Moreover the same authors reported on the reaction of metalated acetylenes and allenes with carbon disulfide and the influence of the alkali metal counterion on the course of the reaction.[385b,386] Vinylketene *S,S'*-acetals **317** can be prepared in high yields by reaction of a 2-alkenyllithium compounds **315** with carbon disulfide and *S,S'*-dimethylation of the resultant 3-butenedithiolate **316** with methyl iodide.[387]



SCHEME 170

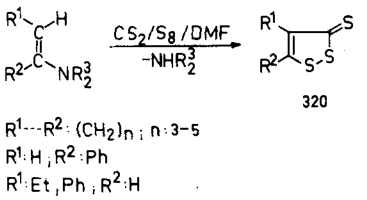
12. REACTIONS WITH ENAMINES AND DIENAMINES

Enamines react with carbon disulfide in DMF to give the 2*H*-thiopyran-2-thiones **319** in moderate yields. These reactions involve the dienamines **318** as intermediates.[388-390] With these dienamines as starting materials the yields of **319** increased.[389]



SCHEME 171

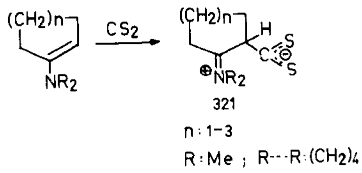
Also enamines of aliphatic methyl ketones afford 2*H*-thiopyran-2-thiones, whereas the corresponding enediamines yield salt-like products.[389,390] Enamines react with carbon disulfide and elemental sulfur at room temperature to give the 3*H*-1,2-dithiole-3-thiones **320**.[389,391-393]



SCHEME 172

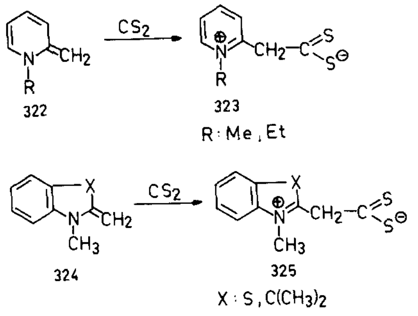
The reaction of a 3-anilino-2-cyclohexen-1-one derived from dimedone with CS_2/NaOH and dimethyl sulfate in DMSO gives enamino dithiocarboxylates.[394a]

Gompper *et al.*[394b] found that enamines of aliphatic 5-, 6- or 7-membered ring ketones react with carbon disulfide to afford the 1,4-dipoles **321**. These compounds react with sulfur to give 3*H*-1,2-dithiole-3-thiones. With heterocumulenes (*e.g.* phenyl isocyanate or phenyl isothiocyanate) cycloaddition and elimination of amine occur to afford 1,3-thiazines.



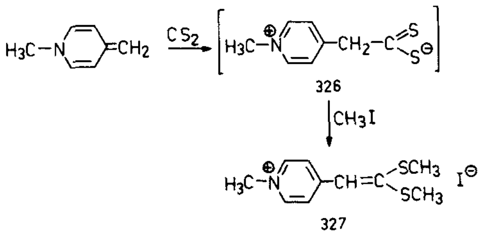
SCHEME 173

The enamine-like methylene bases **322** and **324** yield the dithioacetic acid betaines **323** and **325**[394b–398] which then undergo rearrangement to unsaturated dithioacids.



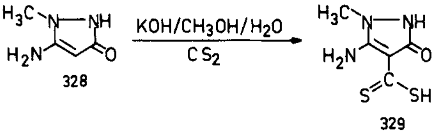
SCHEME 174

In the special case of the pyridinium and quinolinium derivatives **326**, formed in a vinylogous enamine reaction with carbon disulfide, and without additional base a ketene *S*,*S*-acetal **327** is formed.[394b]



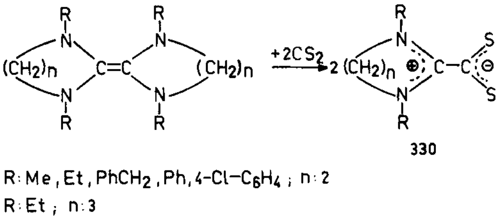
SCHEME 175

The aminopyrazolinone **328** reacts with alkali and carbon disulfide to yield the adduct **329**.[399]



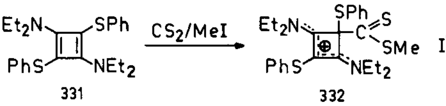
SCHEME 176

Tetraaminoethylenes react violently with carbon disulfide. The deep red zwitterionic dithiocarboxylates **320** can be isolated.[400-402]



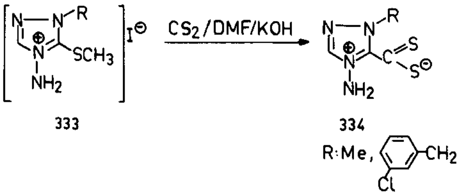
SCHEME 177

The cyclobutadiene **331** also reacts as an enamine and can thus be dithiocarboxylated to form, after methylation, **332**.[403]



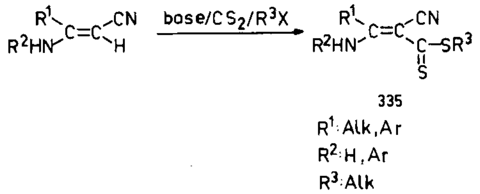
SCHEME 178

By reaction with carbon disulfide the 1,2,4-triazolium iodides **333** yield the dithiocarboxylates **334**.[404]



SCHEME 179

Enaminonitriles react with carbon disulfide in the presence of appropriate bases such as potassium hydroxide or alkali metal alkoxides and subsequent alkylation to give the α-cyano-β-aminodithioacrylates **335**.[405,406]

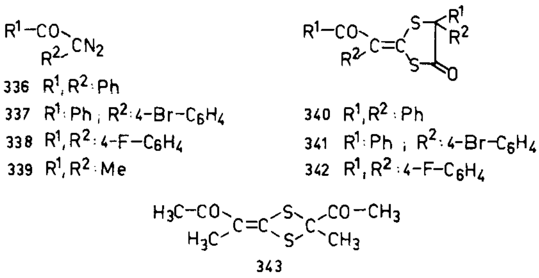


SCHEME 180

Muraoka *et al.*[407] describe the synthesis of β-alkylimino α-cyano dithiocarboxylic acids, 3-alkyl-1,3-thiazine-2,6-dithiones and 1,2-dithiole-3-thiones by reaction of enaminonitriles with carbon disulfide.

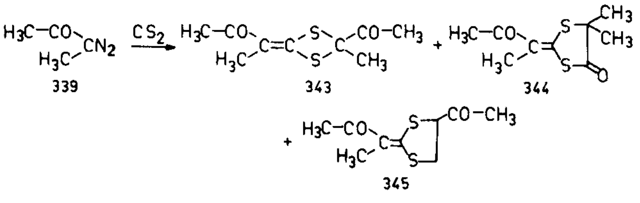
13. REACTIONS WITH DIAZO COMPOUNDS

Reaction of the α-diazo ketones **336** and **337** with boiling carbon disulfide gives the 1,3-dithiolane derivatives **340**[408–411b] and **341**,[412] respectively, and spectroscopic evidence suggests strongly that **338** gives the analogous product **342**.[413] In striking contrast, a product formed from **339** has been shown to be the 1,3-dithietane derivative **343**.[414,415a] The reaction of the diazomethyl anion with carbon disulfide has been studied.[415b]



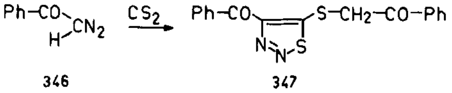
SCHEME 181

Reexamination of the reaction of **339** revealed that, while **343** is the major product (50%), the 1,3-dithiolane **344** is also formed together with a third isomeric product **345**.[416]



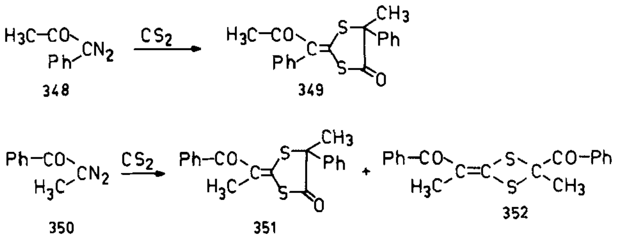
SCHEME 182

Reaction of the α-diazo ketone **346** without any substituent on the diazo carbon atom formed a complex product mixture from which the 1,2,3-thiadiazole **347** was isolated in low yield.[416]



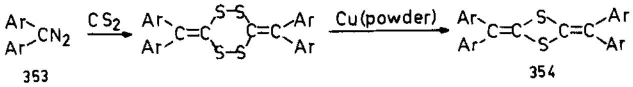
SCHEME 183

The major determining factor of the course of the reactions of α-diazo ketones $R^1COCN_2R^2$ with carbon disulfide is the nature of R^2. When R^2 = Ph, 1,3-dithiolanes are the sole products; when R^2 = Me, both 1,3-dithiolanes and 1,3-dithietanes are formed. Reaction of **348** with carbon disulfide gave the 1,3-dithiolane **349** as the only product, while **350** reacted very much more slowly to give both the 1,3-dithiolane **351** and the 1,3-dithietane **352**.



SCHEME 184

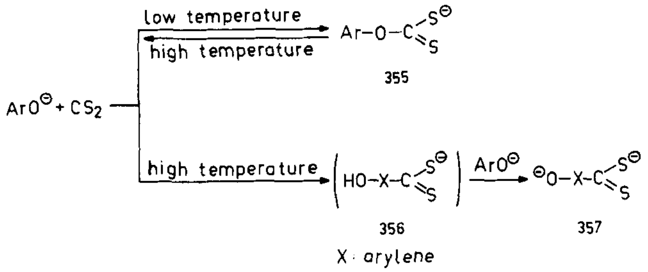
Reaction of diaryldiazomethanes **353** with carbon disulfide affords [after sulfur removal with copper powder] the 1,3-dithietanes **354**.[220]



SCHEME 185

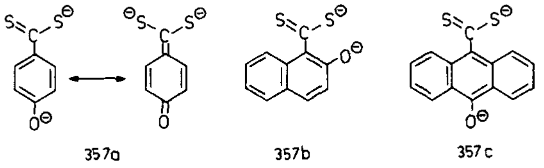
14. REACTIONS WITH PHENOLS

Since phenols and phenoxides are compounds of ambifunctional character the reaction with carbon disulfide may occur at the oxygen atom as well as at the ortho or para carbon atoms. Aprotic dipolar solvents and higher temperatures favor reaction at these carbon atoms.[417–420a] It has been found that with the *o*- and *p*-hydroxy dithiocarboxylates excess alkali favors the relatively stable dianions **357a–c**.



SCHEME 186

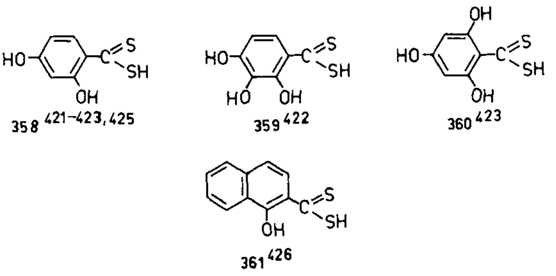
The ambifunctional dianions **357** possess three nucleophilic sites (cf. **357a**). Due to the high nucleophilicity of the sulfur, reaction with one equivalent of alkylating agent always leads to the corresponding alkyl hydroxydithiocarboxylate. As a rule, the dialkylation of **357** yields *O*,*S*-dialkyl derivatives. Due to the stability of the aromatic ring, *S*,*S*-dialkylation to give ω,ω-bis-(alkylthio)quinone methides does not take place readily.[417–419]



SCHEME 187

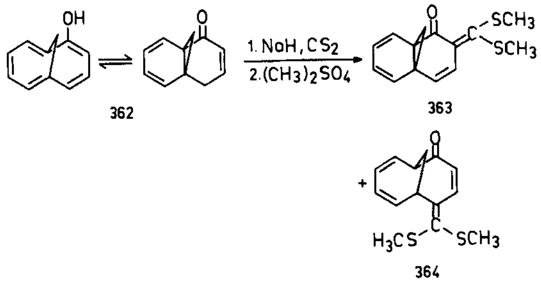
Methyl *o*-hydroxydithiobenzoates have been prepared regiospecifically in a one-pot procedure from phenol methoxymethyl ethers. It involves ortho-metalation with *n*-BuLi, carbon disulfide dithiocarboxylation, sulfur alkylation with methyl iodide, and *in situ* phenol deprotection with aluminum chloride.[420b]

Treatment of an alcoholic solution of the potassium salt of 8-hydroxyquinoline with carbon disulfide leads to the potassium salt of 8-hydroxyquinoline-7-dithiocarboxylic acid.[421–423] The reaction also proceeds if DMF, $AcNMe_2$ or $AcNH_2$ are used as solvents.[424] Dithiocarboxylic acids which have been prepared by nucleophilic attack on carbon disulfide are:



SCHEME 188

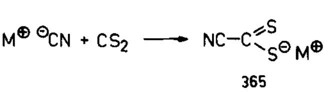
The Kolbe-Schmitt reaction has been extended[424] to the direct dithiocarboxylation of sodium phenoxide with carbon disulfide in DMF at 155–170 °C at atmospheric pressure. 3,5-Di-*t*-butyldithiosalicylic acid, 3-*t*-butyl-5-methyldithiosalicylic acid, and 8-hydroxy-7-quinolinedithiocarboxylic acid have been prepared by this method. The reaction of 2-hydroxy-1,6-methano[10]annulene **362** with NaH/DMSO, CS_2 and subsequent alkylation with dimethyl sulfate gives the *p*-quinonoid ketene *S*,*S*-acetal **364** as well as the *o*-quinonoid isomer **363**.[427,428]



SCHEME 189

15. REACTIONS WITH THE CYANIDE ION

Inorganic cyanides react with carbon disulfide by virtue of the strong nucleophilicity of the cyanide ion to give salts of dithiooxalic acid nitrile **365**.[429–431] In this way alkali metal, thallium, ammonium and heavy-metal salts of **365** are available.



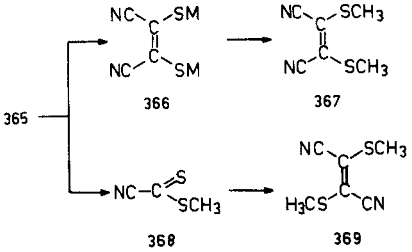
$$M^{\oplus}\,{}^{\ominus}CN + CS_2 \longrightarrow NC{-}C{\overset{\displaystyle S}{\underset{\displaystyle S^{\ominus}}{\lessgtr}}}\;M^{\oplus}$$

365

SCHEME 190

Upon acidification the salts **365** form polymeric dithiooxalic acid nitrile,[432] which in aqueous alkali again gives the monomeric form.[433]

In aqueous solution **365** loses sulfur to yield the bis-salts **366** of 1,2-dimercapto-1,2-dicyanoethylene.[431–432] The tetraalkylammonium salts are more stable than the alkali metal salts.[434,cf.435] The dithioester **368** also desulfurizes to form the *trans*-ethylene derivative **369**.

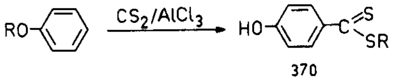


SCHEME 191

It is possible to obtain **366** directly from an aqueous acetone solution at elevated temperature.[436,437]

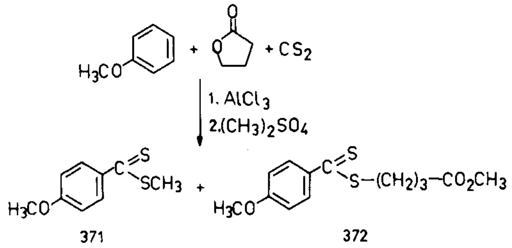
16. PARTICIPATION OF CARBON DISULFIDE IN FRIEDEL-CRAFTS REACTIONS

Carbon disulfide is ordinarily regarded as an excellent solvent for Friedel-Crafts reactions because it is generally believed not to participate in such reactions. However, the reactions of carbon disulfide under Friedel-Crafts conditions have been observed to give rise to the formation of methyl *p*-hydroxydithiobenzoate and ethyl *p*-hydroxydithiobenzoate in poor yields from anisole and phenetole, respectively.[438] Methyl *p*-hydroxydithiobenzoates have been prepared in a one-pot process from anisoles by treatment with carbon disulfide, methyl iodide, and aluminum chloride.[420b] The corresponding phenols give lower yields in this reaction.



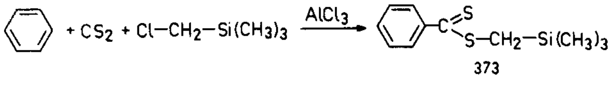
SCHEME 192

Instead of the phenol ethers, also the corresponding phenol and alkyl halide can be used.[439,440] It was found that anisole reacts with carbon disulfide and γ-butyrolactone in the presence of aluminum chloride to furnish, after methylation and esterification with dimethyl sulfate, methyl 4-methoxydithiobenzoate **371** and 3-(methoxycarbonyl)propyl 4-methoxydithiobenzoate **372**.[441]



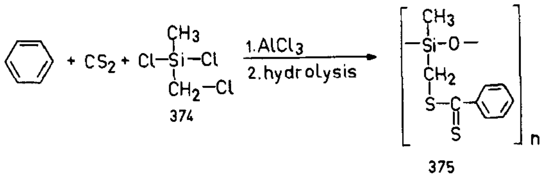
SCHEME 193

However, no corresponding reactivity was noted when anisole was substituted by benzene, toluene, phenol or α-naphthol. Participation of carbon disulfide was also observed in the Friedel-Crafts reaction of (chloromethyl)trimethylsilane with benzene to yield (trimethylsilyl)methyl dithiobenzoate **373**.[442,443]



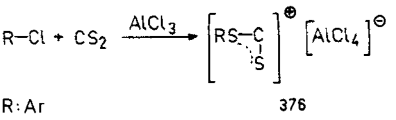
SCHEME 194

Extensive participation of carbon disulfide was also observed in the reaction of (chloromethyl)trimethylsilane with chlorobenzene, 1-octene, isooctane and *n*-octane, always in the presence of an equimolar amount of aluminum chloride. Otherwise the reaction of benzene with carbon disulfide and (chloromethyl)methyldichlorosilane **374** gives the polymeric product **375**.



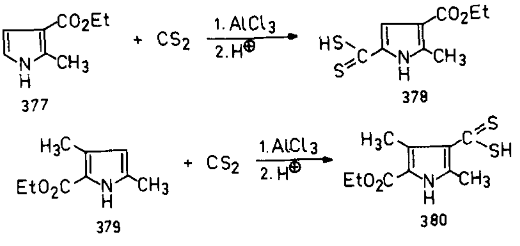
SCHEME 195

A Friedel-Crafts complex **376** can be assumed to be formed as an intermediate and to attack the aromatic system electrophilically.[444]



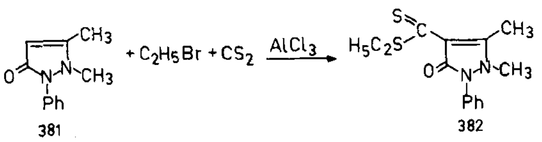
SCHEME 196

The Friedel-Crafts reaction of the pyrroles **377** and **379** gives 2-methyl-3-ethoxycarbonylpyrrole-5-dithiocarboxylic acid **378** and 2,4-dimethyl-5-ethoxycarbonylpyrrole-3-dithiocarboxylic acid **380**.[445]



SCHEME 197

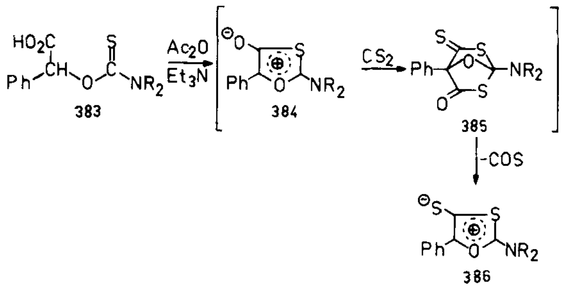
The Friedel-Crafts alkylation of 5-pyrazolone **381** with ethyl bromide in carbon disulfide leads only to the corresponding dithiocarboxylic acid ester **382**.[446,447]



SCHEME 198

17. MISCELLANEOUS REACTIONS

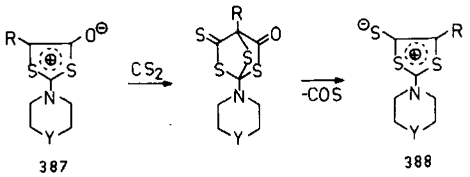
Anhydrocyclization of *N*,*N*-dialkylamino(thiocarbonyloxy)phenylacetic acids **383** in the presence of carbon disulfide affords the 1,3-oxathiolylium-4-thiolates **386**. Obviously, the *in situ* formed mesoionic 1,3-oxathiazoles **384** are trapped during the course of the reaction by [3 + 2] cycloaddition to carbon disulfide with subsequent elimination of carbonyl sulfide from the intermediate **385** to give 1,3-oxathiolylium-4-thiolates **386**.[448]



R: Me,Et
NR$_2$: pyrrolidino, piperidino, morpholino

SCHEME 199

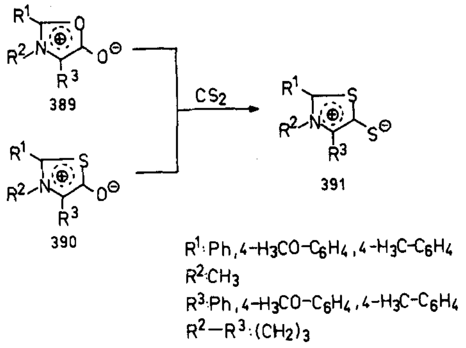
Souizi and Robert[449] describe the easy conversion of the mesoionic 1,3-dithiolylium-4-olates **387** to the mesoionic 1,3-dithiolylium-4-thiolates **388** by reaction with carbon disulfide.



R: aryl
Y: O, CH$_2$

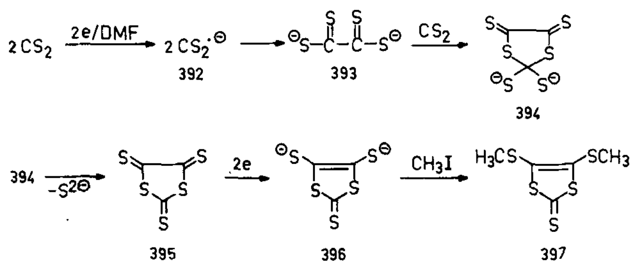
SCHEME 200

1,3-Thiazolylium-5-thiolates **391** are easily prepared by 1,3-dipolar cycladdition of carbon disulfide to the 1,3-oxazolylium-5-olates **389**[450-452] and the 1,3-thiazolylium-5-olates **390**.[453-454]



SCHEME 201

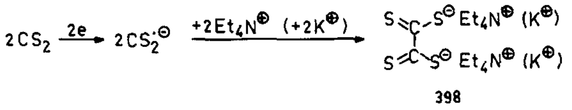
The reduction of carbon disulfide in aprotic media provides synthetic access to multisulfur species based on the 1,3-dithiole ring structure. Although the sodium amalgam reduction of carbon disulfide was studied a long time ago,[455] only in 1974 was the structure of the key product, 4,5-dimercapto-1,3-dithiole-2-thione **396** elucidated by Wawzonek and Heilmann.[456] The electrolytic reduction of carbon disulfide in DMF, followed by alkylation with methyl iodide, gave 4,5-bis(methylthio)-1,3-dithiole-2-thione **397**. The formation of an anion radical **392** from carbon disulfide would be followed by dimerization to the tetrathiooxalate ion **393**. This species would add to carbon disulfide and form 1,3-dithiole-2,4,5-trithione **395** which is reduced electrochemically to the species which is alkylated to form **397**.[456–458]



SCHEME 202

The reaction of carbon disulfide with sodium or potassium in *N*,*N*-dimethylformamide gives 1,3-dithiole-2-thione-4,5-dithiolate **396** in excellent yield.[459,460]

The electrochemical reduction of carbon disulfide in acetonitrile with a mercury cathode and Et_4NBr as conducting salt gave the tetraethylammonium salt **398** of tetrathiooxalic acid.[461] The electrochemical reduction of carbon disulfide at a mercury cathode at 0 °C in acetonitrile saturated with potassium iodide gave the potassium salt **398**.[462]



SCHEME 203

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