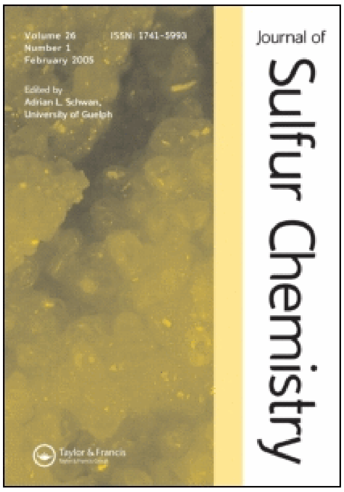

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Acyclic Dithiocarboxylic Acid Esters - Reactions and Syntheses

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ACYCLIC DITHIOCARBOXYLIC ACID ESTERS - REACTIONS AND SYNTHESES

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The present review deals with the reactions and synthetic methods of acyclic dithiocarboxylic acid esters. Their reactions are classified according to reaction sites. The synthetic methods are roughly divided into five classes. The yields and physical properties of the isolated acyclic dithioesters (ca. 500) which have been reported before August 1987 are collected in Tables 1–3.

Key words: Dithiocarboxylic acid esters, dithioesters, acyclic dithioesters.

CONTENTS

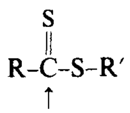
I. INTRODUCTION

Dithiocarboxylic acid esters (RCS_2R') (hereafter called dithioesters) are one type of the possible sulfur isologues of carboxylic acid esters and can be defined as compounds containing one or more C-C(S)S-C moieties in the molecule. The first synthesis and reaction of dithioesters was reported by Houben and Schultze[1] in 1910 who showed that methyl dithioacetate can be synthesized from sodium dithioacetate and methyl iodide and that the methyl dithioate reacts with sodium methoxide and then methyl iodide to give ketene dimethyl dithioacetal. However, little attention was given to this class of compounds for a long time, presumably due to the difficulty of preparation (low yield) and their unpleasant smell, especially of the alkyl derivatives. From the 1960's onwards the chemistry of dithioesters began to develop vigorously. Many studies have been published during the past two decades. Particularly, during the last decade increasing attention has been given to the synthesis of naturally occurring compounds via dithioesters. Numerous reviews have also been published.[2] In this review article, a classification of the synthetic methods leading to acyclic dithioesters is attempted. The literature survey covers papers published before August, 1987.

II. REACTIONS

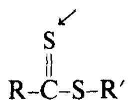
In Figure 1, the reaction sites of dithioesters are shown as found in the period 1850–1987. The reaction patterns of dithioesters principally resemble those of the common carboxylic acid esters. For instance, dithioesters react with nucleophiles such as carbanions, amines, alkoxides, thiolates, etc. at the thiocarbonyl carbon atom (carbophilic attack). However, in their reactions with nucleophiles such as Grignard reagents a unique reaction pattern, *i.e.* nucleophilic attack at the thiocarbonyl sulfur atom, is observed (thiophilic attack). Selective oxidation at the thiocarbonyl sulfur atom is also characteristic of dithioesters and leads to the corresponding sulfine derviates.

1. Attack at thiocarbonyl carbon



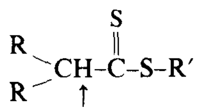
C-, N-, and S-Thioacylation
Dithioacetal formation

2. Attack at thiocarbonyl sulfur



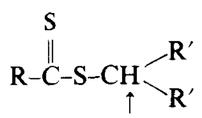
Dithioacetal formation
Sulfine formation

3. Attack at α-hydrogen



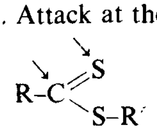
α-Hydrogen abstraction (Ketene dithioacetal formation
Substitution with halogens

4. Attack at α′-hydrogen



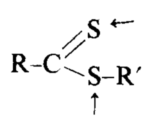
α′-Hydrogen abstraction

5. Attack at the carbon and sulfur atoms of the thiocarbonyl group



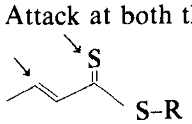
[2 + 2]-*Cycloaddition*
[2 + 3]-*Cycloaddition*
[2 + 4]-*Cycloaddition*

6. Attack at both the thiocarbonyl and the sulfide sulfur atom



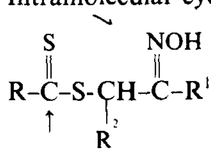
1,3-Dithiane formation
Sulfinyl sulfine formation

7. Attack at both the thiocarbonyl sulfur atom and a β-vinylic carbon atom



[4 + 2]-*Cycloaddition*
[4 + 4]-*Cycloaddition*

8. Intramolecular cyclization

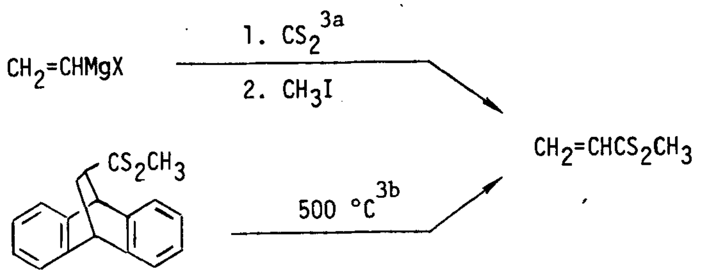


1,3-Thiazole formation

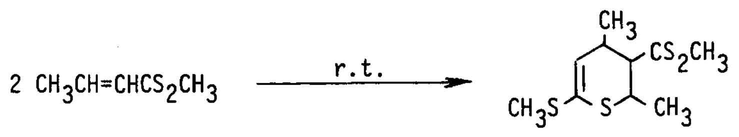
Figure 1. Reaction sites of dithioesters

1. THERMOLYSIS

In general dithioesters are thermally stable. They can be stored at room temperature for over one month. However, α-olefinic dithioesters such as methyl dithioacrylate and dithiocrotonate are thermally too unstable to be isolatable.[3] The latter can be obtained as the *endo*-dimeric form **1** at ambient temperature.[4]



(1)[3]

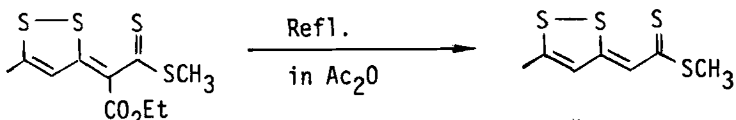


(2)[4]

1

Gas phase pyrolysis of alkyl dithioacetates gives methane, an alkene, and carbon disulfide, which are formed by a concerted monomolecular process.[5] Refluxing of the thiophthene type of dithioesters possessing an α-ethoxycarbonyl group in acetic anhydride leads to the diethoxycarbonylated product **2**.[6]

$$CH_3CS_2R \xrightarrow{584-639\ K} CH_4 + >C=C< + CS_2 \quad (3)^{5}$$



(4)[6]

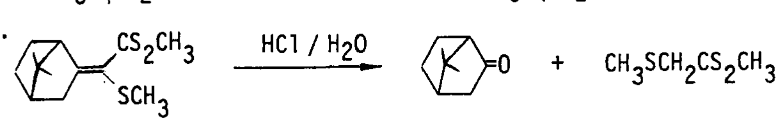
2

2. HYDROLYSIS AND ALCOHOLYSIS

Dithioesters are resistant to water and alcohol at room temperature. However, they are readily hydrolyzed under acidic conditions to give the corresponding carboxylic acid and thiol with evolution of H_2S.[7]

$$4\text{-}HOC_6H_4CS_2Et \xrightarrow{HCl\ /\ H_2O} 4\text{-}HOC_6H_4CO_2H + EtSH \quad (5)^{7}$$

cf.



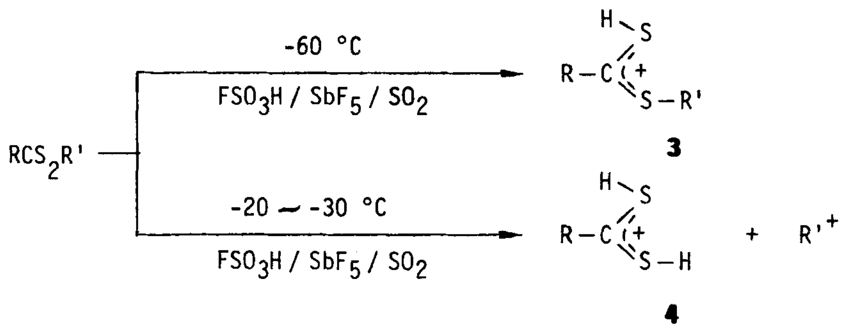
(6)[8]

No reaction occurs upon refluxing of methyl 1-naphthalenedithiocarboxylate in ethanol.[1]

$$1\text{-}C_{10}H_7CS_2CH_3 \xrightarrow[\text{in EtOH}]{\text{Refl.}} \text{No Reaction} \qquad (7)^{1}$$

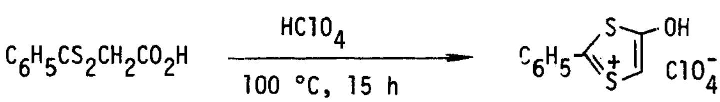
3. REACTION WITH ACIDS

Dithioesters are protonated in $FSO_3H/SbF_5/SO_2$ solution to yield the corresponding carbenium ions **3** or **4**.[9]

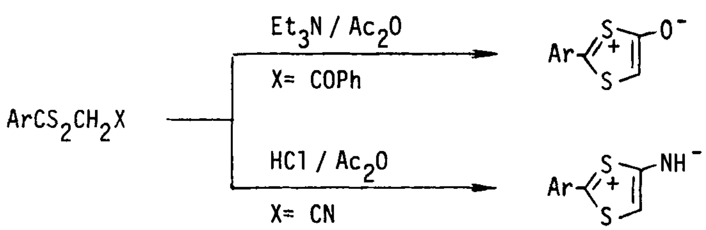


(8)[9]

Treatment of carboxymethyl,[10] phenacyl,[11-15] and cyanomethyl esters[15c] of aromatic dithiocarboxylic acids with strong acids such as conc. sulfuric acid, perchloric acid, or trifluoroacetic acid anhydride produces 1,3-dithiolium salts[10-13] or mesoionic compounds.[14,15]

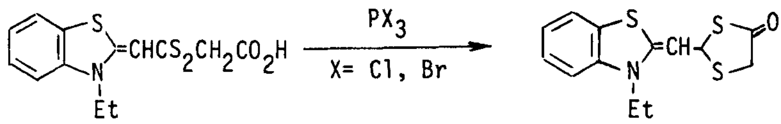


(9)[10]

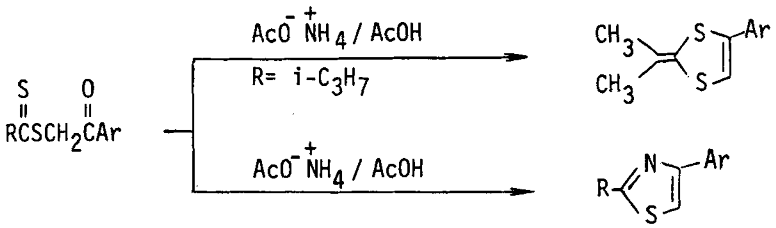


(10)[15]

Similar treatment with phosphorus trihalides and refluxing with acetic acid in the presence of ammonium acetate lead to 1,3-dithiolanes[16,17a] or 1,3-thiazoles.[17a]

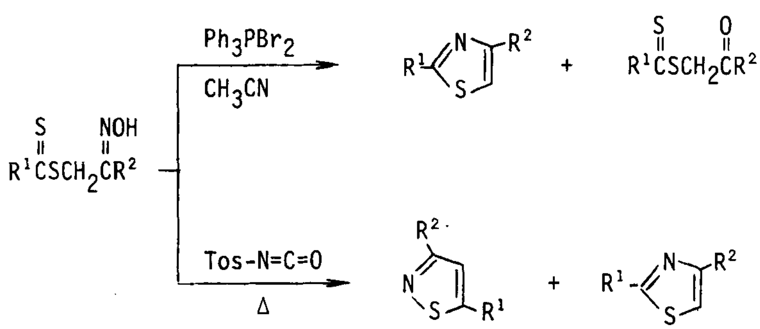


(11)[16]

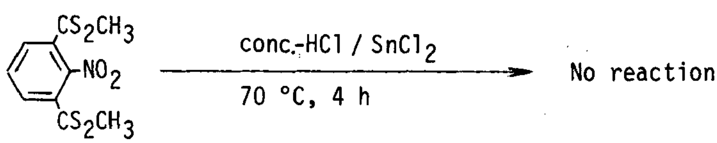


(12)[17]

In addition, 2-hydroxyiminoethyl dithioates are readily cyclized to 1,3-thiazoles[17a] and isothiazoles by treatment with triphenylphosphine dibromide[17b] and with tosyl isocyanate,[17c] respectively. It is noted that treatment of 3-methylthio-thiocarbonyl 2-nitrodithiobenzoic acid methyl ester with conc. HCl at 70 °C leads to no change.[18]



(13)[17b,c]



(14)[18]

4. REACTION WITH ALKALI METAL HYDROXIDES

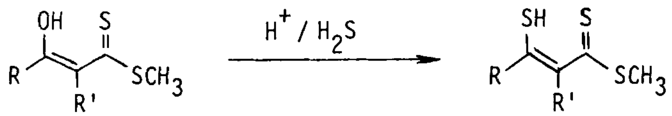
Dithioesters readily react with alkali metal hydroxides to give the corresponding salts of carboxylic and thiocarboxylic acids.[1,7]

$$RCS_2R' \xrightarrow{\text{NaOH or KOH / } H_2O} R\overset{\overset{\displaystyle O}{\|}}{C}E^- \; Na^+ \text{ (or K)} \qquad (15)^{1,7}$$

$$E = O, S$$

5. REACTION WITH H_2S

Generally dithioesters do not react with hydrogen sulfide. However, the β-hydroxy group of methyl dithioacrylates can be readily substituted by a thiol group.[19] Methyl dithiocinnamate reacts with H_2S to give the addition product.[4]



(16)[19]

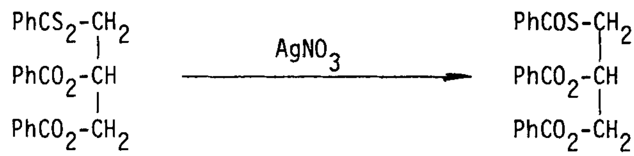
$$PhCH{=}CHCS_2CH_3 \xrightarrow{H_2S} S\begin{cases}CH(Ph)CH_2CS_2CH_3\\CH(Ph)CH_2CS_2CH_3\end{cases} \qquad (17)^{4}$$

6. OXIDATION

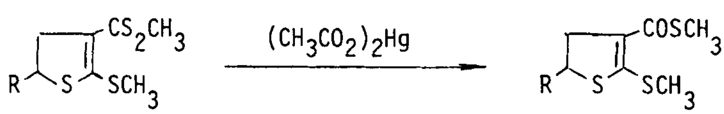
a. Conversion of >C=S to >C=0

Dithioesters are oxidized by alocoholic alkali metal hydroxides,[20,21] Grignard reagents/H_2O,[22] potassium permanganate,[23,24] silver nitrate,[25] mercury acetate,[26] selenenic acid anhydride,[27,28] diaryl telluroxides,[29,30] ozone,[31] $SOCl_2/H_2O$,[32] and $(CH_3)_2SO_4/H_2O$[33] to give the corresponding thiolesters.

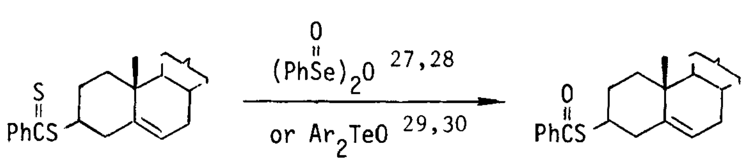
$$ArCS_2R' \xrightarrow[2.\ H_2O]{1.\ alc.\ KOH^{20,21}\ or\ PhMgBr^{22}} ArC(=O)SR' \qquad (18)$$



(19)[25]

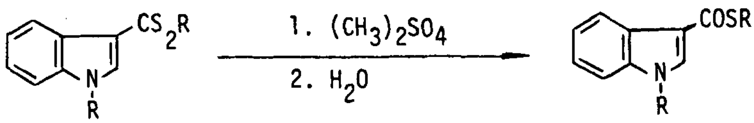


(20)[26]



(21)

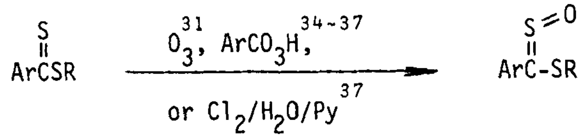
$$RCS_2R' \xrightarrow{O_3} RC(=O)SR' \qquad (22)^{31}$$



(23)[33]

b. Sulfine formation

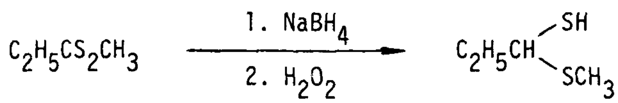
Treatment of dithioesters with ozone,[31] perbenzoic acid[34-37] or Cl_2/H_2O/pyridine[37] under mild conditions leads to sulfine formation.



(24)

7. REDUCTION AND ELECTROLYSIS

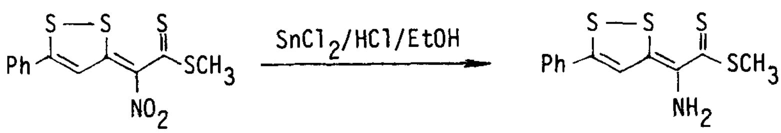
Reduction of dithioesters by $NaBH_4$ produces dithiohemiacetals,[38] whereas Raney-Ni reduction gives the corresponding alkanes.[39]



(25)[38]

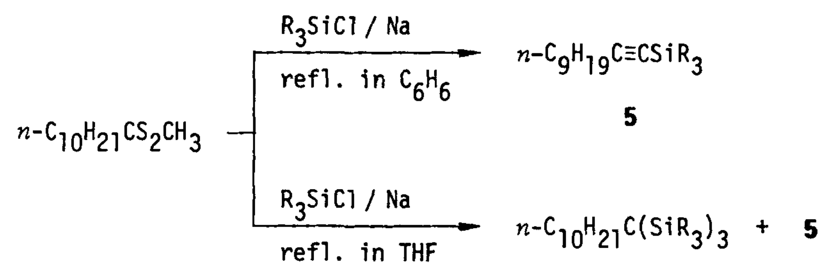
$$C_6H_5CS_2CH_3 \xrightarrow{\text{Raney Ni}} C_6H_5CH_3 \qquad (26)^{39}$$

An α-nitro group of a dithioester is reduced to an amino group by $SnCl_2$/HCl/EtOH without disruption of the S-S bonds of the thiathiophthene system.[40]



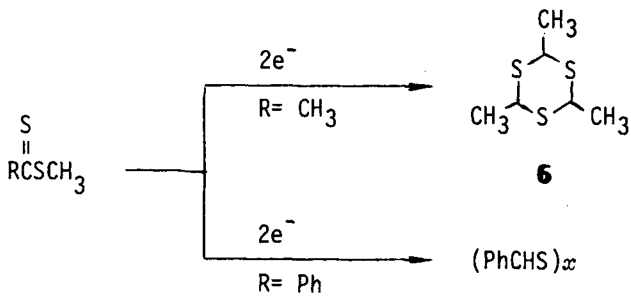
(27)[40]

The Na reduction of dithioesters in the presence of trialkylsilyl chlorides leads to the silylated acetylenes **5**.[41]



(28)[41]

The electroreduction of methyl dithioacetate yields trithiane **6**, whereas methyl dithio-

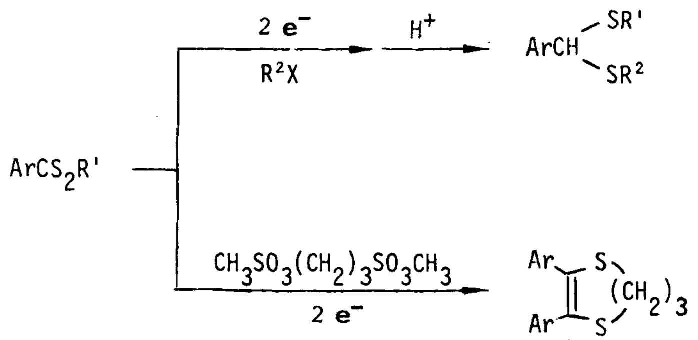


(29)[42]

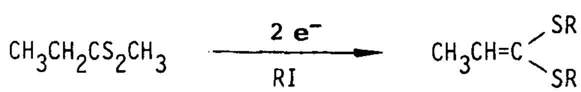
benzoate yields polymeric thiobenzaldehyde.[42] The reactivity towards polarographic reduction of dithioesters (RCS_2CH_3) increases in the following order:[42]

$$R = CH_3 < C_2H_5 < CH(CH_3)_2 < C(CH_3)_3$$

Electroreduction of dithioesters in the presence of alkylating reagents such as alkyl halides gives dithioacetals[43] or ketene dithioacetals.[43a]



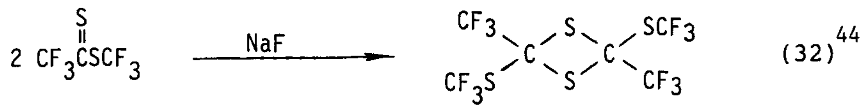
(30)[43]



(31)[43a]

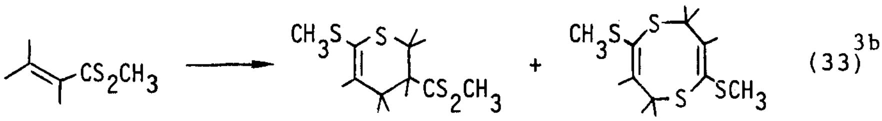
8. DIMERIZATION

The thiocarbonyl group of common dithioesters does not dimerize. Trifluoromethyl dithioacetate, however, affords the [2 + 2]-adduct **7** (head-to-tail) of the thiocarbonyl group in the presence of NaF.[44]

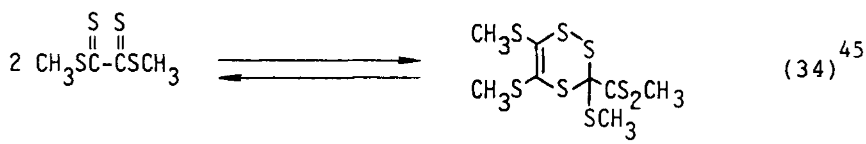


7

In addition, α-olefinic dithioesters and dimethyl tetrathiooxalate give the dimers (**8** and **9**, **10**), resulting from [4 + 2]-[3,45] and [4 + 4]-cycloaddition.[3]



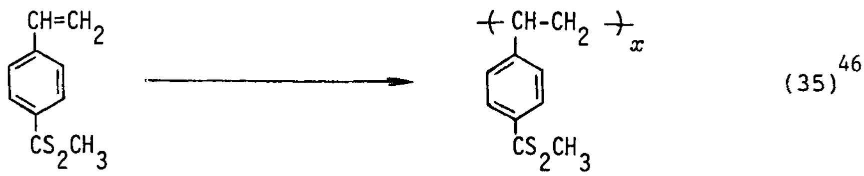
8 **9**



10

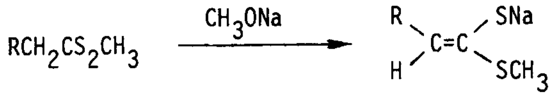
9. POLYMERIZATION

Styrene dithiocarboxylates readily polymerize to give polymers containing a dithiocarboxyl group.[46]

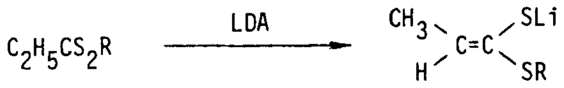


10. ABSTRACTION OF α-HYDROGEN

It was found for the first time by Houben and Schultz in 1910[1] that the α-hydrogen atoms of dithioesters are readily abstracted under basic conditions to give ketene dithioacetals. Since then a number of synthetic applications of this type of reaction have been reported.[47-73] The stereochemistry of the deprotonation of dithioesters also has been investigated.[47,52b,c,d,68] For example, treatment of alkyl dithiopropanoates with lithium diisopropylamide (LDA) in THF leads chiefly to the cis lithium thioenolates, while most carbonyl compounds afford the trans enolates.[47]



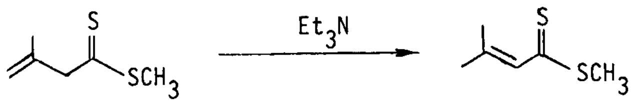
(36)[1]



(37)[47]

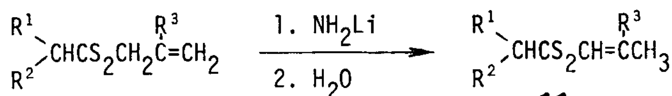
a. Isomerization

β,γ-Unsaturated dithioesters are readily isomerized by base such as triethylamine to α,β-unsaturated ones.[3] Similarly, allyl dithiocarboxylates are isomerized to the vinyl esters **11** by treatment with base.[48]



(38)[3]

cf.

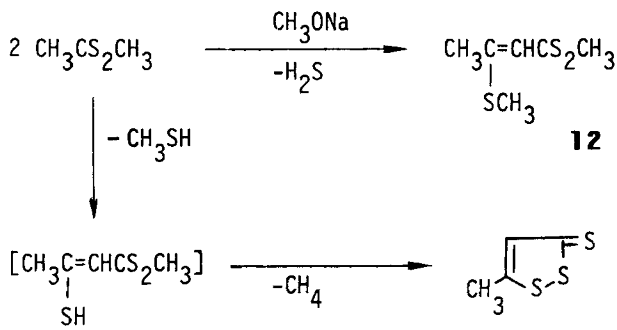


11

(39)[48]

b. Condensation

Treatment of methyl dithioacetate with sodium ethoxide has been found to give condensation products (**12**, **13**).[49]



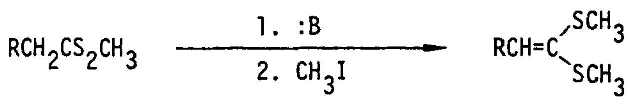
12 **13**

(40)[49]

c. Trapping of thioenolates

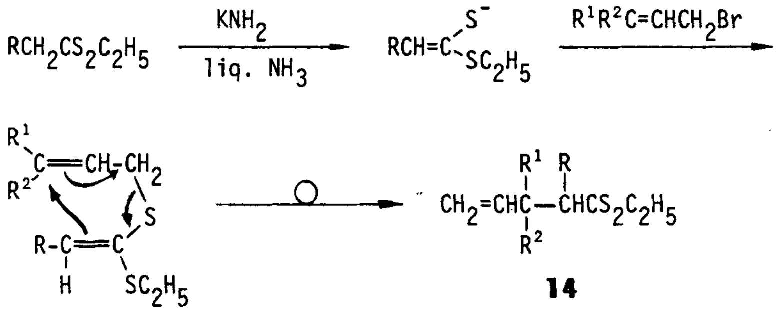
The thioenolates formed by abstraction of the α-hydrogen of dithioesters with base have been trapped with a variety of electrophiles.

(i) With alkyl halides Thioenolates readily react with alkyl halides to give the corresponding dithioacetals.[47,51,53]



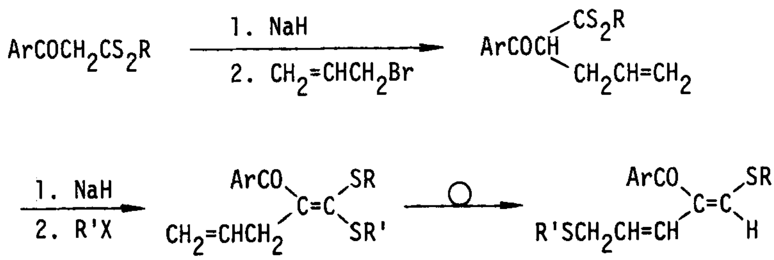
(41)[47,51,52]

(ii) With allyl halides The rearranged products (**14**, **15**) are obtained.[53,54,55]



(42)[53,54]

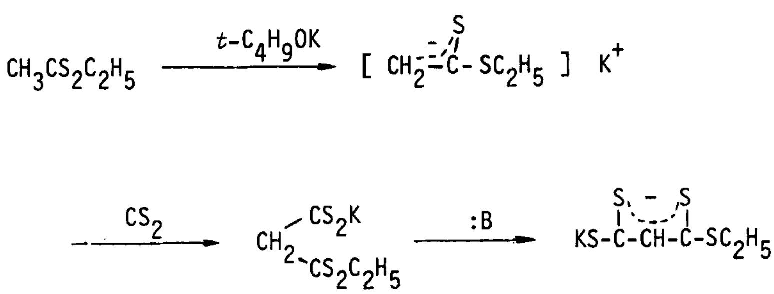
14



(43)[55]

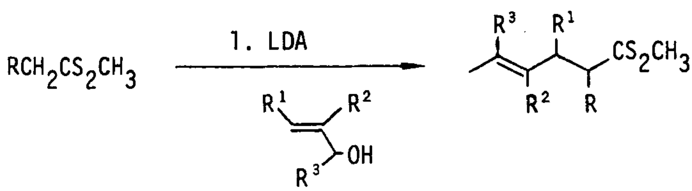
15

(iii) With carbon disulfide.



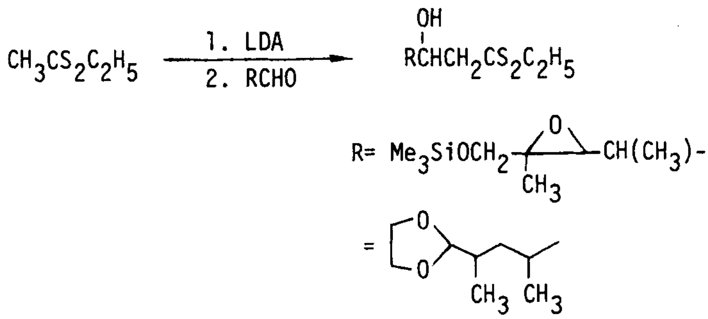
(44)[56]

(iv) With allylic alcohols



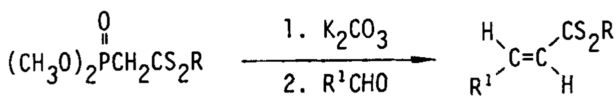
(45)[57]

(v) With aldehydes Treatment of ethyl dithioacetate with LDA, followed by an aldehyde has been used for the synthesis of α-maytansin and maytansinoids.[58-60]



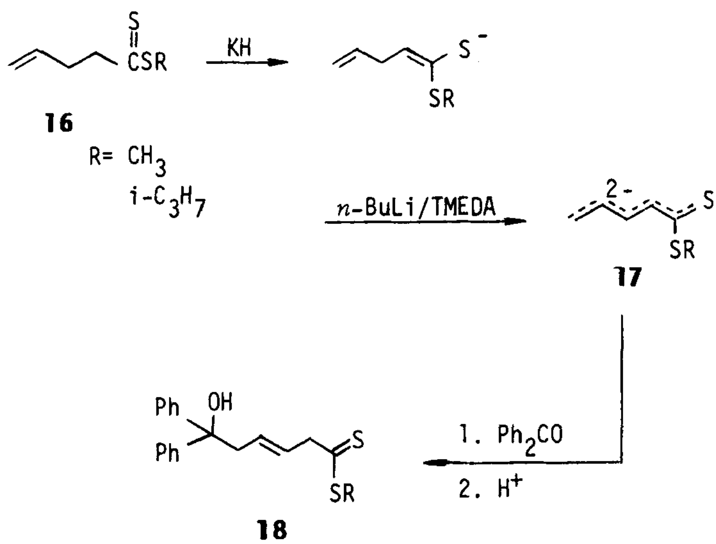
(46)[58-60]

α-(*O,O'*-Dimethylphosphinoyl)dithioacetic esters react with aldehydes in the Horner-Emmons reaction to give alkyl 2-alkenedithioates.[61]



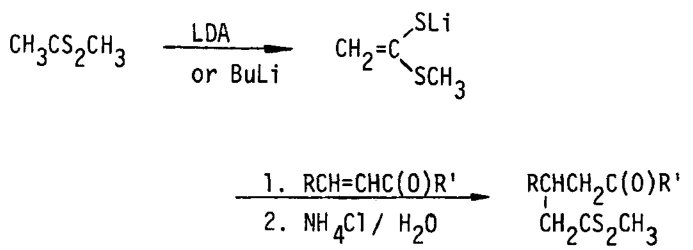
(47)[61]

(vi) With ketones Dithiopentenoic esters **16** are smoothly converted to dienone dianions**17** by sequential treatment with potassium hydride and *n*-BuLi/*N,N,N',N'*-tetramethylethylenediamine. The products **17** react with benozphenone at their terminal carbon atom to give a high yield of the adducts **18**.[62-63]



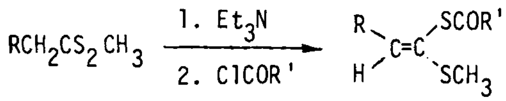
(48)[62,63]

Methyl dithioacetate, after lithiation, undergoes a selective 1,4-C-addition at low temperature to give 5-oxodithioesters.[64-65]



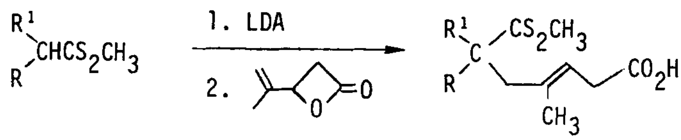
(49)[64,65]

(vii) With acyl and alkoxycarbonyl chlorides



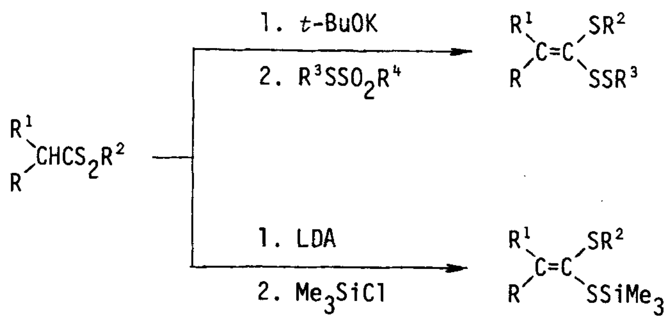
(50)[66,67]

(viii) With 4-vinylbutyrolactone[68]



(51)[68]

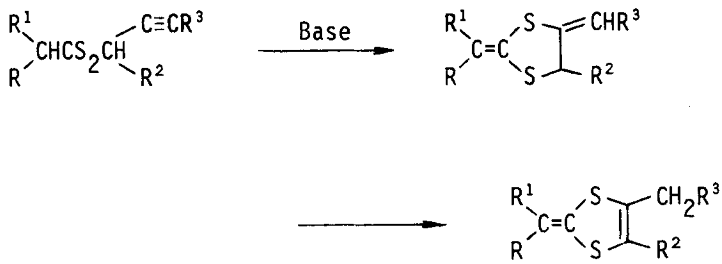
(ix) With alkanethiosulfonates and trimethylsilyl chloride[69]



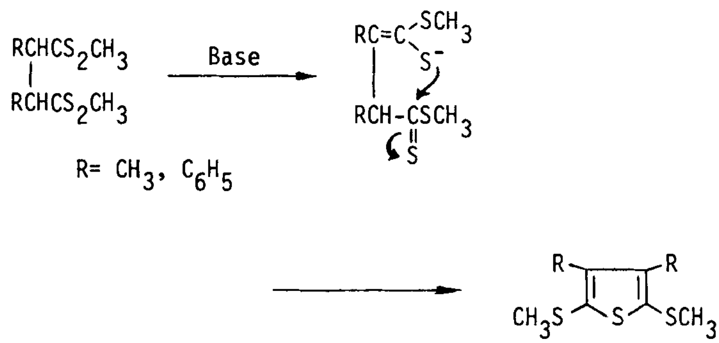
(52)[69]

11. Base-catalyzed cyclization

2-Alkinyl alkanedithioates cyclize in the presence of base to give 1,3-dithioles.[71,72] Dimethyl and diphenyl tetrathiosuccinates, on the other hand, undergo ring closure to thiophenes.[73]



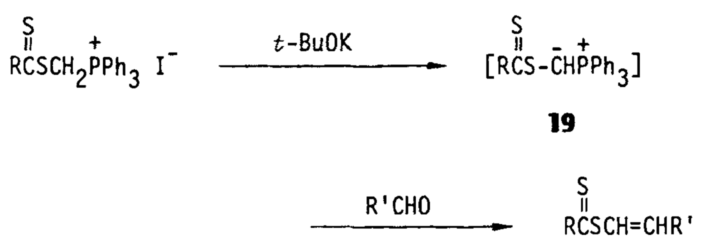
(53)[71,72]



(54)[73]

12. α′-Hydrogen abstraction

In general the abstraction of the α′-hydrogen atoms of dithioesters such as RCS_2CH_2R' is more difficult than that of the α-hydrogen of RCH_2CS_2R' because of their lower acidity. However, treatment of phosphonio-methyl dithiocarboxylates possessing no α-hydrogen with potassium *t*-butoxide generates the ylide **19** which readily reacts with an aldehyde to give the corresponding vinyl ester **20**.[74,75]

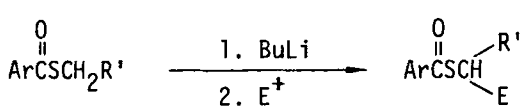


19

20

(55)[74,75]

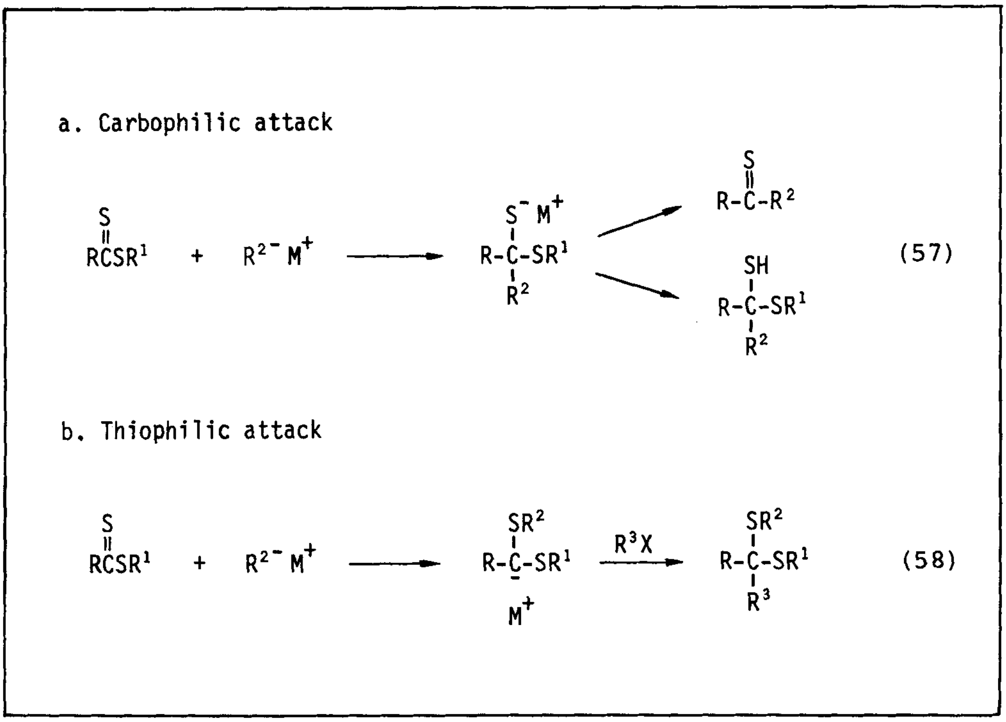
cf.



(56)[76]

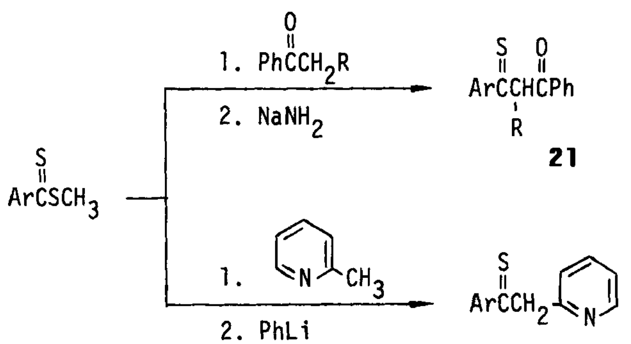
13. REACTION WITH CARBANIONS

In contrast to esters, dithioesters react with carbanions such as alkyllithium and Grignard reagents to give products of both carbophilic and thiophilic attack.



a. Carbophilic attack

(i) Thioketone formation Sodium α-keto carbanions[77-79] and 2-picolyllithium[88] react with methyl esters of aromatic dithiocarboxylic acids to give the corresponding thioketones (**21, 22**).



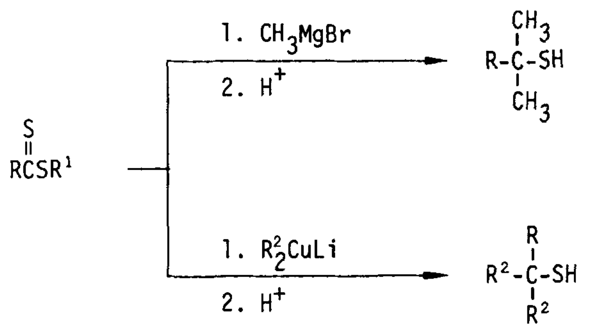
21

22

(59)[77-79]

(60)[80]

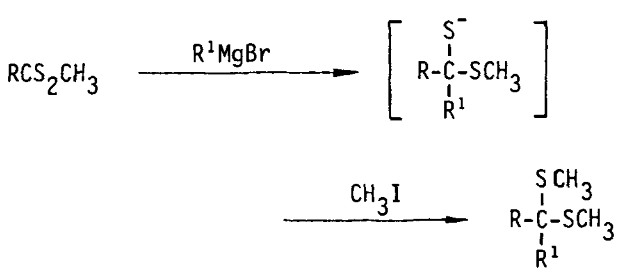
Similar reactions with methylmagnesium bromide[81] and organocuprates[82] lead to tertiary thiols.



(61)[81]

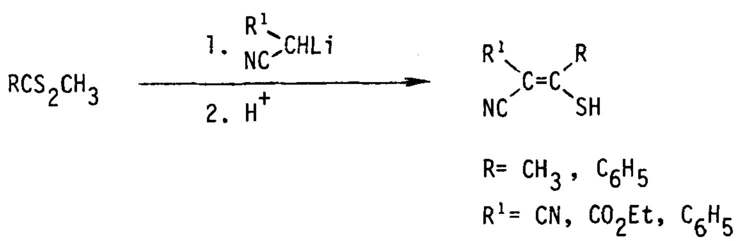
(62)[82]

(ii) Dithioacetal formation It is known that a Grignard reagent adds to both thiocarbonyl carbon and sulfur atoms. However, allyl, benzyl, propargyl, and vinyl Grignard reagents give dithioacetals resulting from carbophilic attack.[83,84]



(63)[83,84]

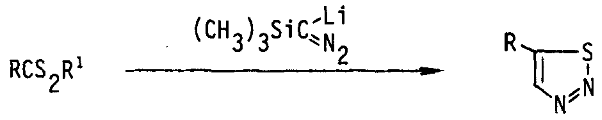
(iii) Thioenolization The reaction of dithioesters with α-cyano carbanions produces 1-alkenethiols.[49,85]



(64)[49,85]

(iv) Others

Treatment with lithio-silyldiazomethane leads to 1,2,3-thiadiazoles **23**, which seem to be formed by carbophilic attack.

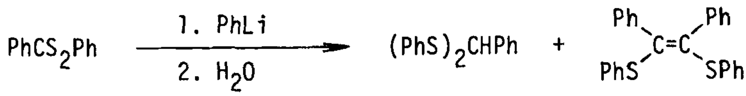


23

(65)[86]

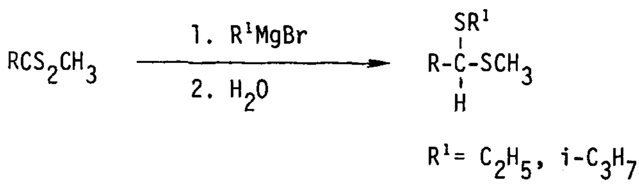
b. Thiophilic attack

Thiophilic addition to the thiocarbonyl group of dithioesters by a formal carbon nucleophile was observed in 1972 by Beak and Worley[87] who reported the addition of phenyllithium to phenyl dithiobenzoate[87-89] and by Leger and Saquet,[81] who reported that the reaction of dithioesters with ethyl- and isopropylmagnesium bromide, followed by methyl iodide, gives ketene dithioacetals.

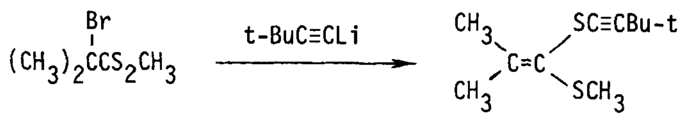


(66)[87]

This has been used by several groups for the synthesis of biologically active compounds such as (–)-maysine etc.[64,88,89,90,91,92]

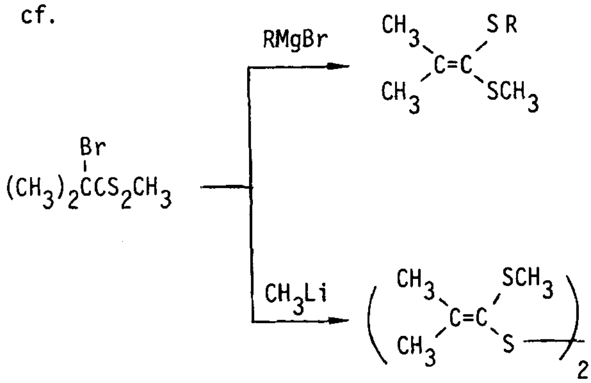


(67)[64,81,88,89]

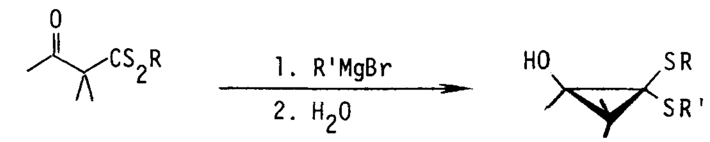


(68)[90]

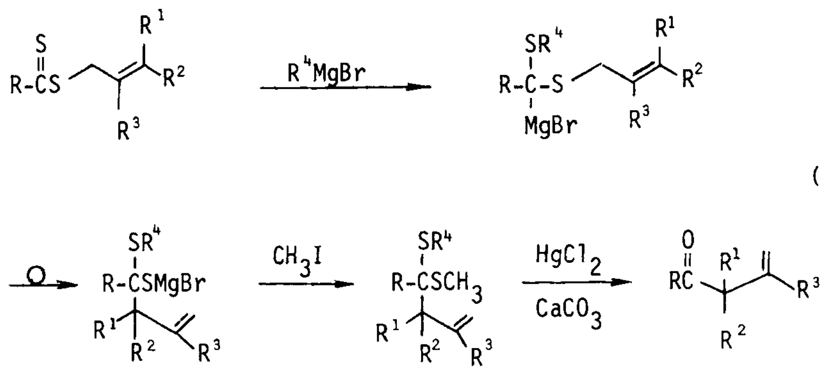
cf.



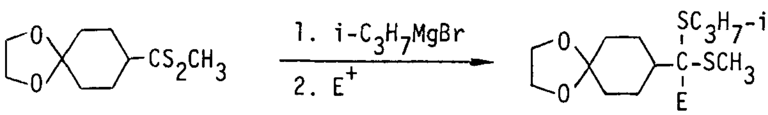
(69)[90]



(70)[91]



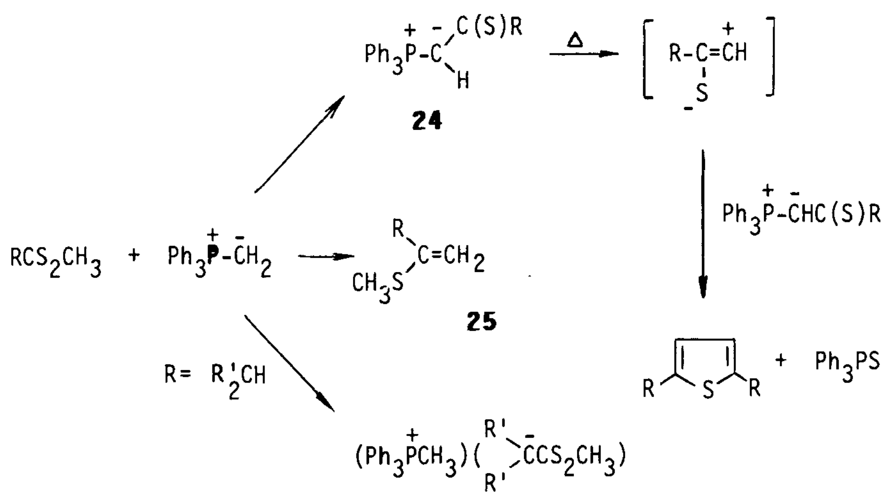
(71)[92]



(72)[64]

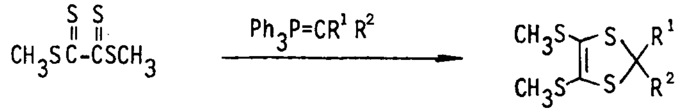
14. REACTION WITH YLIDES

Dithioesters react with alkylidenetriphenylphosphoranes to give the thioacylated ylides **24** and the vinyl sulfides **25** (Scheme 1).[93]



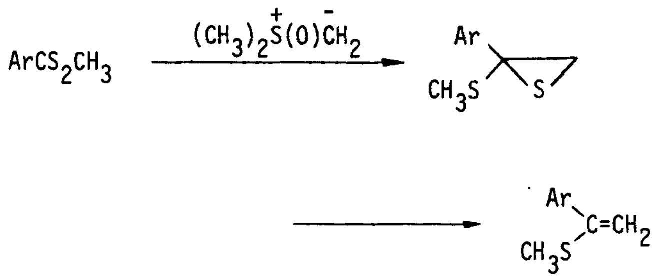
Scheme 1[93]

A similar reaction with dimethyl tetrathiooxalate affords 1,3-dithioles.[94]

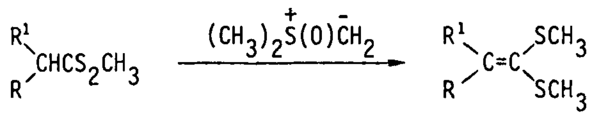


(73)[94]

Treatment of aromatic dithioesters with dimethyloxosulfonium methylide gives vinyl sulfides via an intermediate thiirane, while dithioesters with α-hydrogen atoms yield ketene dithioacetals.[95]

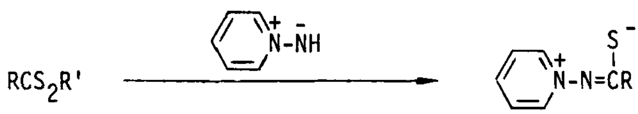


(74)[95]



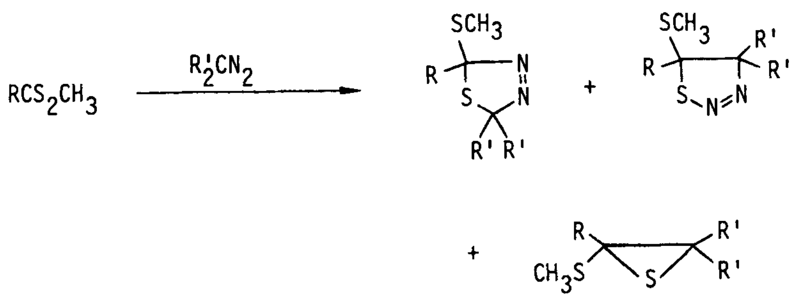
(75)[95]

Reaction with pyridinium N-imide gives the corresponding N'-thioacylated N-imide **26**.[26] Reactions with diazoalkanes,[97] isonitriles,[99] benzonitrile N-(4-nitrobenzylide),[100] and chloramine T[101] have also been investigated.



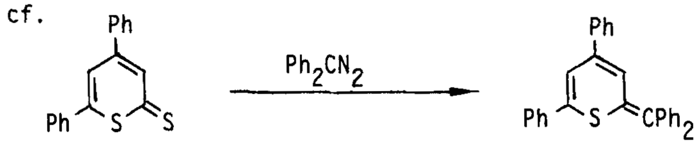
26

(76)[96]

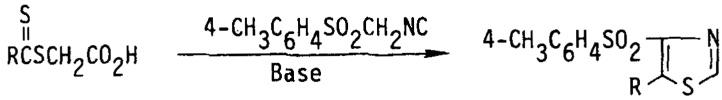


(77)[97]

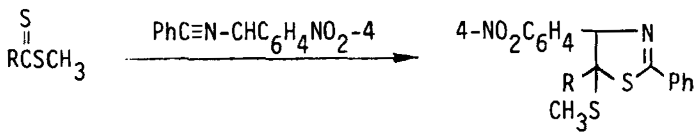
cf.



(78)[98]



(79)[99]



(80)[100]

$$RC(=S)SR' \xrightarrow{\text{Chloramine T}} R\text{-}C(=S{=}NSO_2C_6H_4CH_3\text{-}4)\text{-}SR' \quad (81)^{101}$$

15. REACTION WITH AMINES

a. N-Thioacylation

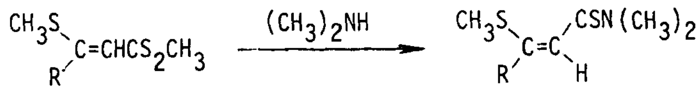
In 1930, Bost and Mattox[102] reported firstly that dithioesters react with ammonium hydroxide to give thioamides. Since then a volumiuous literature has accumulated concerning the use of dithioesters in thioacylation[103-132] and in heterocyclic synthesis via thioamides.[116,117] This thioamide formation proceeds kinetically as a second-order process.[107]

$$4\text{-}CH_3C_6H_4CS_2CH_3 \xrightarrow{NH_4OH} 4\text{-}CH_3C_6H_4C(=S)NH_2 \quad (82)^{102}$$

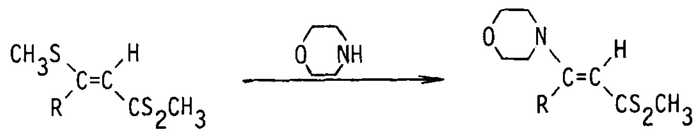
$$RCS_2CH_3 \xrightarrow{NH_2OH} RC(=S)NHOH \quad (83)^{103}$$

$$RCS_2CH_3 \xrightarrow{R'_2NH} RC(=S)NR'_2 \quad (84)^{104-111}$$

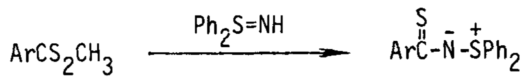
$$HO(R)C{=}CHCS_2CH_3 \xrightarrow{R'NH_2} R'NH(R)C{=}CHCSNHR' \quad (85)^{112}$$



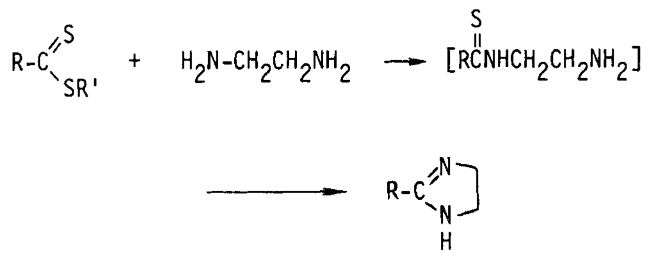
(86)[113]



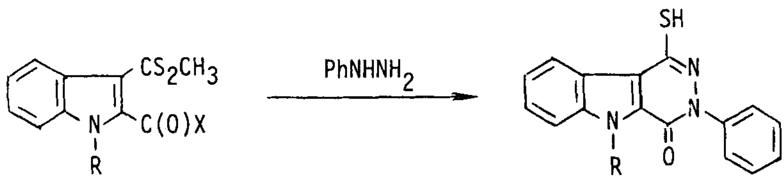
(87)[113]



(88)[114]



(89)[115]

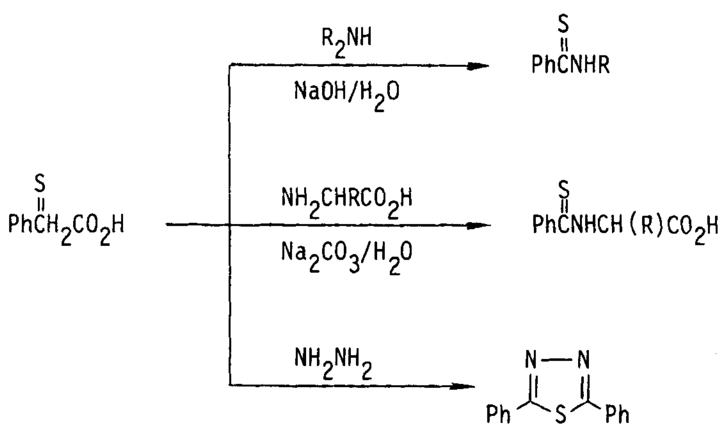


(90)[116]

X= CH_3O, etc.

R= H, CH_3

Since the first report by Holmberg in 1944,[117] carboxymethyl dithiobenzoate has been proven to been one of the most effective thioacylating reagents for amines,[119-132] especially amino acids,[118,123b,126,130] under aqueous conditions.

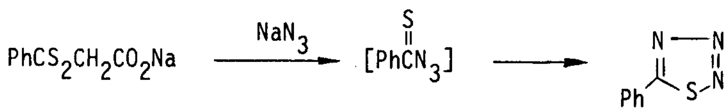


(91)[117-132]

(92)[118,123b,126,130]

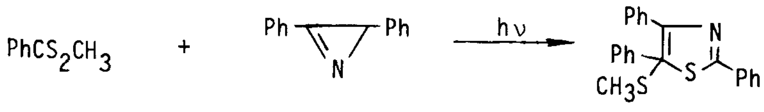
(93)[127]

Sodium carboxymethyl dithiobenzoate reacts with sodium azide to give the thiatriazole **27**.[133] In addition, the photoreaction of methyl dithiobenzoate with 2,3-diphenylaziridine produces the corresponding 1,3-thiazole.[134]



27

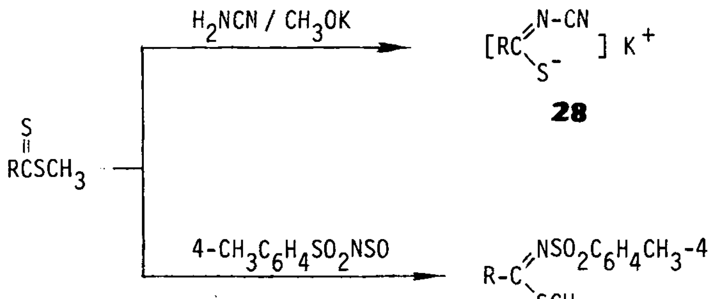
(94)[133]



(95)[134]

b Conversion of >C=S *to* >C=N-

Reaction of dithioesters with cyanamide in the presence of potassium methoxide and with *N*-Sulfinyl-*p*-toluenesulfonamide affords the corresponding imino derivatives **28** and **29**, respectively.[135,136]



(96)[135]

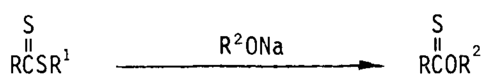
28

(97)[136]

29

16. REACTION WITH ALKOXIDES (*O*-THIOACYLATION)

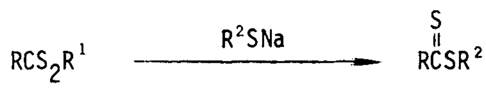
It has been described in the literature that methyl,[26b] allyl,[74] carboxymethyl,[137,138,139,140] ethoxycarbonylmethyl,[138] cyanomethyl,[138] and 2,4-dinitrophenyl esters of dithiocarboxylic acids act as thiacylating reagents towards alcohols.



(98)[26b,74,137-140]

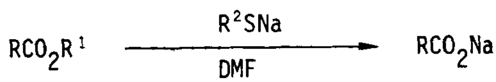
17. REACTION WITH THIOLATES (*S*-THIOACYLATION)

Sodium thiolates have also been thioacylated with methyl[25] and allyl,[74] and carboxymethyl dithioates.[141,142] In contrast, the reaction of carboxylic acid esters with sodium thiolates gives the corresponding carboxylic acid sodium salts.[143]



(99)[25,74,141,142]

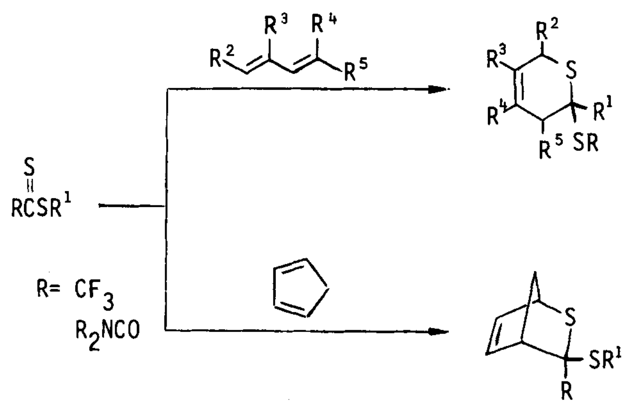
cf.



(100)[143]

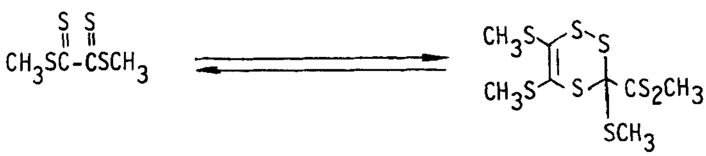
18. REACTION WITH ALKENES

Fluorine-containing dithioesters,[144] methyl esters of α-cyano,[145] α-aminocarbonyl[146] and α-ethoxycarbonyl dithiocarboxylic acids,[147] and α-ethoxycarbonyl dithiocarboxylic acids,[147] and dimethyl tetrathiooxalate[45] react with 1,3-butadienes to give Diels-Alder products. α,β-Unsaturated dithioesters tend to dimerize in part during [4 + 2]-cycloadditions (see eq. 2).[4,148]

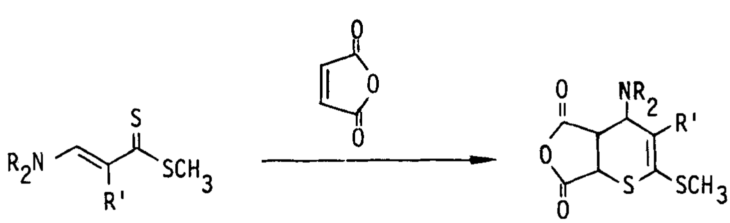


(101)[144-147]

(102)[146]



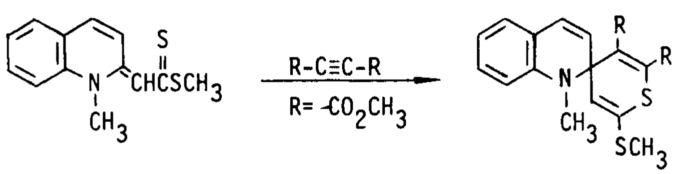
(103)[45]



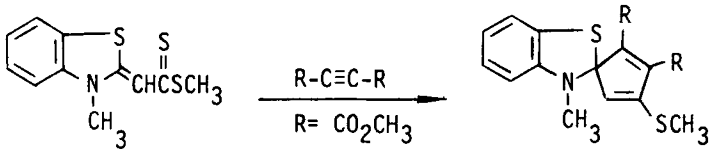
(104)[148]

19. REACTION WITH ALKYNES

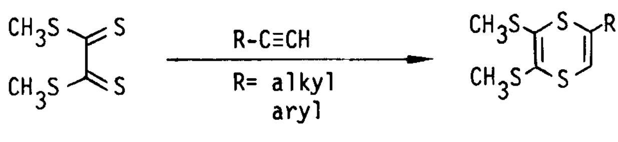
Dithioesters react with alkynes to give Diels-Alder adducts.[149-152] A new cycloaddition accompanied by a sigmatropic shift was found in the reaction of dithioesters with dimethyl acetylenedicarboxylate.[153,154]



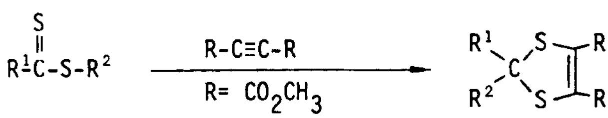
(105)[149]



(106)[150]



(107)[152]



(108)[153,154]

20. REACTION WITH BENZYNE

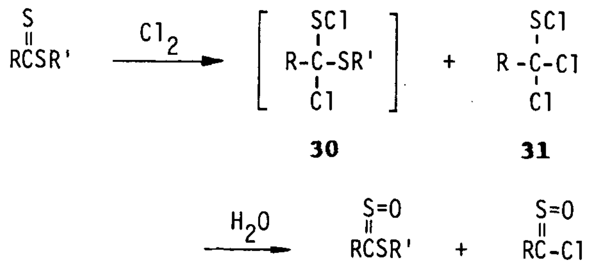
The reaction of dithioesters with benzyne affords the corresponding aldehydes.[155]

(109)[155]

R= *t*-Bu, Ph,
Me(Ph)C=CH-

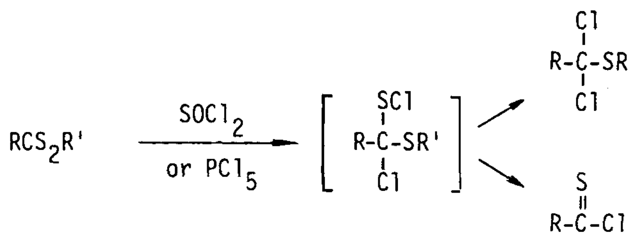
21. REACTION WITH HALOGENS (α-HALOGENATION)

Chlorination of dithioesters with chlorine gives the corresponding sulfenyl chlorides **30** or **31**,[37,156] hydrolysis of which produces the corresponding sulfines.



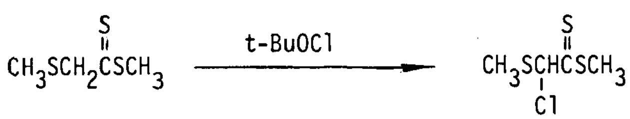
(110)[37,156]

Treatment with thionyl chloride or phosphorus pentachloride gives α,α-dichloro sulfides[98] or thioacyl chlorides.[157]



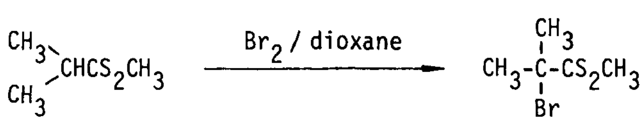
(111)[98,157]

The reaction of methyl α-methylthiodithioacetate with *t*-butyl hypochlorite results in an α-chloro dithioester.[158]

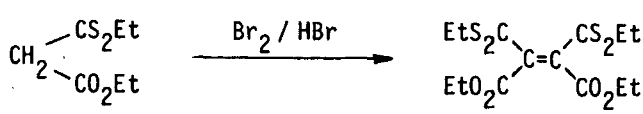


(112)[158]

Dithioesters possessing α-hydrogen atoms can be converted to α-bromo dithioesters by reaction with the complex of bromine and dioxane[90] whereas asymmetric diethyl dithiomalonate forms the olefinic product **32** with bromine/hydrogen bromide.[49]



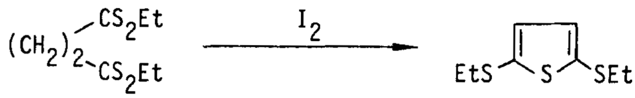
(113)[90]



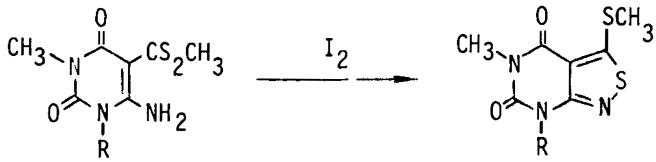
(114)[49]

32

Treatment of diethyl tetrathiosuccinate with iodine produces 2,5-bis(ethylthio)thiophene in good yield.[4] Similar treatment of 6-aminouracil-5-carbodithioate leads to the isothiazole **33**.[159]



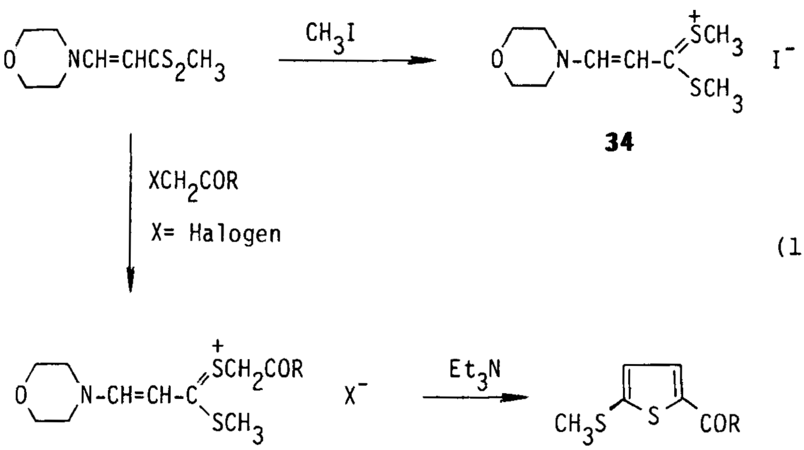
(115)[4]



33

(116)[159]

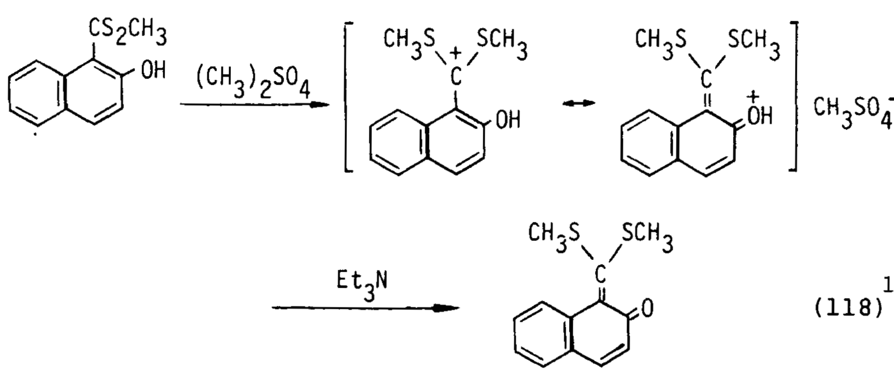
In general dithioesters do not react with alkyl halides. However, methyl α-morpholinodithioacrylate reacts with methyl iodide to give the thionium salt **34**.[160] Further reaction with an α-halocarbonyl compound and triethylamine leads to a 2,5-disubstituted thiophene via the salt **35**.[160] 2-Hydroxy- or 2-methoxy-1-dithionaphthoate reacts with dimethyl sulfate in the presence of triethylamine to give the quinone methide **36**.[161]



34

35

(117)[160]



36

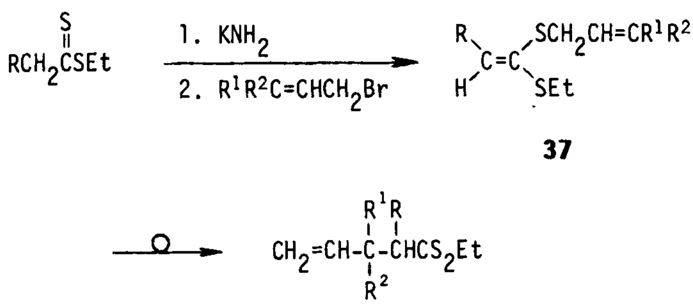
(118)[161]

22. PHOTOREACTIONS

Aromatic dithioesters are inert to photoirradiation. In contrast, the aliphatic ones yield complex, intractable, oily substances. A photo-induced reaction of dithioesters with 2,3-diphenylaziridine yields 1,3-thiazoles (see eq. 95).[134]

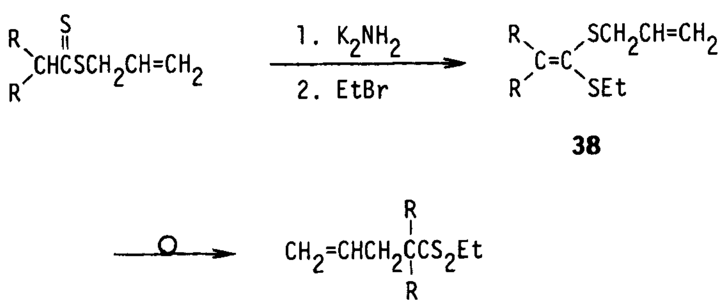
23. REARRANGEMENTS

In 1966, Brandsma and his coworkers reported that γ,δ-unsaturated dithioesters can be obtained by treatment of dithioesters possessing α-hydrogen with potassium amide, followed by allyl bromide.[53] Similar 3,3-[48,55] and 2,3-sigmatropic rearrangements[92] of the corresponding *S*-allyl ketene dithioacetals **37–40** (which are derived from dithioesters) have been described in the literature.



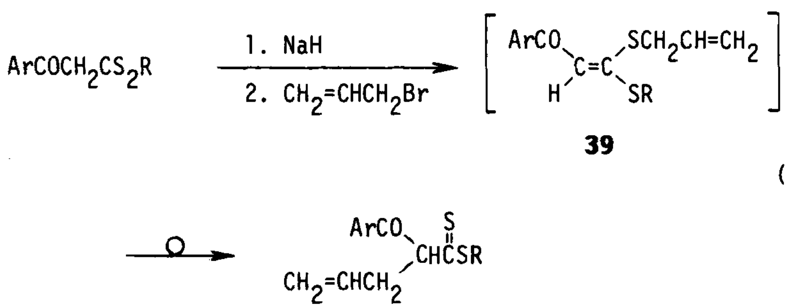
37

(119)[54]



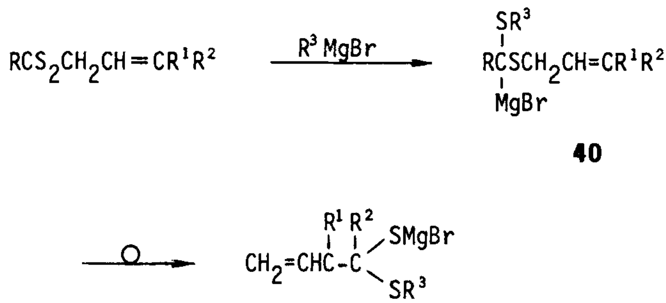
38

(120)[48]



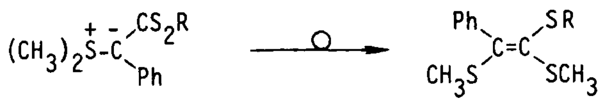
39

(121)[56]



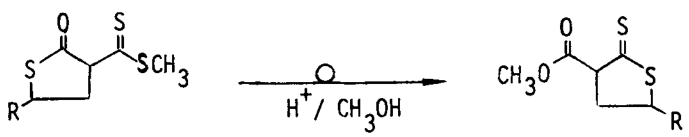
(122)[92]

Another type of sigmatropic rearrangment of allyl dithioates was found in the shape of their cycloaddition reaction with dimethyl acetylenedicarboxylate.[153] Alkylthio-thiocarbonyl-stabilized ylides[162] and methyl 5-oxo-2-methylthiolane-4-carbothioates[163] rearrange to the styrene derivatives **41** and the dithiolactones **42**, respectively. In addition, the mass spectrum of methyl α-nitroacrylate **43** shows clear evidence for rearrangment of **44** through cyclization before fragmentation (Scheme 2).[164]



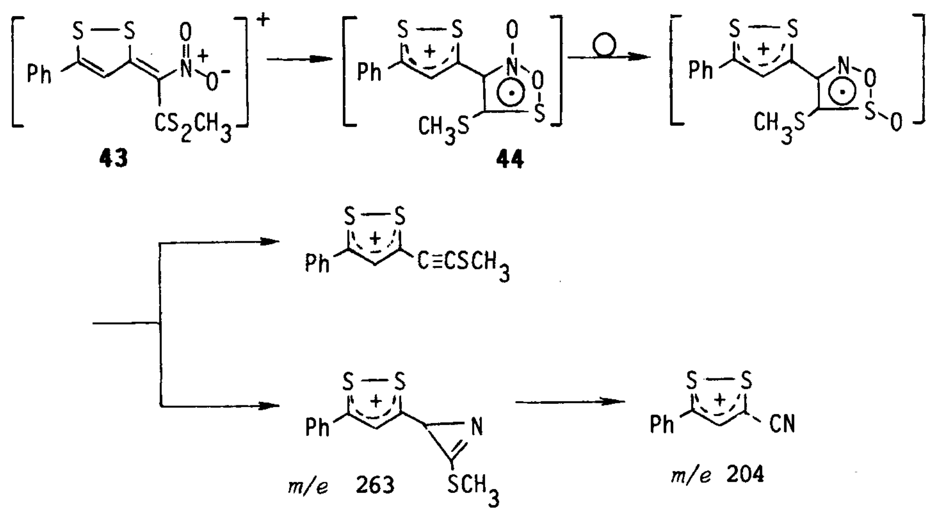
41

(123)[162]



42

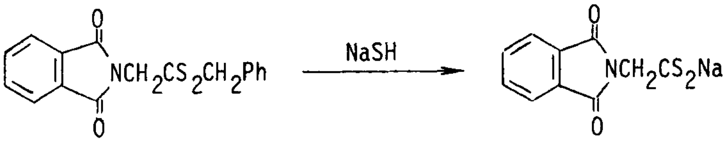
(124)[163]



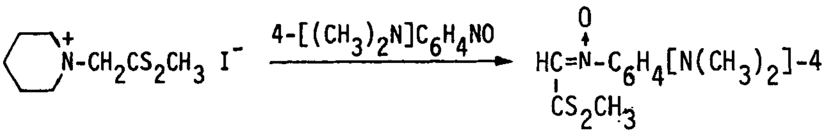
Scheme 2[164]

24. MISCELLANEOUS

The sodium salt of *N*-phthaloyldithioglycine can be obtained by thiohydrolysis of the corresponding benzyl dithioester.[165] Methyl *N*-piperdiniodithioacetate reacts with nitroso-arenes to give α-nitrones such as **45**.[106] Heating of methyl 3-hydroxyindolecarbodithioate and phosphorus pentasulfide produces the 1,2-dithiole-3-thione **46**.[166,167] Reaction of dithioesters with dialkoxydibutyltin produces trialkyl orthocarbonates.[168] Methyl benzoyl- and ethoxycarbonyldithioacetates condense with 3-methyl-1,2-dithiolium salts to give 6*a*-thiathiophtens **47** and thiopyranethiones.[23,169,170] *O*-Thioacylation of α-amino ethers with dithioesters has been reported by Russian chemists.[171]

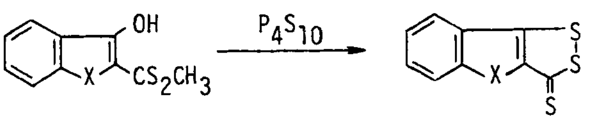


(125)[165]



(126)[106]

45

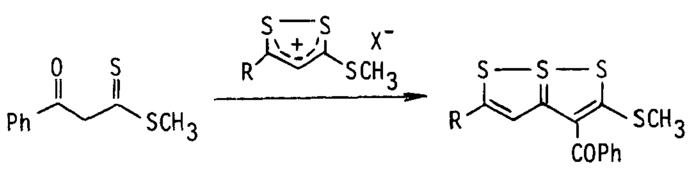


(127)[166,167]

X= NAc, SO_2

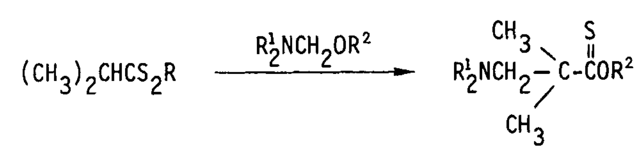
46

$$RCS_2CH_3 \xrightarrow{Bu_2Sn(OR')_2} RC(OR')_3 + Bu_2SnS + Bu_2Sn(SCH_3)_2 \quad (128)^{168}$$



(129)[169,170]

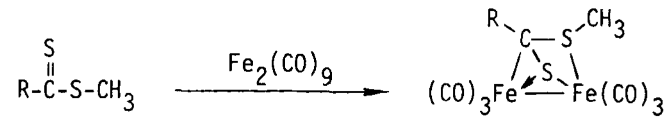
47



(130)[171]

Dithioesters react with dicobalt octacarbonyl in ethanol to give the corresponding alkylidenetricobalt clusters[172] while the reaction with diiron nonacarbonyl affords the binuclear complexes **48** resulting from coordination of the carbon-sulfur double bond to the two iron atoms and donation of two electrons from the *S*-alkyl group to one iron center.[173] In addition, the reactions with a complex containing a molybdenum-molybdenum triple bond at room temperature or upon refluxing in xylene gives the new complexes **49** or **50** possessing a bridging thioacyl or dithioester unit, respectively.[174]

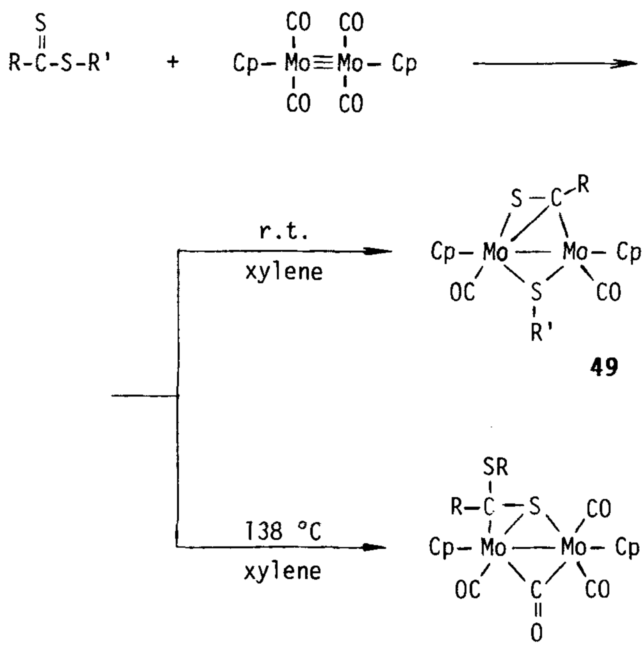
$$RCS_2R' \xrightarrow{Co_2(CO)_8} R\text{-}C(Co)_3(CO)_9 \qquad (131)^{172}$$



R= alkyl, aryl

48

(132)[173]

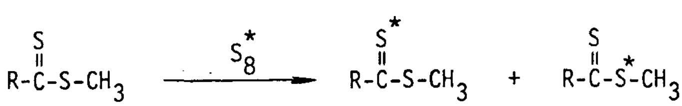


49

50

(133)[174]

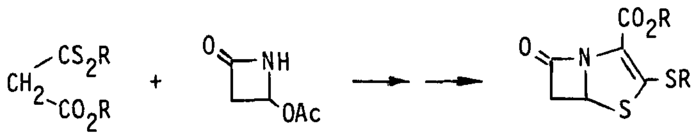
Dithioesters undergo isotopic exchange with elemental $^{35}S_8$.[175]



(134)[175]

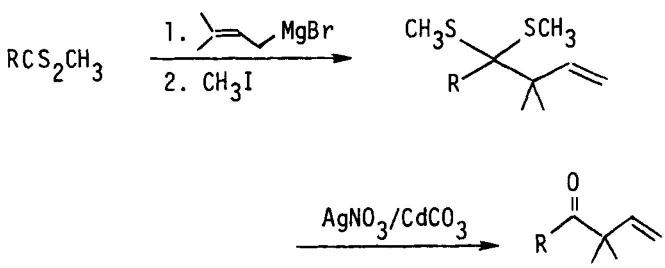
25. APPLICATIONS

Dithioesters have been introduced as useful thioacylating reagents of amino acids,[118,126] 6-aminopenicillanic,[176] and cephalosphoranic acid,[177] and as starting materials for the synthesis of biologically active compounds such as (–)-(E)-lanceol,[52] maytansine and maytansinoids (see eq. 50),[58-60] (–)-maysine,[59] maysines,[88,89] penems (**51**),[178] artemisia ketone (**52**),[84] egomaketone,[179], *ar*-turmerone,[179] manicone (**53**),[180] melanostatin, and leucine enkephalin (amino acid and peptide dithioesters),[181,182] and dyes.[183]



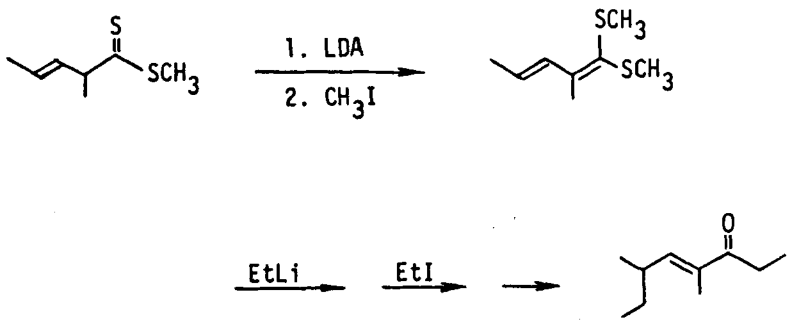
51

(135)[178]



52

(136)[84]



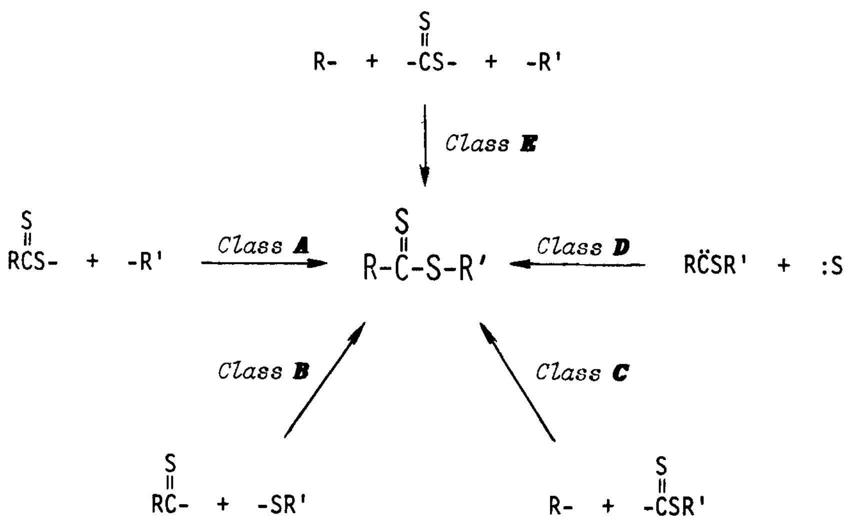
53

(137)[180]

Dithioesters have also been used in industry as photosensitizers,[184,185] vulcanization inhibitors,[186] antioxidants of lubricating oils,[187] bactericidal and fungicidal agents,[188] and for the sequential analysis of peptides by solid-phase techniques.[189]

III. SYNTHETIC METHODS

The synthetic methods of acyclic dithioesters which have been reported hitherto are roughly divided into the following five types (Classes *A* to *E*) on the basis of the final step of bond formation (Scheme 1):



Scheme 1. Synthetic routes to acyclic dithiocarboxylic acid esters

a. Class A (Alkylation of dithiocarboxylic acid salts):

Historically this type of synthetic method is oldest[1] and has been most widely utilized. This type of method is suitable for the alkyl esters (RCS_2R', R′ = alkyl), but not for the 2,4-dinitrophenyl esters. In general the dithio salts used are limited to the Li, Na, K, Mg, Cu, and ammonium ones, showing relatively high reactivity. Among these, the piperidinium salts seem to be most preferable because of their easy preparation and handling.[190] In contrast, other alkali or alkali-earth metal salts are not so easy to isolate,[191] though the reactions proceed cleanly. It is noted that the use of the cuprous salts is effective for alkylation of bulky and α-olefinic dithio salts.[200]

$$RCS_2^- M^+ + R'X \longrightarrow RCS_2R' \qquad (1)$$

R = alkyl,aryl   R' = alkyl
X = Cl, Br, I

Ref. M = Li: 108, 140, 192, 193, 194, etc.
Na: 102, 117, 118, 196a, 196b, 196c, 197
K : 20, 117, 123b, 198
Mg: 199, 200, etc.
Cu: 201
R_4N: 12, 190

Addition of dithio acids to alkenes,[202] and imines[203] gives the corresponding dithioesters.

$$RCS_2H + \ \rangle C{=}C\langle \ \longrightarrow RC(=S)S{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H \qquad (2)^{202}$$

$$RCS_2H + \ \rangle C{=}N{-} \ \longrightarrow RC(=S)S{-}\overset{|}{\underset{|}{C}}{-}N\langle_H \qquad (3)^{203,339}$$

Reaction of dithioacids with sodium methoxide leads to methyl dithioates:

$$RCS_2H + CH_3ONa \longrightarrow RCS_2CH_3 \qquad (4)^{51}$$

cf.

$$RCS_2PPh_2 + CH_3ONa \longrightarrow RCS_2CH_3 \qquad (5)^{204}$$

*b. Class **B** (Thioacylation of thiolates):*

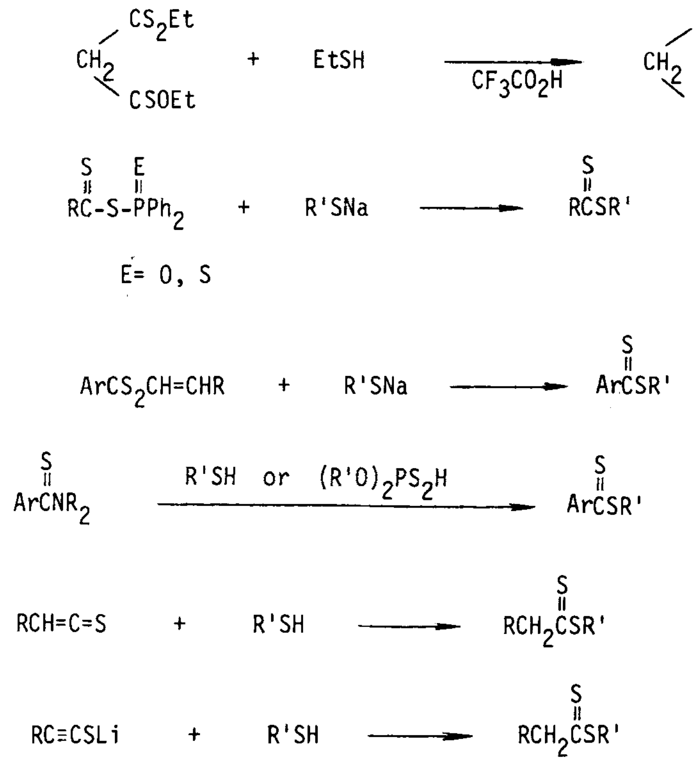
This type of method is useful for the preparation of aryl esters of dithiocarboxylic acids (RCS_2R', R' = aryl). Carboxymethyl dithioates,[25,141] thioacyl chlorides,[205,208] bis-(thioacyl) sulfides,[209] thionesters,[56] thioacyl chlorides,[205,208] bis(thioacyl) sulfides,[209] thioacyl posphinoyl sulfides,[210a] thioacylphosphinothioyl sulfides,[210b] vinyl dithioates,[75] thioamides,[211,212] thioketenes,[213,214,215] and alkynethiolates[53,216] possess thioacylating ability. Among these thioacylating reagents, carboxymethyl dithioates and thioacyl chlorides have been used widely. The former are effective under aqueous conditions, the latter under nonaqueous conditions. When trifluoroacetyl fluoride is used as thioacylating reagent for the preparation of perfluoro dithioates the presence of a catalytic amount of sodium fluoride is effective.[44] Bis(thioacyl) sulfides have been proven to be effective as both aliphatic and aromatic thioacylating reagents.[209]

$$ArC(=S)Cl + RSH \xrightarrow{Py} ArC(=S)SR \qquad (6)^{205,208}$$

$$CF_3C(=S)F + CF_3SH \xrightarrow{NaF} CF_3C(=S)SCF_3 \qquad (7)^{44}$$

$$RC(=S){-}S{-}C(=S)R + R'SNa \longrightarrow RC(=S){-}S{-}R' \qquad (8)^{209}$$

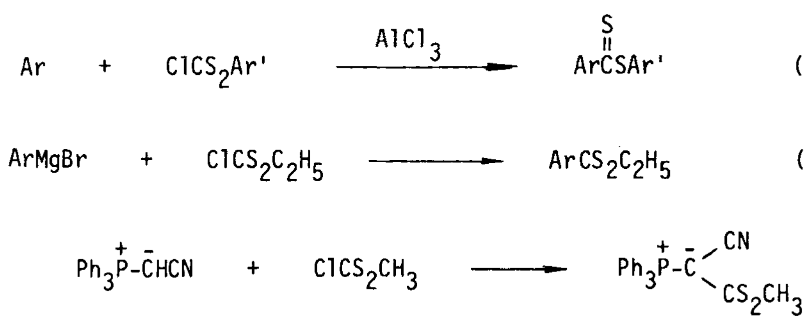
$$RC(=S)SCH_3 + R'SNa \longrightarrow RC(=S)SR' \qquad (9)^{25,141}$$



(10)[56]
(11)[210]
(12)[75]
(13)[211,212]
(14)[213,214,215]
(15)[53,216]

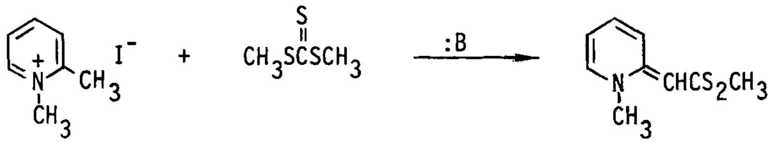
c. Class C (Alkylthio-thiocarbonylation of hydrocarbons):

Chlorodithioformic acid esters[49,217-228] and alkyl trithiocarbonates[164,220] are known as alkylthiothiocarbonylating reagents. The former seem to be effective for the preparation of aryl esters of aromatic dithiocarboxylic acids, especially bulky derivatives such as aryl 2,4,6-trimethyldithiobenzoates.

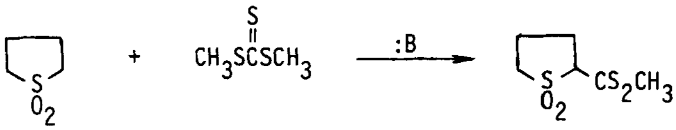


(16)[49,217-226]
(17)[227,228]
(18)[222]

Alkylthio-thiocarbonylation reactions of 1,2-dimethylpyridinium iodide[223] and some other active methylene compounds such as alkyl sulfones,[224,226] thiolactones,[168] acetonitriles,[229,230] cyclopentadiene,[231] and acetophenones,[230] with alkyl trithiocarbonates have been reported.

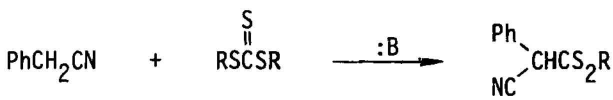


(19)[223]

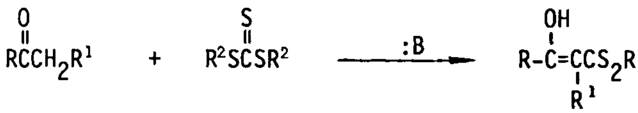


(20)[224,225]

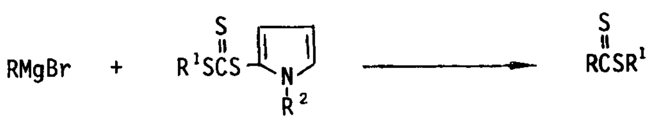
(21)[163]



(22)[229,230]

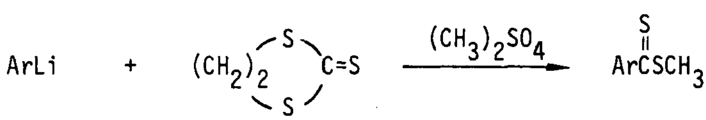


(23)[230]



(24)[221]

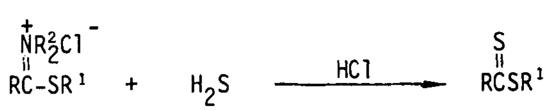
Cyclic trithiocarbonates can also be used as alkylthio-thiocarbonylating reagents.



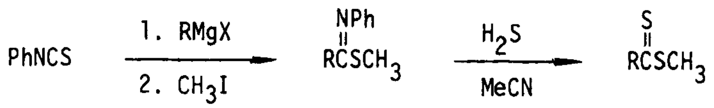
(25)[220]

*d. Class **D** (Substitution of carbonyl oxygen or imino nitrogen by sulfur and thionation of active methylene groups):*

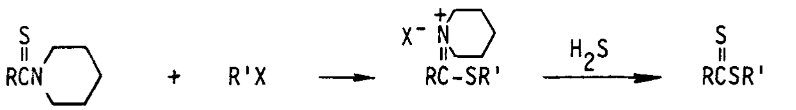
Treatment of iminothioesters with hydrogen sulfide under acidic conditions has been used widely. This type of reaction is effective for the synthesis of dithioesters containing two or more dithio groups. Convenient methods of preparation involving isothiocyanates[3a] and thioamides as the starting compounds have been reported.



(26)[3,21,42,51,105,110,179,189,232-243]

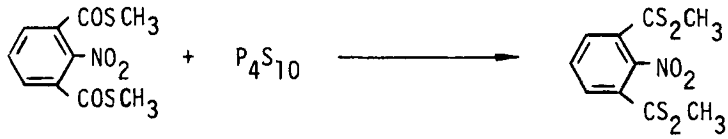


(27)[3a]



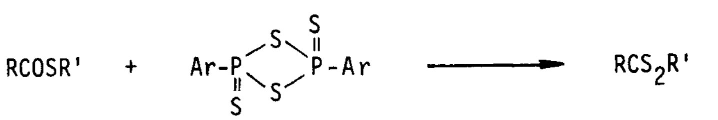
(28)[181,182,241,244]

The thionation of thiolesters with tetraphosphorus decasulfide,[18] *O,O*-dialkyl dithiophosphoric acid,[212,245] and 2,4-bis(aryl)-1,3-dithia-2,4-diphosphetane 2,4-disulfides **54** (Lawesson's reagent),[246,247] has been described in the literatures.



(29)[18]

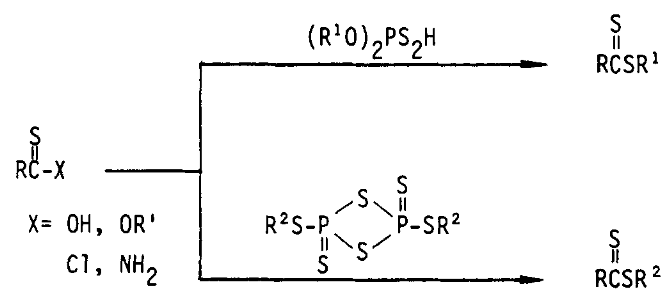
$$RCOSR^1 + (R^2O)_2PS_2H \longrightarrow RCS_2R^1 + RCS_2R^2 \qquad (30)^{212,245}$$



(31)[246,247]

54

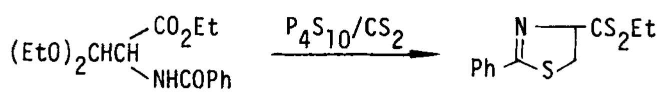
Carboxylic acids,[212,248] acid chlorides,[248] and amides[248] are directly converted to dithioesters by treatment with dithiophosphoric acid,[212,215] and 2,4-bis(alkylthio- or -arylthio)-1,3-dithia-2,4-diphosphetane 2,4-disulfides (**54**, Ar = SR),[249,250] though requiring relatively high reaction temperature.



(32)[212,248]

(33)[245,250]

cf.



(34)[251]

Treatment of active methylene sulfides with elemental sulfur in the presence of tertiary amines produces dithioesters.[252]

$$RCH_2SR' \xrightarrow{S_8/R_3N} RCS_2R' \qquad (35)^{252}$$

*e. Class **E** (Simultaneous bond formation at carbon and sulfur):*

Only one example has been reported, where benzene and carbon disulfide are treated with (trimethylsilyl)methyl chloride in the presence of aluminium chloride.[253]

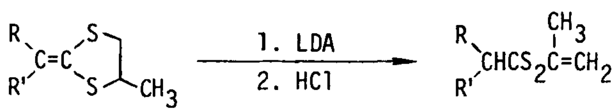
$$C_6H_6 + CS_2 + (CH_3)_3SiCH_2Cl \xrightarrow{AlCl_3} C_6H_5CS_2CH_2Si(CH_3)_3 \qquad (36)^{253}$$

f. Miscellaneous

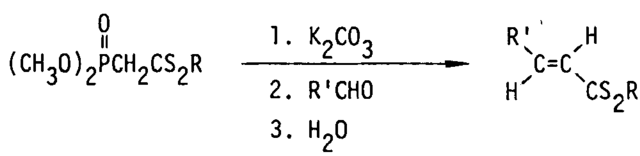
(i) Preparation from a ketone dithioacetal as starting compound or intermediate.

$$ArCH{=}C(SCH_3)(SCH_2OAr) \xrightarrow{HCl} ArCH_2CS_2CH_3 \qquad (37)^{254,255}$$

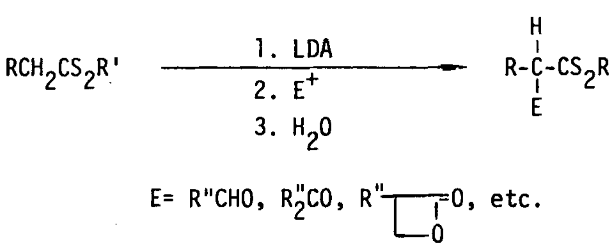
$$(CH_3S)_2C{=}C(SCH_3)_2 \xrightarrow[2.\ H^+]{1.\ CH_3SNa} (CH_3S)_2CHCS_2CH_3 \qquad (38)^{256}$$



(39)[257]

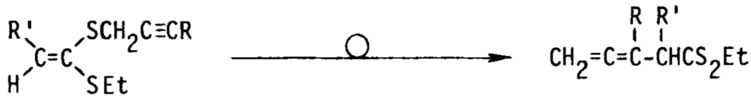


(40)[61]



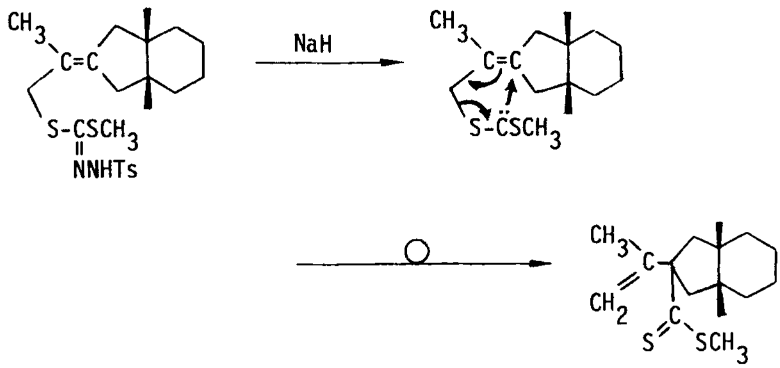
(41)[68,88]

[1,3] Rearrangement[69,258]

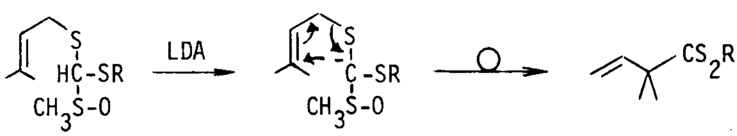


(42)[258]

[2,3] Sigmatropic rearrangement[259,260]

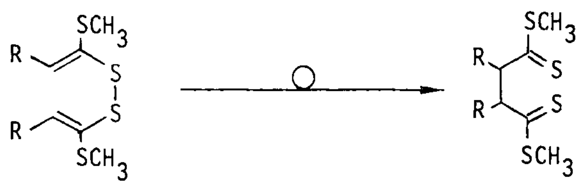


(43)[259]



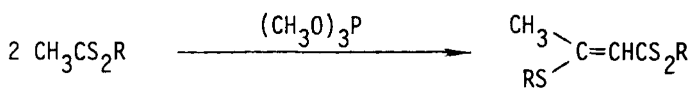
(44)[260]

[3,3] Sigmatropic rearrangement[73]



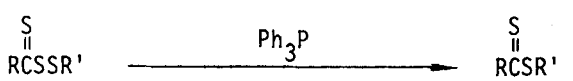
(45)[73]

(ii) Condensation of dithioacetates in the presence of trimethyl phosphite.[261]



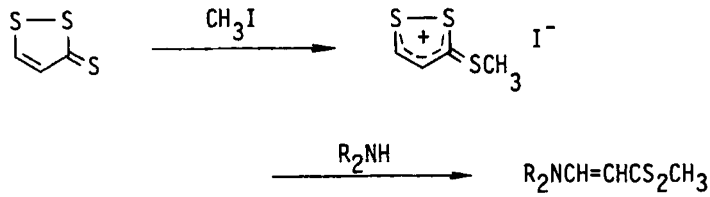
(46)[261]

(iii) Desulfurization of trithioperesters with triphenylphosphine.[262]



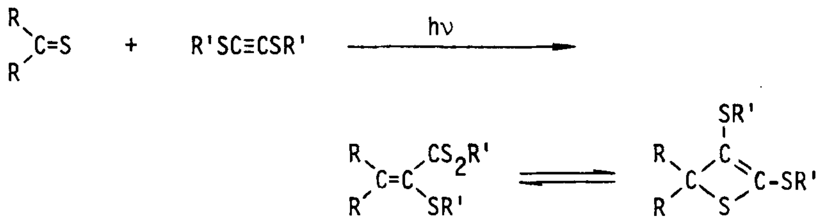
(47)[262]

(iv) Reaction of a 3-methylthio-1,2-dithiolium salt with an amine.[263]



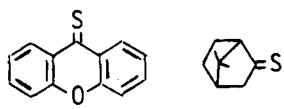
(48)[263]

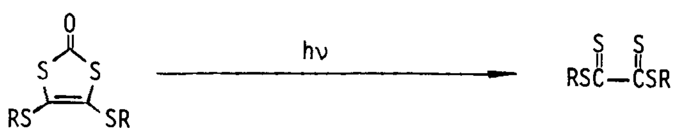
(v) Photoinduced preparation from thioketones and bis(alkylthio)alkyenes or from cyclic dithiocarbonates.[45,264]



(49)[264]

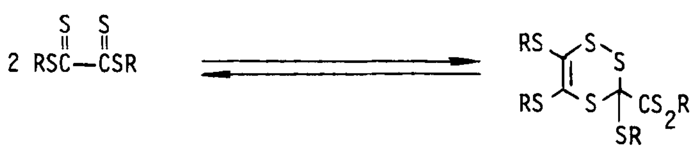
R_2CS :





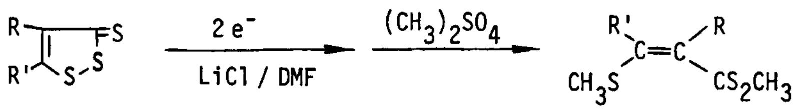
(50)[45]

(vi) Dimerization of dialkyl tetrathiooxalates.[42]



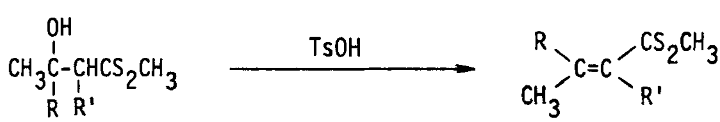
(51)[45]

(vii) Electrolytic reductive methylation of 1,2-dithiol-3-thiones.[265]



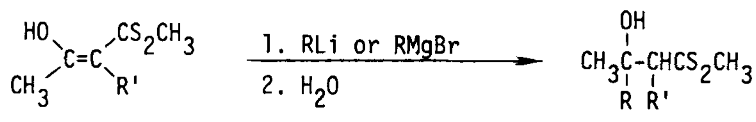
(52)[265]

(viii) Conversion of β-hydroxy dithioesters to α-olefinic dithioesters.[266]



(53)[266]

(ix) Conversion of β-hydroxyl-α-olefinic dithioesters to β-hydroxy dithioesters.[266]



(54)[266]

ACKNOWLEDGEMENT.

We would like to thank Professor Renji Okazaki, The University of Tokyo, for his kind advice during the preparation of this manuscript.

IV. Tables

Table 1. Aliphatic dithiocarboxylic acid esters

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
CH_3	CH_3	142/760,[1] 80-81/95,[1] 40/30,[51] 70-71/70,[267,268] 54-55/40,[268] 53.5-55/39-40,[268] 38-39/24[271]	52,[51] 25,[248] 65,[250] 65[272]	1, 51, 248, 250, 267, 268, 271, 272
	CD_3			273
CD_3	CH_3			273
$^{13}CH_3$	CH_3			273
CH_3	$CH_2C_6H_5$	85-88/0.4,[245] 83/0.4[246]	60,[245] 99,[246] 82[248]	245, 246, 248
	$CH_2\overset{+}{P}Ph_3\ I^-$	70-76	56	74
	CH_2Cl	73-74/12		200
	CH_2CO_2H	80-81,[274] 76-79,[275]	60[274]	274, 275

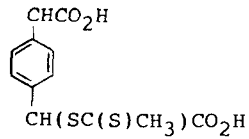
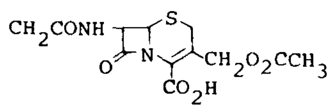
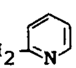
CH_3	$CH_2(C_6H_5)CO_2H$	131-133	73	244
	$CH_2COC_6H_5$			15a
	$CH_2C_6H_4Br$-4	99-99.5,[17a] 97[195]	92[17a]	17a, 195
	$CH(CO_2CH_3)_2$	oil		202
		203	29	276
		150-155		177
	C_2H_5	130-131/760,[5] 42-43/11,[50] 64/24,[141] 52/12,[199] 131/760,[212] 43-46/10,[227] 61/23,[234] 52-53/19[268], 47-50/12,[275] 128-132[277]	70,[199] 40,[212,227] 64,[250] 50[278]	5, 50, 141, 199 212, 227, 234, 250, 268, 275, 277, 278

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
CH_3	CD_2CH_3			273
CD_3	C_2H_5			273
CH_3	CH_2CH_2Cl	89-90/12	72	200
	$CH(C_6H_5)CH_3$	oil		202
	$CH(OC_6H_4CH_3\text{-}4)CH_3$	oil		202
	$CH(O_2CCH_3)CH_3$	oil		202
	$CH(CH_3)CH_2CN$	oil		202
	$CH_2CH_2CO_2H$	oil		202
	$CH_2CH_2N(CH_3)_2$	oil		195
	CH_2CH_2– 	oil		202
	$CH_2CH_2\overset{+}{N}H(CH_3)_2\ Cl^-$	130-132		195
	$CH_2CH_2\overset{+}{N}H(CH_3)_2\ I^-$	172.5-173.5		195

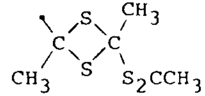
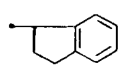
	$CH_2CH(S_2CCH_3)SPh$	oil		202
CH_3		145-147,[268] 148-151,[281]	3,[279] 53[268]	268, 279, 281
	$CH{=}CHCO_2H$	121/760		281
	$CH{=}CHCO_2CH_3$	62-63/760		281
	$CH_2CH_2CH_2Cl$	111-112/12	65	200
	$CH(CH_3)CH_2SPh$	oil		202
	$C(CH_3)_2SPh$	oil		202
	$CH_2CH{=}CH_2$	92-93/20,[48] 65-66/13,[83b] 104/45,[141] 77/1.8,[282] 68/17[268]		48, 83b, 141, 268, 282
	$CH{=}CHCH_3$	68-71/17	85	48
	$CH_2C{\equiv}CH$	38-40/0.001	65	72
	C_4H_9-*n*	32-33/0.05,[5] 36.4/3.5[268]	90[268]	5, 268
	$CH(CH_3)CH_2CH_3$	77/16,[5] 33/5[268]	90[268]	5, 268

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
CH_3	$CH_2CH(CH_3)_2$	86-87/23[234,268]	49.2[234]	234, 268
	C_4H_9-*t*	70-71/16[5]		5
	$(CH_2)_4Cl$	131-132/12	84	245
	$CH{=}C(CH_3)_2$	82-84/17	83	48
	$CH_2CH{=}CHCH_3$			83b
	$CH_2C(CH_3){=}CH_2$	52-53/0.1	85	48
	$CH_2C{\equiv}CCH_3$	50-53/0.001	78	72
	$CH(CH_3)CH(CH_3)_2$		20	284
	$C(CH_3)_2CH_2CH_3$		38	284
	$C(Et){=}CHCH_2CH_3$		35	281
	$CH{=}CHC(CH_3){=}CH_2$		60	281
		oil		202

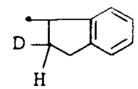
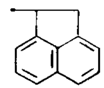
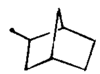
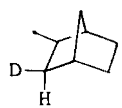
CH_3		oil		284
		oil		202
			80	284
				284
	C_6H_5	63-65/0.5,[245] 64/0.5,[246] 55-60/0.3[249]	85,[245] 90,[246] 72,[248] 44[249]	245, 246, 248, 249
	$-C(Pr\text{-}i)(Pr\text{-}n)(CH_2)_2C(Pr\text{-}i)=CHEt$			284
	$-C(Pr\text{-}i)(Bu\text{-}n)(CH_2)_2CH=C(Pr\text{-}i)(Pr\text{-}n)$			284
$PhCH_2$	CH_3	149/12,[1] 120/1,[235]	68,[248] 65,[250]	1, 235, 248,

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$PhCH_2$		95/0.1,[255] 208/760,[268] 122-125/1[286]	64,[255,268] 98,[268] 23[286]	250, 255, 268, 286
	CH_2Ph		55	250
	CH_2CO_2H	79-80	50	118
	C_2H_5	110/13,[212] 91-92/2.5,[268] 140-144/45[268]	57,[212] 91[268]	212, 268
	C_3H_7-*n*	119-120/4	97	268
	C_3H_7-*i*	118-119/4[268]	51[250]	250, 268
	$(CH_2)_3CO_2CH_3$	oil	40	287
	$CH_2CH{=}CH_2$	96-97/2	96	268
	C_4H_9-*n*	118-119/2.5	63	268
	$CH(CH_3)C_2H_5$	114/3		268
	C_4H_9-*t*	oil	81	288

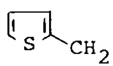
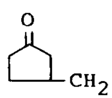
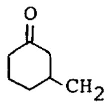
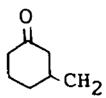
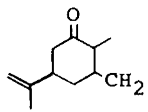
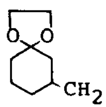
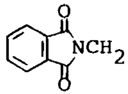
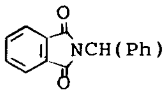
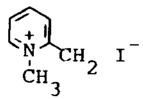
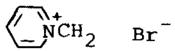
4-$CH_3OC_6H_4CH_2$	CH_3	145/0.3[255]	70[255,268]	255, 268
3,4-$(CH_3O)_2C_6H_3CH_2$	CH_3	185/0.3[255]	69[255,268]	255, 268
4-$ClC_6H_4CH_2$	CH_3	145/0.3[255]	65[255,268]	255, 268
Ph_2CH	CH_3	57-57.5[289,290]	96[290]	289, 290
PhCH(OH)	C_2H_5	oil	32	297
PhCH(SEt)	C_2H_5	oil		297
PhCH(CN)	CH_3	48-49	42	230
1-$C_{10}H_7CH_2$	$(CH_2)_3CO_2H$	oil	40	287
	CH_3	145/0.1	64	255
CH_3COCH_2	CH_3	50/0.11	64	308
	CH_2Ph	128/0.1	21	308
	C_2H_5	63/0.2	42	308
t-$C_4H_9COCH_2$	CH_3	92-94	43	291
	CH_3		78	64

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3		86	64
	C_2H_5		52	64
	CH_3		70	64
	CH_3			64
$(EtO_2C)_2(NC)C$	$CH_2CH{=}CHCH_3$			254
$PhCO_2CH_2$	papain			293
$CH_3CONHCH_2$	papain			293
$PhCH_2CONHCH_2$	papain			293
$PhCH_2CH_2CONHCH_2$	papain			293

$PhCONHCH_2$	CH_2Ph	105-107	25	165
	C_2H_5	98-99[165,243]	40[165,243]	165, 243
	C_6H_5	149-151	21	165
	papain			293
$4\text{-}CH_3C_6H_4CONHCH_2$	C_2H_5			294
$4\text{-}CH_3OC_6H_4CONHCH_2$	C_2H_5			294
$(CH_3O_2C)_2CH$	CH_3	124/0.01	74	292
$(EtO_2C)_2CH$	CH_3	60/10	33	254
	C_2H_5		30	254
	$CH_2CH{=}CH_2$		29	254
$(EtO_2C)_2(NC)C$	$CH_2CH{=}CH_2$			254
$4\text{-}ClC_6H_4CONHCH_2$	C_2H_5			294
$4\text{-}NO_2C_6H_4CONHCH_2$	C_2H_5			294
	papain	oil		295
$PhCH_2OCONHCH_2$	papain			293

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_2Ph	116-117	65	165
	CH_2Ph	121-122	35	165
	CH_3	160	90	345
	CH_2CO_2H	133-135	55	296
	CH_2CO_2H			107
$(EtO)_2P(O)(EtO_2C)CH-$	C_2H_5	oil	5	301
$(CH_3O)_2P(O)(CH_3O)PhC-$	CH_3	65-67	5	301
$(EtO)_2P(O)(CH_3O)PhC-$	CH_3	oil	48	301
	C_2H_5	oil	56	301

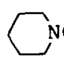
$(CH_3O)_2P(O)$ \ PhC- / C_2H_5O	CH_3	91-93	15	301
$(EtO)_2P(O)$ \ PhC- / C_2H_5O	CH_3	51-53	56	301
NH_2CSCH_2	C_2H_5	oil		295
$PhOCH_2$	CH_3	oil	35	55
	CH_2Ph	oil	24	55
CH_3SCH_2	CH_3	74/0.05,[55] 35/0.06[69]	85,[55] 80[69]	55, 69
$EtSCH_2$	CH_3	42/0.05	80	158
NH_2COCH_2	C_2H_5	125	65	56
$NCSCH_2$	CH_3	151/0.2	81	56
EtO_2CCH_2	C_2H_5	oil	70	56
$CH_3S_2CCH_2$	CH_3	oil	82	56

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
EtS_2CCH_2	C_2H_5	oil	89	56
$PhSCH_2$	CH_3		51	55
EtSCHCl	CH_3			158
$(EtS)_2CH$	CH_3	118/0.05,[158] 64-66/0.05[256]		158, 256
$(CH_3)_2\overset{+}{S}CH_2CS_2CH_3\ ClO_4^-$		60	23	158
$CH_3SO_2CH_2$	CH_3	82	15	224
$PhSO_2CH_2$	CH_3	49	20	224
$(CH_3SO_2)(Ph)CH$	CH_3	103	35	224
$(PhCH_2SO_2)(Ph)CH$	CH_3	134	25	224
$PhCOCH_2SO_2CH_2$	CH_3	127	20	298
$(PhCOCH_2SO_2)(Ph)CH$	CH_3	124	30	298
$4\text{-}CH_3OC_6H_4COCH_2SO_2CH_2$	CH_3	105	25	298

$PhSO_2CH_2$	CH_3	117	50	224
$ClCH_2$	CH_3	oil	25,[248] 43[250]	248, 250
$BrCH_2$	CH_3			90
CF_3	CF_3			44
	C_2H_5	134/760	96	44
ClF_2C	C_2H_5	51-52/5	95	44
	C_6H_5	85-86/1.5	95	44
$(Ph)(Ph_3\overset{+}{P})\overset{-}{C}$	CH_3	179-180	82	300
$(4\text{-}NO_2C_6H_4)(Ph_3\overset{+}{P})\overset{-}{C}$	CH_3	285-286		299
C_2H_5	CH_3	159-160/760,[1,268] 47/11,[1] 86/50,[42] 57-58/17,[51] 55-56/12,[188] 52/12,[199] 40-41/20[268]	68,[3a] 71,[51] 87,[199] 95[268]	1, 42, 51, 188, 199, 268
	CH_2CO_2H	51-52	60	274
	CH_2COPh	oil	95	17a
	$CH_2COC_6H_4Br\text{-}4$	44-44.3	82	17a

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
C_2H_5	CH_2Cl	83-84/12	82	200
	C_2H_5	60-61/10,[50,302] 59/9,[216] 67-70/10,[227] 70-72/20,[234] 150-155/760[268]	40,[216] 32,[227] 50,[234] 20[303]	50, 216, 227, 234, 268, 302, 303
	CH_2CH_2Cl	62-63/0.1	89	200
	$CH=CH_2$	53/0.02	50	257
	$CH=CHCH_3$	81-83/17	83	48
	$CH_2CH=CH_2$	96-97/12,[48] 88/12[199]	90,[48] 80[199]	48, 199
	$CH_2C\equiv CH$	40/0.001,[71] 55-57/0.001[72]	72[71]	71, 72
	$(CH_2)_3Cl$	121-122/12	87	200
	C_4H_9-*t*	70/13	70	234
	$CH_2CH=CHCH_3$	52/13	78	92

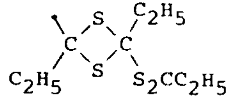
	$CH_2C(CH_3)=CH_2$	85-87/12[48] 96/13[92]	92,[48] 40[92]	48, 92
	$CH=C(CH_3)_2$	95-97/17	83	48
	$CH(CH_3)C\equiv CH$	57-58/0.001	66	72
	$CH_2C\equiv CCH_3$	56-58/0.001	90	72
	$(CH_2)_4Cl$	140-142/2	80	200
	$CH_2C(CH_3)=CHCH_3$	65/0.2	67	92
		67-69	49	268
$CH_3CH(Ph)$	CH_2CO_2H			304
$CH_3CH(OH)$	CH_3			268
$CH_3CH(SCH_3)$	CH_3	45/0.05	80	69
$CH_3CH(COCH_3)$	CH_3	67/0.1	38	306
CH_3CHBr	CH_3			38
$PhCH_2CH_2$	CH_3			41

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$PhCH_2CH_2$	CH_2CO_2H	92-93	55	274
$CH_3SCH_2CH_2$	CH_3	130/11	59	42
EtO_2C CH_3C- CH_3CO	CH_3	105-108/0.2		304
CH_3O_2C CH_3C- $(EtO)_2P(O)$	CH_3	oil	52	301
$CH_2CS_2CH_3$ $CH_2CS_2CH_3$		35	66	240
$CH_2CS_2C_2H_5$ $CH_2CS_2C_2H_5$		oil	81	4
$PhCHCS_2CH_3$ $PhCHCS_2CH_3$				73
$PhC(=NH)CH(CN)$	$C_6H_2(NO_2)_3$-6,4,2	222-224	93	346
• 3-$CH_3C_6H_4C(=NH)CH(CN)$	$C_6H_2(NO_2)_3$-6,4,2	190-201	74	346

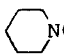
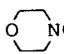
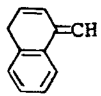
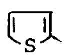
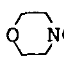
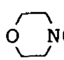
4-$CH_3C_6H_4C(=NH)CH(CN)$	$C_6H_2(NO_2)_3$-6,4,2	166-172	70	346
4-$NO_2C_6H_4CH=CH$	CH_3	31	54	61
3,4-$Cl_2C_6H_3CH=CH$	CH_3	156-157	33	263
PhNHCH=CH	CH_3	86.6-87.6	92	263
	CH_2Ph	120-122	30	263
$(CH_3)_2NCH=CH$	CH_3	99-102	27	263
NCH=CH	CH_3	118-122		263
NCH=CH	CH_3	136.5-138	92	263
	CH_2Ph	94-96		263
4-$CH_3NHC_6H_4CH=C(Ph)$	CH_3	125	63	328
4-$CH_3NHC_6H_4CH=C(C_6H_4CH_3$-4)	CH_3	104	58	328
4-$EtNHC_6H_4CH=C(Ph)$	CH_3	oil		328

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3			233, 329
$(CH_3NH)(Ph)C{=}CH$	CH_3	63	80	110
$(CH_3NH)(4\text{-}CH_3OC_6H_4)C{=}CH$	CH_3	80	90	110
	C_2H_5	59	75	110
$(CH_3NH)(4\text{-}ClC_6H_4)C{=}CH$	CH_3	73	85	110
$[(CH_3)_2N](Ph)C{=}CH$	CH_3	96		110
$[(CH_3)_2N](4\text{-}CH_3OC_6H_4)C{=}CH$	CH_3	148		110
	C_2H_5	102		110
$[(CH_3)_2N](4\text{-}ClC_6H_4)C{=}CH$	CH_3	129		110
(O N)(Ph)C=CH	CH_3	105	85	110
(O N)$(4\text{-}CH_3OC_6H_4)C{=}CH$	CH_3	96	75	110

	C_2H_5	88	90	110
(O N)(4-ClC$_6$H$_4$)C=CH	CH_3	120	75	110
(HO)(Ph)C=CH	CH_3	63-65,[196c] 55-56,[230] 57,[333] 53-56[334]	60,[230] 46,[333] 24[334]	196c, 230, 333, 334
(HO)(Ph)C=CH	C_2H_5	oil	75	55
(HO)(4-CH$_3$C$_6$H$_4$)C=CH	CH_3	59-60,[196c] 54-55[230,333]	62,[230] 39,[333]	196c, 230, 333
(HO)(2-CH$_3$OC$_6$H$_4$)C=CH	CH_3	75-77		196c
(HO)(3-CH$_3$OC$_6$H$_4$)C=CH	CH_3	58-60	55	230
(HO)(4-CH$_3$OC$_6$H$_4$)C=CH	CH_3	59,[19] 52-53,[196c] 75[333]	58[333]	19, 196c, 333
	C_2H_5	42-48	70	55
(HO)(4-EtOC$_6$H$_4$)C=CH	CH_3	57	88-99	230
(HO)(4-ClC$_6$H$_4$)C=CH	CH_3	80-82,[196c] 80-81[230,333]		196c, 230, 333

Table 1. (*Continued*)

RCS$_2$R′ R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
(HO)(4-BrC$_6$H$_4$)C=CH	CH$_3$	71-74	48	333
	CH$_2$Ph	80-81	35	333
	CH$_2$CO$_2$Et	93-94	52	333
	CH$_2$CH$_2$CO$_2$Et	61-63	50	333
	C$_3$H$_7$-i	81-83	66	333
(HO)(4-BrC$_6$H$_4$)C=CH	CH=CHCH$_3$	40	33	333
	CH$_2$C≡CH	70-72	90	333
	CH$_2$CH$_2$CH$_2$CN	79-80	96	333
(HO)()CH=CH	CH$_3$	51-53[196c] 50-51[230]	25[196c] 52[230]	196c, 230
NCH=C(CH$_3$)	CH$_3$	102-104		263
NCH=C(Ph)	CH$_3$	126-128		263

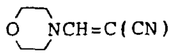
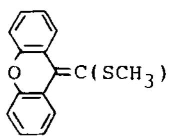
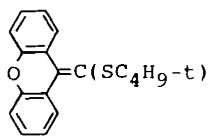
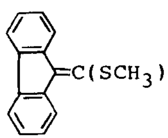
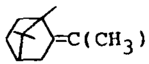
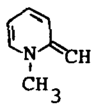
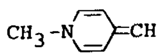
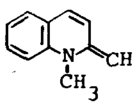
	CH_3	158-159		263
$PhNHCH=C(C_6H_4CH_3\text{-}4)$	CH_3	92		332
$4\text{-}CH_3C_6H_4NHCH=C(CH_3)$	CH_3	82		332
$4\text{-}CH_3C_6H_4NHCH=C(Ph)$	CH_3	131		332
$4\text{-}CH_3C_6H_4NHCH=C(C_6H_4CH_3\text{-}4)$	CH_3	101		332
$4\text{-}CH_3OC_6H_4NHCH=C(C_6H_4CH_3\text{-}4)$	CH_3	106		332
	CH_3	149.5-150	70	330
	$C_4H_9\text{-}t$	131-133		331
$Ph_2C=C(SCH_3)$	CH_3	110-111,[201] 142.5-143.5[330]	98,[201] 36[330]	201, 330
	CH_3	110-111		233, 329

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3	oil	40	8
	CH_3	176	81	223
	CH_3	227	90	223
	CH_3	154	71	223
$(HO)(Ph)C=C(CH_3)$	CH_3	oil		230
$(HO)(Ph)C=C(CH_2CH=CH_2)$	CH_3	oil		230
$(HO)(4\text{-}CH_3C_6H_4)C=C(CH_2CH=CH_2)$	CH_3	oil	75	55
$(HO)(2\text{-}ClC_6H_4)C=C(CN)$	CH_3	100-102	38	335
$(HS)(4\text{-}CH_3OC_6H_4)C=CH$	CH_3	74-76	65	19

$(HS)(4\text{-}CH_3OC_6H_4)C{=}CH$	C_2H_5	59-61	55	19
$(CH_3S)(Ph)C{=}CH$	CH_3	67	75	19
$(CH_3S)(4\text{-}CH_3C_6H_4)C{=}CH$	CH_3	59	75	19
$(CH_3S)(4\text{-}CH_3OC_6H_4)C{=}CH$	CH_3	79	80	19
	C_2H_5	45-47	55	19
$(CH_3S)(4\text{-}ClC_6H_4)C{=}CH$	CH_3	56	70	19
$(C_2H_5S)(4\text{-}CH_3OC_6H_4)C{=}CH$	C_2H_5	92-93	50	19
$(CH_3S)_2C{=}CH$	C_2H_5	87	36	56
$(CH_3S)(C_2H_5S)C{=}CH$	CH_3-(*E*)	oil	25	56
	CH_3-(*Z*)		25	56
$(C_2H_5S)_2C{=}CH$	C_2H_5	57	79	56
$(C_2H_5S)(NH_2)C{=}CH$	C_2H_5	50,[56] 51[295]	73.5[56]	56, 295
$[(CH_3S)_2C{=}N](Ph)C{=}C(SO_2CH_3)$	CH_3	131-132	32	344
	C_2H_5	108-109	41	344
$[(CH_3S)C(SC_2H_5){=}N](Ph)C{=}C(SO_2CH_3)$	CH_3	112-116	60	344

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$[(CH_3S)_2C=N](Ph)C=C(SO_2Ph)$	CH_3	109	18	344
$n-C_3H_7$	CH_3	70-72/10,[188] 64/12,[199] 64/9[216]	78,[199] 50,[216] 56[248]	188, 199 216, 248
	CH_2COPh	oil	80	309
	$CH_2COC_6H_4Br-4$	38-39	35	17a
	C_2H_5	150-155/760,[21] 75/9,[216] 153-155/760,[235] 73-75/10,[245] 74/10[246]	40,[216] 86,[235] 95,[245] 97[246]	21, 216, 235 245, 246
	$CH_2CH=CH_2$	92/13	82	92
	C_4H_9-t	51-53/4	16	209a
	C_6H_5	91-94/1.8	33	209b
	$C_6H_4CH_3-4$	97-100/0.2	37	209a
	C_6H_4Cl-4	110-112/0.8	33	209a

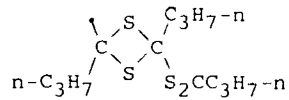
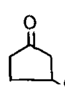
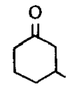
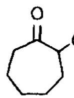
n-C_3H_7		35-37	40	268
$CH_3C(CH_3)_2CH_2$	C_2H_5	90/9	20	216
$PhCH_2CH_2CH_2$	CH_3			41
$CH_3CO(CH_2)_2CH_2$	CH_3		30	64
$PhCOCH_2CH(Ph)CH_2$	CH_3		73	64
$(CH_3)_2C(OH)CH_2$	CH_3		90	311
$CH_3CH_2CH(Ph)$	CH_3		63	250
$CH_3C(CH_3)_2CH(CN)$	CH_3	oil	54	317
$CH_3CHCH_2CS_2CH_3$ S $CH_3CHCH_2CS_2CH_3$		62	65	4
$PhCHCH_2CS_2CH_3$ S $PhCHCH_2CS_2CH_3$		120-122	85	4
 $CH(CH_3)CH_2$	CH_3		80	65

Table 1. (*Continued*)

RCS₂R′ R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
 $CH(CH_3)CH_2$	CH_3		56	65
 $CH(CH_3)CH_2$	CH_3		80	65
$(CH_3)CH=CH$	CH_3		30	4
$(CH_3NH)(CH_3)C=CH$	CH_3	88,[109] 89[110]	65[110]	109, 110
$(PhCH_2CH_2NH)(CH_3)C=CH$	CH_3	75	22	109
(*cyclo*-C_6H_{11} NH)$(CH_3)C=CH$	CH_3	69	25	109
$(PhNH)(CH_3)C=CH$	CH_3	75,[109] 54[332]	25,[109] 40[332]	109, 332
i-C_3H_7	CH_3	67/23,[42] 75/35,[51] 65/13,[81] 58/12,[199] 61-62/10[268]	67,[3a] 42,[51] 70,[199] 58,[250] 80[268]	3a, 42, 51 81, 199, 250, 268
	CH_2CO_2H	48-49		274

i-C_3H_7	CH_2COPh	oil	38	134
	$CH_2C(NOH)C_6H_4Br$-4			17c
	$CH_2COC_6H_4Br$-4	38.5-40.2	46	134
	CH_2Cl	58-63/0.1	70	200
	C_2H_5	36-37/18	75	268
	CH_2CH_2Cl			200
	$CH{=}CH_2$	70/12	55	257
	C_3H_7-n	54/4	96	268
	C_3H_7-i	47-48/6[268]	85,[48] 10[268]	48, 268
	$(CH_2)_3Cl$	125-126/12	68	200
	$CH{=}CHCH_3$	87-89/17	71	48
	$CH_2CH{=}CH_2$	85-86/12[48]	85,[48] 90[268]	48, 268
	$CH_2C{\equiv}CH$	61-64/0.001	78	72
	C_4H_9-n	117-121/29-33	93	268
	C_4H_9-sec	60/4	88	268

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
i-C_3H_7	C_4H_9-t	73-75/4	20	209a
	$(CH_2)_4Cl$	144-146/12	70	200
	$CH_2C(CH_3)=CH_2$	65-68/0.1	83	48
	$CH=C(CH_3)_2$	100-102/17	61	48
	$CH_2C{\equiv}CCH_3$	66-69/0.001	85	72
	$C(CH_3)_2CH_2CH_3$			284
	$CH(CH_3)CH(CH_3)_2$			284
	$CH_2CH=C(CH_3)_2$			284
	$CH_2C(CH_3)=CHCH_3$			284
	$CH_2CH_2C(CH_3)=CH_2$			284
	$CH_2CH(CH_3)CH=CH_2$			284
	$C(CH_3)_2CH=CH_2$			284
	$CH(CH_3)C(CH_3)=CH_2$			284

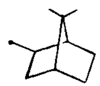
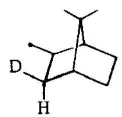
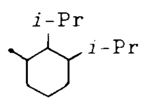
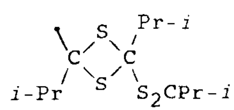
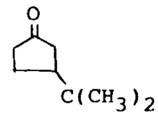
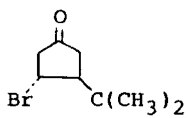
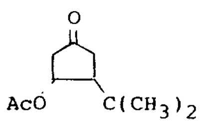
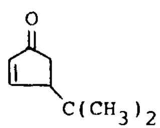
i-C_3H_7	$CH_2C{\equiv}CC_2H_5$	70-75/0.001	80	72
	C_6H_{13}-*n*			257
	$CH_2C{\equiv}CC(CH_3){=}CH_2$	93-95/0.001	81	72
	C(Pr-*i*)(Bu-*n*)-$CH_2CH_2CH{=}C$(Pr-*i*)(Pr-*n*)			284
	C(Pr-*i*)(Pr-*n*)-$CH_2CH_2CH_2C$(Pr-*i*)$=CHCH_2CH_3$			284
				284
				284
				284
		145-146.5[307]	29,[268] 12[307]	268, 307

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
i-C_3H_7	C_6H_5	83-85/0.8	31	209b
	$C_6H_4CH_3$-4	101-103/0.1	53	209b
	C_6H_4Cl-4	93-96/0.08	70	209b
$(CH_3)_2CD$	$CH_2C{\equiv}CCH_3$			71
	C_3H_7-i		70	320
	C_3H_7-i			320
	C_3H_7-i			320
	C_3H_7-i		60	320
$(CH_3CO)(CH_3)_2C$	CH_3	48/0.6	73	306

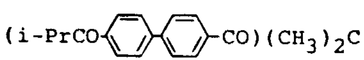
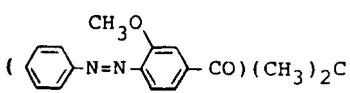
$(CH_3CO)(CH_3)_2C$	CH_2CO_2H	47-48, 134-138/0.6		296
	C_2H_5			90
	C_3H_7-i			90
(i-PrCO)$(CH_3)_2C$	CH_3	65/0.1	73	306
	CH_2CO_2H	78.5-80		296
(PhCO)$(CH_3)_2C$	CH_2CO_2H	137-138		296
(4-EtC_6H_4CO)$(CH_3)_2C$	CH_2CO_2H			296
(4-i-PrC_6H_4CO)$(CH_3)_2C$	CH_2CO_2H	145-146		296
(4-$CH_3OC_6H_4$CO)$(CH_3)_2C$	CH_2CO_2H	105.5-107		296
(4-ClC_6H_4CO)$(CH_3)_2C$	CH_2CO_2H	136-137.5		296
	CH_2CO_2H	82-95		296
	CH_2CO_2H	57-59		296

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$(EtO)_2P(O)(C_2H_5)(CH_3O_2C)C$-	CH_3	oil	52	304
$(HO)(CH_3)_2C$	CH_3			268
$Cl(CH_3)_2C$	CH_3			268
$Br(CH_3)_2C$	CH_3	78-80/0.1		90
$CH_3S_2C-(CH_2)_3-CS_2CH_3$		121/0.05		240
$(CF_3)_2CH$	CH_2Ph	65/0.3	92	214
	C_2H_5	62.6/23	88	214
	C_3H_7-i	62-64/23	85	214
	C_6H_5	37.5-38.5, 100/10	82	214

$(CF_3)_2CH$	C_6H_4Cl-4	34, 74-75/0.5	81	214
$O{=}C[C(CH_3)_2CS_2CH_3]_2$		132-133		268
$(CH_3)CH{=}CH$	CH_3	46-48/0.5,[201]	77,[3a] 95[201]	30, 201
$[(CH_3)_2N](CH_3)C{=}CH$	CH_3	93		110
(O N)$(CH_3)C{=}CH$	CH_3	78	85	110
O NCH=$C(CH_3)$	CH_3	102-104		263
$(HO)(CH_3)C{=}CH$	CH_3	oil	40	230
$(HS)(CH_3)C{=}CH$	CH_3			49
$(CH_3S)(CH_3)C{=}CH$	CH_3-(*E*)	55-57,[262] 106/0.2[49]	18,[49] 13.9[262]	49, 262
	CH_3-(*Z*)	67	75	19
n-C_4H_9	CH_3	84/12,[199] 68-69[268]	83,[199] 53,[248] 91[268]	199, 268, 248

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
n-C_4H_9	CH_2COPh	oil	82	309
	C_2H_5	90/9,[216] 52/10[268]	40,[216] 90[268]	216, 268
	C_3H_7-n	72/2	97	268
	C_3H_7-i	69/3	6	268
	$CH_2CH{=}CH_2$	63-64/2	94	268
	C_4H_9-n	89/4.5	97	268
	C_4H_9-sec	83/5		268
	C_4H_9-t	85-86/7	18	209a
$CH_3CH_2CH(CH_3)$	CH_3	76/12[199]	67,[3a] 48[199]	3a, 199
$(CH_3)_2CHCH_2$	CH_3	37-38/0.1,[83b] 80/50[274]	66[274]	83b, 274
	C_2H_5	88/9,[216] 76/11[235]	28,[216] 71[235]	216, 235
	$CH_2C(CH{=}CH_2){=}CH_2$	72-75/0.1		83b

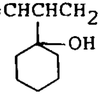
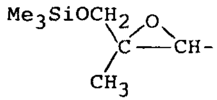
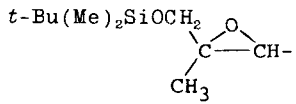
t-C_4H_9	CH_3	75-76/15,[42] 65/13,[81] 185/760,[83b] 74-75/20,[201] 65-65.5/12[274]	59,[3a] 65,[42] 70,[81] 63,[83b] 95,[201] 84,[248] 58,[250] 57,[272] 68[274]	3a, 42, 81, 83b, 201, 248, 250, 272, 274
	$CH(Ph)CO_2H$	140.5-142	70	276
	C_2H_5	185/760	63	83b
$CH_2=CHCH_2CH_2$	CH_3	43-45/1	80	63
	C_3H_7-i	38-40/0.6	81	63
$CH_2=CHCH(CH_3)$	CH_3		77,[3a] 86[52b]	3a, 52b
$CH_2=C(CH_3)CH_2$	CH_3		78,[3a] 47[52b]	3a, 52b
$CH_2=CHCHCH_2$ 	C_3H_7-i		2-10	310
$CH_3COCH_2CH(CH_3)CH_2$	CH_3		74	64
$CH_3COCH(CH_3)CH_2CH_2$	CH_3		73	64
$PhCOCH(CH_3)CH(Ph)CH_2$	CH_3		61	65

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
 $-CH(CH_3)CH(OH)CH_2$	C_2H_5		60	60
 $-CH(CH_3)CH(OH)CH_2$	C_2H_5		62	89
$CH_2=C=C(CH_3)CH_2$	C_2H_5	130/15	60	259
$CH_2=CHC(CH_3)_2$	CH_3		72,[3a,52b] 18[261]	3a, 52b, 261
$(CH_3)_2CHCH(OH)CH_2$	C_2H_5			88
$(CH_3)_2CHCH(OLi)CH_2$	C_2H_5			88
$(HO_2C)CH_2CH=CHCH_2$	CH_3		80	68
$CH_2=C(CO_2Et)CH_2CH_2$	C_2H_5			312
$(EtO)(CH_3)CHO\backslash CHCH_2$ / $i-C_3H_7$	C_2H_5			88

$(CH_3)_3CC(CH_3)(OH)CH_2$	CH_3		95	311
$CH_3COCH(CH_3)CH(CH_3)CH_2$	CH_3		61	65
t-$C_4H_9COCH(CH_3)CH(CH_3)CH_2$	CH_3		64	65
$PhCOCH(CH_3)CH(CH_3)CH_2$	CH_3		64	65
$(HO_2C)CH=C(CH_3)CH_2CH_2$	CH_3		84	68
$(CH_3NH)(t$-$Bu)C=CH$	CH_3	103-105	20	109
$(PhNH)(t$-$Bu)C=CH$	CH_3	90-92	10	109
$(HO)(CH_3)C=C(CH_3)$	CH_3	oil		230
$CH_3CH(OH)CH(CH_3)$	CH_3	90/0.8	65	315
$(CH_3)_2C(OH)CH(CH_3)$	CH_3	42	92	311
$(HO_2C)CH_2CH=CHCH(Ph)$	CH_3		63	68

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$CH_2{=}C(CO_2Et)C(CH_3)_2-$	CH_3			312
$CH_2{=}CHCH_2C(CO_2Et)_2-$	CH_3	120-126/0.1	63	254
$CH_2{=}CHCH_2C(CO_2Et)(CN)-$	CH_3	130-132/0.5	78	254
$HC{\equiv}CC(CH_3)_2-$	CH_3	80/18	80	318
$HC{\equiv}CC(Ph)(CH_3)-$	CH_3	102/0.001	95	318
$(CH_3)_2CHCH_2C[P(O)(OEt)_2](CO_2Et)-$	CH_3	100/0.001	26	301

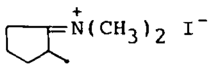
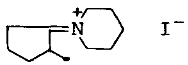
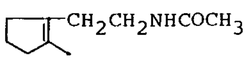
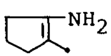
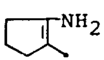
CS_2CH_3–$(CH_2)_4$–CO_2CH_3		94-96/0.1	68	194
$CS_2C_2H_5$–$(CH_2)_4$–$CO_2C_2H_5$		oil	trace	194
	$CS_2CH_2CO_2H$–$(CH_2)_4$–$CS_2CH_2CO_2H$	160-162		296
	$CS_2C_2H_5$–$(CH_2)_4$–$CO_2C_2H_5$	140/0.02	94	56
	$(CH_3)CHCS_2CH_3$–$(CH_3)CHCS_2CH_3$	32		73
	C_2H_5	106/9	48	216
n-C_5H_{11}				
	CH_3	oil	54	317
$Br(CH_2)_5$				
	CS_2CH_3–$(CH_2)_5$–CO_2CH_3	113-116/0.4		194
$CS_2C_2H_5$–$(CH_2)_5$–$CS_2C_2H_5$				240
$(Ph)_2C(OH)CH_2CH{=}CHCH_2$	CH_3	64-66	71	63

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$(Ph)_2C(OH)CH_2CH=CHCH_2$	C_3H_7-*i*	53-55	78	63
$(HO_2C)CH_2CH=CHCH_2CH_2$	CH_3		88	68
$(HO_2C)CH_2CH=CH$ \ CH / CH_3	CH_3		80	68
$(HO_2C)CH_2CH=C(CH_3)CH_2$ \ CH / Ph	CH_3		72	68
$CH_2=C(CO_2Et)CH_2$ \ CH / CH_3	CH_3			312
$CH_2=C(COPh)CH_2$ \ CH / CH_3	CH_3			312
$CH_2=C(COCH_3)CH(Ph)$ \ CH / CH_3	CH_3			312
CH_3 $CH_2=C(COPh)CH_2C$- CH_3	CH_3			312

CH_3 $(HO_2C)CH_2CH=CHC-$ CH_3	CH_3		75	68
EtO_2C $CH_3CH=CHCH_2C-$ EtO_2C	CH_3	130-132/0.5	78	254
EtO_2C $CH_3CH=CHCH_2C-$ NC	CH_3	152-154/0.2	54	254
EtO_2C $CH_3CH=CHCH_2C-$ NC	$CH_2CH=CHCH_3$		29	254
$CH_2=C=C(CH_3)$ CH CH_3	C_2H_5	70-72/0.6	80	259
CH_3 $CH_2=C=CHC-$ CH_3	C_2H_5	131/20	75	259
CH_3 C_2H_5C- $HC\equiv C$	CH_3	98/15	76	318
CH_3 $i\text{-}C_3H_7C-$ $HC\equiv C$	CH_3	75/0.4	86	318

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3			345
	CH_3			345
	CH_3	130-132	25	337
	CH_3	74-75,[336] 77-79[337]	63[337]	336, 337
	CH_2CO_2H	150-151		141
	CH_2NEt_2	97-99	70	337
	$CH_2CH_2CO_2CH_3$	71-72	77	338
	$CH=CHCO_2CH_3$-(*Z*)	240-241	82	338
	$CH_2CH_2COCH_3$	122-123	98	338
	CH_2CH_2CN	104-106	45	338

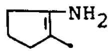
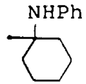
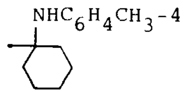
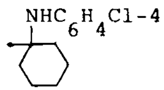
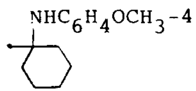
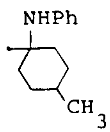
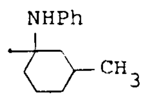
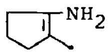
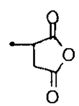
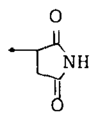
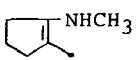
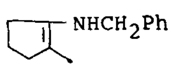
	$CH(CONH_2)CH_2CO_2H$	89	70	338
		111-114	71	339
		98-101	39	339
		98-100	37	339
		108-111	69	339
		119-120	36	339
		106-107	52	339
	$CH(CO_2H)CH_2CONH_2$	147-148	40	338

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	$CHCO_2Et$ CH_2CO_2Et	108-109	39 (from diethyl maleate)	338
	$CHCO_2Et$ CH_2CO_2Et	108-109	72 (from diethyl fumarate)	338
		136-137	93	338
		200-201		338
	$C_6H_3(NO_2)_2$-2,4	141 (dec)		336
	CH_3	143-144	69	337
	CH_2NEt_2	72	58	337
	CH_3	82-84	67	340

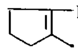
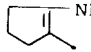
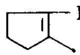
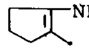
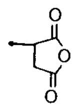
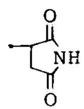
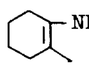
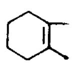
 NHEt	CH_3	96-97.5	47	337
 $NHCH_2CH_2NH_2$	CH_3	94-95	48.5	337
 NHPr-n	CH_3	84	70-80	341
 NHPr-i	CH_3	63-65,[337] 85[341]	67,[337] 70-80[341]	337, 341
 NHBu-*n*	CH_3	54-55,[340] 54[341]	70-80[341]	340, 341
 NHC_6H_{11}-*cyclo*	CH_3	84-86,[337] 82-83[341]	37,[337] 70-80[341]	337, 341
	$CH_2CH_2CO_2CH_3$	75-76	46	338
	$CH=CHCO_2CH_3$	130-131	39	338
	$CH_2CH_2CONH_2$	117-119	64	338

Table 1. (*Continued*)

RCS$_2$R′ R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
 NHC_6H_{11}-*cyclo*	$CHCO_2Et$ / CH_2CO_2Et	70-71	35 (from diethyl maleate) 55 (from diethyl fumarate)	338
	$CHCONH_2$ / CH_2CONH_2	267-268	64	338
		145-146	89	338
		203-204	99	338
 $NHCH_2]_2$	CH_3	210-213	9	337
 NHPr-*n*	CH_3	82-83	70-80	341
 NHPr-*i*	CH_3	99-100	70-80	341

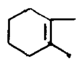
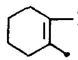
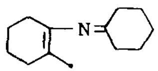
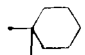
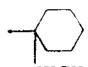
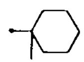
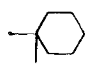
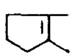
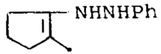
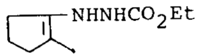
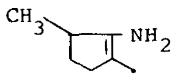
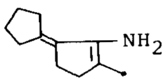
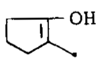
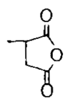
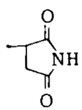
 NHC_6H_{11}-*cyclo*	CH_3	84-85	70-80	341
 NHPh	CH_3	82-86	15	334
	 NH_2	143-144		342
	 $NHCH_3$	204-205		342
	 NHPh	183-184		342
	 NHC_2H_5	201-202		342
 NHPh	CH_3	63-65	80	340

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3	139	33	340
	CH_3	110-111	42	340
	CH_2CO_2H	127		336
	CH_3	148		336
	CH_3	40-41,[230] 39[340]	57,[230] 18-20[340]	230, 340
	$CH=CHCO_2CH_3$	113-115		338
		198-200		338
		144-145		338

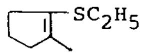
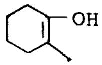
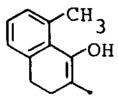
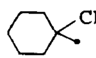
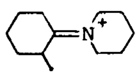
	C_2H_5			163
	CH_3	106/0.08	34	334
	CH_2CO_2H	145-146	31	343
	CH_3	76-77	24	23
n-C_6H_{13}	C_2H_5	115/12,[199] 121/9[216]	80,[199] 40[216]	199, 216
$CH_3(CH_2)_3C(CH_3)(OH)CH_2$	CH_3		9.5	311
HO_2C-$CH(CH_3)(CH_2)_4$	CH_3	109-111/0.4	54	194
$(HO_2C)CH_2CH=C(CH_3)CH_2CH(CH_3)$	CH_3		88	68
$(HO_2C)CH_2CH=C(CH_3)CH_2C(CH_3)_2$-	CH_3		50	68

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$(n\text{-}Bu)_2C{=}CH$	CH_3	94-96/0.6	80	201
$CH_2{=}CHCH_2$ \ CH / $CH_2{=}CH$	CH_3	oil	66	316
$CH_2{=}C(CH_3)CH_2$ \ CH / $CH_2{=}CH$	CH_3	oil	38	316
$CH_2{=}CHCH(CH_3)$ \ CH / $CH_2{=}CH$	CH_3	oil	56	316
$CH_2{=}C(CH_3)CH_2$ \ CH / $CH_2{=}C(CH_3)$	CH_3		80	316
$CH_2{=}CHCH(CH_3)$ \ CH / $CH_2{=}C(CH_3)$	CH_3		61	316
CH_3 $(CH_3)_2C{=}CHCH_2CCH_2$ OH	CH_3		92	311

$CH_2=CHC(CH_3)C(CH_3)(OH)CH_2$	CH_3		88	311
$CH_2=C=C(CH_3)CH(C_2H_5)$	C_2H_5	82-84/0.8	60	259
$CH_2=C=CHCH(i\text{-}C_3H_7)$	C_2H_5	131/20	75	259
$CH_2=C=C(CH_3)CH(i\text{-}C_3H_7)$	CH_3	138/15	71	259
$CH_2=C=CHCH(t\text{-}C_4H_9)$	CH_3	139/15	75	259
$CH_2=C=C(CH_3)CH(t\text{-}C_4H_9)$	CH_3	90-93/0.5	60	259
$(CH_3)_2CHCH_2C(CH_3)(C\equiv CH)-$	CH_3	51-52/0.3[318]	75,[314] 85[318]	314, 318

Table 1. (*Continued*)

RCS$_2$R′ R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
cyclo-C_6H_{11}	CH_3	105/1,[175] 128-130/18,[201] 90/3[217]	5,[175] 100,[201] 68[250]	175, 201, 217, 238, 250
	$CH_2COC_6H_4Br$-4	94-95.5	56	17a
	C_2H_5	oil		114
	$(CH_2)_3CO_2CH_3$	oil	60	287
	$CH(CH_3)CH_2CO_2CH_3$	oil	70	313
2-(HO)-*cyclo*-C_6H_{10}	CH_3	oil	27	315
 $CH=CHCH_2CO_2H$	CH_3		28	68
 I^-	CH_3		90	345
CS_2CH_3–$(CH_2)_6$–CS_2CH_3				326

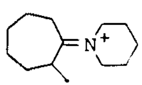
$CS_2C_{12}H_{25}$-*n* / $(CH_2)_6$ / $CS_2C_{12}H_{25}$-*n*		34-35	89	108
n-C_7H_{15}	CH_2CO_2H	58-59.5,[239] 55-56[296]	62[239]	239, 296
	C_2H_5	71/0.1,[141] 136/9[216]	44[141]	141, 216
	$(CH_2)_3CO_2H$	oil	60	287
$(HO_2C)CH_2CH{=}C(CH_3)CH_2C(CH_3)(CH{=}CH_2)$-	CH_3		78	68
$(HO_2C)CH_2CH{=}CHCH_2C(CH_3)(C{\equiv}CH)$-	CH_3		80	68
 I^-	CH_3		90	345
$CS_2CH_2CO_2H$ / $(CH_2)_8$ / $CS_2CH_2CO_2H$		135-136		296

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$CS_2C_2H_5$ $(CH_2)_8$ $CS_2C_2H_5$		oil		141
n-C_7H_{15} CH HO_2C	CH_3		88	193
n-C_7H_{15} CH CH_3O_2C	CH_3		85	193
n-C_9H_{19}	CH_3	90/0.3[193]	65,[193] 61[250]	193, 250
	CH_2CO_2H	64.5-66,[239] 58-59.5[296]	75[239]	239, 296
	C_2H_5			114
n-C_7H_{15} CH CH_3	CH_3	85/0.05	69	193
CH_3 n-C_7H_{15}C- HO_2C	CH_3		77	193

n-$C_{10}H_{21}$	CH_3			41
CH_2=$CH(CH_2)_7CH_2$	CH_3		52	250
$CS_2C_2H_5$ – $(CH_2)_{10}$ – $CS_2C_2H_5$		oil		114
$CS_2C_{12}H_{25}$-n – $(CH_2)_{10}$ – $CS_2C_{12}H_{25}$-n		41.5-42.5	83	108
n-$C_{11}H_{23}$	CH_2CO_2H	72-73,[239] 64.5-66[319]	65[239]	239, 319
	C_2H_5			114
n-$C_9H_{19}C(CH_3)(CO_2CH_3)$-	CH_3	117/0.04	75	193
n-$C_{12}H_{25}$	CH_2CO_2H	77.5-78.5	65	239
n-$C_{13}H_{27}$	CH_3		64	250
n-$C_{15}H_{31}$	CH_3		70	193
	CH_2CO_2H	80.5-81.5	69	239

Table 1. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	C_3H_7-*i*		69	250
n-$C_{14}H_{29}$CH(CO_2H) (HO_2C–CH–$C_{14}H_{29}$-n)	CH_3	67-72	84	193
n-$C_{17}H_{35}$	CH_2CO_2H	80.5-81.5		296

Table 2. Aromatic dithiocarboxylic acid esters

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
C_6H_5	CH_3	125-127.5/5.3,[43b] 141-142/12,[50] 149-150/17,[51] 140-142/12,[77] 110-112/130,[175] 145/12,[199] 120/13,[205] 113/1.2,[220] 86-93/0.2,[227] 105/1,[235] 118/3,[235] 146/15,[245] 97-98/6,[268] 280/760,[283,347] 154-157/22,[347] 76/0.2,[348] 90/0.6,[348] 99-101/0.4,[349] 83/0.3,[350] 75/0.25[351]	50,[43b] 69,[51] 40,[77] 11,[175] 85,[199] 79,[245] 89,[248] 57,[250] 91,[348] 71,[349] 48[351]	43b, 50, 51, 77, 175, 199, 205, 220, 227, 235, 245, 268, 283, 347, 348, 349, 350, 351
	CH_2Ph	55,[197] 159-160/0.3,[141] 156-157/0.2,[245]	81,[245] 99,[246] 24[350]	141, 197, 245, 246, 350, 353
	CH_2Ph	160/0.5,[246] 130/0.1,[350] 179-180/3[353]		
	$CH_2\overset{+}{P}Ph_3\ I^-$	174-178	46	74

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
C_6H_5	CH_2CO_2H	128,[117] 125-127,[192] 127-128,[198] 123-125,[235] 126-127,[274] 125[354]	51,[198] 82,[274] 41[354]	117, 192, 198, 235, 274, 354
	$CH_2CO_2CH_3$	118-119/0.6		141
	$CH_2C(NOH)CH_3$			17c
	$CH_2C(NOH)Ph$	99-101	86	17b
	CH_2COPh	78.5-79.5[17a]	59,[17a] 45[356]	17a, 355, 356
	$CH_2COC_6H_4CH_3$-4	109.5-111	37	17a
	$CH_2COC_6H_4OCH_3$-4	82.5-83.5	61	17a
	$CH_2COC_6H_4Cl$-4	88-89	53	17a
	$CH_2COC_6H_4Br$-4	89.5-91	48	17a
	CH_2CN	80		15b
	$CH_2Si(CH_3)_3$	54-55,[357] 95/0.1[253]	43[253]	253, 357

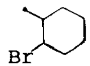
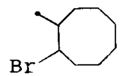
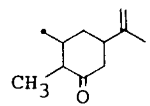
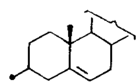
C_6H_5	$CH(CO_2CH_3)_2$			202
	$CH(Ph)CO_2H$	138.5-140		15f
	$CH(C_6H_4CH_3-4)CO_2H$		43	15f
	$CH(C_6H_4Cl-4)CO_2H$			358
	$CH(C_6H_4Br-4)CO_2H$	139-141	30	15f
	$CH(C_6H_4OCH_3-4)CO_2Bu$-*t*	oil	65	15f
	CH(Ph)CN	oil		15b
	CN	50-52		352
	C_2H_5	165-170/19,[7] 117/0.2,[42] 90/0.5,[141] 122-125/70,[196c] 164/12,[199] 150/12,[212,245] 155-160/15,[218] 98-99/0.1,[235] 112-114/4,[268] 158-162/10,[268] 153-154/13,[274] 154/14,[278] 165-168/19[347]	82,[199] 65,[212] 75,[234] 92,[245] 60[278]	7, 42, 142, 196c, 199, 212, 218, 235, 245, 268, 274, 278, 347
	$CH=CHC_6H_4NO_2-4$	135-138	45	74
	$CH(Ph)CH_3$			202

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
C_6H_5	$CH(Ph)CHCOCH_3$	90-91	69	269
	$CH(Ph)CHCOPh$	oil	59	269
	$CH_2CH_2CO_2H$	83.5-85		296
	$CH(CO_2H)CH_3$	87-87.5[358] oil[15f]	48-67[15f]	15f, 358
	$CH_2CH_2NHCSPh$	108.5-109		141
	$CH_2CH_2\overset{+}{N}H(CH_3)_2\ Cl^-$	162-163,[360] 160-161[361]	75[361]	360, 361
	$CH_2CH_2\overset{+}{N}H_3\ Br^-$	156-157	38	359
	$CH_2CH_2\overset{+}{N}(CH_3)_3\ Br^-$	188-189?	3	360
	$CH_2CH_2\overset{+}{N}(CH_3)_3\ I^-$	199-200	45	361
	$CH_2CH_2\overset{+}{P}Ph_3\ Br^-$		30	362
$C_6H_5CS_2$–$(CH_2)_2$–$C_6H_5CS_2$		103-105	55	43b

C_6H_5	C_3H_7-*n*	119/1.4,[141] 162/12[212]	68[212]	141, 212
	C_3H_7-*i*	90/0.2,[42] 88-89/0.2,[141] 164/12[212]	71[212]	42, 141, 212
	$(CH_2)_3CO_2H$	oil	28	287
	$(CH_2)_3CO_2CH_3$	oil	95	287
	$(CH_2)_3Br$	112-114,[231,268] 122-125/70[231]		231, 268
	$CH_2CH{=}CH_2$	96-97/0.6,[141] 118-120/0.4[268]		141, 268
	$CH(CH_3)CH_2CO_2H$	110-111		296
$C_6H_5CS_2-(CH_2)_3-C_6H_5CS_2$		oil	79	43b
C_6H_5	C_4H_9-*t*	105/0.5	97	246
$C_6H_5CS_2-(CH_2)_4-C_6H_5CS_2$		64-65	62	43b

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
C_6H_5	$C(CH_3)_2CH_2COCH_3$	130-135/7	58	268
		oil	16	268
		oil	18	268
		oil	10	268
		oil	56	269
				27
	C_6H_5	60-61,[141] 56-59,[192] 59-60,[218] 60-62,[235] 62,[245] 61,[246] 63-64,[362] 145-150/1[208]	75,[208] 60,[218,235] 59,[245] 90,[246] 33[362]	141, 192, 208, 218, 235, 245, 246, 362

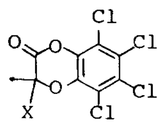
	$C_6H_4CH_3$-4	58-58.5	34	218
C_6H_5	$C_6H_2(CH_3)_3$-6,4,2	65-66	43	34
	$C_6H_3(OCH_3)_2$-3,2	oil	38	269
	$C_6H_3(NO_2)_2$-4,2	98-100	25	138
				
	X = H	161-162	50	358
	CH_3	153.5-154	14	358
	C_6H_5	164-165	88	358
	$C_6H_4OCH_3$-4	87-89	96	358
	C_6H_4Cl-4	160-162	83	358
	X = C_6H_4Br-4	166.5-167.5	72	358
	$C_6H_4NO_2$-4	167-169	63	358
2-$CH_3OC_6H_4$	CH_3	31,[347] 99-101/3[268]		268, 347

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
2-$CH_3OC_6H_4$	CH_2CO_2H	86-98	16	274
	CH_2COPh	85-91	66	17a
	C_2H_5	25-26		347
2-(*n*-C_3H_7O)C_6H_4	CH_2CO_2H	93-94	46	274
2-(*i*-C_3H_7O)C_6H_4	CH_2CO_2H	145-146	40	274
2-(*n*-C_4H_9O)C_6H_4	CH_2CO_2H	108-109	58	274
2-(*i*-C_4H_9O)C_6H_4	CH_2CO_2H	104-105	20	274
3-$CH_3OC_6H_4$	CH_3			268
3-$CH_3OC_6H_4$	C_3H_7-n	128-129/0.2		141
	$CH_2CH{=}CH_2$	141-142/6.5		141
4-$CH_3OC_6H_4$	CH_3	30.5-31,[42] 31,[347] 27-28,[349] 148/0.8[42]	26,[42] 77[349]	42, 347, 349
	$CH_2C_6H_4OCH_3$-2	82	90	287
	$CH_2C_6H_4COCH_3$-4	66-69	20	350

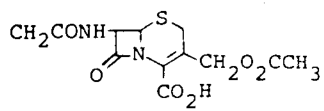
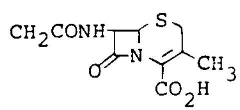
4-$CH_3OC_6H_4$	$CH_2C_6H_4CO_2H$-2	146	41	287
	$CH_2C(NOH)Ph$	117-118	91	17b
	CH_2COPh	122-123	95	17a
	$CH_2COC_6H_4CH_3$-4	116-117	84	268
	$CH_2COC_6H_4OCH_3$-4	127.5-128.5	93	268
	$CH_2COC_6H_4Br$-4	128-129	100	268
	CH_2CO_2H	121-122,[125] 124-125[274]	40,[125] 67[274]	125, 274
	$CH(Ph)CO_2H$	154-155.5	28-40	15f
		165-167		177
		187-190		177

Table 2. (*Continued*)

RCS_2R' R	R'	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$4\text{-}CH_3OC_6H_4$	$CH_2\overset{+}{P}Ph_3\ I^-$	202–205	63	74
	C_2H_5	20–21,[75] 22–25,[235] 22–26,[347] 120–121/0.2,[141] 143–145/0.2,[235] 162–164/4,[268] 158–164/4[349]	81,[75] 75,[235] 78[349]	75, 141, 235, 268, 347, 349
	$CH_2CH_2\overset{+}{N}HEt_2\ Cl^-$	194–194.5	79	361
	$CH_2CH_2\overset{+}{N}HEt_2\ I^-$	198–198.5	74	361
	$CH_2CH_2\overset{+}{P}Ph_3\ Br^-$	131–135	39	74
	CH=CHPh	49–50[74,75]	39[74,75]	74, 75
	$CH{=}CHC_6H_4NO_2\text{-}4$	166–168[74,75]	56[74,75]	74, 75
	$C_3H_7\text{-}n$	128–129/0.2		141
	$(CH_2)_3CO_2H$	90	28	287

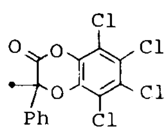
4-$CH_3OC_6H_4$	$(CH_2)_3CO_2CH_3$	oil	54	287
	$(CH_2)_3COCH_3$		54	349
	$CH_2CH=CH_2$	141-142/0.5		141
	$CH=CHCH_3$	oil	65	75
	C_4H_9-*n*	168-172/0.5	56	268
	C_4H_9-*t*	37.5-39.5[75]	51,[75] 66[209b]	75, 209b
	$CH=CHCH_2CH_3$	oil	28	75
	CH=CH-CH=CHPh	95-97	46	75
	$CH=CH-CH=CHC_6H_4NO_2$-2	96-100[74,75]	94[74,75]	74, 75
	$CH=CH-CH=CHC_6H_4NO_2$-4	192-194[74,75]	88[74,75]	74, 75
4-$CH_3OC_6H_4$	C_6H_5	79.5-83,[75] 83[218]	46,[75] 89[218]	75, 218
		130-131.5	93	358

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
4-(*n*-BuO)C_6H_4	CH_3	38-38.5	63	274
	CH_2CO_2H	104-105	20	274
2,4-$(CH_3O)_2C_6H_3$	C_6H_5	89.5-90.5	73	218
2-CH_3O,4-HOC_6H_3	CH_3	126.5-128	38	363
	CH_2CO_2Et	106-107	18	363
3,4-$(CH_3O)_2C_6H_3$	CH_3	65-66	40	351
2-$CH_3C_6H_4$	CH_3	116/2[42,157]	66[42]	42, 157
	CH_2Ph	168/0.3	25	327
	$CH_2C(NOH)Ph$			17c
	CH_2CO_2H	122-124	46	248
	CN	oil		352
	C_2H_5	90/0.4	30	327
	C_6H_5			270

$3\text{-}CH_3C_6H_4$	CH_3	111/1.3[42,157]	28,[42] 67[349]	42, 157, 349
	CH_2CO_2H	122-124	46	274
	$C_4H_9\text{-}n$	159-163/5	50	349
$4\text{-}CH_3C_6H_4$	CH_3	126-127,[42] 130/3,[102] 116-118/4[268]	41,[42] 60[349]	42, 102, 268, 349
	$CH_2C_6H_4NO_2\text{-}4$	70.5		102
	CH_2CO_2H	117-118,[125] 118-119[274]	43,[125] 34[274]	125, 274
	$CH(Ph)CO_2H$	165.5-167.5	33-35	15f
	$CH_2C(NOH)Ph$	122-124	86	17b
	CH_2COPh	108-109	98	17a
	$CH_2COC_6H_4CH_3\text{-}4$	123-125	64	17a
	$CH_2COC_6H_4OCH_3\text{-}4$	124-126	57	17a
	$CH_2COC_6H_4Cl\text{-}4$	109.5-111.5	58	17a
	$CH_2COC_6H_4Br\text{-}4$	117-118	61	17a
	$CH_2\overset{+}{P}Ph_3\ I^-$	179-182	72	74

Table 2. (*Continued*)

RCS_2R' R	R'	mp [°C] bp [°C/torr]	Yield [%]	Ref.
4-$CH_3C_6H_4$	C_2H_5	132/3,[102] 114/12,[212] 111-114/4,[268] 132-134/4,[269] 160-165/85[277]	67,[75] 60[212]	75, 102, 212, 268, 269, 277
	$CH_2CH_2\overset{+}{N}H(CH_3)_2$ citrate$^-$	120.5-130	55	361
	$CH_2CH_2\overset{+}{P}Ph_3$ Br^-	120-124	45	268
	CH=CHPh	50-51	75	74
	CH=CH$C_6H_4CH_3$-4	110-114	74	74
	CH=CH$C_6H_4NO_2$-4	122-128	89	74
	CH=CH-CH=CHPh	143-146	76	74
	$CH_2CH=CH_2$	121-123/0.4	60	268
	$(CH_2)_3PPh_3$ ClO_4^-	58-60	63	268
	C_4H_9-*n*	196/3,[102] 158-164/4[349]		102, 349

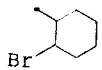
	C_4H_9-*t*	83-86/0.05	52	209b
		oil	15	268
	C_6H_5	83-84	95	218
2,4-$(CH_3)_2C_6H_3$	C_6H_5	44-46	60	218
2,6-$(CH_3)_2C_6H_3$	CH_3	47, 86-87/0.2	26	327
	CN	54-55		352
2-CH_3-6-(*i*-C_3H_7)C_6H_3	CH_3	167-168/8		304
	C_2H_5	141-142/3		34
2,4,6-$(CH_3)_3C_6H_2$	CH_3	20-30, 96-97/0.25	77	227
	CN	solid		352
	C_2H_5	45.5-47.5	86	34
	C_6H_5	93-94.5	75	218
	$C_6H_2(CH_3)_3$-6,4,2	142-143	90	34

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
2,4,6-$(CH_3)_3C_6H_2$	$C_{10}H_7$-1	137-139	86	34
3,5-$(CH_3)_2$-4-$(CH_3O)C_6H_2$	C_6H_5	oil	77	34
3,5-$(CH_3)_2$-4-$HOC_6H_2CH_2CONH_2$	CH_3	109	96	161
2-CH_3-4-(i-C_3H_7)C_6H_3	CH_3			152
3,5-$(CH_3)_2$-4-HOC_6H_2	CH_2CONH_2	142-143	63	161
2,6-$(CH_3)_2$-3-(*i*-C_3H_7)-4-$CH_3OC_6H_4C_2H_5$	C_2H_5	119-120	25	34
	$C_6H_2(CH_3)_3$-6,4,2	161-163	45	34
	$C_{10}H_7$-1	121-122	25	34
4-$CF_3C_6H_4$	CH_3	98/0.9	31	42
4-$C_2H_5C_6H_4$	CH_3	141/7.4	59	42
4-CH_2=CHC_6H_4	CH_3			46
	4-CH_2=CHC_6H_4-$^{13}CS_2CD_3$	36-38	22	365
	4-(*t*-C_4H_9)$C_6H_4C^{33}S_2CD_3$	37-38	15	365

4-(*t*-C_4H_9)$C_6H_4C^{33}S_2CH_2CO_2H$		119-122	37	365
4-(*t*-C_4H_9)$C_6H_4CS_2C_6H_5$				270
2,4,6-(*t*-Bu)$_3C_6H_2$	CD_3	107-108	50	365
2,6-(*t*-Bu)$_2$,4-HOC_6H_2	CH_2Ph	120-121.5	57	363
	CH_2CO_2Et	101-102	61	363
2-HOC_6H_4	CH_3	61,[7] 10-20[347]		7, 347
	CH_2CO_2H	124-125	16	274
	$CH(Ph)CO_2H$	134-138		14
	$CH_2COC_6H_4Br$-4	122-123		361
	C_2H_5	oil		347
	$CH_2CH_2\overset{+}{N}H(CH_3)_2$ citrate$^-$	147-148		361
	$CH_2CH_2\overset{+}{N}(CH_3)_3\ I^-$	187.5	65	361
4-HOC_6H_4	CH_3	60-61	60	218
	CH_2CO_2H	194-197	32	274

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
4-HOC_6H_4	C_2H_5	57		7
	$CH_2CH_2\overset{+}{N}H(CH_3)_2\ Cl^-$	157-158.5		361
	$CH_2CH_2\overset{+}{N}(CH_3)_3\ I^-$	194-195	55	361
	C_6H_5	92.5-93	68	218
2,4-$(HO)_2C_6H_3$	CH_3	96	88	161
2-HO-4-$CH_3OC_6H_3$	CH_3	60	33	161
3-HO,4-$CH_3OC_6H_3$	$CH_2C_6H_4Br$-4	131-132		361
	$CH_2CH_2\overset{+}{N}(CH_3)_3\ I^-$	172-173	55	361
2-FC_6H_4	C_6H_5			270
3-FC_6H_4	C_6H_5			270
4-FC_6H_4	CH_3	106.5/1.2	62	42
	CH_2CO_2H			239
	C_6H_5			270

$2\text{-}ClC_6H_4$	CH_3	184-186/0.5	25	268
	$CH_2CH_2\overset{+}{N}H(CH_3)_2\ Cl^-$	171-172	76	361
	$CH_2CH_2\overset{+}{N}(CH_3)_3\ I^-$	158-159	80	361
	C_6H_5			270
$3\text{-}ClC_6H_4$	CH_3	105-107/0.4		268
	CH_2CO_2H	124-126	95	274
	$C_4H_9\text{-}n$	126-129/0.3	54	268
	C_6H_5			270
$4\text{-}ClC_6H_4$	CH_3	133-135,[42] 120-122,[269] 118-122,[349] 72/0.25[351]	64,[42] 55,[349] 87.9[351]	42, 269, 349, 351
	$CH_2C_6H_4Cl\text{-}4$	49-51	28	350
	CH_2CO_2H	117.5-118.5,[125] 115-117,[274] 118-120[366]	82,[274] 36-45[366]	125, 274, 366
	$CH_2C(NOH)CH_3$			17c
	$CH_2C(NOH)Ph$	98-100	74	17b

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
4-ClC_6H_4	CH_2COPh	117-120	97	17a
	$CH_2COC_6H_4OCH_3$-4	138-140	81	17a
	$CH_2COC_6H_4CH_3$-4	104.5-106	53	17a
	$CH_2COC_6H_4Cl$-4	119-120	54	17a
	$CH_2COC_6H_4Br$-4	109-110	65	17a
	$CH_2\overset{+}{P}Ph_3\ I^-$	171-175	39	74
	C_2H_5	31-32,[141] 102-104/0.1[141]	88[268]	141, 268
	$CH_2CH_2\overset{+}{N}H(CH_3)_2$ citrate$^-$	140.5-141.5		361
	$CH_2CH_2\overset{+}{N}(CH_3)_3\ I^-$	209.5-210	60	361
	$CH_2CH_2\overset{+}{P}Ph_3\ Br^-$		38	268
4-ClC_6H_4	$CH{=}CHC_6H_4NO_2$-4	139-141	13	268
	C_3H_7-n	113-115/0.1		141

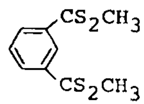
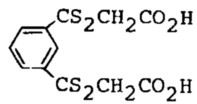
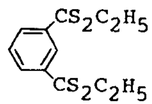
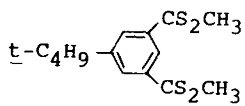
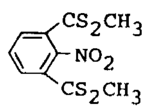
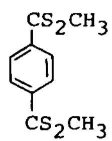
	$CH_2CH{=}CH_2$	129-132/0.5	53	268
	C_4H_9-n	145-150/0.5	53	268
	C_4H_9-t	oil	25	209b
	C_6H_5	97-98.5	43	218
2-BrC_6H_4	C_6H_5			270
4-BrC_6H_4	CH_3	53-54,[42] 164-165/3[269]	38[42]	42, 269
	$CH_2C_6H_4Br$-4	61-63	40	350
	$CH(Ph)CO_2H$	169-171.5	75	155
	C_6H_5	73	40	218
4-IC_6H_4	CH_3	81.5	66	42
2-$NO_2C_6H_4$	C_6H_5			270
3-$NO_2C_6H_4$	CH_3	68	36	327
	CH_2CC_2H	145-147,[274] 112-114[296]	71[274]	274, 296

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$3\text{-}NO_2C_6H_4$	C_2H_5	52.5-53.5, 140/0.2		141
	$CH_2CH{=}CH_2$	137-138/0.2		141
$4\text{-}NO_2C_6H_4$	CH_3		56	248
	$CH_2C_6H_4NO_2\text{-}4$	109-111	9	350
	$CH(Ph)CO_2H$	oil	55	15f
	C_2H_5	150-153/0.3	94	124
	$CH_2CH_2CO_2H$	113-114	89	239
	C_6H_5			270
$4\text{-}(NC)C_6H_4$	CH_3			270
$2\text{-}(Ph)C_6H_4$	CH_2CO_2H	109	36	176
$4\text{-}(Ph)C_6H_4$	CH_2CO_2H	123-124	36	218
$3\text{-}(EtO_2C)C_6H_4$	C_2H_5	200</0.1	30	367
$4\text{-}(CH_3O_2C)C_6H_4$	CH_3	90,[42] 89-90[367]	84,[42] 30[367]	42, 367

4-$NH_2C_6H_4$	$CH_2COC_6H_4Br$-4	175		361
	$CH_2CH_2\overset{+}{N}H_3$ citrate$^-$	162-162.5		361
4-[$(CH_3)_2N$]C_6H_4	CH_3	132	91	42
4-$(CH_3)_2NC_6H_4$	$CH(Ph)CO_2H$	171-173	51	15f
	$CH_2CH_2\overset{+}{N}H(CH_3)_2$ Cl^-	226		361
	$CH_2CH_2\overset{+}{N}(CH_3)_3$ I^-	202-203	56	361
4-$(CH_3CONH)C_6H_4$	CH_2CO_2H	206-208	94	274
	C_2H_5	127-128		141
	$CH_2CH{=}CH_2$	oil		141
4-$(PhN{=}N)C_6H_4$	CH_2CO_2H	158-158.5	71	239
	C_2H_5	58-59		141
4-$(PhCO_2)C_6H_4$	C_2H_5	80		7
4-(4-$NO_2C_6H_4CO_2)C_6H_4$	CH_3	119		7

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
				114
		184-185		296
		174-175/0.1,[141] 170</0.1[367]		141, 367
		170</0.1	36	367
		138-139	71	18
		134-135,[351] 133-135[367]	41.7,[351]	351, 367

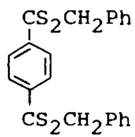
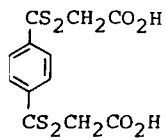
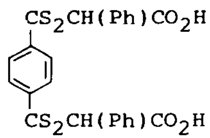
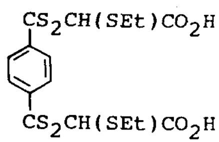
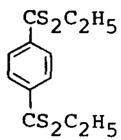
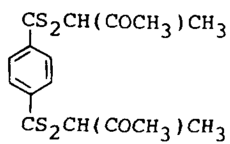
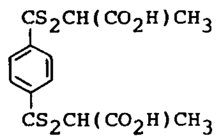
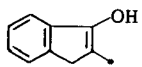
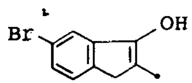
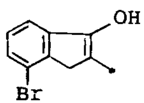
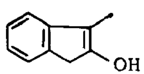
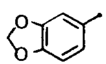
	148-150	84	12
	212-214	58	296
	169-171	63	280
	oil	47	280
			114
	90-91	65	13

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
		183-184	65	280
$1\text{-}C_{10}H_7$	CH_3	54,[42,50] 49.5-53,[218] 55,[368] 210/15[50]	58[42]	42, 50, 218, 368
	CH_2Ph	180-184/0.1		141
	CH_2COPh	78.5-80.5	68	17a
	CH_2CO_2H	142-144	54	274
	$CH_2\overset{+}{P}Ph_3\ I^-$	118-121	96	268
	C_2H_5	39-40,[50] 37-38.5[141]	43,[50] 33-35[218]	50, 141, 218
	$(CH_2)_3CO_2H$	96		287
	$(CH_2)_3\overset{+}{P}Ph_3\ Br^-$		72	268
	$CH_2CH{=}CH_2$	141-142/0.2		141

1-$C_{10}H_7$	$(CH_2)_3CO_2H$	96		287
	C_6H_5	111-112	41	249
2-HO-1-$C_{10}H_6$	CH_3	86[363]	42[161]	161, 363
	CH_2CO_2Et	117-118.5	25	363
4-HO-1-$C_{10}H_6$	CH_3	119-114	19	363
	$CH_2CO_2CH_3$	118.5-119.5	27	363
2,4-$(HO)_2$-1-$C_{10}H_5$	CH_2CONH_2	169	68	161
2-CH_3O-1-$C_{10}H_6$	CH_3	110-111	60	161
4-CH_3O-1-$C_{10}H_6$	CH_3	87	30	161
2-$C_{10}H_7$	CH_3	88-89,[77] 91.5[152]	25[77]	77, 152
	CH_2CO_2H	145-147,[139] 147-148[274]	15[274]	139, 274
	$CH(Ph)CO_2H$	115	35	287
	C_2H_5	200-205/45		277
	$(CH_2)_3CO_2H$	101	22	287

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
1-HO-2-$C_{10}H_6$	CH_3	75-77,[363] 77[369]	12[363]	363, 369
	CH_2CO_2Et	69-70.5	4	363
	CH_3	138-140		369
	CH_3	192		369
	CH_3	148		369
	CH_3	92	77	369
	CH_3	77-79	42	364
	$CH_2CH_2\overset{+}{N}H(CH_3)_2\ Cl^-$	189-190		361

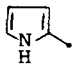
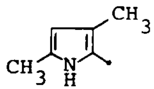
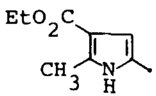
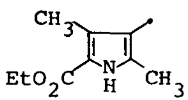
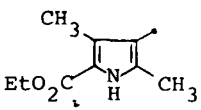
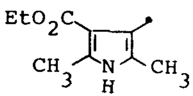
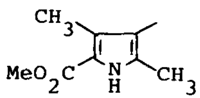
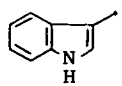
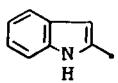
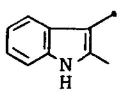
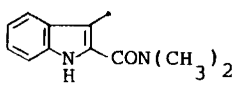
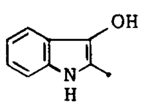
	CH_3	oil		370
	CH_2CO_2H	140-141	21	274
	C_2H_5	119-120/64,[221] 162-164/3[371]	24[371]	221, 371
	CH_3	45-46		370
	C_2H_5	92-94		370
	CH_3	131-133		370
	C_2H_5	96-97,[372] 150/1[370]		370, 372
	CH_3	142-143		370
	CH_3	131-134		370
	C_2H_5	110-112		370
	CH_3	152-153	16	370

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3	142–143		370
	CH_3	63–65		112
	CH_2CO_2H	163–166	22	274
	CH_3	209–210	65	373
	CH_3	167–168	90	373
	CH_3	185		166

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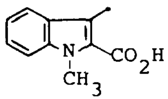
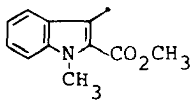
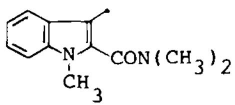
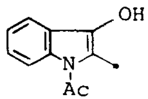
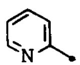
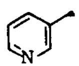
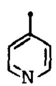
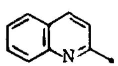
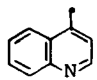
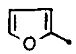
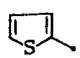
	CH_3	200	75	373
	CH_3	105	45	373
	CH_3	66-68	75	373
	CH_3	151	35	166
	CH_3	51	2	283
	CH_3	oil	1	283
	CH_3	oil	1	283
	C_2H_5			285

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	C_2H_5		72.2	285
	CH_3			305
	CH_2CO_2H	132-133	21	274
	C_2H_5	72-73/0.1,[141] 89-90/0.1[218]		141, 218
	C_3H_7-*n*	78-79/0.1		141
	$CH_2CH{=}CH_2$	81-82/0.2		141
	C_6H_5	65-70/0.3,[249] 85/1[305]	37,[249] 75[305]	249, 305
	CH_3	120/1,[42] 94-99/0.6,[77] 158/12[199]	50,[42] 80,[77] 68[199]	42, 77, 199
	CH_2CO_2H	123-124	46	274

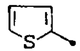
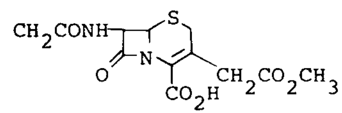
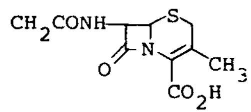
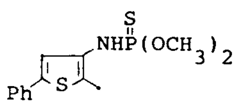
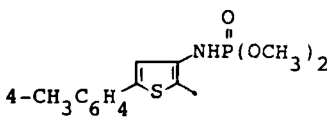
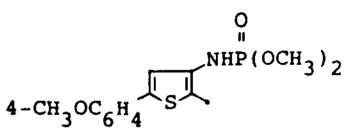
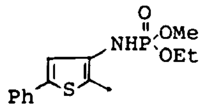
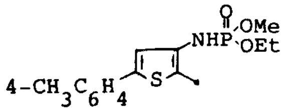
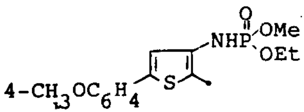
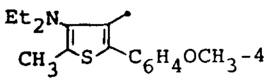
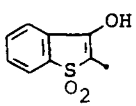
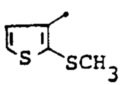
		120-135		177
		190-193		177
	C_6H_5	oil	84	218
	CH_3	94	40-70	374
	CH_3	118		374
	CH_3	104		374

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3	88		374
	CH_3	82		374
	CH_3	102		374
	C_2H_5	76		374
	CH_3	126	6	375
	CH_3	207	80	167
	CH_3	120[26a,b]	14,[26a] 80[26b]	26a, 26b

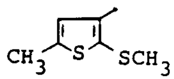
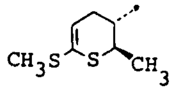
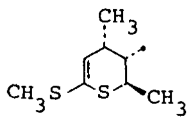
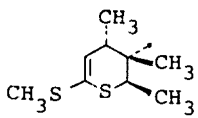
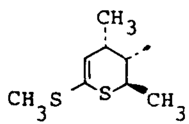
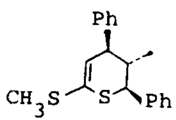
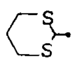
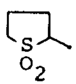
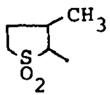
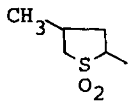
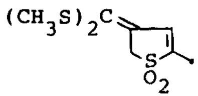
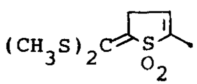
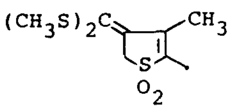
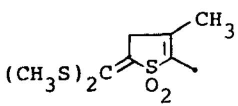
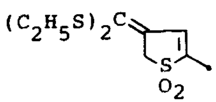
	CH_3	92,[26a] 93[26b]	68,[26a] 70[26b]	26a, 26b
	CH_3			3b
	CH_3		15	3b
	CH_3			3b
	CH_3	71	66	4
	CH_3	52	79	4
	CH_3	125	85	309
	CH_3	93	40	225

Table 2. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3	107	15	225
	CH_3	72	17	225
	CH_3	169	8	225
	CH_3	120	25	225
	CH_3	150	2	225
	CH_3	104	25	225
	C_2H_5	70	7	225

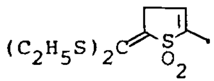
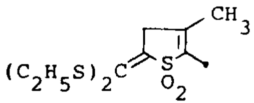
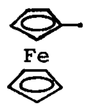
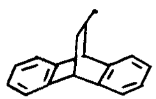
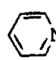
	C_2H_5	69	30	225
	C_2H_5	59	15	225

Table 3. Dithiocarboxylic acid esters (miscellaneous)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_2Ph	67-68	10	376
	COC_6H_4Br-4	140-150	87	376
	CH_2CO_2H	100-101	16	376
	CONHPh	101-103	84	376
	CH_3			3b
C_6H_5CO	CH_3	32-33, 135-137/0.6	60	321
4-$CH_3OC_6H_4CO$	CH_3	26-28	43	321
3,4-$(HO)_2C_6H_3CO$	CH_3	145.5-145	70	321
4-ClC_6H_4CO	CH_3	31-32	52	321
4-BrC_6H_4CO	CH_3	40-42	60	321
4-PhC_6H_4CO	CH_3	87-88	40	321

2-$C_{10}H_7CO$	CH_3	100-101	69	321
NH_2CO	CH_3	104-105	60	322
	CH_2Ph	100-102	48	322
	C_2H_5	76-77.5	58	322
cyclo-$C_6H_{11}NHCO$	CH_3			322
PhNHCO	CH_3	78-79.5	55	322
	CH_2Ph	80-82	36	322
4-$CH_3C_6H_4NHCO$	CH_3			322
4-$CH_3OC_6H_4NHCO$	CH_3			322
1-$C_{10}H_7NHCO$	CH_3	123-124.5	46	322
2-$C_{10}H_7NHCO$	CH_3			322
Ph(CH_3)NCO	CH_3	133/0.1	58	322
	CH_2Ph	liq.	55	322
Ph_2NCO	CH_3			322
4-(Ph-N=N-)C_6H_4NHCO	CH_3			322

Table 3. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
EtO_2C	CH_3	73/0.7	50	323
	C_2H_5	74/0.8	52	323
$CH_3OC(=S)$	CH_3 (trans)	42-43	95	324
CH_3S_2C	CH_3 (cis)	71-72,[45] 71.5,[325] 210/0.1[325]	60[326]	45, 325, 326
CH_3S_2C	CH_3 (cis)	101.5		325
EtS_2C	C_2H_5	90-93/42		325
 $\overset{+}{N}$-$\overset{-}{C}HCS_2CH_3$				107
$Ph_3\overset{+}{P}$-$\overset{-}{C}(CN)CS_2CH_3$		240-241	99	222
$Ph_3\overset{+}{P}$-$\overset{-}{C}(CN)CS_2C_2H_5$		206-207	98	222
$Ph_3\overset{+}{P}$-$\overset{-}{C}(C_6H_4NO_2$-$4)CS_2C_2H_5$		285-286	18	299
$(CH_3)_2\overset{+}{S}$-$\overset{-}{C}(Ph)CS_2CH_2Ph$		121	82	162

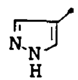
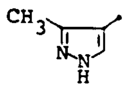
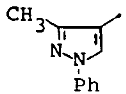
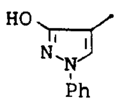
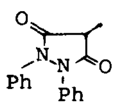
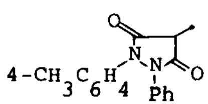
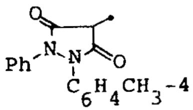
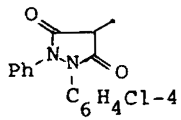
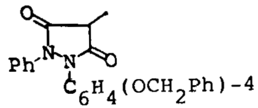
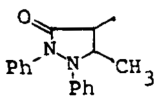
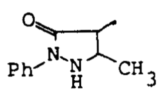
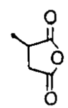
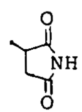
	$(CH_3)_2\overset{+}{S}-\overset{-}{C}(CS_2CH_2COPh)(CO_2Et)$	85-85.5	75	162
	C_2H_5	184-185		377
	C_2H_5	186	40	377
	C_2H_5	81-82	20	377
	C_2H_5	114		377
	CH_3	155-157,[378] 152-154[379]		378, 379
	C_2H_5	150-152		379
	CH_3	184		380
	C_2H_5	168-170		379

Table 3. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3	184		380
	CH_3	186-188		380
	CH_3	140		380
	$CH=CHCO_2CH_3$ (*cis*)	170	80	338
	$CH=CHCO_2CH_3$ (*trans*)	156-158		338
		181-182	84	338
		186-189	93	338

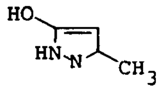
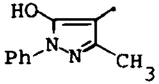
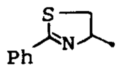
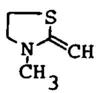
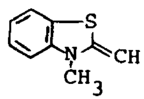
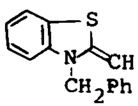
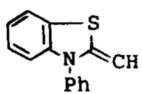
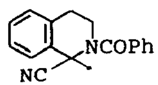
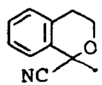
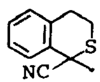
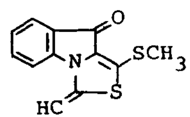
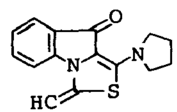
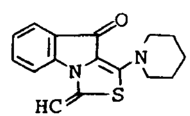
	CH_3	196-198		379
	C_2H_5	185-186		379
	CH_3	97-98		379
	C_2H_5	86-87		379
	C_2H_5			251
	CH_3			149
	CH_3	187[223]	60[223]	149, 223
	CH_3			149
	CH_2CO_2H	198	81.6	16

Table 3. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3	174–176	99	381
	CH_2Ph	139–141	99	381
	CH_3	123–125	80	104
	CH_3	86–87	44	104
	CH_3	265	13	166
	CH_3	228	50–60	166
	CH_3	237	50–60	166

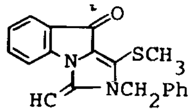
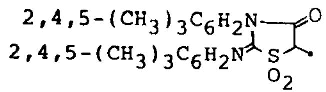
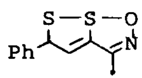
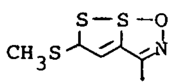
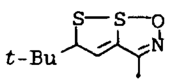
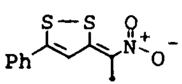
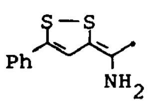
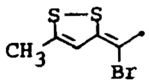
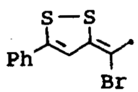
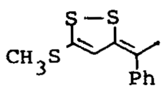
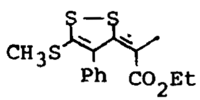
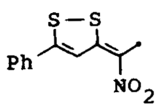
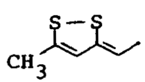
	CH_3	248	57	166
	CH_3			226
	CH_3	138-140[382]		164, 382, 383, 384
	CH_3	100-101[382]		382, 383, 384
	CH_3	124.5-125	40	291
	CH_3		164	
	CH_3		40	

Table 3. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
	CH_3	95-96		6
	CH_3	135-136		6
	CH_3	138.5-140[170] 138[385]		170, 385
	CH_3	150-152		170
	CH_3			40, 164
	CH_3	139-140		6

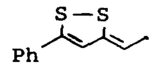
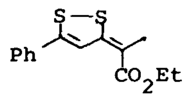
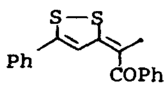
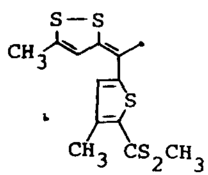
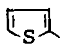
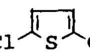
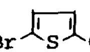
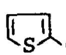
	CH_3	125-126[6,170]	6, 170
	CH_3	112-113[6,170]	6, 170
	CH_3	163-164,[6] 163[170]	6, 170
	CH_3		40, 386
$(CH_3COCHCS_2CH_3)_2Cu$		152	196b
$(C_6H_5COCHCS_2CH_3)_2Cu$		203	196b
$(4\text{-}CH_3OC_6H_4COCHCS_2CH_3)_2Cu$		213	196b
$(4\text{-}CH_3C_6H_4COCHCS_2CH_3)_2Cu$		165	196b

Table 3. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$(4\text{-}ClC_6H_4COCHCS_2CH_3)_2Cu$		210		196b
( $COCHCS_2CH_3)_2Cu$		193		196b
(Cl  $COCHCS_2CH_3)_2Cu$		192		196b
(Br  $COCHCS_2CH_3)_2Cu$		168		196b
$(CH_3COCHCS_2CH_3)_2Zn$		210		196b
$(C_6H_5COCHCS_2CH_3)_2Zn$		206		196b
$(4\text{-}CH_3OC_6H_4COCHCS_2CH_3)_2Zn$		210		196b
$(4\text{-}CH_3C_6H_4COCHCS_2CH_3)_2Zn$		228		196b
$(4\text{-}ClC_6H_4COCHCS_2CH_3)_2Zn$		252		196b
( $COCHCS_2CH_3)_2Zn$		262		196b

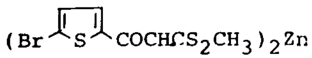
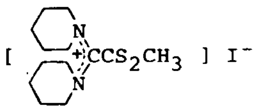
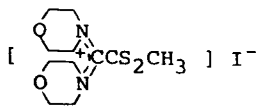
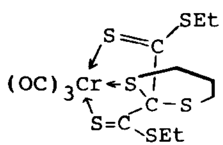
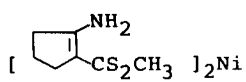
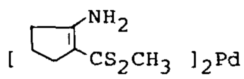
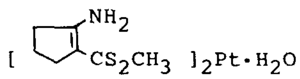
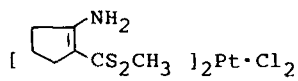
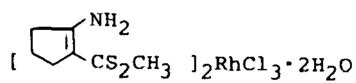
	264		196b
	272		196b
			387
			387
	150	24	388
$(i\text{-}C_3H_7CS_2)[(OC)_3Fe]_2$			173
$\overline{Ph}CH_2CS_2CH_3$ / Fe^+Cp			364
$PhCH(CH_3)CS_2CH_3$ / Fe^+Cp		40	364

Table 3. (*Continued*)

RCS_2R' R	R′	mp [°C] bp [°C/torr]	Yield [%]	Ref.
$PhC(CH_3)_2CS_2CH_3$ (Fe⁺Cp attached to Ph)			65	364
$(CH_3COCHCS_2CH_3)_3Co$		136		196b
$(C_6H_5COCHCS_2CH_3)_3Co$		236		196b
$(4\text{-}CH_3OC_6H_4COCHCS_2CH_3)_3Co$		195		196b
$(4\text{-}CH_3C_6H_4COCHCS_2CH_3)_3Co$		174		196b
$(4\text{-}ClC_6H_4COCHCS_2CH_3)_3Co$		160		196b
				196b
		255		196b
		258		196b
			99	349

	80	349
	70	349
	70	349
	70	349

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