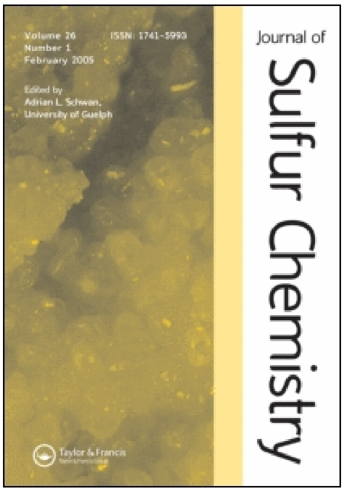

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The Formation of Heterocyclic Compounds from Carbon Disulfide

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THE FORMATION OF HETEROCYCLIC COMPOUNDS FROM CARBON DISULFIDE

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Carbon disulfide has been readily available since the earliest days of organic chemistry and has proved to be a versatile building block for construction of a wide variety of heterocyclic compounds. In this review we have aimed to present the most important examples of reactions in which a heterocycle is formed either from CS_2 or from a readily formed adduct such as a xanthate, dithiocarbamate, trithiocarbonate or trialkylphosphine adduct. The material is ordered so that the heterocyclic products appear in order of: (i) increasing ring size, (ii) increasing number of heteroatoms and, (iii) decreasing priority of heteroatoms.

Keywords: Carbon disulfide, heterocycles, synthesis

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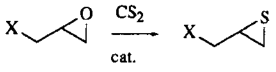
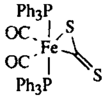
1. FORMATION OF THREE-MEMBERED RINGS

Treatment of some simple epoxides with CS_2 and a catalyst results in formation of the corresponding thiiranes.[1] Thus both epichlorohydrin and propylene oxide can be converted into the thiiranes **1** by CS_2 and triethylamine at 100 °C,[2] and the latter transformation has also been reported in the presence of other catalysts.[3]



1 X = Cl, H



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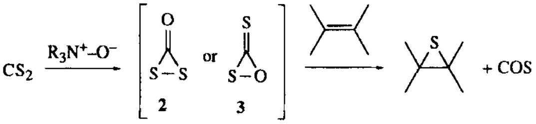
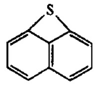


Various tertiary amine *N*-oxides react with CS_2 by transfer of oxygen to give an intermediate which may be either the dithiiranone **2** or the oxathiiranethione **3**. When the reaction is carried out in the presence of an alkene, this intermediate transfers sulfur to it to give the thiirane and COS.[4,5] Oae and coworkers favour structure **2** based on hydrolysis results.[4] The interaction of diphenylnitrone with CS_2 to produce benzylideneaniline and COS was also proposed to proceed by way of **3** some time earlier.[6] The unusual three-membered metallacycle **4** is formed upon treatment of $Fe(CO)_5$ with CS_2 and Ph_3P.[7]

2. FORMATION OF FOUR-MEMBERED RINGS

2.1. Thietanes

When 1,8-didehydronaphthalene is generated from treatment of the ring-fused 1-amino-1,2,3-triazine with $Pb(OAc)_4$ in the presence of CS_2, the products include the fused thiete **5**.[8] The high pressure reaction of quadricyclane **6** with CS_2 gives only the 1 : 1 adduct **7** at high pressures and with excess CS_2, while at lower pressures and higher temperatures the 2 : 1 adduct **8** is favoured.[9] It is interesting to note that norbornadiene does not react under these conditions. The phosphoranylideneketene, $Ph_3P{=}C{=}C{=}O$, reacts readily with CS_2 to generate the thietane **9** but this spontaneously loses COS to give $Ph_3P{=}C{=}C{=}S$.[10] The related product **10**, formed by the corresponding reaction of $Ph_3P{=}C{=}C(OEt)_2$, undergoes an unusual rearrangement upon heating at 100 °C to afford **11**.[11] The regioisomeric [2+2] adducts **12** and **13** are formed upon photolysis of the corresponding silacyclopentadiene with CS_2, although only **12** could be isolated in pure form.[12] Finally in this section, base-induced condensation of *tert*-butyl acetate and of substituted toluenes with sodium *tert*-amyloxide and CS_2 in DMF is claimed to give the thietanedithiones **14** and **15**, respectively.[13]



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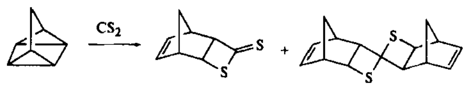
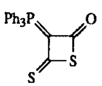


6 **7** **8**



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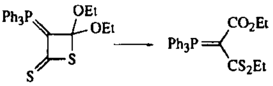
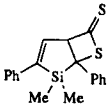


10 **11**



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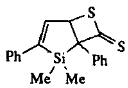

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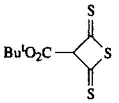

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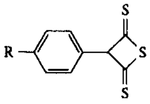

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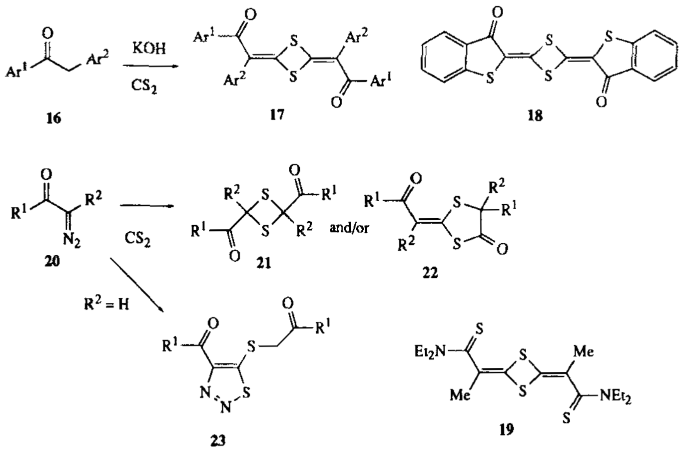
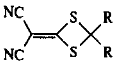
2.2. 1,3-Dithietanes

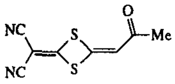
The earliest work in this area involves the treatment of deoxybenzoins **16** with CS_2 and KOH to give bright yellow compounds which were named 'desaurins' derived from desoxybenzoin and their golden colour.[14,15] Propiophenone and 2-propionylthiophene were later found to react similarly.[16] It was not until 1971 that the structure of these products was unambiguously shown to be **17**.[17] A similar product **18** is also formed from 2,3-dihydrobenzothiophen-3-one.[18] Treatment of $MeC{\equiv}CNEt_2$ with CS_2 also gives the desaurin type structure **19**.[19]



The reaction of α-diazo ketones **20** with CS_2 gives both four- and five-membered ring products depending on the substituents present. The dithietane structure **21** was demonstrated for the major product from **20** ($R^1 = R^2 = Me$) by X-ray methods,[20] disproving a previous report that the product was **22**,[21] but a later study showed both **21** and **22** to be formed for this and a variety of other diazo ketones.[22] Where both R^1 and R^2 are aromatic, only **22** is formed and where $R^2 = H$, the reaction takes a different course to give the thiadiazole **23**.[22]

Reaction of acidic methylene compounds with base and CS_2 affords the corresponding enedithiolate salts. When these are treated with 1,1-dihaloalkanes, 2-alkylidene-1,3-dithietanes are formed. Thus, for example, malononitrile reacts with CS_2, base and dichlorodiphenylmethane to give **24**,[23] and with diiodomethane to give **25**.[24] With 2,2-dichlorovinyl methyl ketone as the electrophile, reaction in DMF or DMSO gives the expected product **26**, but in ethanol or acetonitrile a five-membered ring product is formed.[25] Treatment of trialkyl phosphonacetates with base and CS_2 followed by phosgene gives the dithietanones **27**.[26] Reaction of 2,6-di-*tert*-butylphenol with CS_2, KOH and 1,1-dihalo compounds gives interesting quinonoid products such as **28** and **29**.[27] Aromatic aldehydes can also be suitable electrophiles as illustrated by the formation of **31** from the pyrazolone **30** upon treatment with CS_2, KOH and ArCHO.[28]


24 R = Ph
25 R = H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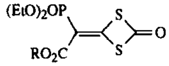
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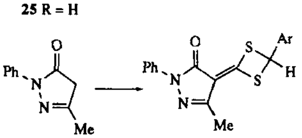
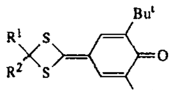
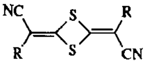
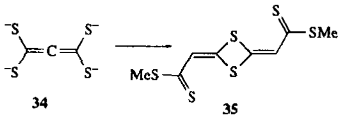

30 **31**

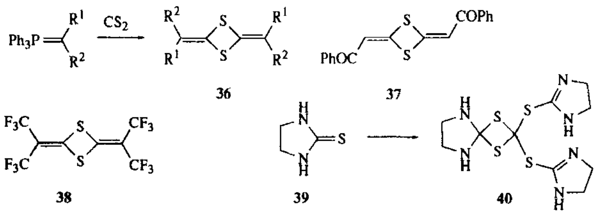

28 $R^1 = R^2 = Ph$
29 $R^1 = H$, $R^2 = CO_2Et$


32 $R = CO_2Me$
33 R = COPh


34 **35**

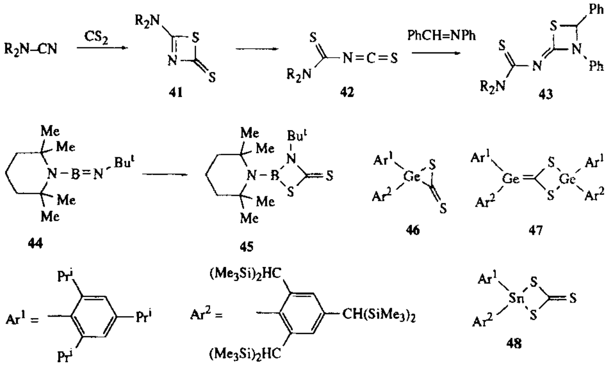
In the presence of an oxidising agent rather than a conventional electrophile, the enedithiolates may undergo coupling with loss of sulfur. Thus, for example, treatment of methyl cyanoacetate with CS_2, sodium methoxide and an oxidant such as ammonium persulfate gives **32**,[23] while reaction of α-cyanoacetophenone with CS_2/NaH and then methyl chloroformate gives **33**.[29] A related process is the treatment of dithioacetic acid with base and CS_2 to generate the tetraanion **34** which upon reaction with methyl iodide and CS_2 gives **35**.[30]

Reaction of various ylides and carbenes with CS_2 can also give 1,3-dithietanes. Both benzylidene- and fluorenylidenetriphenylphosphorane react with CS_2 to give products of type **36**,[31,32] and the stabilised sulfur ylide, $Me_2S{=}CHCOPh$, similarly affords **37** in chloroform, although a 1,2,4-trithiolane is produced when the reaction is performed in ethanol.[33] A very recent paper describes the formation of **38** by treatment of CF_3CHFCF_3 with ammonium fluoride and CS_2.[34] In a rather remarkable reaction, imidazolidine-2-thione **39** reacts with NaH and CS_2 in HMPA and diethyl carbonate to afford the spiro dithietane **40**.[35]



2.3. Other Four-membered Rings

Reaction of cyanamides with CS_2 under high pressure first results in formation of the thiazetes **41** but this ring opens to afford the thiocarbamoyl isothiocyanates **42** which can be trapped by added benzylideneaniline to give the thiazetidines **43**.[36] Carbon disulfide has proved useful in trapping unusual heteroatom double bonded compounds. Thus the B=N double bond of **44** reacts readily with CS_2 to give **45** whose X-ray structure has been reported.[37] The hindered diarylgermylene, Ar^1Ar^2Ge:, reacts with CS_2 to give **46** but this undergoes further reaction with the germylene to finally give the 2 : 1 adduct **47**.[38] Reaction of the first Sn=S double bonded compound, $Ar^1Ar^2Sn{=}S$, with CS_2 gave the 1 : 1 adduct **48**.[39]



3. FORMATION OF FIVE-MEMBERED RINGS

3.1. One Heteroatom

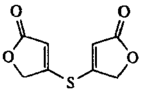
3.1.1. Furans

A rare example of this type is the reaction of 4-hydroxy-2-butynoic acid, $HOCH_2C{\equiv}CCO_2H$, with an aqueous suspension of dithiocarbamic acid to give the 4,4′-thiodibutenolide **49** in 20% yield.[40]

3.1.2. *Thiophenes*

Under extreme conditions CS_2 reacts with a variety of simple organic compounds to give thiophenes. Thus, for example, reaction with acetylene in a flow system at 700 °C gives thiophene in 10% yield.[41] Reaction of CS_2 with simple alkanes, alkenes, ketones and alcohols over a catalyst may also lead to thiophenes as illustrated by formation of 3-methylthiophene in 70% yield from 3-methylbutan-1-ol.[42] Reaction with CS_2 at 500 °C in the presence of a catalyst results in formation of thiophene from butan-1-ol or crotonaldehyde,[43] 3-methylthiophene from isoprene, 2-methylthiophene from pentane,[44] and 1,3-dihydrobenzo[*c*]thiophene from 2-methylbenzyl alcohol.[45]

When 1,8-didehydronaphthalene is generated from treatment of the ring-fused 1-amino-1,2,3-triazine with $Pb(OAc)_4$ in the presence of CS_2, the products include the fused dithiolactone **50**.[8] Generation of benzyne from phthalic anhydride in a glow discharge in the presence of CS_2 leads to formation of dibenzothiophene in 10% yield.[46] The spirocyclopropenes **51** react with CS_2 at 140 °C to give the products **52**.[47] An early study describes the reaction of the diazo compound $PhCOC(N_2)Ph$ with CS_2 to give a product which was assigned the structure **53** based on hydrolysis studies.[48]



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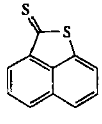

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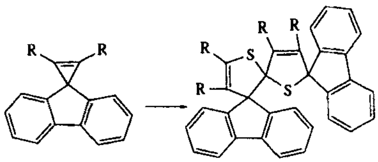

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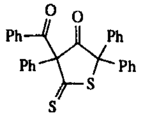

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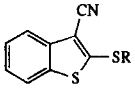

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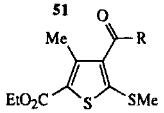

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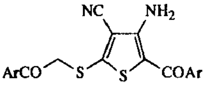

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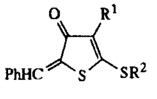

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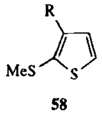

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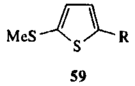

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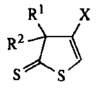

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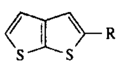

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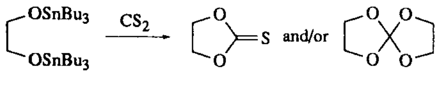
A variety of reactions of carbanions with CS_2 result in formation of products containing a thiophene ring. Thus, for example, reaction of *o*-chloro- or *o*-bromophenylacetonitrile with NaH and CS_2, followed by an alkyl halide, RX, gives the benzothiophenes **54**.[49] Sequential treatment of 1,3-diketones, $MeCOCH_2COR$, with CS_2/KOH, ethyl bromoacetate, MeI and aqueous KOH affords the tetrasubstituted thiophenes **55**.[50] In a similar reaction, treatment of malononitrile with CS_2 and base followed by α,p-dibromoacetophenone affords the thiophene **56**.[51] The acetylenic ketones, $PhC{\equiv}CCOCH_2R^1$, react with CS_2/NaH followed by an alkyl halide, R^2X, to give **57**.[52] A number of reports of the reaction of metallated allenes with CS_2 followed by an electrophile have appeared. Thus the lithiated allenes $RCH{=}C{=}CHLi$, which are in equilibrium with the isomeric form $RC(Li){=}C{=}CH_2$, generally react with CS_2 and MeI to give the thiophenes **58** while for $R = Bu^t$, the isomeric product **59** is formed.[53] With disubstituted allenes, $R^1R^2C{=}C{=}CH_2$, lithiation and reaction with CS_2 gives **60** ($X = H$).[54] The silver derivatives of allenes behave similarly and reaction with CS_2 followed by a suitable electrophile has been used to obtain **60** ($X = H$, D, Cl and Br).[55,56] Finally in this section, metallation of 1,3-diynes, $MeC{\equiv}C{-}C{\equiv}CR$, with $BuLi/KOBu^t$ followed by reaction with CS_2 gives the thienothiophenes **61**.[57]

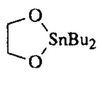
3.2. Two Heteroatoms

3.2.1. *Dioxolanes*

A series of studies by Sakai and coworkers on the formation of dioxolanes using CS_2 have appeared. Reaction of the organotin compound **62** gives **63** and/or **64** depending on the conditions used.[58] The same product **64** can also be formed by treatment of the cyclic organotin compound **65** with CS_2.[59] The unsaturated organotin compounds **66** react with CS_2 to give the dioxolethiones **67**.[60] The dithallium derivative of ethylene glycol, $TlOCH_2CH_2OTl$, reacts with CS_2 to give **64**.[61]



62 **63** **64**



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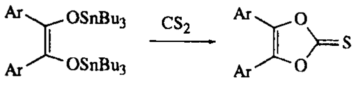
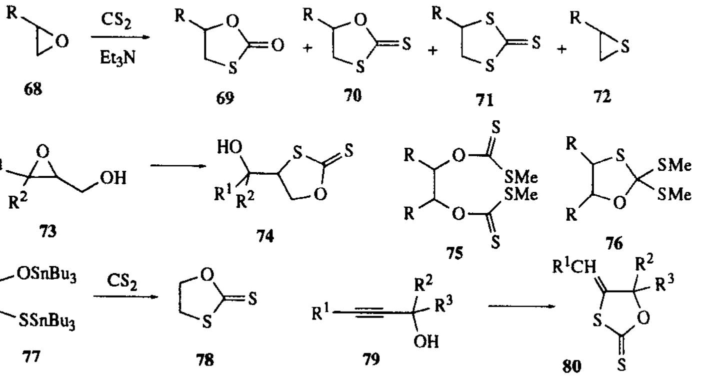


66 **67**

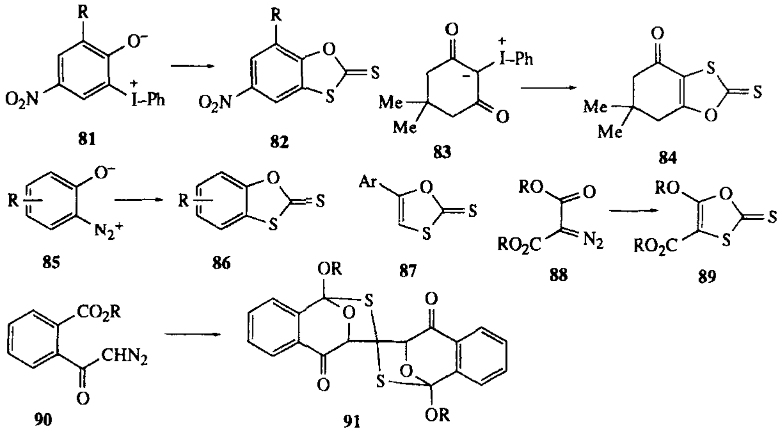
3.2.2. Oxathiolanes

The high pressure reaction of simple epoxides **68** with CS_2 and triethylamine produces both the oxathiolanones **69** and the oxathiolanethiones **70** in addition to the dithiolanethiones **71** and thiiranes **72**.[62] Similar reaction of epoxides such as epichlorohydrin and propylene oxide at 100 °C gives mixtures of stereoisomers of the corresponding oxathiolane-2-thiones in addition to the thiiranes mentioned earlier,[2] and the reaction has been extended to epoxides bearing heteroaryl substituents.[63] Recently the epoxides **73** of allylic alcohols have been treated with CS_2 to afford the oxathiolanethiones **74** and by starting with chiral epoxides from Sharpless epoxidation, the chiral heterocycles can be obtained.[64] Reaction of 1,2-diols with CS_2 and methyl iodide under basic conditions gives the bis(dithiocarbonates) **75**, which upon heating cyclise with loss of COS to form the oxathiolanes **76**.[65]



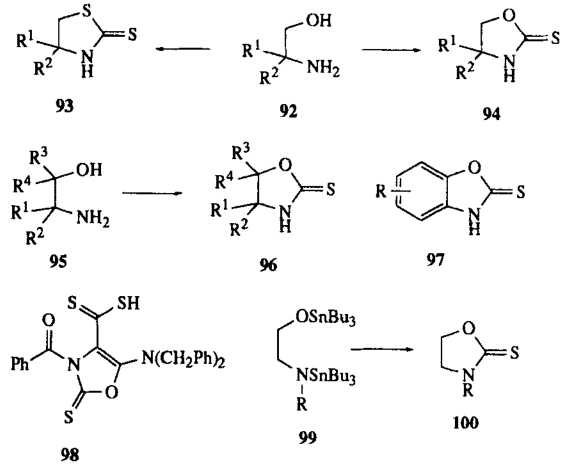
The approach used to form dioxolanes in Section 3.2.1 may also be adapted to produce oxathiolane systems. Thus, the organotin compound **77** reacts with CS_2 by elimination of $(Bu_3Sn)_2S$ to give 1,3-oxathiolane-2-thione **78**.[66,67] Acetylenic alcohols **79** react with CS_2 and sodium hydride to give the oxathiolanethiones **80**,[68–70] and the same reaction has recently been brought about with potassium fluoride supported on alumina as the base.[71]

Photolysis of the iodoniophenoxide **81** in CS_2 gives the benzoxathiolethione **82**,[72] and the iodonium ylide **83** similarly affords **84** either photochemically[72] or upon thermolysis in the presence of a copper catalyst.[73] In earlier work the diazoniophenoxides **85** were found to react readily with CS_2 to give **86**.[74] The α-diazoacetophenones, $ArCOCHN_2$, react with CS_2 in the presence of a rhodium catalyst to give the oxathiolethiones **87**, and diazomalonates **88** similarly give **89**.[75] Where the aryl group has an *ortho* ester function as in **90**, the reaction takes a more complex course to give the spirobis(oxathiolanes) **91** as the main products.[76]



3.2.3. *Oxazolines and Oxazolidines*

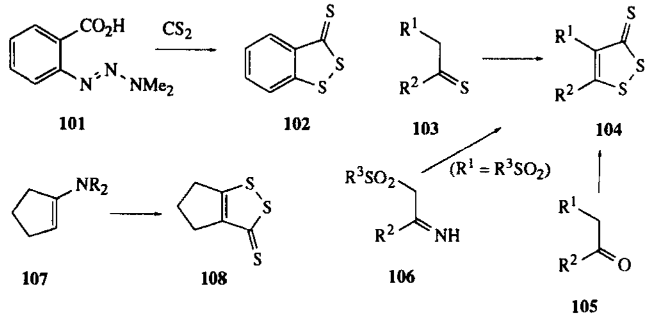
The majority of reactions of this type involve treatment of 2-amino alcohols with CS_2 under basic conditions. This reaction is not straightforward however and depending on various factors it can produce either the oxazolidine-2-thione or the thiazolidine-2-thione or a mixture of the two. The situation has been discussed in detail in a recent paper by Le Corre.[77] Reaction of primary amino alcohols **92**, including ethanolamine itself, with CS_2 and NaOH or KOH in aqueous ethanol or methanol generally gives the thiazolidinethiones **93**.[78,79] A number of ways have been found to divert the reaction in favour of the oxazolidinethiones **94** including treatment of **92** with CS_2 and NaOH and then a lead salt followed by thermolysis,[80,81] reaction with CS_2 and KOH in DMSO,[82] reaction with CS_2 and triethylamine at room temperature,[83] and reaction with CS_2 and an oxidant such as iodine which forms an intermediate thiuram disulfide[84] or hydrogen peroxide which forms an intermediate isothiocyanate.[85] In general terms, oxazolidinethione formation is favoured by mild conditions and a weak base such as triethylamine, whereas thiazolidinethione formation is favoured by stronger bases such as KOH and an excess of CS_2. The presence of a substituent on nitrogen leads to exclusive formation of the thiazolidinethione.[77,86] Many examples have been reported of the conversion of amino alcohols of type **95** into the oxazolidinethiones **96** using CS_2 and KOH or NaOH in aqueous alcohols,[79,87–89] CS_2 and NaH in DMSO,[90] and CS_2 in DMF followed by heating.[91] Reliable procedures for conversion of *o*-aminophenol[92] and substituted derivatives[93] into the corresponding benzoxazolinethiones **97** using CS_2 and a base have also been described.



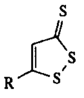
In an unusual reaction, the *N*,*N*-dibenzylamide of *N*-benzoylglycine reacts with CS_2 and NaH to give oxazoline-2-thione **98**.[94] Finally in this section, the organotin method previously mentioned for dioxolanes and oxathiolanes can also be applied to formation of oxazolidinethiones **100** from **99**.[95]

3.2.4. 1,2-Dithiole-3-thiones

Benzyne may react with CS_2 to give various products depending on the conditions used for its generation. As will be seen in the following section, most routes lead to formation of 1,3-benzodithiol-2-ylidene which goes on to further reactions. Heating the triazene precursor **101** in the presence of CS_2, in contrast, gives 1,2-benzodithiole-3-thione **102** as the main product,[96] and this is also formed when the benzyne is generated by flash vacuum pyrolysis of phthalic anhydride at 700 °C.[97] A wide variety of functionalised carbanions and their equivalents react with CS_2 to afford 1,2-dithiole-3-thiones. Thus for example, thioketones **103** react with CS_2, sulfur and triethylamine in DMF to give the products **104**,[98,99] and these can alternatively be formed from ketones **105** by reaction with CS_2 and base followed by P_2S_5[100] or form α-sulfonylimines **106** with CS_2 and base.[101] A variety of enamines such as **107** also react with CS_2 and sulfur in alkali or DMF to give the dithiolethiones **108**.[102–105]



Further routes to 5-substituted 1,2-dithiole-3-thiones **109** include treatment of either alkynyltelluride anions, $RC{\equiv}C{-}Te^-$[106] or sulfoxonium thioketones **110**[107] with CS_2 at room temperature. Reaction of ethyl dithioacetate with CS_2 and KOBu^t followed by iodine gives **111**,[108] while similar reaction of dithio acids, RCH_2CS_2H, with CS_2, base, iodine and then $Bu_4N^+F^-$ gives **112**.[30] The α-anions of thioamides $RCH_2C({=}S)NR^1_2$, react directly with CS_2 to give the products **113**,[109,110] while the product **114** may be prepared either by reaction of malononitrile or 2-cyanothioacetamide with CS_2 and sulfur with an amine catalyst,[111] or from malononitrile with CS_2 in liquid ammonia followed by acetic acid.[112] Reaction of $MeC{\equiv}CNEt_2$ with CS_2 and sulfur also gives **113** (R = Me, R^1 = Et).[19] Treatment of dithiolethiones **115** with CS_2 and a base followed by methyl iodide affords access to the trithiapentalenes **116**.[113] A recent report describes the remarkable reaction of tetramethylammonium fluoride with CS_2 in wet DMF to give a complex salt containing the dianion **117** as determined by X-ray crystallography.[114]



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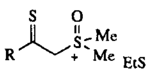

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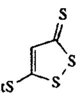

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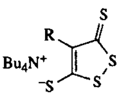

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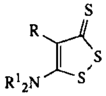

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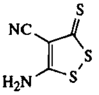

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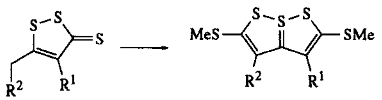
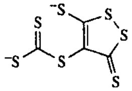


115 **116**



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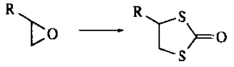
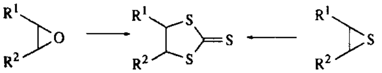
3.2.5. 1,3-Dithioles and Dithiolanes

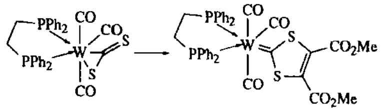
In Section 3.2.2 the reaction of epoxides **68** with CS_2 and triethylamine under high pressure to give products including the dithiolanethiones **71** was described,[62] but by the use of exactly 1 equiv. of CS_2 the 1,3-dithiolan-2-ones **118** can be produced.[115] Conversion of epoxides **119** into the dithiolanethiones **120** can be achieved by treatment with CS_2 either in the presence of trimethylamine[116] or of NaOH or KOH in methanol or ethanol,[117–120] in which case the process involves *in situ* generation of the xanthates.[121] The same products can also be formed from the corresponding thiiranes **121** with CS_2 and triethylamine at 100 °C under pressure,[2,122] or from the appropriate 1,3-dioxolan-2-ones, 1,3-dioxolane-2-thiones or 1,3-dithiolan-2-ones by treatment with a xanthate.[123] The coordinated CS_2 of the tungsten complex **122** undergoes cycloaddition with DMAD to give the product **123**.[124]



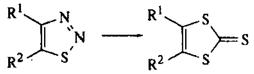
68 **118**



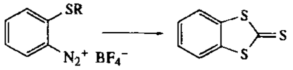
119 **120** **121**



122 **123**



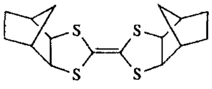
124 **125**



126 **127**

A variety of 1,2,3-thiadiazoles **124** are converted into the 1,3-dithiole-2-thiones **125** by treatment with CS_2 either alone at high temperature,[125,126] or with KOH in ethanol under milder conditions.[127] Treatment of the *o*-alkylthiobenzenediazonium salts **126** with sodium iodide and CS_2 produces **127** by a radical mechanism.[128]

Reactive alkenes and alkynes react directly with CS_2 to afford one of the most direct routes to the important tetrathiafulvalene (TTF) skeleton. For the strained double bond in norbornene this requires extremely high pressures and gives a product with structure **128** or **129**.[129] Substituted norbornenes react similarly while norbornadiene gives an isomer of **130** or, with an excess of CS_2, a polymer **131**. The reaction of alkynes, $RC{\equiv}CR$, with CS_2 to afford **132** has been reported for $R = CF_3$,[130,131] CO_2Me,[130-132] $SiMe_3$,[133,134] and 2-pyridyl,[133,135] with most of the studies using high pressure conditions. For $R = CF_3$ and CO_2Me the more complex products **133** and **134** may also be formed with the ratio depending upon the conditions used.[130,131,136] Terminal alkynes, $RC{\equiv}CH$ also react to afford mixtures of **135** and **136** for $R = CO_2Me$ or CO_2H,[133,137] and $SiMe_3$.[133,134] If the reactions are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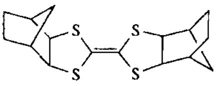
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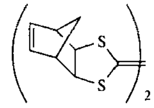
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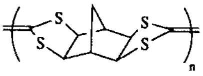
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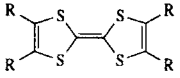
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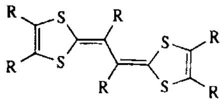
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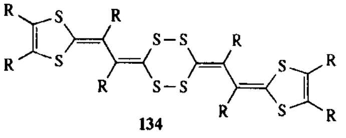
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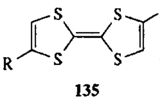
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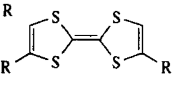
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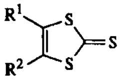
carried out in the presence of sulfur[138,139] or diamino disulfides,[140,141] the intermediates can be trapped to afford the dithiolethiones **137**, while with methanol present, **138** is produced.[130,131] Treatment of metallated terminal alkynes, $RC{\equiv}C^-M^+$, with sulfur and CS_2 gives the dithiolethiones **139**.[142,143] The bis(dialkylamino)carbenes readily formed by thermal dissociation of tetrakis(dialkylamino)ethylenes react with CS_2 and an alkyne, $R^1C{\equiv}CR^2$ to give **140**.[144] The highly reactive cycloalkynes **141**,[145] **142**[146] and **143**[147] react readily with CS_2 to give TTF derivatives and for **142**, addition of sulfur or methanol leads to products of the type **137** and **138**, respectively.

As mentioned briefly in Section 3.2.4, benzyne generally reacts with CS_2 to generate the carbene **144**. While this may dimerise to give dibenzo TTF to some extent, it usually reacts with another compound by insertion. Generation of benzyne by lead tetraacetate oxidation of 1-aminobenzotriazole in the presence of CS_2 for example gives mainly **145** and **146** from reaction of **144** with acetic acid.[148] Generation by reaction of anthranilic acid with amyl nitrite likewise gives **147** from reaction with amyl alcohol,[149] a reaction which has been extended to substituted benzynes[150] and methylenedibenzyne,[151] and **144** can also be trapped by electrophilic substitution on phenol or *N*,*N*-dimethylaniline.[96]



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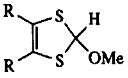

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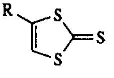

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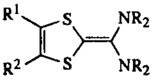

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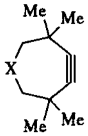
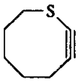


141 X = CH_2
142 X = S



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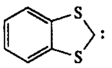

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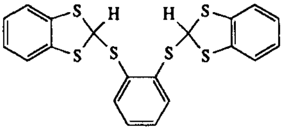

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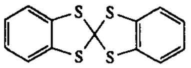

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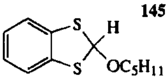
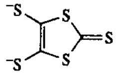


147

Reduction of CS_2 with sodium amalgam or sodium in liquid ammonia was investigated at an early date,[152] but the outcome was rather complex and could not be understood fully. It is now known that the reduction either by electrochemical methods[153,154] or with sodium[155–157] or potassium[158] in DMF gives salts of the dianion **148** which is called DMIT. The mechanism of the process which also gives the metal trithiocarbonate has been examined in detail[159] and the great value of DMIT in preparing further heterocyclic compounds is summarised in two comprehensive reviews.[160,161] Treatment of CS_2 with sodium cyanide followed by phosgene also leads to formation of the heterocyclic product **149**.[162]

As already mentioned in Section 2.2, the reaction of aromatic α-diazo ketones **150** with CS_2 gives the 1,3-dithiolan-4-ones **151** and, because of the controversy surrounding their structure, this was demonstrated conclusively by several methods including an X-ray determination.[163–166]

The dithiocarbonates of general structure **152** which are formed by treatment of R^1CH_2X with potassium ethyl xanthate, react readily with a base, CS_2 and an alkyl halide, R^2X, to give dithiolethiones **153**.[167–169] In a related process, the compounds **154** and **155** formed from an α-halo ketone and either $KOPr^i$ or $NaSBu^t$ together with CS_2, undergo acid catalysed cyclisation to afford the dithiolones **156**[170] and dithiolethiones **157**,[171] respectively. A similar sequence starting from α-halo acids provided the first synthesis of 1,3-dithiolane-2,4-diones **158**.[172] Treatment of propargyl[173] or allyl[174] halides with $NaSBu^t$ and CS_2 followed by further steps has also been used to obtain substituted 1,3-dithiole-2-thiones and 1,3-dithiol-2-ones.



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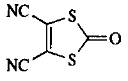

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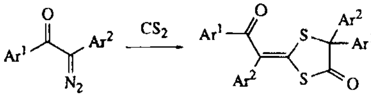
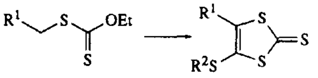
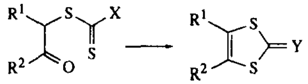


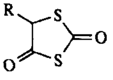
150 **151**



152 **153**



154 X = OPr^i
155 X = SBu^t
156 Y = O
157 Y = S



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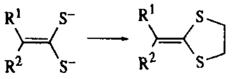
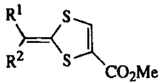


159 **160**

A wide variety of acidic methylene compounds react with base and CS_2 to give salts of the dianions **159** and these react with 1,2-dibromoethane to give the 2-alkylidene-1,3-dithiolanes **160**.[23,51,175–179] Other types of electrophile can also be used including methyl propiolate which leads to **161**,[180] 1,4-dichlorobut-2-ene which gives **162** in addition to the expected seven membered ring product[181] and 2,4-dinitrochlorobenzene which gives **163**.[28] The same reaction is also applicable to amines and related compounds where the salts **164** provide access to 2-imino-1,3-dithiolanes **165** and this has been reported for amines,[182] amides,[183] hydroxylamine,[184] hydrazines[185] and cyanamide.[186] In the last case further reaction of **165** (R = CN) with α,ω-dithiols gave the spiro compounds **166** and **167**.[187] Again different electrophiles can be used as illustrated by formation of **168** from an amine, CS_2 and 2,3-dichloronaphthoquinone.[188] Reaction of secondary amines with CS_2, base and a halomethyl ketone gives intermediates **169** which cyclise in perchloric acid to give the dithiolium salts **170**.[189] Interaction of metal sulfides with CS_2 gives the metal trithiocarbonates, $S{=}C(S^-M^+)_2$, and these react with dibromoethane to give 1,3-dithiolane-2-thione,[190] with oxalyl chloride to give the 4,5-dione **171**,[191] and with 2,3-dichlorohexafluorobut-2-ene to give **172**.[138]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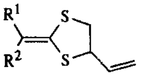
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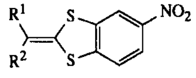
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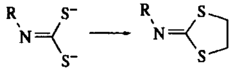
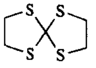

164 **165**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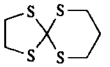
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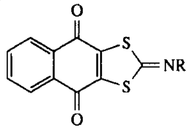
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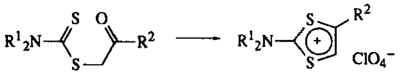
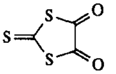

169 **170**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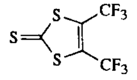
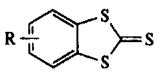

172

Reaction of arene-1,2-dithiols with base and CS_2 affords the corresponding fused 1,3-dithiole-2-thiones and examples such as **173**,[192–194] **174**,[195,196] and **175**[197] have been prepared in this way.

The red crystalline adduct **176** formed from tributylphosphine and CS_2 undergoes cycloaddition to alkynes to give the phosphoranylidenedithioles **177**. These can be trapped by Wittig reaction with aldehydes[198,199] or ketones[200] to give **178** and with nitroso compounds to give **179**.[201] When R^1 is CO_2H, intramolecular proton transfer affords the salts **180**,[202] while intermolecular protonation by added HBF_4 gives the stable salts **181**[200] which can be used to regenerate **177** by treatment with triethylamine and this has allowed **177** to be used in construction of a variety of extended TTF analogues of interest as components of organic conductors.[203,204] In the absence of any trap, **177** reacts with a second molecule of alkyne to give **182**.[205,206]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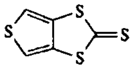
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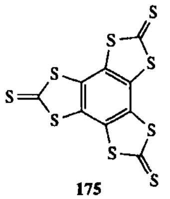
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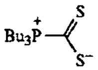
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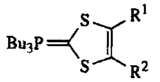
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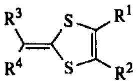
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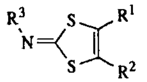
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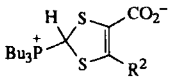
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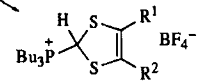
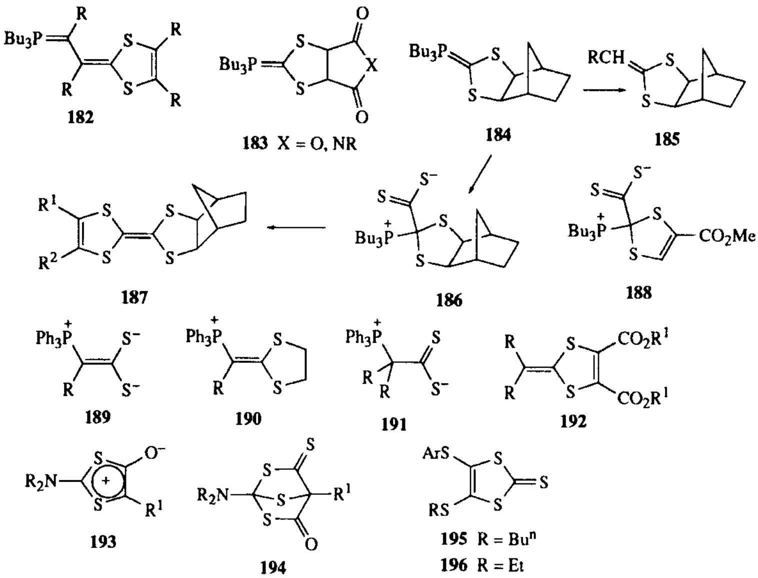

181

Hartzler described the reaction of **176** with dimethyl maleate in methanol to afford dimethyl succinate[198] and in the light of more recent reports[207,208] this probably involves dissociation of **176** and conjugate addition of the resulting tributylphosphine to give an ylide which undergoes methanolysis. There has been some evidence for formation of adducts such as **183** from maleic anhydride and maleimides but these could not be isolated in pure form.[207,208] The strained double bond of norbornene and substituted norbornenes does undergo cycloaddition with **176** and in the presence of an aldehyde the ylide **184** can be trapped to give **185**.[209,210] The reaction can also be extended to norbornadiene and di- and trialdehydes to give a variety of sulfur-rich heterocyclic systems.[211] In the absence of any trap, **184** reacts with CS_2 from dissociation of **176** to give the solid compound **186**. When an acetylenic dipolarophile is added to this, cycloaddition occurs with loss of tributylphosphine to give the dihydroTTFs **187**.[212] A similar mechanism involving **188** probably explains the earlier report that reaction of methyl propiolate with Bu_3P and an excess of CS_2 directly gives dimethyl TTFdicarboxylate.[213]

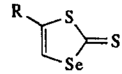


Phosphorus ylides, $Ph_3P{=}CHR$, react with CS_2 to give the anion **189** which can be trapped by added 1,2-dibromoethane to give the dithiolanes **190**.[214] In contrast, ylides of the type $Ph_3P{=}CR_2$ react with CS_2 to give the zwitterionic species **191** and this undergoes cycloaddition with an acetylenic ester to give **192** and Ph_3P.[215,216]

The mesoionic 1,3-dithiolium-4-olates **193** react with CS_2 to give the corresponding dithioliumthiolates and COS by way of the bicyclic intermediate **194**.[217] In an unusual reaction, treatment of the highly hindered 2,4,6-tri-*tert*-butylbromobenzene with Bu^nLi and CS_2 affords **195** while use of Bu^tLi, CS_2 and EtI gives **196**.[218]

3.2.6. 1,3-Thiaselenoles

The alkyneselenolates, $RC{\equiv}C{-}Se^{-}M^{+}$, which can be formed either by treatment of a terminal alkyne with base and selenium[219,220] or by base-induced fragmentation of a 1,2,3-selenadiazole,[221–224] react readily with CS_2 to give the thiaselenolethiones **197**. Thermolysis of 1,2,3-selenadiazoles **198** in the presence of CS_2 has also been used to obtain thiaselenolethiones **199**.[225,226] Treating an amidine of phenylpropiolic acid with CS_2, selenium and pyridine gives the products **200**,[139] while the high pressure reaction of DMAD with CS_2 and CSe_2 gives the diselenadithiafulvalene **201**.[227]



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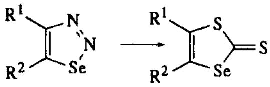
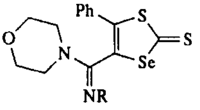


198 **199**



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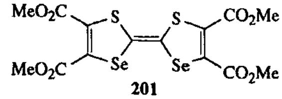
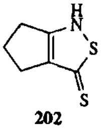


201

3.2.7. Isothiazoles and Isothiazolines

Reaction of cyclopentanone with CS_2, sulfur and ammonium hydroxide gives **202** while with cyclohexanone the intermediate **203** is formed which can be trapped with base and CS_2 to give **204** or with a carbonyl compound to give **205**.[228] A range of acyclic ketones, $R^1COCH_2R^2$, also react with CS_2, sulfur and ammonium hydroxide to give intermediates which can be trapped by an alkyl halide R^3X to give isothiazoles **206**.[229] Treatment of cyclohexanone with a primary amine and CS_2 followed by iodine gives the isothiazolinethiones **207**,[230] and the *N*-phenylimine of cyclohexanone reacts with CS_2 and sulfur in DMF to give **207** (R = Ph).[103] Sequential reaction of 6-amino-1,3-dimethyluracil with CS_2 and NaOH, dimethyl sulfate and then iodine results in formation of **208**.[231]



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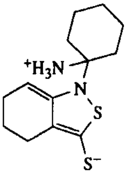

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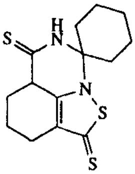

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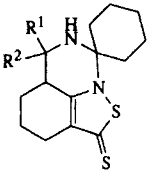

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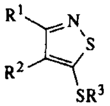

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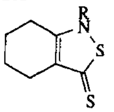

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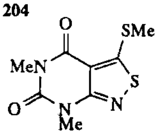
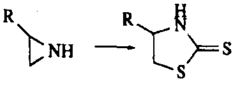
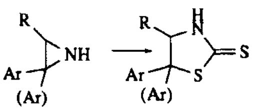


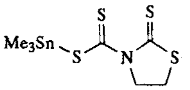
208

3.2.8. *Thiazolines and Thiazolidines*

One of the earliest examples of this type to be studied was the highly energetic reaction of aziridine and simple derivatives with CS_2 to give the thiazolidine-2-thiones although the aziridines were thought to have the isomeric vinylamine structure at that time.[232,233] The regiochemistry of the process has been of some interest and 2-substituted aziridines **209** usually give the 4-substituted products **210**.[234–237] In cases of the type **211**, the products **212** are formed.[238] Several other examples have been reported including the 2,3-dimethyl case,[239] and both *cis*- and *trans*-2,3-dialkyl aziridines where the reaction proceeds with inversion of the relative stereochemistry of the groups.[240,241] With 1-arylaziridines, treatment with CS_2 gives mainly a dithiocarbamate polymer together with the expected thiazolidinethione in low yield.[242] With *N*-trimethylstannylaziridine the reaction takes an unexpected course and treatment with CS_2 gives **213**.[243] Aziridine may also be converted into thiazolidine-2-thione by treatment with a xanthate to give the isolable compounds **214** followed by heating to eliminate the alcohol.[244]


209 **210**


211 **212**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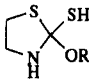
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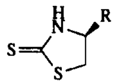
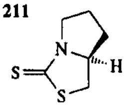

215 R = Et, Pr^i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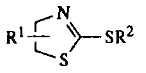
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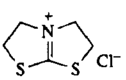
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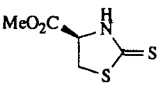
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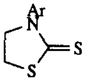
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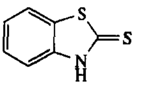
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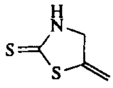
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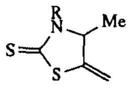
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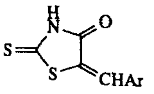
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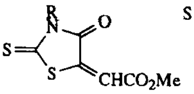
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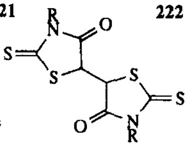
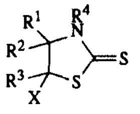

226

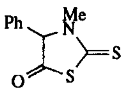
As already described in Section 3.2.3, reaction of 2-amino alcohols with CS_2 and a base often gives the thiazolidine-2-thiones **93**, although the oxazolidine-2-thiones **94** may be formed in addition or instead depending on the conditions used and the substituents present. Reaction of amino acid derived chiral amino alcohols in this way has been used to obtain thiazolidinethiones such as **215** and **216**.[245,246] Reaction of amino alcohols with CS_2 and an alkyl halide, R^2X, followed by ring closure with thionyl chloride gives the 2-alkylthiothiazolines **217**.[247] Thiazolidine-2-thiones have also been prepared by reaction of 2-chloroalkylamines with CS_2 and base[248] or with a xanthate[89] and treatment of 2-aminoalkyl hydrogen sulfates with xanthate is also effective.[249] Reaction of bis(2-chloroethyl)amine with CS_2 and NaOH gives the bicyclic salt **218**.[250] A variety of 2-mercaptoalkylamines similarly form thiazolidine-2-thiones upon treatment with CS_2 and a base,[251] and examples include **219** formed from cysteine methyl ester[83,252] and the *N*-aryl compounds **220**.[253,254] The reaction of 2-aminothiophenol with CS_2 to give **221** was reported at an early date,[255] and this has been extended to substituted examples [256] and to pyridine and quinoline fused analogues.[257]

A variety of propargylic amines react with CS_2 to give 5-methylene-thiazolidine-2-thiones. Thus, the parent propargylamine gives **222**,[258] while the compounds RNHCH(Me)C≡CH react with CS_2 and NaOH to afford **223**.[259] The acetylenic amides, ArC≡C–CONH$_2$, similarly give **224**.[260] Ammonium *N*-alkyldithiocarbamates react with DMAD to give not only the 1 : 1 adduct **225** but also the 1 : 2 adduct **226**.[261]

Several α-amino carbonyl compounds also react with CS$_2$ to give thiazolidinethione products as exemplified by reaction of α-amino ketones to give **227**,[262] α-amino oximes to give **228**[263] and the ethyl ester of *N*-methylphenylglycine to give **229**.[264] Aminoacetaldehyde dimethyl acetal reacts with CS$_2$ and an alkyl halide, RX, to give an intermediate which can be cyclised to **230**.[265] Sequential treatment of glycine ethyl ester hydrochloride with CS$_2$, MeI and NaOH followed by KOBu^t or NaOBu^t, CS$_2$ and RX gives the thiazoles **231**.[266,267] The dehydrovaline ethyl ester **232** reacts with CS$_2$ to give **233**[268] and treatment of the chloropyrimidine **234** with CS$_2$ in DMF gives **235**.[269]



227 X = OH
228 X = NHOH



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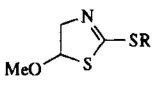

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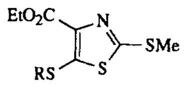

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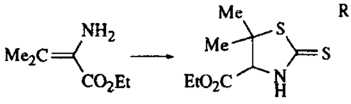
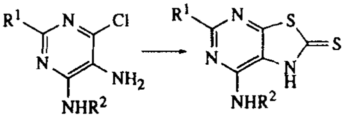
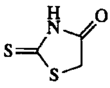


232 **233**



234 **235**

A large number of synthetic methods involving reaction of dithiocarbamates with α-halo carbonyl compounds to give thiazolinethiones or thiazolidinethiones are known. The parent ammonium dithiocarbamate reacts with sodium chloroacetate to give **236**[270] and the reaction has been extended to formation of **237** by treatment of heteroaromatic amines with CS$_2$ and triethylamine then sodium chloroacetate[271] and the products may be trapped with an added aldehyde, R^{1}CHO, to give **238** in a one pot procedure.[272] Treatment of ammonium dithiocarbamate with chloroacetaldehyde gives the thiazolinethione **239** in 65% yield.[273] The reaction of α-halo ketones with dithiocarbamates, which may be formulated in general as **240** and **241** giving **242**, is very general and numerous examples have been described.[274–279] For α-halo esters **240** (R^1 = alkoxy) the reaction takes a slightly different course to give products **243**.[274] Treatment of hydrazines with CS$_2$ and base followed by sodium chloroacetate similarly affords the *N*-amino compounds **244**.[280,281]



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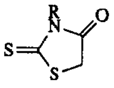

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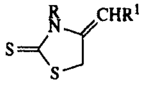

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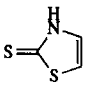

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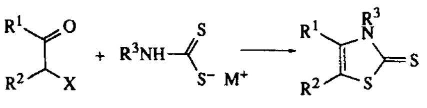
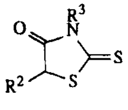
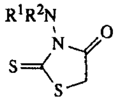


240 **241** **242**

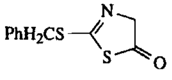


243

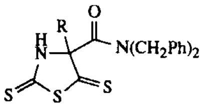


244

A variety of α-amino acid derivatives undergo reaction with CS_2 to afford heterocyclic products. When glycine is treated with CS_2 and benzyl chloride and then PBr_3, **245** is formed.[282] Reaction of the *N*,*N*-dibenzylamides of *N*-benzoyl amino acids with CS_2 and NaH leads to formation of the thiazolidine-3,5-dithiones **246**.[94] The α-amino acid amides generally react with CS_2 followed by HCl to give **247**.[283] On the other hand α-amino nitriles **248** react with CS_2 to give the aminothiazolinethiones **249**.[284–288] Where there is a competition, as in the case of aminocyanoacetamide, it is the nitrile function which reacts to give **250**.[289,290] Direct reaction of benzaldehyde with CS_2, HCN and ammonia at room temperature affords **251**.[285] Treatment of cyanamide with CS_2 and base followed by an α-halo ketone gives the aminothiazoles **252**.[51,291] Reaction of isonitriles, R^1CH_2NC, with base and CS_2 followed by an alkyl halide, R^2X, gives the thiazoles **253**.[292,293]



245



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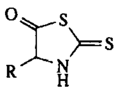

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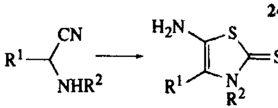
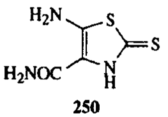


248 **249**



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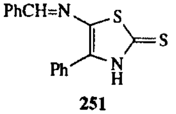

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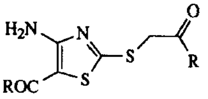

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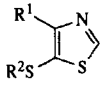
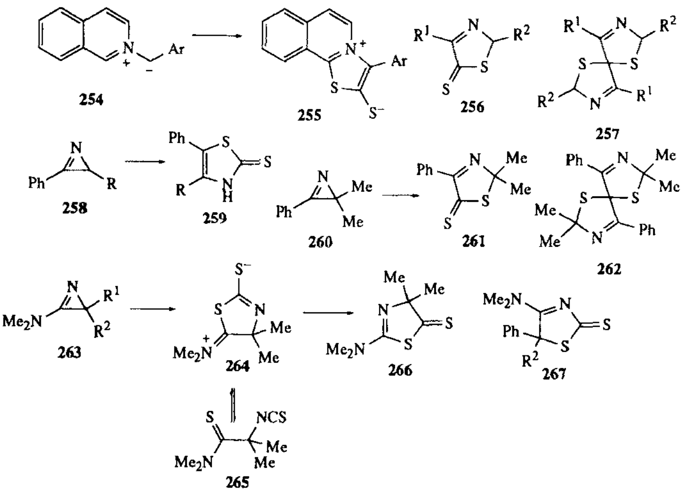


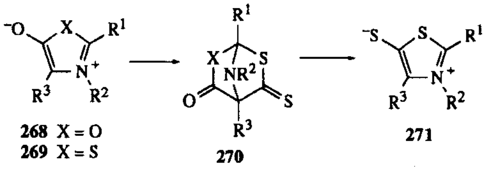
253

The double bond of CS_2 may act as a 1,3-dipolarophile and such dipoles as **254** react readily to give the mesoionic products **255**.[294–297] Nitrile ylides also add to CS_2 and in this case the initial adduct **256** can react further to give **257**.[298–300] Heating the azirine **258** with CS_2 in a sealed tube at 100 °C gives the thiazolinethiones **259**.[301] Photolysis of azirines is well established to give nitrile ylides and when this is performed in the presence of CS_2 it gives the 2 : 1 adduct by further reaction of the initial 1 : 1 adduct. For azirine **260** for example, these have structures **261** and **262**, respectively,[302] despite an earlier report that they had isomeric structures.[303] The 2-aminoazirines such as **263** react with CS_2 in a more complex way. For $R^1 = R^2 = Me$, the initial product is **264** which is in equilibrium with the thiocarbamoyl isothiocyanate **265** and undergoes thermal isomerisation to **266**.[304,305] In contrast where $R^1 = Ph$ and $R^2 = Me$ or Et, the isomeric products **267** are formed.[306]

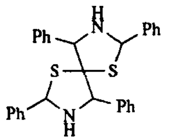


Both the oxazolium-5-olates **268**[307,308] and the thiazolium-5-olates **269**[309] react with CS_2 to afford the corresponding thiazolium-5-thiolates **271** by way of bicyclic intermediates **270**. Treatment of dibenzylamine with base and CS_2 is reported to give the spiro compound **272** in 31% yield.[310] Reaction of *o*-azidobenzenediazonium fluoroborate with CS_2 and sodium iodide gives a 13% yield of benzothiazoline-2-thione

221.[311] Treatment of the indolone **273** with NaH and CS_2 gives the thiazoliumthiolate **274**,[312] while reaction of **275** with CS_2 and NaOH affords **276**.[313]



268 X = O
269 X = S
270
271



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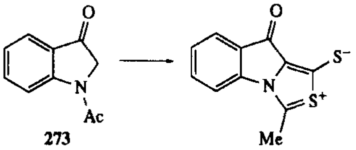
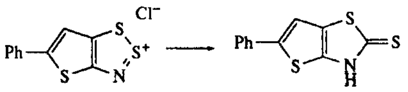


273
274



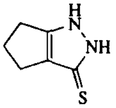
275
276

3.2.9. *Pyrazolines*

A rare example of this type is provided by the reaction of cyclopentanone with CS_2 and KOH followed by hydrazine to give **277**.[28]

3.2.10. *Imidazoles, Imidazolines and Imidazolidines*

The reaction of ethylenediamine with CS_2 to give imidazolidine-2-thione **278** is well known, [314] and *N*,*N*′-dialkylethylenediamines react similarly.[315] The hypervalent silicon compounds **279** react with CS_2 to give mainly **280**.[316] Treatment of *o*-phenylenediamine with CS_2 and a base or with a xanthate gives benzimidazoline-2-thione **281**[92] and the reaction has been extended to substituted examples[317] and to the thiophene-,[318] pyridine-,[319] pyridazine-,[320] and pyrimidine-fused analogues.[269,321–323] In the case of 3-amino-2-hydrazinopyridine reaction with CS_2 and triethylamine gives the *N*-amino compound **282**.[324] Treatment of 1,2-diimines such as **283** with sodium metal and CS_2 affords the imidazolinethiones **284**.[325] Reaction of glycine with CS_2 and aqueous NaOH followed by HCl produces **285** in 49% yield.[326] Ketones, R^1COR^2, react with a combination of CS_2 and ammonium cyanide in methanol to give the imidazolidine-2,4-dithiones **286**.[327,328]



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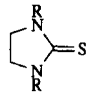
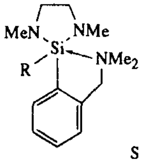


278 R = H
280 R = Me



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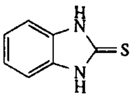

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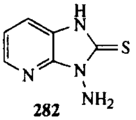

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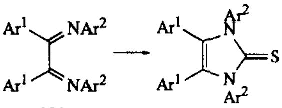
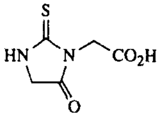


283 **284**



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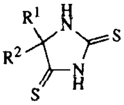

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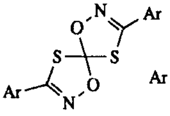
3.3. Three Heteroatoms

3.3.1. Oxathiazolines and Oxathiazolidines

Aromatic nitrile oxides undergo cycloaddition to CS_2 at 100 °C to give the bis adducts **287** but these are unstable and fragment with loss of ArNCS to give the 1,4,2-oxathiazolin-5-ones **288**.[329] A uracil derived nitrone was also reported to add to CS_2 to give **289**,[330] but later work by Black has cast doubt on this result and shown that such adducts are generally unstable and lose COS to give thioamides as exemplified by the formation of **291** in 62% yield from reaction of **290** with CS_2.[331]



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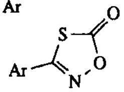

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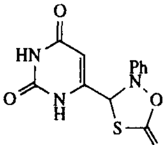

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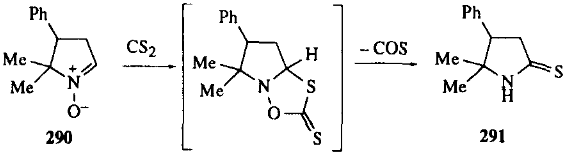
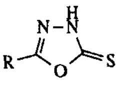


290 **291**

3.3.2. Oxadiazoles and Oxadiazolines

A variety of acid hydrazides, $RCONHNH_2$, react with CS_2 with or without base present to give the corresponding 1,3,4-oxadiazoline-thiones **292** and this has been described for R = Ph,[332] and a variety of heterocyclic and other groups.[333–336] Reaction of **293** with CS_2 and

DCCI gives the mesoionic product **294**.[337] The phosphinimine substituted pyridone **295** reacts with CS_2 to give **296**.[338]



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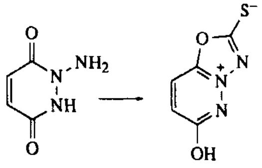
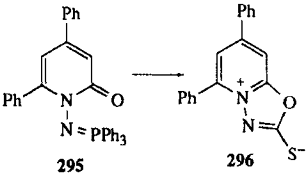


293 **294**

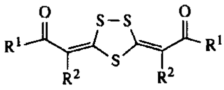


295 **296**

3.3.3. Trithiolanes

The compounds in this section have largely been obtained by one of two routes. The first of these involves treatment of an acidic methylene compound with CS_2 and base followed by oxidation. This has already been mentioned in Section 2.2 as a route to 1,3-dithietanes but, depending on the conditions used and the nature of the oxidant, the 1,2,4-trithiolanes may be obtained instead. In this way a wide variety of trithiolanes **297** have been prepared from the appropriate $R^1COCH_2R^2$ using oxidants such as bromine, iodine, hydrogen peroxide and ammonium persulfate.[23,29,112,339–342]

The second major route is reaction of carbenes or their equivalent with CS_2. Treatment of either bis(trifluoromethyl)diazirine or 2-diazohexafluoropropane with CS_2 at 180 °C gives **298** which probably arises by thermal extrusion of sulfur from the tetrathiane formed by reaction of two molecules of the carbene with 2 CS_2.[343,344] Rhodium catalysed decomposition of diazomalonates in the presence of CS_2 may also give some trithiolanes of type **297** in addition to the products **89** mentioned earlier in Section 3.2.2.[75] Both phosphonium[345–347] and sulfonium[33] ylides may also react with CS_2 to afford 1,2,4-trithiolane products. In an unusual reaction, treatment of ruthenium(III) tris(dimethyldithiocarbamate) with BF_3 in the presence of oxygen gives the salt **299**.[348]



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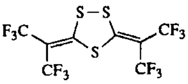

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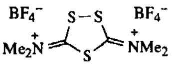
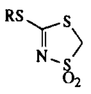


299

3.3.4. *Dithiazoles and Dithiazolines*

Treatment of chloromethanesulfonamide with CS_2 and base followed by an alkyl halide gives the 1,3,4-dithiazole 3,3-dioxide **300**.[349] In a somewhat similar reaction, the 1-alkynesulfonamides, $ArC{\equiv}CSO_2NH_2$, react with CS_2 and base followed by dimethyl sulfate to give **301**.[350] The earliest reaction of this type was that of **302** with CS_2 which gives **303**[351] and the kinetics of this process have been examined in detail.[352] Related processes include the reaction of **304** to give **305**[351] and of **306** to give **307**.[353,354] The simpler isothiourea derivative **308** also reacts with CS_2 to give **309**.[355] In some cases addition of CS_2 may be accompanied by extrusion of another heterocumulene fragment as exemplified by formation of **312** either from **310** with loss of PhNCS[355] or from **311** with loss of Bu^{t}NCO.[356]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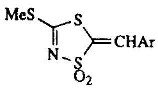
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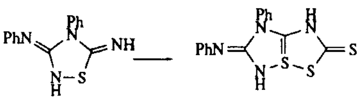
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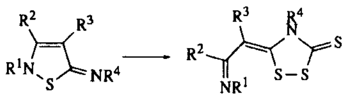
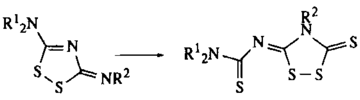
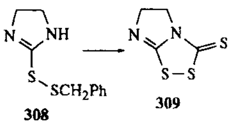
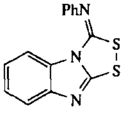

304 **305**


306 **307**


308 **309**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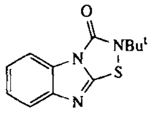
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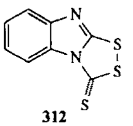
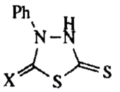
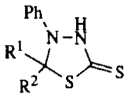

312

3.3.5. *Thiadiazoles and Thiadiazolines*

The reaction of phenylhydrazine with CS_2 in the presence of base to give the thiadiazolidinedithione **313** was reported at an early date, and in the presence of added phosgene, the product **314** was formed.[357,358] Carrying out the same reaction in the presence of an aldehyde or ketone, R^1COR^2, gives the thiadiazolidinethiones **315**[359–361] while with an acid chloride, RCOCl, the mesoionic thiadiazoliumthiolates **316** are produced.[362,363] Alkylhydrazines may also react with CS_2 and base to give heterocycles as exemplified by formation of **317** from 1,2-dimethylhydrazine[364] and **318** from the bicyclic hydrazines.[365] The reaction of *N*-alkylhydrazones of ketones with base also gives cyclic products of the type **319**, isomeric with **315**.[366,367] Thioacyl hydrazides such as PhC(=S)NHNH$_2$ react with CS$_2$ and base to give thiadiazolinethiones **320**,[335,368] but where N-1 is alkylated, as in R^{1}C(=S)N(R^2)NH$_2$, the mesoionic products **321** are formed.[369,370] In a related reaction, treatment of the amidrazone **322** with CS$_2$ affords **323**.[371] Thiosemicarbazide reacts in a similar way to give **324**[372,373] and its alkylated analogues have also been examined.[373] The *N*-aminotriazole derivatives **325** react with CS$_2$ and base to afford **326**.[374] The dihydrazone of oxalamide H$_2$N–N=C(NH$_2$)–C(NH$_2$)=N–NH$_2$, reacts with CS$_2$ to give **327** in excellent yield.[375] Treatment of hydrazine hydrate with CS$_2$ and pyridine gives the dipyridinium salt of **328** while under the same conditions thiosemicarbazide gives the salt of **324** and thiocarbohydrazide, (NH$_2$NH)$_2$CS, gives the salts of both **329** and **330**.[376]



313 X = S
314 X = O



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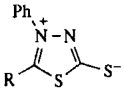

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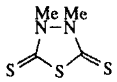

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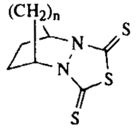

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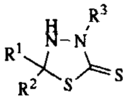

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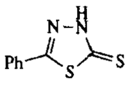

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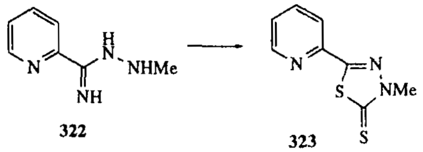

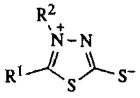

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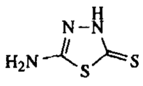

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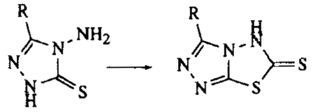

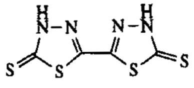

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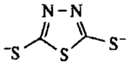

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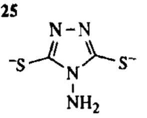

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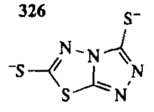
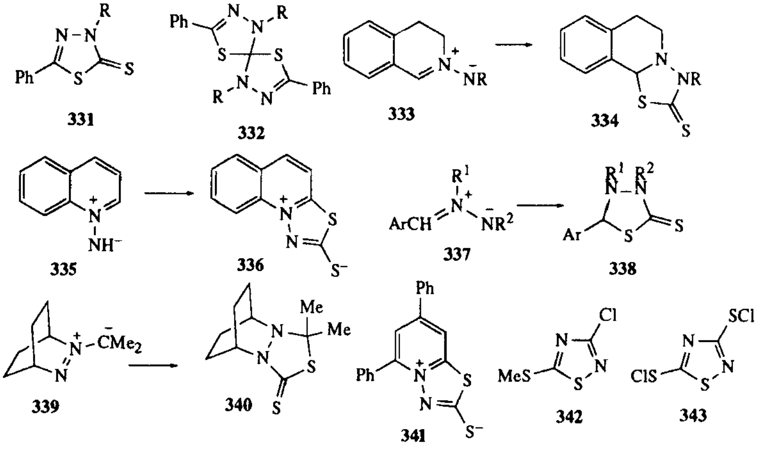


330

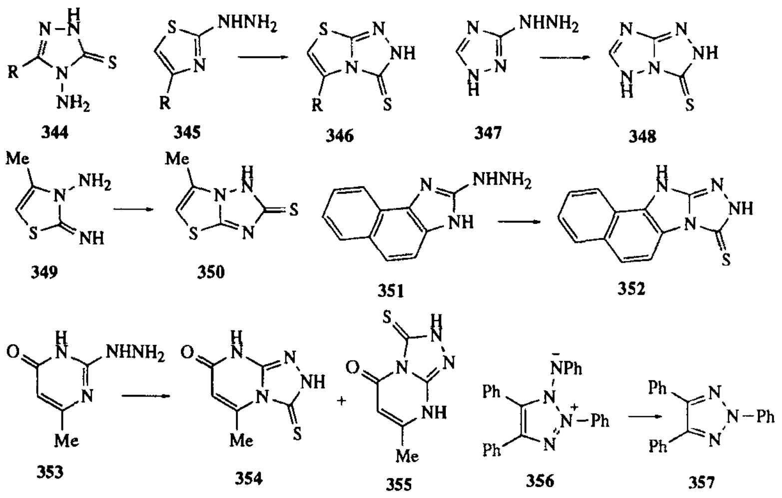
A second major group of reactions leading to heterocycles of this type is 1,3-dipolar cycloaddition of nitrile imines and azomethine imines. Addition of PhC≡N$^+$–NR$^-$ proceeds to give the 2 : 1 adducts **332** for

R = Ph,[377–379] but stops at the 1 : 1 adducts **331** for R = Me or CH_2Ph.[380,381] The reason for this discrepancy is unclear.[381] Reaction of the dihydroisoquinoline based dipoles **333** proceeds in a simple manner to give **334**[382] but for the related quinoline system **335** it is accompanied by oxidation to afford the mesoionic products **336**.[383,384] The azomethine imines **337** formed by reaction of benzaldehyde with 1,2-dialkylhydrazines add to CS_2 to give **338**,[385,386] and the azo ylide **339** adds to give **340**.[365] The pyridine-2-thione analogous to **295** reacts with CS_2 to give **341**.[338] Finally in this section, the reaction of cyanamide with CS_2 and base followed by an electrophile and a halogenating agent gives 1,2,4-thiadiazoles such as **342** and **343**[186,387,388]



3.3.6. *Triazoles*

Treatment of acylhydrazines, $RCONHNH_2$, with CS_2 and KOH followed by hydrazine gives the *N*-aminotriazolinethione products **344**.[389] A variety of heterocyclic hydrazines react with CS_2 and base to afford fused triazoles as exemplified by the conversion of **345** into **346**,[390] **347** into **348**,[391] **349** into **350**,[392] and **351** into **352**.[393] In the case of **353**, the isomeric products **354** and **355** are formed in equal amounts.[394] The reaction of the 1,2,3-triazolium *N*-phenylimide **356** with CS_2 takes an unusual course. Cycloaddition is followed by loss of PhNCS and sulfur to give the triazole **357**.[395]



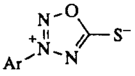
3.4. Four Heteroatoms

3.4.1. Oxatriazoles

A rare example of this type is provided by the reaction of arylhydrazines with CS_2 followed by nitrous acid to give the mesoionic oxatriazolium thiolates **358**.[396]

3.4.2. Thiatriazoles and Thiatriazolines

All the examples of this type involve interaction of azide anion with CS_2. The interaction of metal azides with CS_2 was described at an early date but the structure of the metal "azidodithioformates" was unclear.[397–400] It was not until the advent of IR spectroscopy that clear evidence was obtained for the cyclic structure **359** for these salts. They undergo *S*-alkylation with alkyl halides to give **360**,[401,402] but *N*-alkylation with acid chlorides, trityl chloride and benzhydryl bromide to give **361**.[401–404] The dimer formed by oxidation of the metal salt was also shown to have the disulfide structure **362**.[402] Formation of heterocycles of this type may take place within the coordination sphere of a transition metal and has been carried out both by treating azide complexes of copper, silver and gold[405] and palladium[406] with CS_2 and by treating a tungsten CS_2 complex with azide anion.[124]



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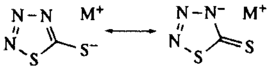

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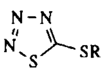

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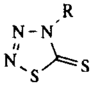

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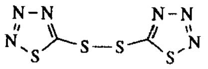

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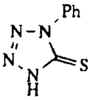


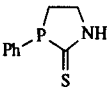
363

3.4.3. Tetrazoles

A product of this type is **363** which is formed by treatment of aniline with CS_2 and sodium azide under basic conditions followed by acidification.[407]

3.5. Five-membered Rings Containing Less Common Atoms

Reaction of (2-aminoethyl)phenylphosphine with CS_2 gives the azaphospholidinethione **364**.[408] A range of 2-aminoalkylarsines similarly give **365**[409] and the benzo fused compounds **366** have been prepared in an analogous way.[410] The 1,2-diphosphetine **367** reacts with lithium metal, CS_2 and then methyl iodide to give **368**[411] and the arsenic analogue **369** similarly affords **370**.[412] The tetraazadiborinanes **371** react with CS_2 to give products including **372** and **373**.[413]



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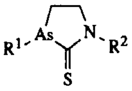

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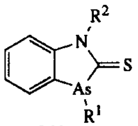

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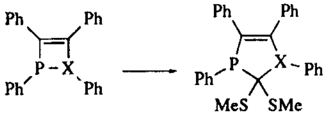
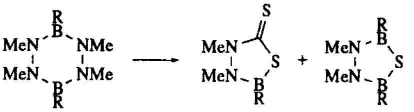


367 X = P
369 X = As

368 X = P
370 X = As



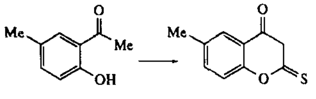
371 **372** **373**

4. FORMATION OF SIX-MEMBERED RINGS

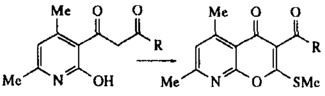
4.1. One Heteroatom

4.1.1. Pyrans

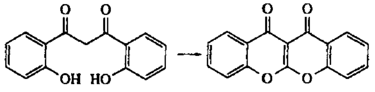
Treatment of *o*-hydroxyacetophenones such as **374** with CS_2 and base results in cyclisation to give the pyranone **375**.[340] The same process also occurs for 1,3-diketones bearing *o*-hydroxyaryl or heteroaryl groups as illustrated by formation of **377** from **376**[414] and of the double cyclisation product **379** from **378**[415] by reaction with CS_2 and base followed by dimethyl sulfate. By starting from an appropriately difunctionalised benzene, **380** can be obtained in a similar way.[416]



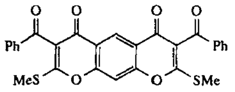
374 **375**



376 **377**



378 **379**



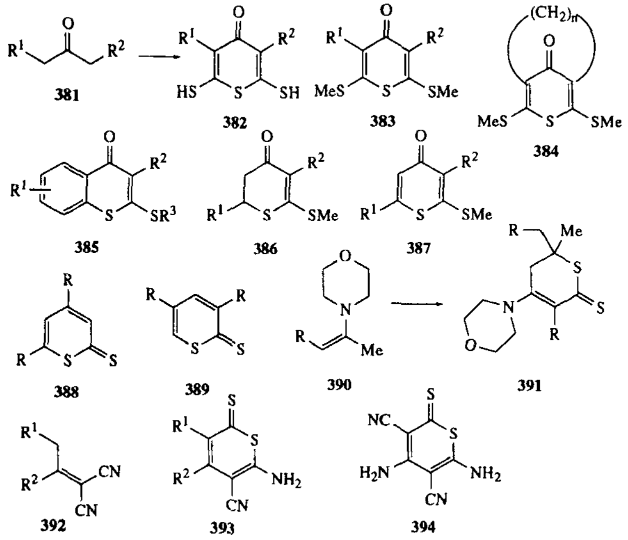
380

4.1.2. Thiopyrans

The reaction of ketones **381** with CS_2 and a base to give the thiopyranones **382** was reported at an early stage[417] and has since been extended to a wide variety of examples[418–420] with subsequent addition of methyl iodide being used to obtain **383** in some cases.[421,422] By the use of large ring cyclic ketones the products **384** have been obtained for $n = 7$–13.[100,423] The *o*-halophenyl ketones can similarly be converted into thiobenzopyranones **385**.[424,425] By use of α,β-unsaturated ketones, $R^1CH{=}CHCOCH_2R^2$, products of the type **386** are obtained,[426,427] while with acetylenic ketones, $R^1C{\equiv}CCOCH_2R^2$, the main product is **387**.[52]

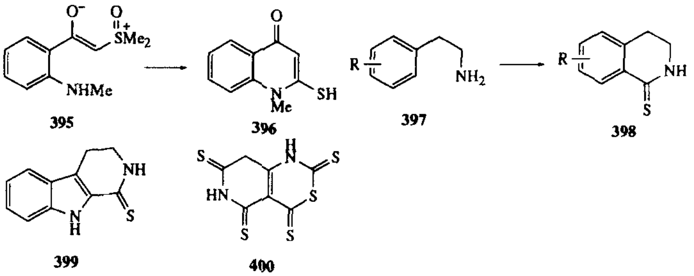
Enamines react in a 2 : 1 ratio with CS_2 to give thiopyran-2-thiones. The α-substituted type, $RC({=}CH_2)NR^1_2$ give the 4,6-disubstituted products **388** while the β-substituted enamines, $RCH{=}CHNR^1_2$, give the 3,5-disubstituted products **389**.[428,429] With both α- and β-substituents as in **390**, the reaction takes a more complex course to afford **391**.[430]

Dicyanoalkenes of the general structure **392** react with CS_2 and a base to afford the thiopyran-2-thiones **393**[431] and treatment of malononitrile with CS_2 and aqueous alkali similarly gives the product **394**.[432]



4.1.3. Pyridines

The stabilised ylide **395**, formed from *N*-methylisatoic anhydride and dimethylsulfoxonium methylide, reacts with CS_2 to give the dihydroquinolinone product **396**.[433] Treatment of 2-arylethylamines **397** with CS_2, triethylamine and ethyl chloroformate gives the tetrahydroisoquinolinethiones **398** and the corresponding indole derivative likewise affords **399**.[434] The reaction of the imine of cyanoacetone, MeC(=NH)CH_2CN, with CS_2 and base in DMF takes a complex course to eventually give **400**.[435]



4.2. Two Heteroatoms

4.2.1. *Dioxanes*

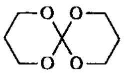
The methods of Sakai and coworkers mentioned in Section 3.2.1. are also applicable to formation of spiro dioxanes. Thus, **401** can be prepared by treatment of either the organotin compound $Bu_3SnO(CH_2)_3OSnBu_3$[58] or of the thallium compound $TlO(CH_2)_3$-OTl[61] with CS_2.

4.2.2. *Oxathianes*

Thermolysis of the bis(dithiocarbonate) **402**, obtained by reaction of propane-1,3-diol with CS_2 and base and then methyl iodide, affords the oxathiolane product **403**.[65]

4.2.3. *Oxazines*

Treatment of *o*-aminobenzyl alcohol with CS_2 in ethanol gives the benzoxazinethione product **404**.[436] The reaction of 3-aminopropanol with CS_2 and triethylamine gives **405** and the process has been extended to a variety of cyclic 3-amino alcohols leading to bicyclic tetrahydro-1,3-oxazine-2-thiones.[437]



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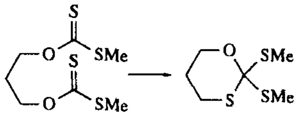
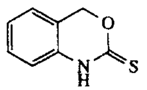


402 **403**



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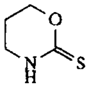

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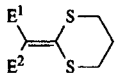

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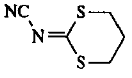

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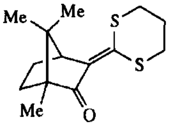

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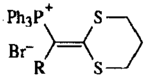

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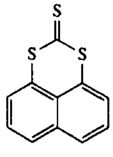
4.2.4. *Dithiins and Dithianes*

A wide variety of acidic methylene compounds react with CS_2 and a base followed by 1,3-dibromopropane to give dithianes **406**[51,179] and the reaction is also applicable to cyanamide to afford **407**.[186,187] Reaction of camphor in this way affords **408**.[438] Treatment of the ylides

$Ph_3P{=}CHR$ with CS_2 and 1,3-dibromopropane likewise gives the phosphonium salts **409**.[214]

The products from reaction of 1,8-didehydronaphthalene with CS_2 include **410**.[8] The rather unstable compound **411** can be generated by treatment of trithiocarbonic acid with malonyl dichloride.[439] Reaction of dithiocarboxylic acids, RCH_2CS_2H, with base and CS_2 gives the alkyltetrathiomalonic acid which undergoes dimerisation to form the unusual adamantane type structure **412**.[30] Treatment of 2,3-dichloronaphthoquinone with aqueous ammonium dithiocarbamate gives the pentacyclic structure **413**.[188] Dibenzyl sulfone reacts with CS_2 and NaH followed by methyl iodide to give the 1,4-dithiin *S*,*S*-dioxide **414**[440] and the *o*-chloroaryl sulfones **415** similarly cyclise to give **416**.[441] Treatment of the dialkynyl sulfides, $MeC{\equiv}C{-}S{-}C{\equiv}CR$ with BuLi/KOBu^t followed by CS_2 allowed the first access to the thienodithiin ring system **417**.[57]



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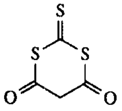

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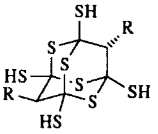

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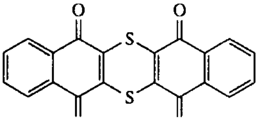

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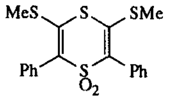

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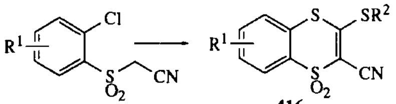
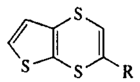


415 **416**



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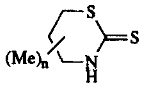
4.2.5. Thiazines

The earliest reactions of this type were those of azetidine and simple methylated derivatives, generated by base treatment of 3-haloalkyl amines, with CS_2 to give the tetrahydro-1,3-thiazine-2-thiones **418**.[442-444] The reaction of *o*-aminobenzyl alcohol with CS_2 in the presence of KOH gives **419** while in the absence of base the product **404** is formed as mentioned earlier.[445] The triazole derivatives **420** react with CS_2 in the presence of triethylamine and pyridine to give the thiazinethiones **421**.[446]

Simple aliphatic ketones react with CS_2 and aqueous ammonia to give products such as **422** obtained from acetone and **423** from methyl ethyl ketone although, as will be seen in the following section, these are easily converted into pyrimidinethiones by thermal rearrangement.[447] The reaction of cyclic ketones with CS_2 and aqueous ammonia has been examined in detail. With cyclohexanone and cycloheptanone the spiro compounds **424** and **425** are produced.[230,448] Starting from cyclopentanone, the initial product can be trapped by an added ketone, R^1COR^2, to give **426**,[449] by an *N*-arylimine of cyclohexanone to give **427**,[450] or by a heterocumulene such as phenyl isothiocyanate to give **428**.[451] Treatment of a cyclopentanone derived enamine with CS_2 followed by phenyl isothiocyanate provides an alternative route to **428** and the reaction is also successful for cyclohexanone and cyclopentanone derived enamines and with other heterocumulenes such as phenyl isocyanate and diphenylcarbodiimide.[104] Reaction of phloroglucinol with CS_2, aqueous ammonia and triethylamine affords **429** while the aza analogues **430** give **431**.[452] The products from reaction of the *β*-imino sulfones, $R^1C(=NH)CH_2SO_2R^2$, with CS_2 and a base in DMF include **432**.[101]



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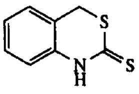

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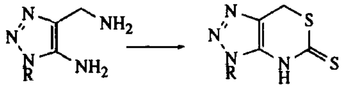
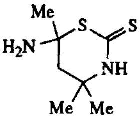


420 **421**



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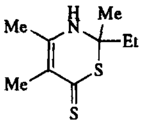

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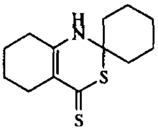

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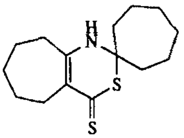

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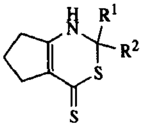

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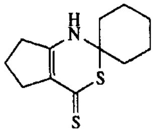

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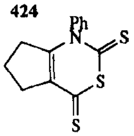

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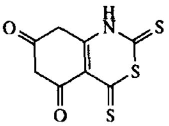

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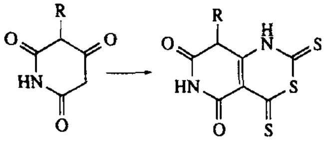
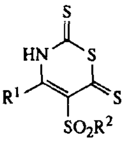
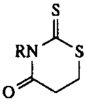


430 **431**



432

Dithiocarbamates react with β-propiolactone to give products which may be cyclised to **433**[453] and the reaction has been extended to alkylated propiolactones.[454] The reaction of α,β-unsaturated amides with CS_2 and NaH gives **434**.[455] A variety of α,β-unsaturated carbonyl compounds react with dithiocarbamates to give cyclic products. Thus, the acid chlorides, $R^1CH{=}C(R^2)COCl$, give products **435**,[456] while mesityl oxide gives **436**, the ketones PhCH=CHCOR give **437** and methyl acrylate gives **433** (R = H).[457] In related processes, **438** reacts with CS_2 and methyl iodide to give **439**,[458] treatment of ethyl 4-hydroxy-2-butynoate $HOCH_2C{\equiv}CCO_2Et$, with dithiocarbamic acid gives **440**,[40] and the amino ketone $Me_2C(NH_2)CH_2COMe$ reacts with CS_2 followed by sulfuric acid to afford **441**.[459]



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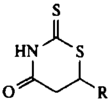

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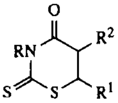

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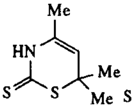

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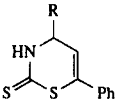

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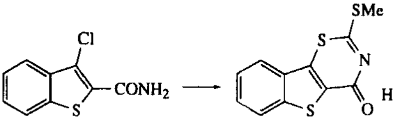
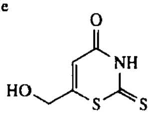


438 **439**



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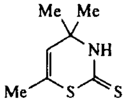
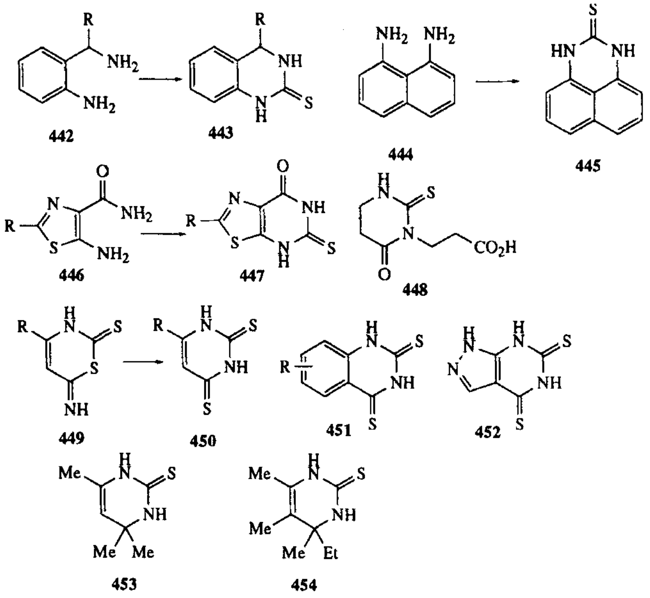


441

4.2.6. *Pyrimidines*

A variety of 1,3-diamines react with CS_2 to give the corresponding pyrimidine-2-thiones. Examples include the conversion of **442** into **443**,[460,461] and **444** into **445**.[462] The thiazole derivatives **446** similarly give **447** after reaction with CS_2 and pyridine for several days.[290] Treatment of β-alanine with CS_2 and base followed by thermal cyclisation affords **448**.[326] A suitably placed cyano group can also lead to products of this type as exemplified by the reaction of β-imino cyanides, $RC({=}NH)CH_2CN$, with CS_2 and base to afford **450** by rearrangement of the initial adducts **449**.[435] By starting from substituted *o*-aminobenzonitriles and 3-aminopyrazole-4-carbonitrile the products **451** and **452** are formed upon treatment with CS_2 and pyridine.[463] The product **422** formed from acetone, CS_2 and aqueous ammonia readily undergoes thermal rearrangement with loss of H_2S to afford **453** and the reaction of methyl ethyl ketone with the same reagents at room temperature gives **454**.[447]



4.3. Three Heteroatoms

4.3.1. Trithianes

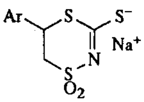
A very early report describes the reduction of CS_2 with zinc and HCl to give 1,3,5-trithiane.[464]

4.3.2. Dithiazines

The styrylsulfonamides, $ArCH{=}CHSO_2NH_2$, react with CS_2 and NaOH to give the salts **455** which can be trapped by various electrophiles.[465] The pyrazole-sulfonamide **456** reacts under similar conditions to afford **457**.[466]

4.3.3. Thiadiazines

Treatment of arylhydrazines with CS_2 and base then 1,2-dibromoethane gives the products **458**.[357,360] With chloroacetic acid as the electrophile, the reaction gives **459** while with α-chloroketones, $R^1COCH(Cl)R^2$, **460** is formed.[467] Treatment of alkylhydrazines with CS_2 and β-nitrostyrenes, $ArCH{=}CHNO_2$, takes place in a different way to give **461**.[468] Intramolecular cyclisation occurs upon treatment of 1,1-bis(2-chloroethyl)hydrazine with CS_2 to afford **462**.[469] Treatment of *N*,*N*′-dialkylethylenediamines with CS_2 followed by oxidation with iodine and potassium iodide gives the cyclised products **463**.[315] The interaction of an amine and an aldehyde with CS_2 may also give products of this type as illustrated by the formation of **464** from formaldehyde, methylamine and CS_2 and **465** from aniline, methylamine, CS_2 and formaldehyde.[470] The thiadiazinethione **466** may be formed by treatment of either cyanoguanidine or of the related imino ester with CS_2.[471,472] The reaction of imidazolidine-2-thione **39** with NaH and CS_2 is reported to give either **467**[473] or the isomeric structure **468**[35] in addition to the product **40** mentioned earlier. Finally in this section, Diels–Alder reaction of the diazadienes **469** with CS_2 gives **470**.[474]



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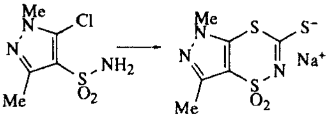
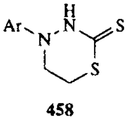


456 **457**



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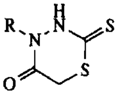

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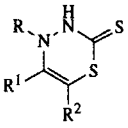

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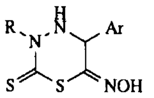

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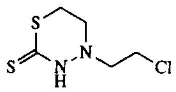

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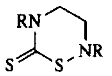

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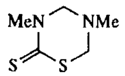

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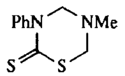

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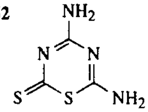

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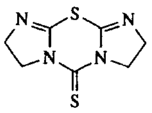

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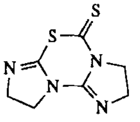

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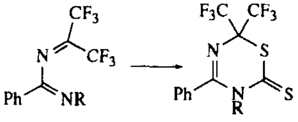
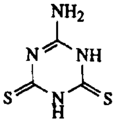


469 **470**

4.3.4. *Triazines*

The thiadiazinethione **466** formed by treatment of cyanoguanidine with CS_2 readily rearranges to the triazinedithione **471**.[471] Reaction of the pyridine derivative **472** with CS_2 and base followed by methyl iodide affords the pyridotriazine **473**.[475] The benzimidazole hydrazide **474** is reported to react with CS_2 to form **475**.[476]



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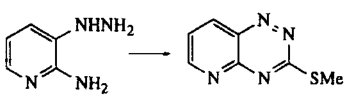
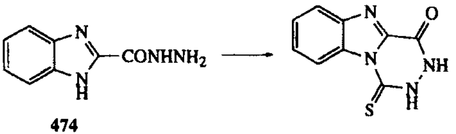


472 **473**



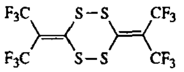
474 **475**

4.4. Four Heteroatoms

The synthesis of 1,2,4,5-tetrathianes by various methods including reactions with CS_2 has already been covered in a recent review in this journal[477] and so it will only be treated briefly here. The formation of **134** from either DMAD or $CF_3C{\equiv}CCF_3$ and CS_2 has already been noted.[130,131,136] The formation of both **298**[343,344] and **299**[348] as already described is accompanied by formation of the corresponding tetrathianes **476** and **477**, and for **477** and the tetraethyl analogue several alternative synthetic routes have been reported.[478–480] Reaction of the iodonium ylide **83** with CS_2 at room temperature gives **478**,[73] while the acyclic iodonium ylide, $(PhSO_2)_2C^{-}{-}I^{+}Ph$, similarly affords **479**.[481] Treatment of indene with CS_2 and base followed by oxidation with 1,2-dibromotetrachloroethane affords **480**.[176] Treatment of an arylhydrazine with CS_2 followed by oxidation using hydrogen peroxide or iodine gives the tetrathiane **481**.[482] Diphenyldiazomethane reacts with CS_2 to give **482** and 9-diazofluorene behaves similarly.[32] The reaction of camphor with base and CS_2 followed by oxidation with thionyl chloride gives **483** and its *E* isomer.[483,484] The dioxaphosphole **484** reacts with CS_2 to afford the tetrathiane **485**.[21]

4.5. Six-membered Rings Containing Heavier Atoms

Treatment of 3-aminoalkylphosphines, $RPH(CH_2)_3NH_2$, with CS_2 gives the heterocyclic products **486**.[408] Bis(pentamethylcyclopentadienyl)silylene, $(Cp^{*})_2Si{:}$, reacts with CS_2 to give **487**.[485]



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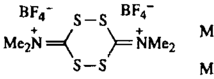

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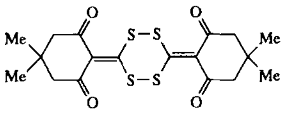

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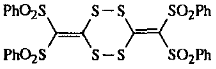

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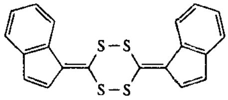

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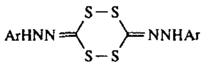

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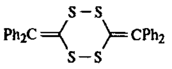

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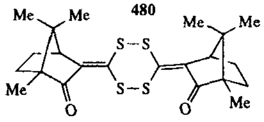

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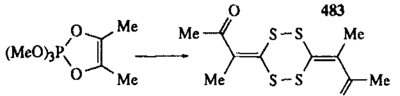
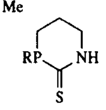


484 **485**



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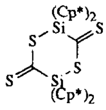
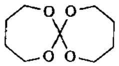


487

5. FORMATION OF SEVEN- AND EIGHT-MEMBERED RINGS

The methods of Sakai and coworkers mentioned in Sections 3.2.1 and 4.2.1 are also applicable to formation of spiro dioxepanes. Thus, **488** can be prepared by treatment of either the organotin compound $Bu_3SnO(CH_2)_4OSnBu_3$[58] or of the thallium compound $TlO(CH_2)_4$-OTl[61] with CS_2. Treatment of ylides $Ph_3P{=}CHR$ with CS_2 followed by 1,4-dibromobutane affords the salts **489**[214] while dithiepanes such as **490**[179] and **491**[438] have been prepared by reaction of the appropriate acidic methylene compounds with CS_2 and base followed by dibromobutane. With 1,4-dichlorobut-2-ene as the electrophile, products of the type **492** can be formed in addition to **162** mentioned earlier.[181]



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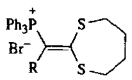

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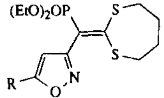

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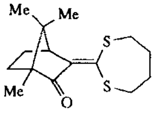

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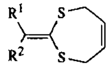

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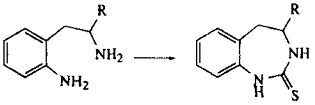
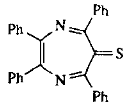


493 **494**



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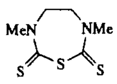

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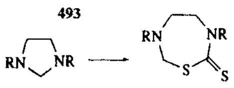
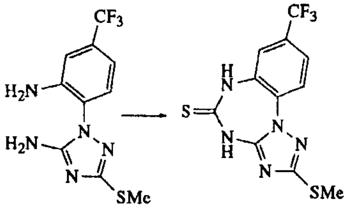
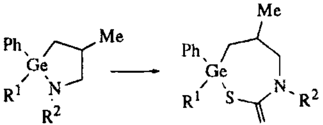


497 **498**

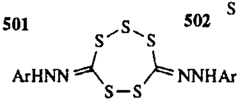
Reaction of diamines **493** with CS_2 gives the benzodiazepinethiones **494**,[460,461] while treatment of the dibenzylimine of benzil with sodium metal and CS_2 followed by air oxidation gives the diazepinethione **495**.[325] Reaction of the hypervalent silicon compounds **279** with CS_2 gives some of the thiadiazepine product **496** in addition to **280** mentioned earlier.[316] The closely related thiadiazepines **498** are formed upon treatment of imidazolidines **497** with CS_2.[486] Reaction of the triazole containing diamine **499** with CS_2 affords the fused triazepinethione **500**.[487] The unusual germanium containing heterocycles **501** react with CS_2 to give **502** but the reaction is reversible since attempted distillation of **502** leads to regeneration of **501**.[488] Treatment of arylhydrazines with CS_2 and ammonia followed by iodine oxidation may give the pentathiepines **503** instead of the more usual tetrathianes **481** mentioned earlier.[482]



499 **500**



501 **502**



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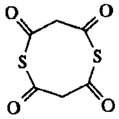

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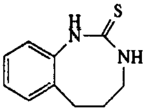

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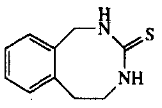

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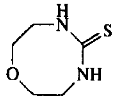

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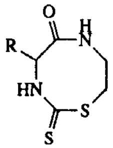

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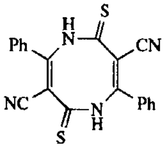


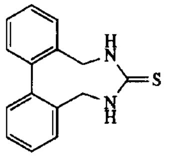
509

The unstable product **411** formed from trithiocarbonic acid and malonyl dichloride undergoes dimerisation with loss of CS_2 to afford the dithiocanetetraone **504**.[439] The isomeric benzodiazocanethiones **505**[460,489] and **506**[490] are formed from the appropriate diamines and

CS_2 while similar reaction of bis(2-aminoethyl) ether gives the oxadiazocane system **507**.[491,492] Esters of α-amino acids react with CS_2 and triethylamine followed by 2-bromoethylamine hydrobromide to give the thiadiazocane products **508**.[493] The reaction of PhC(=NH)CH_2CN with CS_2 and base which normally gives **450** by rearrangement of the initial adducts **449** instead gives the diazocane product **509** when an excess of base is used.[435]

6. FORMATION OF NINE-MEMBERED AND LARGER RINGS

The few examples of this type all involve reaction of suitable diamines with CS_2 to give the cyclic thiourea products. Thus, the dibenzodiazonine system **510** is formed from the corresponding diamine with CS_2 and iodine in pyridine,[494] while treatment of *p*-phenylenediamine with CS_2 gives **511**.[495] Reaction of bis(2-aminoethyl) ether gives not only the oxadiazocane system **507** mentioned in the last section, but also the 16-membered ring product **512** and by starting with ethylene glycol bis(2-aminoethyl) ether, both the 11- and 22-membered ring products **513** and **514** can be obtained.[491]



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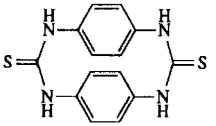

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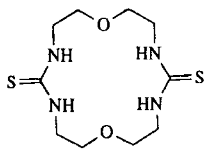

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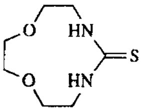

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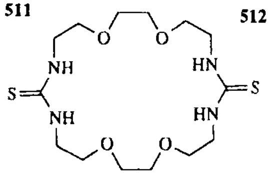

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References

[1] L. N. Grobov, A. P. Sineokov and V. S. Etlis, *Usp. Khim.*, **35**, 1574 (1966); *Chem. Abstr.*, **66**, 46261 (1967).
[2] G. A. Razuvaev, V. S. Etlis and L. N. Grobov, *Zh. Obshch. Khim.*, **33**, 1366 (1963); *Chem. Abstr.*, **59**, 9827 (1963).

[3] R. C. Vander Linden, J. M. Salva and P. A. C. Smith, *US Pat.* 3,542,808 (1970); *Chem. Abstr.*, **74**, 53498 (1971).
[4] T. Yoshimura, K. Asada and S. Oae, *Bull. Chem. Soc. Jpn.*, **55**, 3000 (1982).
[5] M. F. Zipplies, M.-J. De Vos and T. C. Bruice, *J. Org. Chem.*, **50**, 3228 (1985).
[6] M. Hamana, B. Umezawa and S. Nakashima, *Chem. Pharm. Bull.*, **10**, 969 (1962).
[7] M. Ngounda, H. Le Bozec and P. Dixneuf, *J. Org. Chem.*, **47**, 4000 (1982).
[8] J. Nakayama, S. Dan and M. Hoshino, *J. Chem. Soc., Perkin Trans. 1*, 413 (1981).
[9] G. Jenner and M. Papadopoulos, *Tetrahedron Lett.*, **26**, 725 (1985).
[10] G. H. Birum and C. N. Matthews, *J. Am. Chem. Soc.*, **90**, 3842 (1968).
[11] H. J. Bestmann and R. W. Saalfrank, *J. Chem. Res. (S)*, 313 (1979).
[12] Y. Nakadaira, Y. Ohkura, S. Kyushin, M. Ohashi, H. Sakurai, K. Ueno and S. Kanouchi, *Tetrahedron Lett.*, **33**, 4013 (1992).
[13] M. Muraoka, T. Itoi and T. Yamamoto, *J. Chem. Res. (S)*, 256 (1982).
[14] V. Meyer and H. Wege, *Ber.*, **24**, 3535 (1891).
[15] P. Petrenko-Kritschenko, *Ber.*, **25**, 2239 (1892).
[16] C. Kelber and A. Schwarz, *Ber.*, **45**, 137 (1912).
[17] P. Yates, D. R. Moore and T. R. Lynch, *Can. J. Chem.*, **49**, 1456 (1971).
[18] Y. Tominaga, Y. Morita, Y. Matsuda and G. Kobayashi, *Chem. Pharm. Bull.*, **23**, 2390 (1975).
[19] A. Senning and R. G. Hazell, *Sulfur Lett.*, **2**, 173 (1984).
[20] J. A. Kapecki, J. E. Baldwin and I. C. Paul, *J. Am. Chem. Soc.*, **90**, 5800 (1968).
[21] A. J. Kirby, *Tetrahedron*, **22**, 3001 (1966).
[22] P. Yates and J. A. Eenkhorn, *Heterocycles*, **7**, 961 (1977).
[23] R. Gompper and W. Töpfl, *Chem. Ber.*, **95**, 2861 (1962).
[24] D. C. Dittmer, H. E. Simmons and R. D. Vest, *J. Org. Chem.*, **29**, 497 (1964).
[25] V. N. Drozd and E. N. Komarova, *Zh. Org. Khim.*, **24**, 1773 (1988); *Chem. Abstr.*, **111**, 115080 (1989).
[26] E. Schaumann and F.-F. Grabley, *Liebigs Ann. Chem.*, 1715 (1979).
[27] R. Gompper, R. R. Schmidt and E. Kutter, *Liebigs Ann. Chem.*, **684**, 37 (1965).
[28] T. Takeshima, N. Fukada, E. Okabe, F. Mineshima and M. Muraoka, *J. Chem. Soc., Perkin Trans. 1*, 1277 (1975).
[29] W.-D. Rudorf, E. Günther and M. Augustin, *Tetrahedron*, **40**, 381 (1984).
[30] K. Hartke, N. Rettberg, D. Dutta and H.-D. Gerber, *Liebigs Ann. Chem.*, 1081 (1993).
[31] G. Purrello and P. Fiandoca, *J. Chem. Soc., Perkin Trans. 1*, 692 (1976).
[32] A. Schönberg, E. Frese and K.-H. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).
[33] Y. Hayashi, T. Akazawa, K. Yamamoto and R. Oda, *Tetrahedron Lett.*, 1781 (1971).
[34] S. Rüdiger and K. Seppelt, *J. Fluorine Chem.*, **82**, 29 (1997).
[35] M. Yokoyama, S. Ohtuki, M. Muraoka and T. Takeshima, *Tetrahedron Lett.*, 3823 (1978).
[36] T. Tsuchiya, M. Yasumoto, I. Shibuya, Y. Taguchi, K. Yonemoto and M. Goto, *Chem. Lett.*, 1423 (1990).
[37] D. Männig, C. K. Narula, H. Nöth and U. Wietelmann, *Chem. Ber.*, **118**, 3748 (1985).
[38] N. Tokitoh, K. Kishikawa and R. Okazaki, *J. Chem. Soc., Chem. Commun.*, 1425 (1995).
[39] N. Tokitoh, M. Saito and R. Okazaki, *J. Am. Chem. Soc.*, **115**, 2065 (1993); M. Saito, N. Tokitoh and R. Okazaki, *Organometallics*, **15**, 4531 (1996).
[40] R. N. Warrener and E. N. Cain, *Aust. J. Chem.*, **24**, 785 (1971).
[41] H. V. A. Briscoe, J. B. Peel and P. L. Robinson, *J. Chem. Soc.*, 2857 (1928).
[42] N. R. Clark and W. E. Webster, *Ger. Pat.* 2,225,443 (1973); *Chem. Abstr.*, **78**, 111110 (1973).
[43] F. Azizian and J. S. Pizey, *J. Chem. Tech. Biotechnol.*, **30**, 429 (1980); *Chem. Abstr.*, **94**, 121207 (1981).
[44] F. Azizian and J. S. Pizey, *J. Chem. Tech. Biotechnol.*, **30**, 648 (1980); *Chem. Abstr.*, **94**, 139535 (1981).

[45] F. Azizian and J. S. Pizey, *J. Chem. Tech. Biotechnol.*, **31**, 163 (1981); *Chem. Abstr.*, **95**, 150293 (1981).
[46] H. Suhr and A. Szabo, *Liebigs Ann. Chem.*, **752**, 37 (1971).
[47] G. Ege, K. Gilbert and F. W. Nader, *Chem. Ber.*, **114**, 1074 (1981).
[48] J. Meyer, *Helv. Chim. Acta*, **8**, 38 (1925).
[49] W.-D. Rudorf, A. Schierhorn and M. Augustin, *J. Prakt. Chem.*, **321**, 1021 (1979).
[50] K. Clarke, W. R. Fox and R. M. Scrowston, *J. Chem. Soc., Perkin Trans. 1*, 1029 (1980).
[51] K. A. Jensen and L. Henriksen, *Acta Chem. Scand.*, **22**, 1107 (1968).
[52] W.-D. Rudorf and R. Schwarz, *Tetrahedron Lett.*, **28**, 4267 (1987).
[53] R. L. P. de Jong and L. Brandsma, *J. Chem. Soc., Chem. Commun.*, 1056 (1983).
[54] A. Commerçon and G. Ponsinet, *Tetrahedron Lett.*, **26**, 5131 (1985).
[55] H. Westmijze, K. Ruitenberg, J. Meijer and P. Vermeer, *Tetrahedron Lett.*, **21**, 1771 (1980).
[56] J. Meijer, K. Ruitenberg, H. Westmijze and P. Vermeer, *Synthesis*, 551 (1981).
[57] R. L. P. de Jong and L. Brandsma, *J. Organomet. Chem.*, **238**, C17 (1982).
[58] S. Sakai, Y. Kiyohara, K. Itoh and Y. Ishii, *J. Org. Chem.*, **35**, 2347 (1970).
[59] S. Sakai, Y. Kobayashi and Y. Ishii, *J. Org. Chem.*, **36**, 1176 (1971).
[60] S. Sakai, M. Murata, N. Wada and T. Fujinami, *Bull. Chem. Soc. Jpn.*, **56**, 1873 (1983).
[61] S. Sakai, Y. Kuroda and Y. Ishii, *J. Org. Chem.*, **37**, 4198 (1972).
[62] Y. Taguchi, K. Yanagiya, I. Shibuya and Y. Suhara, *Bull. Chem. Soc. Jpn.*, **61**, 921 (1988).
[63] V. A. Mullin, A. N. Zolotov and V. I. Shishkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **23**, 41 (1980); *Chem. Abstr.*, **93**, 7939 (1980).
[64] J. Uenishi, M. Motoyama, Y. Nishiyama and S. Wakabayashi, *J. Chem. Soc., Chem. Commun.*, 1421 (1991).
[65] A. Faure and G. Descotes, *Synthesis*, 286 (1978).
[66] S. Sakai, H. Niimi and Y. Ishii, *J. Organomet. Chem.*, **25**, C23 (1970).
[67] S. Sakai, H. Niimi and Y. Ishii, *J. Organomet. Chem.*, **72**, 103 (1974).
[68] K. Tomita, M. Nagano and H. Oka, *Chem. Pharm. Bull.*, **16**, 914 (1968).
[69] K. Tomita and M. Nagano, *Chem. Pharm. Bull.*, **16**, 1324 (1968).
[70] K. Tomita and M. Nagano, *Chem. Pharm. Bull.*, **17**, 2442 (1969).
[71] D. Villemin and A. Ben Alloum, *Synth. Commun.*, **22**, 1351 (1992).
[72] M. Papadopoulou, S. Spyroudis and A. Varvoglis, *J. Org. Chem.*, **50**, 1509 (1985).
[73] L. P. Hadjiarapoglou, *Tetrahedron Lett.*, **28**, 4449 (1987).
[74] R. Huisgen, G. Binsch and H. König, *Chem. Ber.*, **97**, 2868 (1964).
[75] T. Ibata and H. Nakano, *Bull. Chem. Soc. Jpn.*, **63**, 3096 (1990).
[76] H. Nakano, H. Tamura and T. Ibata, *Bull. Chem. Soc. Jpn.*, **64**, 771 (1991).
[77] D. Delaunay, L. Toupet and M. Le Corre, *J. Org. Chem.*, **60**, 6604 (1995).
[78] L. Knorr and P. Rössler, *Ber.*, **36**, 1278 (1903).
[79] D. Lednicer and D. E. Emmert, *J. Med. Chem.*, **11**, 1258 (1968).
[80] M. G. Ettlinger, *J. Am. Chem. Soc.*, **72**, 4792 (1950).
[81] M. Viscontini and K. Adank, *Helv. Chim. Acta*, **33**, 2251 (1950).
[82] M. Chanon, F. Chanon and J. Metzger, *J. Chem. Soc., Chem. Commun.*, 425 (1974).
[83] C.-N. Hsiao, L. Liu and M. J. Miller, *J. Org. Chem.*, **52**, 2201 (1987).
[84] A. A. Rosen, *J. Am. Chem. Soc.*, **74**, 2994 (1952).
[85] G. Li and T. Ohtani, *Heterocycles*, **45**, 2471 (1997).
[86] R. A. Aitken, D. P. Armstrong, S. T. E. Mesher and R. H. B. Galt, *Tetrahedron Lett.*, **35**, 6143 (1994); *J. Chem. Soc., Perkin Trans. 1*, 2139 (1997).
[87] H. A. Bruson and J. W. Eastes, *J. Am. Chem. Soc.*, **59**, 2011 (1937).
[88] E. Schipper, E. Chinery and J. Nichols, *J. Org. Chem.*, **26**, 4145 (1961).
[89] H. J. Roth and H. Schlump, *Arch. Pharm. (Weinheim, Ger.)*, **296**, 213 (1963); *Chem. Abstr.*, **59**, 6379 (1963).
[90] M. Skulski, D. L. Garmaise and A. F. McKay, *Can. J. Chem.*, **34**, 815 (1956).

[91] A. I. Meyers and M. E. Ford, *J. Org. Chem.*, **41**, 1735 (1976).
[92] J. A. Van Allan and B. D. Deacon, *Org. Synth.*, **30**, 56 (1950).
[93] L. Katz and M. S. Cohen, *J. Org. Chem.*, **19**, 758 (1954).
[94] I. Shahak, Y. Sasson and Y. Wolman, *Synthesis*, 281 (1974).
[95] S. Sakai, Y. Asai, Y. Kiyohara, K. Itoh and Y. Ishii, *Organomet. Chem. Synth.*, **1**, 45 (1970/1971); *Chem. Abstr.*, **74**, 76483 (1971).
[96] J. Nakayama, *J. Chem. Soc., Perkin Trans. 1*, 525 (1975).
[97] E. K. Fields and S. Meyerson, *Tetrahedron Lett.*, 629 (1970).
[98] R. Couturier, D. Paquer and A. Thuillier, *C. R. Seances Acad. Sci., Ser. C*, **270**, 1878 (1970).
[99] J.-L. Burgot and J. Vialle, *Bull. Soc. Chim. Fr.*, 137 (1974).
[100] A. Thuillier and J. Vialle, *Bull. Soc. Chim. Fr.*, 2194 (1962).
[101] M. Muraoka, T. Yamamoto, T. Ebisawa, W. Kobayashi and T. Takeshima, *J. Chem. Soc., Perkin Trans. 1*, 1017 (1978).
[102] J. Fabian, K. Gewald and R. Mayer, *Angew. Chem., Int. Ed. Engl.*, **2**, 45 (1963).
[103] R. Mayer, P. Wittig, J. Fabian and R. Heitmüller, *Chem. Ber.*, **97**, 654 (1964).
[104] R. Gompper, B. Wetzel and W. Elser, *Tetrahedron Lett.*, 5519 (1968).
[105] Y. Tominaga, H. Norisue, C. Kamio, T. Masunari, Y. Miyashiro and A. Hosomi, *Heterocycles*, **31**, 1 (1990).
[106] V. Z. Laishev, M. L. Petrov and A. A. Petrov, *Zh. Org. Khim.*, **17**, 2064 (1981); *Chem. Abstr.*, **96**, 122329 (1982).
[107] H. Yoshida, T. Yao, T. Ogata and S. Inokawa, *Bull. Chem. Soc. Jpn.*, **49**, 3128 (1976).
[108] K. Hartke and R. Hoffman, *Liebigs Ann. Chem.*, 483 (1980).
[109] V. A. Bobylev, M. L. Petrov and A. A. Petrov, *Zh. Org. Khim.*, **17**, 1392 (1981); *Chem. Abstr.*, **96**, 6625 (1982).
[110] V. A. Bobylev, M. L. Petrov and A. A. Petrov, *Zh. Org. Khim.*, **18**, 274 (1982); *Chem. Abstr.*, **96**, 199558 (1982).
[111] K. Gewald, *Z. Chem.*, **3**, 26 (1963).
[112] M. Yokoyama, *Bull. Chem. Soc. Jpn.*, **43**, 2938 (1970).
[113] C. Portail and J. Vialle, *Bull. Soc. Chim. Fr.*, 3187 (1966).
[114] D. Lentz, S. Rüdiger and K. Seppelt, *J. Fluorine Chem.*, **84**, 103 (1997).
[115] Y. Taguchi, M. Yasumoto, I. Shibuya and Y. Suhara, *Bull. Chem. Soc. Jpn.*, **62**, 474 (1989).
[116] J. A. Durden, H. A. Stansbury and W. H. Catlette, *J. Am. Chem. Soc.*, **82**, 3082 (1960).
[117] C. C. J. Culvenor, W. Davies and K. H. Pausacker, *J. Chem. Soc.*, 1050 (1946).
[118] S. M. Iqbal and L. N. Owen, *J. Chem. Soc.*, 1030 (1960).
[119] C. G. Overberger and A. Drucker, *J. Org. Chem.*, **29**, 360 (1964).
[120] M. V. Jesudason and L. N. Owen, *J. Chem. Soc., Perkin Trans. 1*, 2024 (1974).
[121] M. E. Ali, N. G. Kardouche and L. N. Owen, *J. Chem. Soc., Perkin Trans. 1*, 748 (1975).
[122] Y. Taguchi, K. Yanagiya, I. Shibuya and Y. Suhara, *Bull. Chem. Soc. Jpn.*, **60**, 727 (1987).
[123] N. G. Kardouche and L. N. Owen, *J. Chem. Soc., Perkin Trans. 1*, 754 (1975).
[124] W. A. Schenk, T. Schwietzke and H. Müller, *J. Organomet. Chem.*, **232**, C41 (1982).
[125] S. Hünig and E. Fleckenstein, *Liebigs Ann. Chem.*, **738**, 192 (1970).
[126] H. K. Spencer, M. P. Cava, F. G. Yamagishi and A. F. Garito, *J. Org. Chem.*, **41**, 730 (1976).
[127] A. Shafiee, M. Vosooghi and I. Lalezari, *J. Heterocycl. Chem.*, **17**, 545 (1980).
[128] L. Benati and P. C. Montevecchi, *J. Org. Chem.*, **42**, 2025 (1977).
[129] H. Plieninger, C. C. Heuck and R. Bühler, *Tetrahedron*, **28**, 73 (1972).
[130] H. D. Hartzler, *J. Am. Chem. Soc.*, **92**, 1412 (1970).
[131] H. D. Hartzler, *J. Am. Chem. Soc.*, **95**, 4379 (1973).
[132] B. P. Bespalov, Yu. N. Porshnev and V. V. Titov, *Khim. Geterotsikl. Soedin.*, 338 (1976); *Chem. Abstr.*, **85**, 32903 (1976).

[133] J. E. Rice, P. Wojciechowski and Y. Okamoto, *Heterocycles*, **18**, 191 (1982).
[134] Y. Okamoto, H. S. Lee and S. T. Attarwala, *J. Org. Chem.*, **50**, 2788 (1985).
[135] T. Nagawa, Y. Zama and Y. Okamoto, *Bull. Chem. Soc. Jpn.*, **57**, 2035 (1984).
[136] D. L. Coffen, *Tetrahedron Lett.*, 2633 (1970).
[137] J. E. Rice and Y. Okamoto, *J. Org. Chem.*, **46**, 446 (1981).
[138] C. G. Krespan and D. C. England, *J. Org. Chem.*, **33**, 1850 (1968).
[139] W. Ried and H. Wegwitz, *Liebigs Ann. Chem.*, 89 (1975).
[140] F. M. Benitez and J. R. Grunwell, *Tetrahedron Lett.*, 3413 (1977).
[141] F. M. Benitez and J. R. Grunwell, *J. Org. Chem.*, **43**, 2917 (1978).
[142] R. Mayer and B. Gebhardt, *Chem. Ber.*, **97**, 1298 (1964).
[143] K. Takimiya, A. Morikami and T. Otsubo, *Synlett*, 319 (1997).
[144] H. Behringer and J. Falkenberg, *Tetrahedron Lett.*, 1895 (1967).
[145] A. Krebs and H. Kimling, *Angew. Chem., Int. Ed. Engl.*, **10**, 509 (1971).
[146] A. Krebs and H. Kimling, *Liebigs Ann. Chem.*, 2074 (1974).
[147] E. Stavridou, H. Schuhmacher and H. Meier, *Liebigs Ann. Chem.*, 435 (1989).
[148] J. Nakayama, *J. Chem. Soc., Chem. Commun.*, 166 (1974).
[149] J. Nakayama, *Synthesis*, 38 (1975).
[150] J. Nakayama, E. Seki and M. Hoshino, *J. Chem. Soc., Perkin Trans. 1*, 4681 (1978).
[151] J. Nakayama, A. Sakai and M. Hoshino, *J. Org. Chem.*, **49**, 5084 (1984).
[152] B. Fetkenheuer, H. Fetkenheuer and H. Lecus, *Ber.*, **60**, 2528 (1927).
[153] S. Wawzonek and S. M. Heilmann, *J. Org. Chem.*, **39**, 511 (1974).
[154] M. F. Hurley and J. Q. Chambers, *J. Org. Chem.*, **46**, 775 (1981).
[155] G. Steimecke, R. Kirmse and E. Hoyer, *Z. Chem.*, **15**, 28 (1975).
[156] G. Steimecke, H. J. Sieler, R. Kirmse and E. Hoyer, *Phosphorus Sulfur*, **7**, 49 (1979).
[157] T. Otsubo and F. Ogura, *Bull. Chem. Soc. Jpn.*, **58**, 1343 (1985).
[158] K. Hartke, T. Kissel, J. Quante and R. Matusch, *Chem. Ber.*, **113**, 1898 (1980).
[159] E. K. Moltzen, A. Senning, R. G. Hazell and H. Lund, *Acta Chem. Scand. B*, **40**, 593 (1986).
[160] R.-M. Olk, B. Olk, W. Dietzsch, W. Kirmse and E. Hoyer, *Coord. Chem. Rev.*, **117**, 99 (1992).
[161] N. Svenstrup and J. Becher, *Synthesis*, 215 (1995).
[162] E. Ciganek and C. G. Krespan, *J. Org. Chem.*, **33**, 541 (1968).
[163] P. Yates and L. L. Williams, *Tetrahedron Lett.*, 1205 (1968).
[164] J. E. Baldwin and J. A. Kapecki, *J. Org. Chem.*, **34**, 724 (1969).
[165] K. Dichmann, D. Bichan, S. C. Nyburg and P. Yates, *Tetrahedron Lett.*, 3649 (1971).
[166] P. Yates, B. G. Christensen and L. L. Williams, *Can. J. Chem.*, **49**, 1691 (1971).
[167] M. Augustin, W. Dölling and A. Vogt, *Z. Chem.*, **23**, 333 (1983).
[168] W. Dölling, A. Vogt and M. Augustin, *Monatsh. Chem.*, **120**, 879 (1989).
[169] W. Dölling and A. Hildebrandt, *J. Prakt. Chem.*, **331**, 439 (1989).
[170] A. K. Bhattacharya and A. G. Hortmann, *J. Org. Chem.*, **39**, 95 (1974).
[171] N. F. Haley and M. W. Fichtner, *J. Org. Chem.*, **45**, 175 (1980).
[172] H. R. Kricheldorf, *Angew. Chem., Int. Ed. Engl.*, **10**, 726 (1971).
[173] N. F. Haley, *Tetrahedron Lett.*, 5161 (1978).
[174] N. F. Haley and M. W. Fichtner, *J. Org. Chem.*, **45**, 2959 (1980).
[175] R. Gompper and E. Kutter, *Chem. Ber.*, **98**, 2825 (1965).
[176] Z. S. Ariyan, C. I. Courduvelis, J. T. O'Brien and W. D. Spall, *J. Chem. Soc., Perkin Trans. 1*, 447 (1974).
[177] G. Sabbioni, A. Otter, R. W. Millar and M. Neuenschwander, *Helv. Chim. Acta*, **68**, 1543 (1985).
[178] D. Ladurée, D. Paquer and P. Rioult, *Recl. Trav. Chim. Pays-Bas*, **96**, 254 (1977).
[179] R. Neidlein, T. Eichinger and G. Nkusi, *J. Prakt. Chem./Chem.-Ztg.*, **334**, 432 (1992).
[180] E. N. Komarova, D. S. Yufit, Yu. T. Struchkov and V. N. Drozd, *Zh. Org. Khim.*, **25**, 1512 (1989); *Chem. Abstr.*, **112**, 77003 (1990).

[181] W.-D. Rudorf, R. Schwarz and M. Augustin, *J. Prakt. Chem.*, **328**, 215 (1986).
[182] Y. Ueno, T. Nakai and M. Okawara, *Bull. Chem. Soc. Jpn.*, **43**, 162 (1970).
[183] M. Richter and W. Richter, *Z. Chem.*, **29**, 16 (1989).
[184] C. W. Voigt and G. Gattow, *Z. Anorg. Allg. Chem.*, **438**, 195 (1978).
[185] M. Busch and E. Lingenbrink, *J. Prakt. Chem.*, **61**, 336 (1900).
[186] R. J. Timmons and L. S. Wittenbrook, *J. Org. Chem.*, **32**, 1566 (1967).
[187] J. J. D'Amico and R. H. Campbell, *J. Org. Chem.*, **32**, 2567 (1967).
[188] N. K. Sundholm and A. E. Smith, *J. Am. Chem. Soc.*, **73**, 3459 (1951).
[189] E. Campaigne and N. W. Jacobsen, *J. Org. Chem.*, **29**, 1703 (1964).
[190] S. M. Gurvich and R.Ya. Belova, *Zh. Obshch. Khim.*, **31**, 1631 (1961); *Chem. Abstr.*, **55**, 22129 (1961).
[191] B. Krebs and G. Gattow, *Angew. Chem.*, **75**, 978 (1963).
[192] L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1733 (1959).
[193] E. Klingsberg, *Synthesis*, 29 (1972).
[194] G. S. Bajwa, K. D. Berlin and H. A. Pohl, *J. Org. Chem.*, **41**, 145 (1976).
[195] S. Gronowitz and P. Moses, *Acta Chem. Scand.*, **16**, 105 (1962).
[196] L.-Y. Chiang, P. Shu, D. Holt and D. Cowan, *J. Org. Chem.*, **48**, 4713 (1983).
[197] A. M. Richter, N. Beye and E. Fanghänel, *Synthesis*, 1149 (1990).
[198] H. D. Hartzler, *J. Am. Chem. Soc.*, **93**, 4961 (1971).
[199] J. E. Mulvaney and D. M. Chang, *Macromolecules*, **13**, 240 (1980).
[200] M. Sato, N. C. Gonnella and M. P. Cava, *J. Org. Chem.*, **44**, 930 (1979).
[201] E. C. Taylor and R. Dötzer, *J. Org. Chem.*, **56**, 1816 (1991).
[202] C. U. Pittman and M. Narita, *J. Chem. Soc., Chem. Commun.*, 960 (1975).
[203] T. Sugimoto, H. Awaji, I. Sugimoto, Y. Misaki, T. Kawase, S. Yoneda, Z. Yoshida, T. Kobayashi and H. Anzai, *Chem. Mater.*, **1**, 535 (1989).
[204] M. Salle, A. Belyasmine, A. Gorgues, M. Jubault and N. Soyer, *Tetrahedron Lett.*, **32**, 2897 (1991).
[205] R. A. Aitken, G. Ferguson and S. V. Raut, *J. Chem. Soc., Chem. Commun.*, 812 (1991).
[206] R. A. Aitken, S. V. Raut and G. Ferguson, *Tetrahedron*, **48**, 8023 (1992).
[207] R. A. Aitken, T. Massil and S. V. Raut, *Phosphorus, Sulfur Silicon*, **77**, 172 (1993).
[208] Yu. G. Shtyrlin, N. I. Tyryshkin, G. G. Iskhakova, V. V. Gavrilov, V. D. Kiselev and A. I. Konovalov, *Zh. Obshch. Khim.*, **65**, 1101 (1995); *Chem. Abstr.*, **124**, 146288 (1996).
[209] R. A. Aitken, T. Massil and S. V. Raut, *J. Chem. Soc., Chem. Commun.*, 2603 (1994).
[210] R. A. Aitken, K. Carcas, L. Hill, T. Massil and S. V. Raut, *Tetrahedron*, **53**, 2261 (1997).
[211] R. A. Aitken, L. Hill, T. Massil, M. B. Hursthouse and K. M. A. Malik, *Tetrahedron*, **53**, 10441 (1997).
[212] R. A. Aitken, L. Hill and P. Lightfoot, *Tetrahedron Lett.*, **38**, 7927 (1997).
[213] L. R. Melby, H. D. Hartzler and W. A. Sheppard, *J. Org. Chem.*, **39**, 2456 (1974).
[214] H. J. Bestmann, R. Engler, H. Hartung and K. Roth, *Chem. Ber.*, **112**, 28 (1979).
[215] V. N. Drozd and A. S. Vyazgin, *Zh. Org. Khim.*, **19**, 2210 (1983); *Chem. Abstr.*, **100**, 51486 (1984).
[216] V. N. Drozd and A. S. Vyazgin, *Zh. Org. Khim.*, **21**, 1335 (1985); *Chem. Abstr.*, **104**, 34020 (1986).
[217] A. Souizi and A. Robert, *Synthesis*, 1059 (1982).
[218] R. Okazaki, T. Fujii and N. Inamoto, *J. Phys. Org. Chem.*, **1**, 75 (1988); *Chem., Abstr.*, **111**, 194816 (1989).
[219] R. Mayer and A. K. Müller, *Z. Chem.*, **4**, 384 (1964).
[220] E. M. Engler and V. V. Patel, *J. Org. Chem.*, **40**, 387 (1975).
[221] A. Shafiee, I. Lalezari and F. Savabi, *Synthesis*, 764 (1977).
[222] M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, **45**, 2632 (1980).
[223] V. Z. Laishev, M. L. Petrov and A. A. Petrov, *Zh. Org. Khim.*, **18**, 514 (1982); *Chem. Abstr.*, **97**, 6235 (1982).
[224] A. Shafiee, M. Anaraki and A. Bazzaz, *J. Heterocycl. Chem.*, **23**, 861 (1986).

[225] R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, **98**, 3916 (1976).
[226] E. M. Engler, V. V. Patel, J. A. Andersen, R. R. Schumaker and A. A. Fukushima, *J. Am. Chem. Soc.*, **100**, 3769 (1978).
[227] Y. Okamoto and P. S. Wojciechowski, *US Pat.* 4,465,845 (1984); *Chem. Abstr.*, **101**, 211154 (1984).
[228] T. Takeshima, K. Tazaki, N. Fukada and M. Muraoka, *J. Chem. Res. (S)*, 410 (1979).
[229] N. Fukada, T. Mori, M. Muraoka, T. Yamamoto and T. Takeshima, *Bull. Chem. Soc. Jpn.*, **61**, 4443 (1988).
[230] N. Fukada, K. Arai, T. Takeshima and M. Muraoka, *Synthesis*, 566 (1980).
[231] H. Okuda, Y. Tominaga, Y. Matsuda and G. Kobayashi, *Heterocycles*, **12**, 485 (1979).
[232] S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895).
[233] S. Gabriel and C. F. von Hirsch, *Ber.*, **29**, 2747 (1896).
[234] S. Gabriel and H. Ohle, *Ber.*, **50**, 804 (1917).
[235] L. B. Clapp and J. W. Watjen, *J. Am. Chem. Soc.*, **75**, 1490 (1953).
[236] V. I. Markov, S. I. Burmistrov and O. N. Dolgopolov, *Zh. Obshch. Khim.*, **35**, 162 (1965); *Chem. Abstr.*, **62**, 13078 (1965).
[237] S. C. Clough, R. Salomon, E. Crews, L. Jaques, A. Johnson and J. Forehand, *J. Heterocycl. Chem.*, **19**, 1489 (1982).
[238] K. Kotera, S. Miyazaki, H. Takahashi, T. Okada and K. Kitahonoki, *Tetrahedron*, **24**, 3681 (1968).
[239] E. Strauss, *Ber.*, **33**, 2825 (1900).
[240] F. Winternitz, M. Mousseron and R. Dennilauler, *Bull. Soc. Chim. Fr.*, 1228 (1956).
[241] T. A. Foglia, L. M. Gregory, G. Maerker and S. F. Osman, *J. Org. Chem.*, **36**, 1068 (1971).
[242] A. P. Sineokov, F. N. Gladysheva and V. S. Etlis, *Khim. Geterotsikl. Soedin.*, 611 (1970); *Chem. Abstr.*, **73**, 66351 (1970).
[243] M. E. Bishop and J. J. Zuckerman, *Inorg. Chem.*, **16**, 1749 (1977).
[244] F. Drawert and K.-H. Reuther, *Chem. Ber.*, **93**, 3066 (1960).
[245] Y. Nagao, Y. Hagiwara, T. Kumagai, M. Ochiai, T. Inoue, K. Hashimoto and E. Fujita, *J. Org. Chem.*, **51**, 2391 (1986).
[246] R. A. Aitken, K. Ali and S. T. E. Mesher, *Tetrahedron Lett.*, **38**, 4179 (1997).
[247] J. C. Crawhall and D. F. Elliott, *J. Chem. Soc.*, 3094 (1952).
[248] J. R. Piper and T. P. Johnston, *J. Org. Chem.*, **28**, 981 (1963).
[249] C. S. Dewey and R. A. Bafford, *J. Org. Chem.*, **30**, 491, 495 (1965).
[250] W. Schulze, G. Letsch and H. Willitzer, *J. Prakt. Chem.*, **291**, 101 (1962).
[251] J. L. Corbin and D. E. Work, *J. Org. Chem.*, **41**, 489 (1976).
[252] Y. Nagao, M. Yagi, T. Ikede and E. Fujita, *Tetrahedron Lett.*, **23**, 201 (1982).
[253] Yu. K. Yurév and S. V. Dyatlovitskaya, *Zh. Obshch. Khim.*, **27**, 3152 (1957); *Chem. Abstr.*, **52**, 9077 (1958).
[254] Yu. K. Yurév, S. V. Dyatlovitskaya and L. G. Bulavin, *Zh. Obshch. Khim.*, **27**, 3271 (1957); *Chem. Abstr.*, **52**, 9077 (1958).
[255] A. W. Hofmann, *Ber.*, **20**, 1788 (1887).
[256] J. M. F. Leaper, *J. Am. Chem. Soc.*, **53**, 1891 (1931).
[257] I. Tanasescu and I. Dénes, *Chem. Ber.*, **91**, 1601 (1958).
[258] W. Hanefeld and E. Bercin, *Liebigs Ann. Chem.*, **58** (1985).
[259] J. W. Batty and B. C. L. Weedon, *J. Chem. Soc.*, 786 (1949).
[260] W.-D. Rudorf and R. Schwarz, *Heterocycles*, **24**, 3459 (1986).
[261] H. Nagase, *Chem. Pharm. Bull.*, **21**, 279 (1973).
[262] J. C. Jochims and A. Abu-Taha, *Chem. Ber.*, **109**, 139 (1976).
[263] T. I. Orlova, S. P. Epshtein, V. P. Tashchi, A. F. Rukasov, L. Ya. Bogel'fer and Yu. G. Putsykin, *Khim. Geterotsikl. Soedin.*, 549 (1986); *Chem. Abstr.*, **106**, 84466 (1987).
[264] E. Fourneau and A. Vila, *Bull. Soc. Chim. Fr.*, **9**, 985 (1911).
[265] K.-J. Lee, J. U. Jeong, D. O. Choi, S. H. Kim and H. Park, *Synthesis*, 494 (1991).

[266] C. Alvarez-Ibarra, E. Dávila, A. Mateo, P. Ortiz and M. L. Quiroga, *Tetrahedron Lett.*, **28**, 6667 (1987).

[267] W. Dölling, P. Kindt and M. Augustin, *Z. Chem.*, **27**, 212 (1987).

[268] I. M. Heilbron and A. H. Cook, *Br. Pat.* 584,813 (1947); *Chem. Abstr.*, **41**, 4173 (1947).

[269] R. W. Balsiger, A. L. Fikes, T. P. Johnston and J. A. Montgomery, *J. Org. Chem.*, **26**, 3386 (1961).

[270] C. E. Redemann, R. N. Icke and G. A. Alles, *Org. Synth.*, **27**, 73 (1947).

[271] E. B. Knott, *J. Chem. Soc.*, 1644 (1956).

[272] W. I. Stephen and A. Townshend, *J. Chem. Soc.*, 5127 (1965).

[273] P. Bastianelli, M. Chanon and J. Metzger, *Bull. Soc. Chim. Fr.*, 1948 (1967).

[274] J. von Braun, *Ber.*, **35**, 3368 (1902).

[275] B. Groth and B. Holmberg, *Ber.*, **56**, 289 (1923).

[276] P. Sykes and A. R. Todd, *J. Chem. Soc.*, 534 (1951).

[277] J. J. D'Amico, *J. Am. Chem. Soc.*, **75**, 102 (1953).

[278] J. J. D'Amico and T. W. Bartram, *J. Org. Chem.*, **25**, 1336 (1960).

[279] C. M. Roussel, R. Gallo, M. Chanon and J. Metzger, *Bull. Soc. Chim. Fr.*, 1902 (1971).

[280] F. C. Brown, C. K. Bradsher, B. F. Moser and S. Forrester, *J. Org. Chem.*, **24**, 1056 (1959).

[281] W. Hanefeld and M. A. Jalili, *Arch. Pharm.* (*Weinheim, Ger.*), **320**, 329 (1987); *Chem. Abstr.*, **108**, 94449 (1988).

[282] A. H. Cook, G. Harris, I. Heilbron and G. Shaw, *J. Chem. Soc.*, 1056 (1948).

[283] A. C. Davis and A. L. Levy, *J. Chem. Soc.*, 2419 (1951).

[284] A. H. Cook, I. Heilbron and A. L. Levy, *J. Chem. Soc.*, 201 (1948).

[285] A. H. Cook, I. Heilbron and A. L. Levy, *J. Chem. Soc.*, 1598 (1947).

[286] A. H. Cook, I. Heilbron and E. S. Stern, *J. Chem. Soc.*, 2031 (1948).

[287] H. C. Carrington, *J. Chem. Soc.*, 1619 (1948).

[288] A. H. Cook and S. F. Fox, *J. Chem. Soc.*, 2337 (1949).

[289] A. H. Cook, I. Heilbron and E. Smith, *J. Chem. Soc.*, 1440 (1949).

[290] A. H. Cook and E. Smith, *J. Chem. Soc.*, 2329 (1949).

[291] K. Gewald, P. Blauschmidt and R. Mayer, *J. Prakt. Chem.*, **309**, 97 (1967).

[292] U. Schöllkopf, P.-H. Porsch and E. Blume, *Liebigs Ann. Chem.*, 2122 (1976).

[293] A. M. van Leusen and J. Wildeman, *Synthesis*, 501 (1977).

[294] F. Kröhnke and H. Steuernagel, *Angew. Chem.*, **73**, 26 (1961).

[295] R. Huisgen, R. Grashey and E. Steingruber, *Tetrahedron Lett.*, 1441 (1963).

[296] F. Kröhnke and H. H. Steuernagel, *Chem. Ber.*, **97**, 1118 (1964).

[297] J. A. Duncan, M. L. Bossé and J. M. Masnovi, *J. Org. Chem.*, **45**, 3176 (1980).

[298] R. Huisgen, H. Stangl, H. J. Sturm and H. Wagenhofer, *Angew. Chem.*, **74**, 31 (1962).

[299] K. Bunge, R. Huisgen, R. Raab and H. J. Sturm, *Chem. Ber.*, **105**, 1307 (1972).

[300] K. Burger, H. Goth and E. Daltrozzo, *Z. Naturforsch., Teil B*, **37**, 473 (1982).

[301] V. Nair and K. H. Kim, *J. Org. Chem.*, **40**, 1348 (1975).

[302] D. Obrecht, R. Prewo, J. H. Bieri and H. Heimgartner, *Helv. Chim. Acta*, **65**, 1825 (1982).

[303] A. Padwa and S. I. Wetmore Jr., *J. Am. Chem. Soc.*, **96**, 2414 (1974).

[304] S. Chaloupka, H. Heimgartner, H. Schmid, H. Link, P. Schönholzer and K. Bernauer, *Helv. Chim. Acta*, **59**, 2566 (1976).

[305] E. Schaumann, E. Kausch, S. Grabley and H. Behr, *Chem. Ber.*, **111**, 1486 (1978).

[306] E. Schaumann, S. Grabley, K.-D. Siedel and E. Kausch, *Tetrahedron Lett.*, 1351 (1977).

[307] R. Huisgen, E. Funke, F. C. Schäfer, H. Gotthardt and E. Brunn, *Tetrahedron Lett.*, 1809 (1967).

[308] E. Funke, R. Huisgen and F. C. Schäfer, *Chem. Ber.*, **104**, 1550 (1971).

[309] G. C. Barrett and R. Walker, *Tetrahedron*, **32**, 579 (1976).

[310] T. Kauffmann and R. Eidenschink, *Chem. Ber.*, **110**, 651 (1977).

[311] L. Benati and P. C. Montevecchi, *J. Org. Chem.*, **46**, 4570 (1981).

[312] Y. Tominaga, C. Tamura, S. Sato, T. Hata, R. Natsuki, Y. Matsuda and G. Kobayashi, *Chem. Pharm. Bull.*, **21**, 1651 (1973).

[313] P. I. Abramenko, T. K. Ponomareva and G. I. Priklonskikh, *Khim. Geterotsikl. Soedin.*, 477 (1979); *Chem. Abstr.*, **91**, 74518 (1979).

[314] C. F. H. Allen, C. O. Edens and J. van Allen, *Org. Synth.*, **26**, 34 (1946).

[315] R. A. Donia, J. A. Shotton, L. O. Bentz and G. E. P. Smith, *J. Org. Chem.*, **14**, 946 (1949).

[316] R. J. P. Corriu, G. F. Lanneau and V. D. Mehta, *J. Organomet. Chem.*, **419**, 9 (1991).

[317] A. T. James and E. E. Turner, *J. Chem. Soc.*, 1515 (1950).

[318] F. Outurquin and C. Paulmier, *Bull. Soc. Chim. Fr. II*, 159 (1983).

[319] M. Israel and A. R. Day, *J. Org. Chem.*, **24**, 1455 (1959).

[320] G. B. Barlin, *Aust. J. Chem.*, **34**, 1361 (1981).

[321] B. R. Baker, J. P. Joseph and R. E. Schaub, *J. Org. Chem.*, **19**, 631 (1954).

[322] A. G. Beaman, J. F. Gerster and R. K. Robins, *J. Org. Chem.*, **27**, 986 (1962).

[323] H. Uno, A. Irie and K. Hino, *Chem. Pharm. Bull.*, **21**, 34 (1973).

[324] G. A. Mokrushina, I. Ya. Postovskii and S. K. Kotovskaya, *Khim. Geterotsikl. Soedin.*, 411 (1977); *Chem. Abstr.*, **87**, 53170 (1977).

[325] K. N. Mehrotra and G. Singh, *Synthesis*, 1001 (1980).

[326] E. J. Tarlton and A. F. McKay, *Can. J. Chem.*, **36**, 496 (1958).

[327] H. C. Carrington, *J. Chem. Soc.*, 681 (1947).

[328] H. C. Brimelow, H. C. Carrington, C. H. Vasey and W. S. Waring, *J. Chem. Soc.*, 2789 (1962).

[329] W. O. Foye and J. M. Kauffman, *J. Org. Chem.*, **31**, 2417 (1966).

[330] T. Sasaki and M. Ando, *Bull. Chem. Soc. Jpn.*, **41**, 2960 (1968).

[331] D. St. C. Black, R. F. Crozier and V. C. Davis, *Synthesis*, 205 (1975).

[332] E. Hoggarth, *J. Chem. Soc.*, 4811 (1952).

[333] R. W. Young and K. H. Wood, *J. Am. Chem. Soc.*, **77**, 400 (1955).

[334] C. Ainsworth, *J. Am. Chem. Soc.*, **78**, 4475 (1956).

[335] H.-B. König, W. Siefken and H. A. Offe, *Chem. Ber.*, **87**, 825 (1954).

[336] A. Shafiee, I. Lalezari, M. Mirrashed and D. Nercesian, *J. Heterocycl. Chem.*, **14**, 567 (1977).

[337] D. J. Jean, S. C. Shin and Y. Y. Lee, *Heterocycles*, **45**, 2101 (1997).

[338] P. Molina, M. Alajarin, A. Arques and R. Benzal, *J. Chem. Soc., Perkin Trans. 1*, 351 (1982).

[339] P. Yates and T. R. Lynch, *Can. J. Chem.*, **49**, 1477 (1971).

[340] F. M. Dean, D. B. Frankham, N. Hatam and A. W. Hill, *J. Chem. Soc. (C)*, 218 (1971).

[341] E. Klingsberg, *J. Org. Chem.*, **37**, 3226 (1972).

[342] T. Takeshima, N. Fukada, T. Ishii and M. Muraoka, *J. Chem. Soc., Perkin Trans. 1*, 1706 (1976).

[343] M. S. Raasch, *J. Chem. Soc., Chem. Commun.*, 577 (1966).

[344] M. S. Raasch, *J. Org. Chem.*, **35**, 3470 (1970).

[345] U. Kunze and R. Merkel, *J. Organomet. Chem.*, **219**, 69 (1981).

[346] U. Kunze, R. Merkel and W. Winter, *Angew. Chem., Int. Ed. Engl.*, **21**, 291 (1982).

[347] U. Kunze, R. Merkel and W. Winter, *Chem. Ber.*, **115**, 3653 (1982).

[348] S. H. Wheeler, B. M. Mattson, G. L. Miessler and L. H. Pignolet, *Inorg. Chem.*, **17**, 340 (1978).

[349] K. Dickoré, R. Wegler and K. Sasse, *Angew. Chem.*, **74**, 874 (1962).

[350] K. Hasegawa, S. Hirooka, H. Kawahara, A. Nakayama, K. Ishikawa, N. Takeda and H. Mukai, *Bull. Chem. Soc. Jpn.*, **51**, 1805 (1978).

[351] E. Fromm and R. Heyder, *Ber.*, **42**, 3804 (1909).

[352] A. R. Butler, *J. Chem. Res. (S)*, 50; *(M)*, 0855 (1978).

[353] J. Goerdeler, R. Büchler and S. Sólyom, *Chem. Ber.*, **110**, 285 (1977).

[354] J. E. Oliver and R. T. Brown, *J. Org. Chem.*, **39**, 2228 (1974).
[355] R. J. S. Beer, N. H. Holmes and A. Naylor, *J. Chem. Soc., Perkin Trans. 1*, 2909 (1979).
[356] D. Martin and F. Tittelbach, *Tetrahedron*, **39**, 2311 (1983).
[357] M. Busch, *Ber.*, **27**, 2507 (1894).
[358] D. S. Tarbell, C. W. Todd, M. C. Paulson, E. G. Lindstrom and V. P. Wystrach, *J. Am. Chem. Soc.*, **70**, 1381 (1948).
[359] M. Busch, *Ber.*, **28**, 2635 (1895).
[360] F. Best, *J. Prakt. Chem.*, **60**, 225 (1899).
[361] A. Stern, *J. Prakt. Chem.*, **60**, 233 (1899).
[362] M. Busch and S. Schneider, *J. Prakt. Chem.*, **67**, 246 (1903).
[363] W. Baker, W. D. Ollis, A. Phillips and T. Strawford, *J. Chem. Soc.*, 289 (1951).
[364] G. D. Thorn, *Can. J. Chem.*, **38**, 1439 (1960).
[365] J. P. Snyder, M. Heyman and M. Gundestrup, *J. Org. Chem.*, **43**, 2224 (1978).
[366] U. Antoni, C. Larsen and P. H. Nielsen, *Acta Chem. Scand.*, **24**, 179 (1970).
[367] J. Motoyoshiya, M. Nishijima, I. Yamamoto, H. Gotoh, Y. Katsube, Y. Ohshiro and T. Agawa, *J. Chem. Soc., Perkin Trans. 1*, 574 (1980).
[368] K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, **15**, 1124 (1961).
[369] R. Grashey, M. Baumann and W.-D. Lubos, *Tetrahedron Lett.*, 5881 (1968).
[370] L. B. Kier and M. K. Scott, *J. Heterocycl. Chem.*, **5**, 277 (1968).
[371] S. Kubota, Y. Koida, T. Kosaka and O. Kirino, *Chem. Pharm. Bull.*, **18**, 1696 (1970).
[372] Rhône-Poulenc, *Br. Pat.* 726,045 (1955); *Chem. Abstr.*, **50**, 5037 (1956).
[373] P. C. Guha, *J. Am. Chem. Soc.*, **44**, 1510 (1922).
[374] K. T. Potts and R. M. Huseby, *J. Org. Chem.*, **31**, 3528 (1966).
[375] H. D. Rupp and H. Mägerlein, *Ger. Pat.* 1,814,772 (1970); *Chem. Abstr.*, **73**, 45512 (1970).
[376] J. Sandström, *Acta Chem. Scand.*, **15**, 1295 (1961).
[377] R. Huisgen, R. Grashey, M. Seidel, H. Knupfer and R. Schmidt, *Liebigs Ann. Chem.*, **658**, 169 (1962).
[378] J. Sauer and K. K. Meyer, *Tetrahedron Lett.*, 325 (1968).
[379] H. Gotthardt and F. Reiter, *Tetrahedron Lett.*, 2749 (1971).
[380] K.-H. Pfoertner and J. Foricher, *Helv. Chim. Acta*, **63**, 653 (1980).
[381] W. Fliege, R. Grashey and R. Huisgen, *Chem. Ber.*, **117**, 1194 (1984).
[382] R. Huisgen, R. Grashey, P. Laur and H. Leitermann, *Angew. Chem.*, **72**, 416 (1960).
[383] R. Huisgen, R. Grashey and R. Krischke, *Tetrahedron Lett.*, 387 (1962).
[384] R. Huisgen, R. Grashey and R. Krischke, *Liebigs Ann. Chem.*, 506 (1977).
[385] R. Grashey, *Angew. Chem., Int. Ed. Engl.*, **4**, 701 (1965).
[386] R. Grashey, R. Huisgen, K. K. Sun and R. M. Moriarty, *J. Org. Chem.*, **30**, 74 (1965).
[387] W. A. Thaler and J. R. McDivitt, *J. Org. Chem.*, **36**, 14 (1971).
[388] L. S. Wittenbrook, G. L. Smith and R. J. Timmons, *J. Org. Chem.*, **38**, 465 (1973).
[389] J. R. Reid and N. D. Heindel, *J. Heterocycl. Chem.*, **13**, 925 (1976).
[390] K. T. Potts and S. Husain, *J. Org. Chem.*, **36**, 10 (1971).
[391] K. T. Potts and C. Hirsch, *J. Org. Chem.*, **33**, 143 (1968).
[392] K. Pilgram and G. E. Pollard, *J. Heterocycl. Chem.*, **13**, 1225 (1976).
[393] I. N. Getsova, L. L. Sribnaya and N. P. Bednyagina, *Khim. Geterotsikl. Soedin.*, 129 (1965); *Chem. Abstr.*, **63**, 4282 (1969).
[394] C. F. H. Allen, G. A. Reynolds, J. F. Tinker and L. A. Williams, *J. Org. Chem.*, **25**, 361 (1960).
[395] K. B. Sukumaran, C. S. Angadiyavar and M. V. George, *Tetrahedron*, **28**, 3987 (1972).
[396] R. N. Hanley, W. D. Ollis and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 732 (1979).
[397] F. Sommer, *Ber.*, **48**, 1833 (1915).
[398] A. W. Browne, A. B. Hoel, G. B. L. Smith, F. H. Swezey and C. W. Mason, *J. Am. Chem. Soc.*, **45**, 2541 (1923).

[399] G. B. L. Smith, F. Wilkoxon, A. W. Browne and C. W. Mason, *J. Am. Chem. Soc.*, **45**, 2604 (1923).

[400] G. B. L. Smith, P. Warttman, A. W. Browne and C. W. Mason, *J. Am. Chem. Soc.*, **52**, 2806 (1930).

[401] E. Lieber, C. N. Pillai, J. Ramachandran and R. D. Hites, *J. Org. Chem.*, **22**, 1750 (1957).

[402] E. Lieber, E. Oftedahl and C. N. R. Rao, *J. Org. Chem.*, **28**, 194 (1963).

[403] C. Christophersen, *Acta Chem. Scand.*, **25**, 1160 (1971).

[404] C. Christophersen, *Acta Chem. Scand.*, **25**, 1162 (1971).

[405] R. F. Ziolo, J. A. Thich and Z. Dori, *Inorg. Chem.*, **11**, 626 (1972).

[406] W. Beck and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.*, **6**, 169 (1967).

[407] H. Löster and E. Lippmann, *E. Ger. Pat.* 106,645 (1974); *Chem. Abstr.*, **82**, 72998 (1975).

[408] H. Oehme, E. Leissring and R. Thamm, *J. Prakt. Chem.*, **320**, 600 (1978).

[409] A. Tzschach and J. Heinicke, *J. Prakt. Chem.*, **318**, 193 (1976).

[410] J. Heinicke, *Z. Chem.*, **28**, 250 (1988).

[411] N. Maigrot, L. Ricard, C. Charrier and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, **29**, 534 (1990).

[412] M. L. Sierra, C. Charrier, L. Ricard and F. Mathey, *Bull. Soc. Chim. Fr.*, 521 (1993).

[413] F. Kumpfmüller, D. Nölle, H. Nöth, H. Pommerening and R. Staudigl, *Chem. Ber.*, **118**, 483 (1985).

[414] F. Eiden and G. Rademacher, *Arch. Pharm. (Weinheim, Ger.)*, **318**, 926 (1985); *Chem. Abstr.*, **104**, 168392 (1986).

[415] F. Eiden and H.-D. Schweiger, *Synthesis*, 511 (1974).

[416] F. Eiden and G. Rademacher, *Arch. Pharm. (Weinheim, Ger.)*, **318**, 181 (1985); *Chem. Abstr.*, **102**, 131992 (1985).

[417] H. Apitzsch, *Ber.*, **38**, 2888 (1905).

[418] A. Thuillier and J. Vialle, *Bull. Soc. Chim. Fr.*, 2187 (1962).

[419] A. Schönberg and R. von Ardenne, *Chem. Ber.*, **99**, 3327 (1966).

[420] A. M. Arishkevich, A. I. Danilevskaya and Yu. I. Usatenko, *Khim. Geterotsikl. Soedin.*, 232 (1965); *Chem. Abstr.*, **63**, 9908 (1965).

[421] I. Shahak and Y. Sasson, *Tetrahedron Lett.*, 4207 (1973).

[422] R. K. Dieter, Y. J. Lin and J. W. Dieter, *J. Org. Chem.*, **49**, 3183 (1984).

[423] C. Portail and J. Vialle, *Bull. Soc. Chim. Fr.*, 3790 (1968).

[424] W.-D. Rudorf, *Tetrahedron*, **34**, 725 (1978).

[425] W.-D. Rudorf, A. Schierhorn and M. Augustin, *Tetrahedron*, **35**, 557 (1979).

[426] M. Augustin, G. Jahreis and W.-D. Rudorf, *Synthesis*, 472 (1977).

[427] W. Dölling, M. Augustin and H. Bohrer, *Z. Chem.*, **25**, 176 (1985).

[428] R. Mayer and J. Wehl, *Angew. Chem., Int. Ed. Engl.*, **4**, 246 (1965).

[429] R. Mayer, G. Laban and M. Wirth, *Liebigs Ann. Chem.*, **703**, 140 (1967).

[430] J. P. Sauvé and N. Lozac'h, *Bull. Soc. Chim. Fr.*, 2016 (1970).

[431] K. Gewald, *J. Prakt. Chem.*, **31**, 205 (1966).

[432] T. Takeshima, M. Yokoyama, N. Fukada and M. Akano, *J. Org. Chem.*, **35**, 2438 (1970).

[433] A. M. van Leusen and E. C. Taylor, *J. Org. Chem.*, **33**, 66 (1968).

[434] P. Benovsky and J. R. Stille, *Tetrahedron Lett.*, **38**, 8475 (1997).

[435] M. Muraoka, T. Yamamoto, S. Yamaguchi, F. Tonosaki, T. Takeshima and N. Fukada, *J. Chem. Soc., Perkin Trans. 1*, 1273 (1977).

[436] C. Paal and E. Laudenheimer, *Ber.*, **25**, 2978 (1892).

[437] F. Fülöp, G. Csirinyi, G. Bernáth and J. A. Szabó, *Synthesis*, 1149 (1985).

[438] A.-M. Lamazouère, J. Sotiropoulos and P. Bédos, *C. R. Seances Acad. Sci., Ser. C*, **268**, 186 (1969).

[439] B. Krebs and G. Gattow, *Angew. Chem., Int. Ed. Engl.*, **5**, 250 (1966).

[440] D. Ladurée, P. Rioult and J. Vialle, *Bull. Soc. Chim. Fr.*, 637 (1973).

[441] W.-D. Rudorf and D. Janietz, *Synthesis*, 854 (1984).

[442] S. Gabriel and W. E. Lauer, *Ber.*, **23**, 87 (1890).
[443] A. Luchmann, *Ber.*, **29**, 1420 (1896).
[444] M. Kahan, *Ber.*, **30**, 1318 (1897).
[445] C. Paal and O. Commerell, *Ber.*, **27**, 2427 (1894).
[446] A. Albert, *J. Chem. Soc., Perkin Trans. 1*, 2009 (1980).
[447] T. Takeshima, T. Inamoto, M. Yokoyama, K. Yamamoto and M. Akano, *J. Org. Chem.*, **33**, 2877 (1968).
[448] T. Takeshima, T. Hayashi, M. Muraoka and T. Matsuoka, *J. Org. Chem.*, **32**, 980 (1967).
[449] T. Takeshima, M. Yokoyama, T. Inamoto, M. Akano and H. Asaba, *J. Org. Chem.*, **34**, 730 (1969).
[450] N. Fukada, M. Kato, H. Seki, M. Kawana and T. Takeshima, *J. Chem. Soc., Perkin Trans. 1*, 558 (1978).
[451] T. Takeshima, T. Miyauchi, N. Fukada, S. Koshizawa and M. Muraoka, *J. Chem. Soc., Perkin Trans. 1*, 1009 (1973).
[452] M. Muraoka, T. Yamamoto and T. Takeshima, *Bull. Chem. Soc. Jpn.*, **48**, 2462 (1975).
[453] T. L. Gresham, J. E. Jansen and F. W. Shaver, *J. Am. Chem. Soc.*, **70**, 1001 (1948).
[454] W. Hanefeld, *Arch. Pharm. (Weinheim, Ger.)*, **307**, 476 (1974); *Chem. Abstr.*, **81**, 77858 (1974).
[455] T. Takeshima, N. Fukada, E. Ohki and M. Muraoka, *J. Chem. Res. (S)*, 212 (1979).
[456] W. Hanefeld and G. Glaeske, *Liebigs Ann. Chem.*, 1388 (1981).
[457] J. E. Jansen and R. A. Mathes, *J. Am. Chem. Soc.*, **77**, 2866 (1955).
[458] M. Richter, M. Augustin and K. Strauss, *J. Prakt. Chem.*, **326**, 633 (1984).
[459] J. E. Jansen and R. A. Mathes, *J. Am. Chem. Soc.*, **77**, 5431 (1955).
[460] J. Spindler and G. Kempter, *Z. Chem.*, **27**, 36 (1987).
[461] G. Kempter, H.-J. Ziegner and G. Moser, *Z. Chem.*, **11**, 12 (1971).
[462] F. Sachs, *Liebigs Ann. Chem.*, **365**, 135 (1909).
[463] E. C. Taylor, A. McKillop and R. N. Warrener, *Tetrahedron*, **23**, 891 (1967).
[464] A. Girard, *Liebigs Ann. Chem.*, **100**, 306 (1856).
[465] K. Hasegawa, T. Sasaki and S. Hirooka, *Bull. Chem. Soc. Jpn.*, **46**, 696 (1973).
[466] C. C. Deane, *J. Chem. Res. (S)*, 388 (1986).
[467] R. A. Mathes, *J. Org. Chem.*, **17**, 877 (1952).
[468] U. Petersen and H. Heitzer, *Liebigs Ann. Chem.*, 944 (1973).
[469] W. Schulze, G. Letsch and H. Willitzer, *J. Prakt. Chem.*, **291**, 324 (1962).
[470] A. D. Ainley, W. H. Davies, H. Gudgeon, J. C. Harland and W. A. Sexton, *J. Chem. Soc.*, 147 (1944).
[471] H. Bieling and A. Pogadl, *Z. Chem.*, **7**, 106 (1967).
[472] S. Lotz and G. Gattow, *Z. Anorg. Allg. Chem.*, **584**, 143 (1990); *Chem. Abstr.*, **113**, 211361 (1990).
[473] M. Yokoyama, K. Motozawa, E. Kawamura and T. Inamoto, *J. Chem. Soc., Perkin Trans. 1*, 2499 (1981).
[474] K. Burger, U. Wassmuth, B. Forster and S. Penninger, *Z. Naturforsch., Teil B*, **39**, 1442 (1984).
[475] I. Ya. Postovskii, Yu. A. Azev and G. A. Mokrushina, *Khim. Geterotsikl. Soedin.*, 1140 (1976); *Chem. Abstr.*, **86**, 5417 (1977).
[476] H. Graubaum and D. Martin, *J. Prakt. Chem.*, **328**, 515 (1986).
[477] W. Franek, *Sulfur Rep.*, **10**, 193 (1991).
[478] J. Willemse and J. J. Steggerda, *J. Chem. Soc., Chem. Commun.*, 1123 (1969).
[479] E. W. Ainscough and A. M. Brodie, *J. Chem. Soc., Dalton Trans.*, 565 (1977).
[480] L. Yu. Ukhin, Z. S. Morkovnik, Zh. I. Orlova and V. N. Komissarov, *Khim. Geterotsikl. Soedin.*, 1420 (1983); *Chem. Abstr.*, **100**, 51488 (1984).
[481] L. Hadjiarapoglou, S. Spyroudis and A. Varvoglis, *J. Am. Chem. Soc.*, **107**, 7178 (1985).
[482] L. Cambi, G. Bargigia, L. Colombo and E. Paglia Dubini, *Gazz. Chim. Ital.*, **99**, 780 (1969).

[483] J. Sotiropoulos, A.-M. Lamazouère and P. Bédos, *C. R. Seances Acad., Sci., Ser. C*, **265**, 99 (1967).

[484] J. Sotiropoulos and A.-M. Lamazouére, *C. R. Seances Acad. Sci., Ser. C*, **276**, 1115 (1973).

[485] P. Jutzi and A. Möhrke, *Angew. Chem., Int. Ed. Engl.*, **28**, 762 (1989).

[486] R. A. Donia, J. A. Shotton, L. O. Bentz and G. E. P. Smith, *J. Org. Chem.*, **14**, 952 (1949).

[487] J. Reiter, L. Pongo, P. Krajcsi, K. Esses-Reiter, P. Sohar, H. Monar and P. Dvortsak, *J. Heterocycl. Chem.*, **24**, 927 (1987).

[488] M. Rivière-Baudet, P. Rivière, J. Satgé and G. Lacrampe, *Recl. Trav. Chim. Pays-Bas*, **98**, 42 (1979).

[489] I. A. Nicholls, P. F. Alewood, R. I. Brinkworth, S. F. Morrison and P. R. Andrews, *J. Chem. Res.* (*S*), 408 (1993).

[490] P. Thompson and P. Alewood, *J. Chem. Res.* (*S*), 319 (1991).

[491] A. V. Bogatsky, N. G. Lukyanenko and T. I. Kirichenko, *Tetrahedron Lett.*, 313 (1980).

[492] E. Brzezinska, R. Glinka, A. Szadowska and M. B. Kielek, *Acta Pol. Pharm.*, **45**, 400 (1988); *Chem. Abstr.*, **111**, 97201 (1989).

[493] R. Bao, W. Huang, Y. Zhen and B. He, *Synth. Commun.*, **20**, 2675 (1990).

[494] R. R. Hiatt, M.-J. Shaio and F. Georges, *J. Org. Chem.*, **44**, 3265 (1979).

[495] C. E. Bolser and E. B. Hartshorn, *J. Am. Chem. Soc.*, **45**, 2349 (1923).