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THE CHEMISTRY OF THIOKETENS

ERNST SCHAUMANN
Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6,
D-2000 Hamburg 13, West Germany

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CONTENTS

INTRODUCTION AND SCOPE

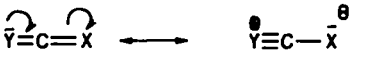
Thioketens are examples of heteroallenes or, in more general terms, heterocumulenes. The common feature of these compounds is an array of two or three orthogonal, non-conjugated double bonds in a three- or four-centre unit incorporating at least one heteroatom. In spite of the formally identical electronic structure, heterocumulenes have a vast range of stability and reactivity depending on the

nature of the heteroatoms and on the substituents. Heterocumulenes with a carbonyl, thiocarbonyl, or imine unit can be subdivided into two classes based on whether the other terminus of the heterocumulene moiety is an electron-acceptor or -donor. The first type has six interacting electrons and includes ketens (X = O), thioketens (X = S), and ketenimines (X = NR); these heteroallenes are usually difficult to isolate and highly reactive.

(1)

X = O, S, NR

In heterocumulenes with an electron-donating terminus, eight electrons are involved in the resonance interaction:



(2)

X = O, S, NR
Y = eg. R_2C, Ph_3P, RN, O, S

Heterocumulenes of this class are usually only moderately reactive, unless substituted by electron-withdrawing groups. Typical representatives are isocyanates (X = O, Y = NR), isothiocyanates (X = S, Y = NR) as well as carbon dioxide and its heteroanalogs (X and/or Y = O, S). In addition, this group includes compounds such as carbon subsulphide, S=C=C=C=S[1] or its recently generated mono-oxygen analog,[1a] triphenylphosphoranylidenethioketen, Ph_3P=C=C=S,[2] or (aminoalkylidene)thioketens, $R^1(R^2_2N)$C=C=C=S.[3,4] Here, a very high contribution of the zwitterionic resonance structure of Eq. 2 is probable and the thioketen nomenclature is used for convenience only.[5] As with other heterocumulenes of this class, these "thioketens" are relatively stable and, in their reactions, show striking differences to their congeners with the resonance interaction of Eq. 1. For example, typical thioketens (Eq. 1, X = S) give thiocarbonyl *S*-oxides on oxidation (cf. 4.1.1), whereas all attempts to convert thiocarbonyl-containing heterocumulenes with a resonance as represented by Eq. 2 into defined oxidation products have so far met with failure. This review will mainly be concerned with the chemistry of the common thioketens which follow Eq. 1 and with that of the closely related thioketen *S*-oxides (Eq. 1 with X = S=O), whereas alkylidene thioketens will only be considered for comparison.

Based on the classification in Eq. 1, only limited stability can be expected for ketens as well as thioketens. However, for thioketens an additional complication stems from the size difference between carbon and sulphur allowing only relatively inefficient overlap of *p* orbitals. Consequently, the chemistry of ketens has been thriving since the beginning of this century, whereas for thioketens, great progress has been made on all fronts only in the last two decades. Though the first claim of a thioketen synthesis dates back to 1877,[6] this was later refuted[7] and the pioneer days of thioketen chemistry have been reviewed.[8,9] In the meantime, the accessibility of thioketens,[10] the understanding of their structure and the knowledge of their reactions have been highly improved and call for the present critical overview.

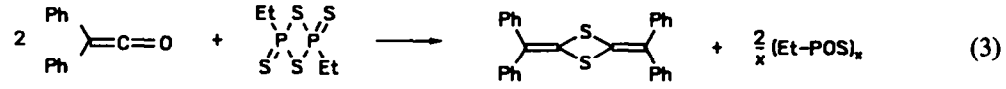
1. PREPARATION OF THIOKETENS

Attempts to synthesize thioketens are rendered difficult by the high tendency of most thioketens to dimerize or oligomerize. Dimers of disubstituted thioketens are always of the 2,4-bis(alkylidene)-1,3-dithietane type (cf. e.g. Eq. 3). To obtain monomeric thioketens or for synthetic uses of thioketens, special measures have to be taken, i.e. flash-vacuum pyrolysis (e.g. Eqs 13, 14, 22, 31 and 45); generation at low temperatures (e.g. Eqs 15–18); generation under conditions which allow trapping-reactions (e.g. Eqs 21, 30, 33, 34 and 41).

Due to limitations in the method or in the availability of precursors, there is no general thioketen synthesis. As a guide to the best route to a specific thioketen, the tabular survey (Part 2) should prove helpful.

1.1. *From carboxylic acid derivatives via thionation*

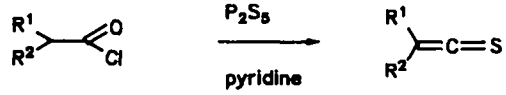
The conversion of a carbonyl into a thiocarbonyl function by the action of phosphorus pentasulphide or a similar inorganic sulphide is a well-established method.[11] With thioketens being the target, ketens are the apparent precursors which may be used as such or generated *in situ* from acyl chlorides by some tertiary amine. In his attempts to obtain diphenylthioketen, Staudinger tried to thionate the corresponding keten with phosphorus pentasulphide but was unable to isolate a defined product;[12] use of the milder reagent triphenylphosphane sulphide led to the polymeric thioketen.[13] With a perthiophosphoric acid anhydride in xylene, dimeric diphenylthioketen can be obtained in 83% yield:[14]



(3)

Similarly, only a dimer is isolated on treatment of bis(trifluoromethyl)keten with triphenylphosphane sulphide.[15,16]

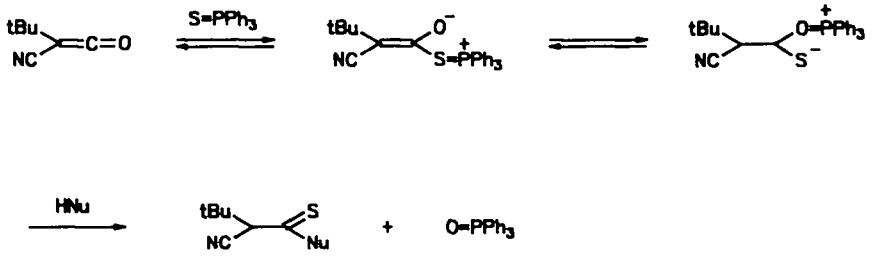
One of the first of the successful syntheses of a thioketen was the generation of the di-tert.butyl derivative from the corresponding acyl chloride with P_2S_5 in pyridine solution.[17] The work-up procedure could be improved[18] and the approach extended to various sterically hindered and consequently quite stable, beautifully purple thioketens:[18,19]



(4)

Interestingly, the yield is higher if the acyl chloride is used as starting material rather than the keten;[17] this and the isolation of side products indicate that the mechanism is more complex than keten formation followed by oxygen/sulphur exchange. The method fails for thioketens with substituents which are less voluminous than tert.butyl plus isopropyl.[18] The otherwise useful[11] Lawesson reagent (cf. Eq. 3) cannot be employed.[18]

When a solution of tert.butyl(cyano)keten[20] in benzene is treated with triphenylphosphane sulphide (5 h, 20°C), the resulting mixture shows reactions which are expected for the corresponding thioketen.[21,22] However, spectra do not confirm the presence of the thioketen. This suggests that a thioketenoid species may be present:

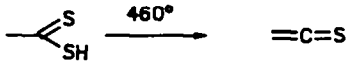


(5)

1.2. *From (di)thiocarboxylic acid derivatives*

1.2.1. *From dithiocarboxylates*

Thioketen could be detected in a photoelectron spectrometer on thermolysis of dithioacetic acid:[23,24]

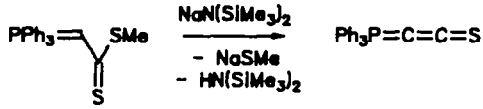


(6)

However, heating of diphenyldithioacetic acid only provided dimeric diphenylthioketen.[25]

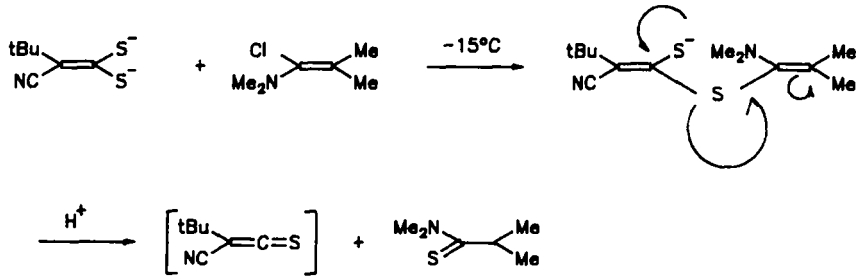
Pyrolysis of *O*- or *S*-methyl thioacetate[26] and even of *O*-silyl thiocarboxylates provides mainly ketens.[27] By comparison, phenyl diphenyl(di)thiocarboxylate can be cleaved at 250–280°C to yield

dimeric diphenylthioketen,[28] and the base-induced elimination of thiol from a dithioester-substituted phosphorus ylide furnishes triphenylphosphoranylidenthioketen:[29]



(7)

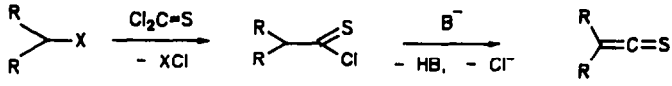
Ghosez's elegant keten synthesis[30] can in principle be applied to thioketen generation. Thus, an *S*-vinyl thiocarboxylate is formed from a dithiocarboxylate dianion[31] by addition of an α-chloro enamine and *in situ* unzips to tert.butyl(cyano)thioketen along with a thioamide which is isolated in high yield. However, the thioketen polymerizes under the reaction conditions.[32]



(8)

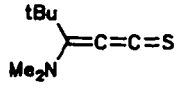
The scope of this thioketen synthesis remains to be explored.

The use of thioacyl chlorides as thioketen precursors is hampered by the unavailability and instability of these thiocarbonyl derivatives.[33] Usually, thiophosgene is used to introduce the thioacyl chloride moiety. For non-cumulated thioketens, the method only led to thioketen dimers or polymers.[34]

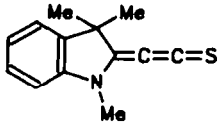


(9)

However, triphenylphosphoranylidenthioketen[35,36] and aminoalkylidenethioketens of the following type have been successfully obtained by the approach of Eq. 9:



ref. 3



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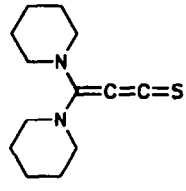
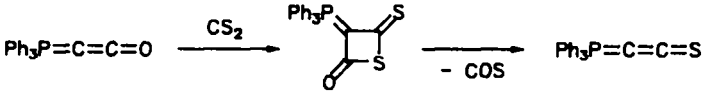


ref. 4

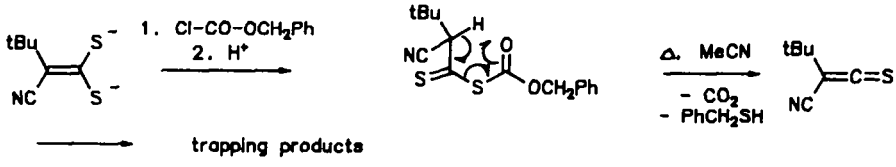
In another synthesis of triphenylphosphoranylidenethioketen a mixed cyclic anhydride is generated *in situ*:[37]



(10)

Very recently, a related reaction allowed synthesis of a thiophosphoryl-substituted thioketen.[38]

An acyclic dithioanhydride offers a possibility to generate and trap tert.butyl(cyano)thioketen:[32]



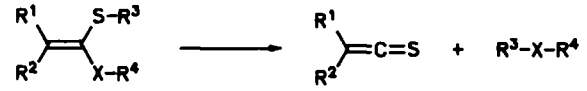
(11)

So far, this case represents the only example for this promising approach.

Elimination of amines from thioamides usually requires very high temperatures; consequently, thioketen dimers are formed.[39]

1.2.2. *From ketene acetals*

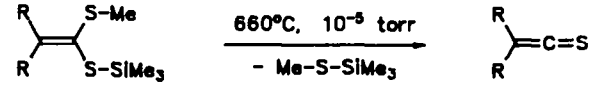
Ketene *S*,X-acetals may lead to thioketens in a β-elimination reaction, if R^3 can be attached to a potential leaving-group XR^4:



(12)

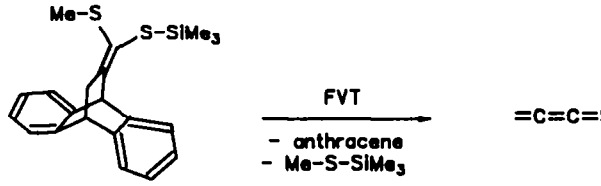
Ketene *O*,*S*-acetals (X = O) so far have only allowed access to dimeric thioketens as derived from diphenylthioketene[40] or bis(trifluoromethyl)thioketene.[41] Similarly, cleavage of a keten *S*,*N*-acetal provided only secondary products of bis(*N*-arylaminocarbonyl)thioketen.[42]

A successful synthesis of monomeric dialkylthioketens employs keten *S*-methyl-*S*-(trimethylsilyl)acetals in a flash-vacuum thermolysis (FVT):[43]



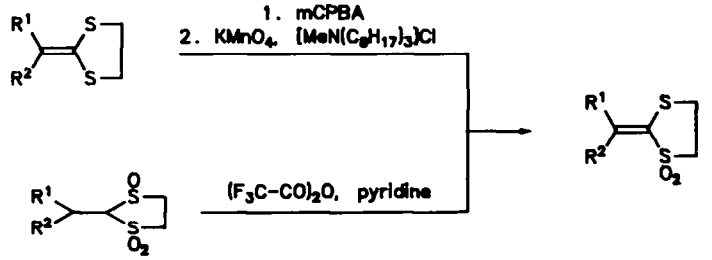
(13)

In combination with a retrograde (4+2) cycloaddition, the method allows generation of methylenethioketen:[43]



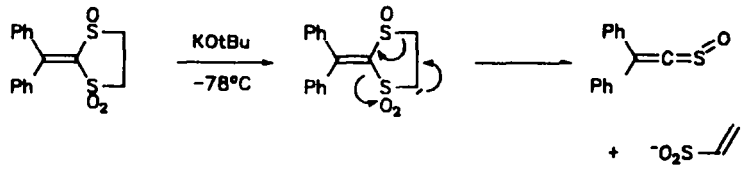
(14)

In a convenient, non-pyrolytic thioketen synthesis, 2-alkylidene-1,3-dithiolane 1,1-dioxides are used. For examples with at least one electron-withdrawing substituent (phenyl, acyl, cyano), these sulphones are obtained in two oxidation steps from the corresponding keten *S*,*S*-acetals.[32,44] The parent compound and simple alkyl derivatives are synthesized from the thioacetal *S*,*S*,*S*′-trioxides in a Pummerer reaction as induced by trifluoroacetic anhydride.[45,46] The ketenthioacetal *S*,*S*-dioxides are deprotonated at −78°C by use of butyl lithium or potassium tert.butoxide. The resulting carbanion unzips in a (3+2) cycloreversion around −50°C as judged from a colour change of the reaction mixture. The resulting thioketens are conveniently trapped by amines or C=N systems.



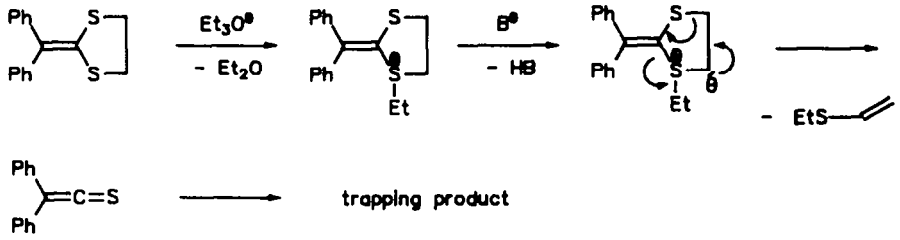
(15)

Remarkably, if a dithiolane-derived ketenthioacetal *S*,*S*,*S*′-trioxide is submitted to the procedure of Eq. 15, a thioketen *S*-oxide can be detected via trapping reactions:[45,47]



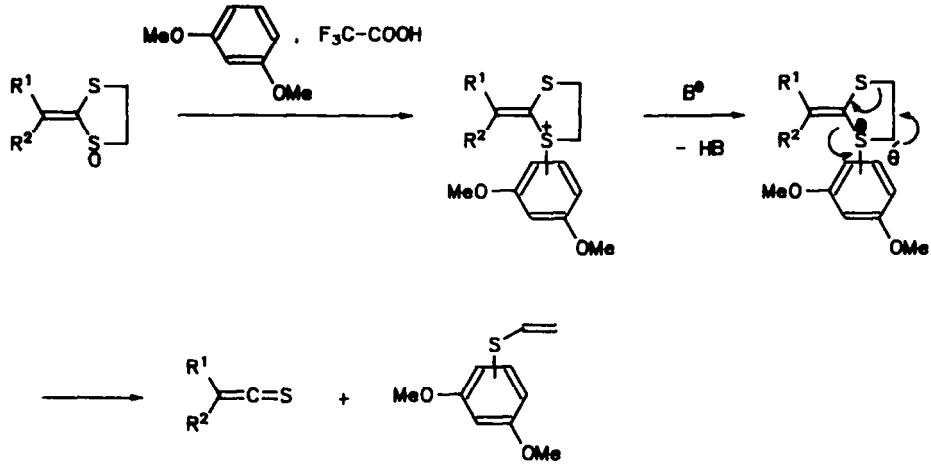
(16)

In a modification of the method in Eq. 15. dithiolane-based sulphur ylides are employed.[48] Interestingly, deprotonation of an *S*-ethyl dithiolanium salt occurs selectively at the ring position as shown by the synthesis and trapping of diphenylthioketen:



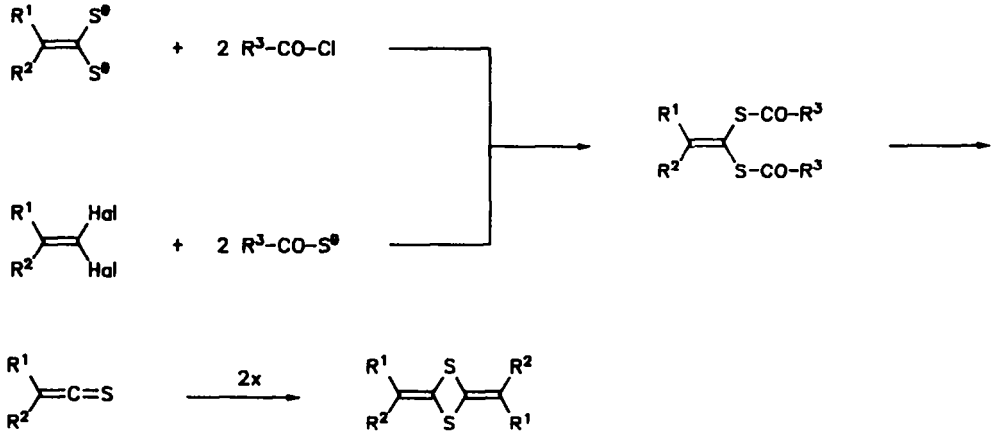
(17)

Alternatively, *S*-arylation of ketenthioacetal *S*-monoxides using 1,3-dimethoxybenzene under acid-catalysis provides *S*-aryl dithiolanium salts. Deprotonation is then achieved by potassium hydride or an amine which will also serve as the trapping-reagent for the generated thioketen.[45,48]



(18)

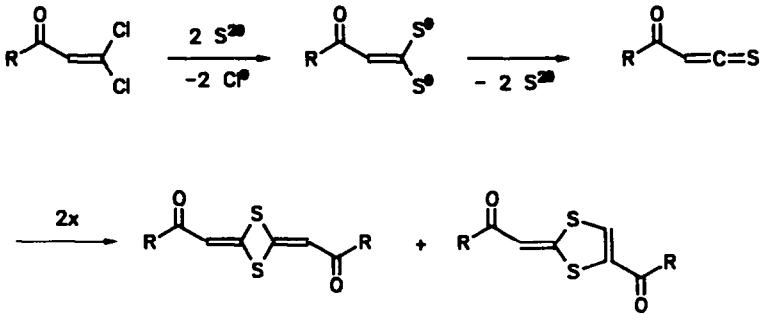
An example of Eq. 12 can be seen in the acylation of dithiocarboxylate dianions with acyl chlorides (R^3, R^4 = acyl groups) which usually provides thioketen dimers.[49–52] However, the mechanism of the elimination has not yet been investigated and may well involve monomeric thioketens. The best yields of dithietane derivatives are usually obtained when alkoxycarbonyl chlorides are used.[53,54]



(19)

In an alternative approach to the intermediate diacylated ketenthioacetals, the halogen atoms in 1,1-dihaloalkenes are substituted by thiocarboxylate residues (Eq. 19). This exchange reaction follows an addition/elimination mechanism and is favoured by electron-withdrawing groups R^1, R^2 to accommodate the negative charge in the anionic intermediate. Thus, bis(trifluoromethyl)thioketen could be obtained from perfluoro-2-methylpropene.[55]

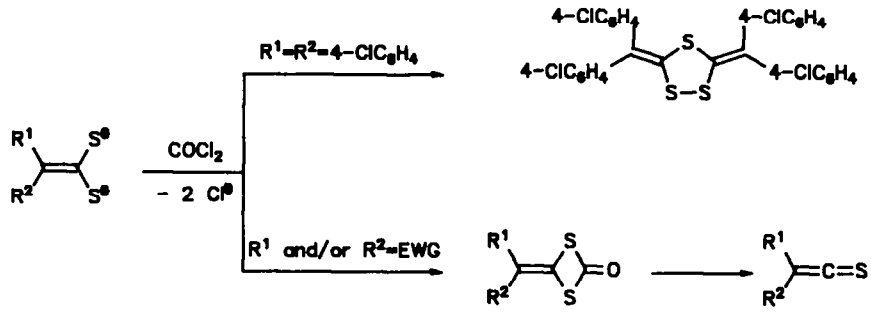
It may be mentioned that dithiocarboxylate dianions, one of the thioketen precursors in Eq. 19, may lead directly to thioketen dimers. The known examples are monosubstituted by acyl groups and provide, besides the usual thioketen dimers of the dithietane type, 2H-1,3-dithiol-derived dimers:[56]



(20)

Besides sodium sulphide, tetraethylammonium hydrogen sulphide has been proven to be useful for the chlorine/sulphur exchange step.[57] The claim that the reaction of Eq. 20 allows isolation of monomeric thioketens[58] could not be verified.[59]

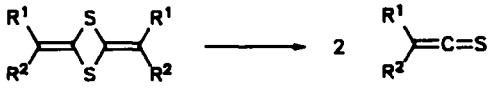
Contrary to other acyl chlorides, the cyclic acylation product from dithiocarboxylate dianions and phosgene can often be isolated (Eq. 21).[31,50,59,60] A prerequisite is that at least one electron-withdrawing group ("EWG", e.g. acyl,[59] alkoxycarbonyl,[60] cyano,[31,60] diethoxyphosphoryl[50]) is present and reduces the nucleophilicity of the dianion. Otherwise, the anionic thioketen precursor will react with the formed dithietanone or with the thioketen as shown for the bis(4-chlorophenyl) derivative.[57]



(21)

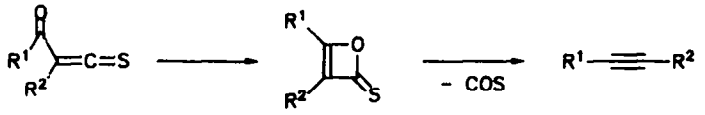
The (2+2) cycloreversion[61] of 2-alkylidene-1,3-dithietan-2-ones to give thioketens is a facile process (Eq. 21). It can be induced thermally, photochemically, by Lewis bases, or by surface-active materials. However, in trapping reactions with nucleophiles, the reacting species may be the dithietanone rather than the thioketen (Eq. 88).[31] In flash-vacuum experiments employing the corresponding dithietanones at 510–550°C, dicyanothioketen[62] and tert.butyl(cyano)thioketen[31] could be collected on a cold finger at −196°C in a solvent matrix, but decomposed on melting the matrix. The formation of the former thioketen was also confirmed by photoelectron spectroscopy.[62] Alternatively, tert.butyl(cyano)thioketen was generated on photolysis (254 nm) of the corresponding dithietanone in an argon matrix at 10 K and characterized by IR and UV spectroscopy.[31,63]

The (2+2) cycloreversion[61] of 2,4-bis(alkylidene)-1,3-dithietanes, i.e. of thioketen dimers, presents another application of Eq. 12 for thioketen synthesis:



(22)

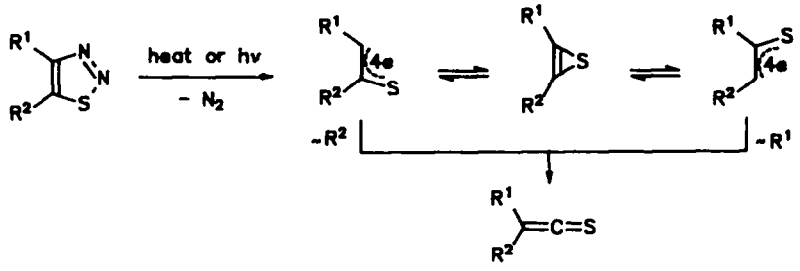
Even when dimerization is a ready reaction for a given thioketen, small equilibrium concentrations of the monomer may be detected. Thus, dimeric diphenylthioketen develops the purple colour of the monomer on standing in aromatic solvents,[64] and trapping products which are derived from the monomer have been isolated from dimeric dicyano or alkoxycarbonyl(cyano)thioketen.[53,65] The most prominent case for generation of the thioketen by cracking the dimer is bis(trifluoromethyl)thioketen; for a good yield, the reaction requires 750°C.[15,16,66] The dimer of diphenylthioketen is cleaved at 800 C in a flash-vacuum thermolysis, whereas dimeric 9-thiocarbonylfluorene is not sufficiently volatile.[67] Carbonyl-substituted thioketens are decomposed to acetylenes in a secondary reaction at the high cracking temperature of 800–875 C:[67]



(23)

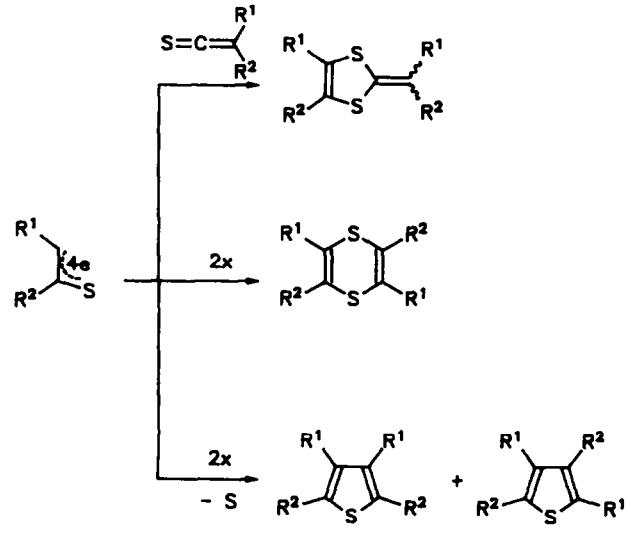
1.3. *From 1,2,3-thiadiazoles*

The Wolff rearrangement of α-diazoketones is one of the most important routes to ketens.[68] However, the sulphur analogues, α-diazothioketones, are not known.[69] They exist in the form of 1,2,3-thiadiazoles, i.e. of cyclic valence tautomers. With 1,2,3-thiadiazoles being aromatic compounds, the loss of nitrogen is not a facile reaction: it requires rather high temperatures or irradiation.[70] The resulting four-electron species may be considered as a thioacyl carbene,[71,72] a 1,3-dipole,[73] or a 1,3-diradical.[74] It may cyclize to a formally antiaromatic thiirene and reopen to give the isomeric four-electron fragment. Migration of R^1 or R^2 eventually leads to the thioketen. Mechanistic efforts have focused on the detection of the thiirene species,[75-77] while synthetic work has been aiming at trapping reactions of the four-electron species or at generation of thioketens.



(24)

The *photolysis* of 1,2,3-thiadiazoles was first studied by Kirmse and Horner[71] for derivatives with aromatic substituents; these authors isolated 1,3-dithiafulvenes[78] which were supposed to result from the reaction of the four-electron species with the thioketen. In addition, dimerization of the intermediate to give 1,4-dithiins and thiophene formation were observed.



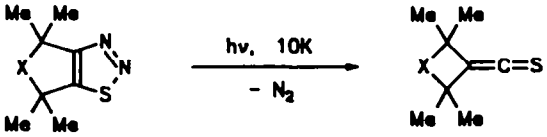
(25)

(26)

(27)

The work of Kirmse and Horner[71] was continued and expanded by Meier covering a broader range of derivatives as well as the parent.[74,79–81] The formation of isomeric thiophenes (Eq. 27) and other isomers[82] may be explained in terms of scrambling of substituents via a thiirene intermediate. Additional evidence as to thiirene participation was seen in the substitution pattern of thiophenes formed during thiadiazole photolysis in the presence of alkynes.[83,84] However, it was noted that an unambiguous interpretation of the results is clouded by our ignorance of the behaviour of alkynes with alternative C_2H_2S species.[85]

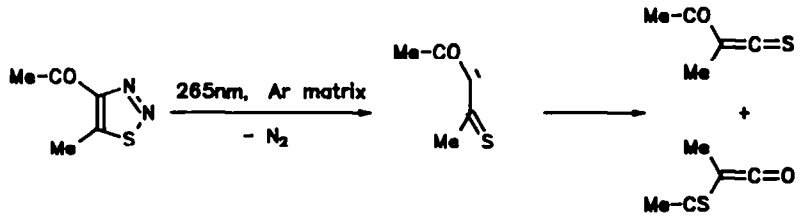
More reliable evidence regarding thiirene formation on 1,2,3-thiadiazole photolysis (Eq. 24) comes from low-temperature irradiation of matrix-isolated precursors. Data that could be interpreted in terms of thiirenes were obtained for the parent and simple alkyl derivatives,[85–88] trifluoromethyl-,[88] acyl-,[72] or ester-substituted derivatives,[88,89] and for the tert.butyl/cyano-substituted compound, which proved to be stable up to 160 K.[63,90] The final products of these irradiations are the corresponding thioketens and, in several instances, thioketens are formed directly without any apparent thiirene involvement. This is true for tert.butylthioketen,[89] di-tert.butylthioketen,[63] and the following examples:[63,91]



(28)

X = $(CH_2)_2$, O, CH_2SCH_2

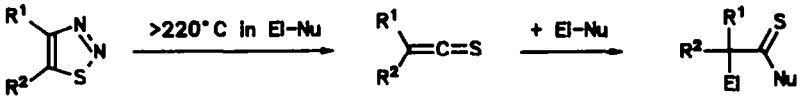
Photolysis of 4-acetyl-5-methyl-1,2,3-thiadiazole in an argon matrix produces a mixture of a keten and a thioketen. Obviously, a common intermediate permits the usual carbonyl carbene Wolff rearrangement as well as the analogous thiocarbonyl process to take place:[72]



(29)

For 4,5-diphenyl-1,2,3-thiadiazole, a slow decomposition to give diphenylthioketen has been observed on exposure to sunlight.[67]

Without special precautions, *thermolysis* of 1,2,3-thiadiazoles yields the same complex pattern of products as photolysis (cf. Eqs 25–27).[81,92,93] Trapping reactions aiming at evidence for thiirene formation (cf. Eq. 24) were carried out with alcohols[82,94,95] or diphenylacetylene[95] and were interpreted as phenyl- or 1-methyl-2-phenyl-thiirene being involved. Successful trapping of the thioketen intermediates is achieved by heating 1,2,3-thiadiazoles in a high-boiling alcohol[82,93–96] or, for 4-monosubstituted thiadiazoles, with a C=N compound (c.f. Section 4.3.2.2.1.).[97,98]

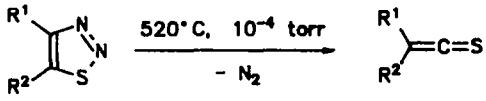


(30)

El-Nu = H-OR, R_2C=NR

Application of the flash-vacuum thermolysis (FVT) technique[99,100] to 1,2,3-thiadiazoles allows isolation even of rather unstable thioketens, when the pyrolysis product is collected on a cold finger.[67,101,102] For clean thioketen formation, a furnace temperature of 520–530°C and a pressure of 10^{-2} to 10^{-4} torr are required. The cold finger of the apparatus is precoated with an inert solvent such as dichloromethane or trichlorofluoromethane;[67,101] during the pyrolysis, more solvent may be applied to provide a matrix for the thioketen. Thus, on melting, a thioketen solution is obtained

which can be used directly for spectroscopic studies or for reactions. An apparatus which allows production of up to 10 g of thioketen in a single run has been described;[103] a simplified version with external heating allows generation of up to 2 g of thioketen.[102]



(31)

The method tolerates the presence of some functional groups such as ethylthio,[104] trifluoromethyl,[64,105] trimethylsilyl,[106] and cyano.[102] Starting from carbonyl-substituted thiadiazoles, thioketen formation may be followed by the secondary reaction of Eq. 23;[67] however, flow thermolysis at 360–410°C allows access to acetyl(methyl) and ethoxycarbonyl(methyl)thioketen.[89] Contrary to photolysis (Eq. 28),[63] the thermal pathway (Eq. 31) fails to provide 2,2,4,4-tetramethyl-1-thiocarbonyloxetane[64] and gives only trace amounts of tert.butyl(cyano)thioketen.[102,107] Pyrolysis of 4,5-di-tert.butyl-1,2,3-thiadiazole yields a complex product mixture with only 24% di-tert.butylthioketen.[108]

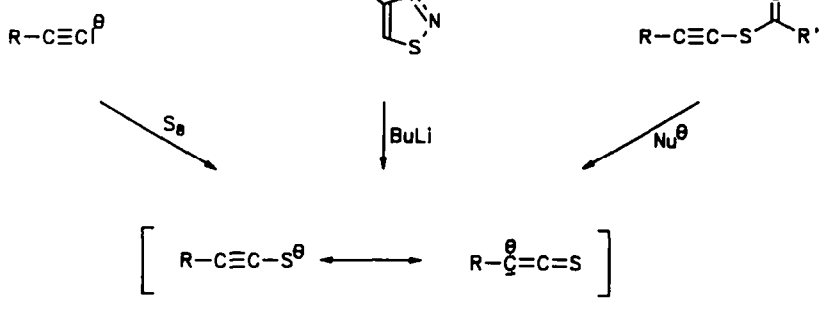
The host of examples for thioketen synthesis following Eq. 31 includes various 5-substituents R^2, but fails to give any clue as to migratory aptitudes. Thus, tert.butyl(phenyl)thioketen is obtained in the same excellent yield from both isomeric thiadiazole precursors,[102] though the tert.butyl group is known not to migrate in the Wolff rearrangement.[109] Similarly, the cyano group seems to migrate in thioketen formation from 4-phenyl-1,2,3-thiadiazole-5-carbonitrile, but barely does so on thermolysis of the corresponding 4-tert.butyl derivative.[102] These and other inconsistencies can be explained when a facile isomerization of the primary fragment occurs which is formed after nitrogen loss from the thiadiazole precursor. This process requires a thiirene intermediate (Eq. 24). The possibility of R^1/R^2 exchange in the four-electron species (Eq. 24) implies that, for the synthesis of a specific thioketen, the more readily available thiadiazole can be chosen and migratory aptitudes are of no concern.

Besides synthetic applications, the clean thioketen formation on gas-phase thermolysis of 1,2,3-thiadiazoles (Eq. 31) allows measurement of microwave,[110,111] UV,[112] or photoelectron spectra.[23,24,113,114] Besides studying the parent[24,110,112,115] and simple alkyl derivatives,[111] the PES investigation of 1-thiocarbonyl-2,4-cyclopentadiene was possible.[114]

1.4. *From alkynyl sulphides*

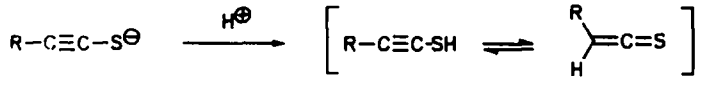
1.4.1. *From alkynyl thiols or silyl sulphides*

Alkynyl thiolates can be looked upon as aldothioketen anions. They are accessible via addition of sulphur[116] to acetylide anions,[117-120] via nitrogen elimination from 4-monosubstituted 1,2,3-thiadiazoles as induced by butyl lithium,[121,122] or via cleavage of *S*-alkynyl thiocarboxylates with amines or thiolates:[123]



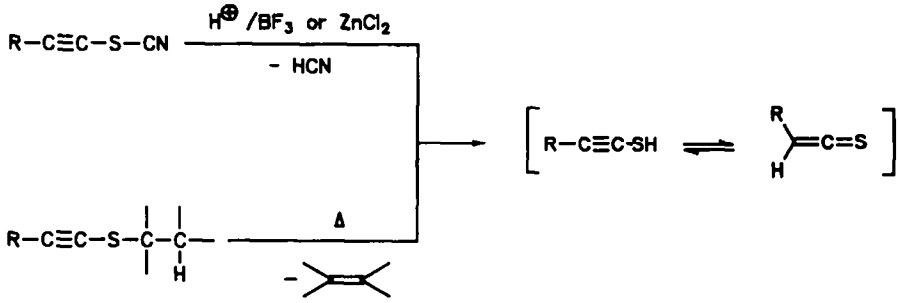
(32)

Protonation of alkynyl thiolates or addition of tert.butylbromide as a mild proton source[118] yields the thiols which, via a 1,3-hydrogen shift, tautomerize to aldothioketens (cf. Part 3):



(33)

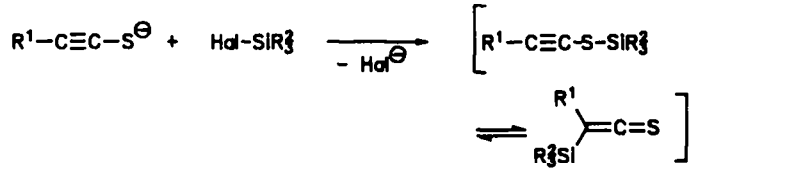
Alternatively, alkynyl thiols have been obtained from alkynyl thiocyanates by protolysis[124] or from alkynyl alkyl sulphides in thermolysis reactions:[117,125–128]



(34)

Only the last-mentioned approach allows isolation of aldothioketens as such. In the other cases, trapping has been achieved, in particular with amines, alcohols, or thiols (cf. Section 4.2). The main competing reaction is aldothioketen dimerization which usually provides 2-alkylidene-1,3-dithiols (cf. Eq. 20).[124] An alternative use of alkynyl thiolates is addition of ketones to give C-hydroxyalkylation which, after cyclization and loss of carbonyl sulphide eventually leads to alkenes.[120]

Silylation of alkynyl thiolates (Eq. 32) gives alkynyl silyl sulphides which may rearrange to silylthioketens:



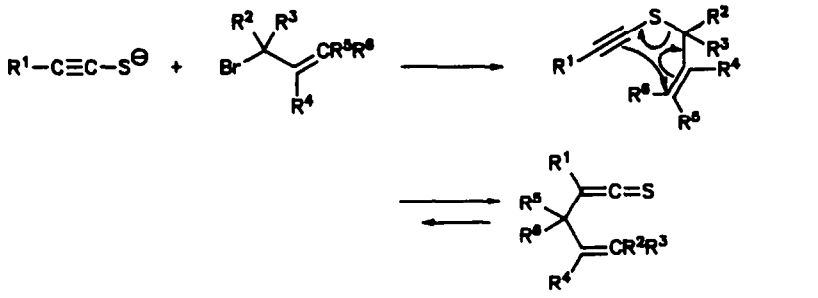
(35)

The tendency of alkynyl silyl sulphides to rearrange to silylthioketens depends on R^1 (which may also be a silyl group) and R^2. The rearrangement is favoured for R^1 = trimethyl-,[129,130] tert.-butyldimethyl-,[97] or triethylsilyl;[129] for the trimethylsilyl case, the sulphide can be isolated only for Hal = bromide (Eq. 35).[130] The S to C silyl shift is then induced thermally[130] or by Lewis bases.[131] The approach can be extended to the synthesis of germyl- and stannylthioketens, but again with the silyl residue being the migrating group.[129,132] On the other hand, the isomerization is not favoured for R^1 = tert.butyl as, even after flash-thermolysis at 550°C, only 30% thioketen can be detected.[106] Similarly, R^2 groups on the silicon other than methyl, i.e. triethylsilyl or tert.butyldimethylsilyl, prevent the rearrangement.[97] In reactions with nucleophiles, alkynyl silyl sulphides show a thioketenoid behaviour.[133–137]

Another pathway from alkynyl sulphides, the intermediates in Eq. 35, to thioketens is S-desilylation by a protic agent to give an aldothioketen. This behaviour was seen on addition of methanol to trimethylsilylethinyl triethylsilyl sulphide (Eq. 67).[129] The presence of a silyl group greatly enhances the stability of the thioketen system. Thus, bis(trimethylsilyl)thioketen is not known to dimerize.

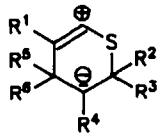
1.4.2. *From alkynyl allyl sulphides*

The Thia–Cope rearrangement of alkynyl allyl sulphides to allyl thioketens represents the most facile access to thioketens. The precursors are readily available by allylation of alkynyl thiolates (cf. Eq. 32):



(36)

In an early report by a Dutch group,[138] the generated thioketen (R^1 = Bu, R^2–R^6 = H) was trapped by amines. Steric stabilization[17,18,139] of the thioketen targets by bulky groups R^1–R^3 allowed, at room temperature or on gentle heating, actual detection or even isolation of the thioketens.[140,141] However, the rearrangement fails for the "di-tert.butyl" thioketen-type target with R^1 = tBu, R^2 = R^3 = Me.[140] In other cases, the rearrangement leads to an equilibrium between sulphide and thioketen[136] and, beyond that, deterioration of the thioketen product may compete with its formation.[140] For R^1–R^6 = alkyl, the optimum combination of ease of rearrangement and steric stabilization of the thioketen is found for allyl(tert.butyl)thioketen, which can be isolated in a pure form.[140] On the other hand, thioketen formation is highly encouraged by R^1 = silyl[134,142] or by an electron-withdrawing substituent R^4.[143] This suggests a highly polarized transition state or an intermediate of the type:



As to functional groups in the R^1 position, the rearrangement of Eq. 36 has been seen for R^1 = tBuS,[143] but for R^1 = Ph(Me)N no thioketen was detected.[135]

A rearrangement that is similar to Eq. 36 has been shown for alkynyl propargyl[141,144] or alkynyl allenyl sulphides.[145] Formation of thioketens was inferred from isolation of thioamides on addition of amines.

(37)

(38)

Interestingly, the formal [3,3]-sigmatropic shift which operates in Eqs 36–38 can also be employed for the synthesis of silyl(allyl)selenoketens.[146]

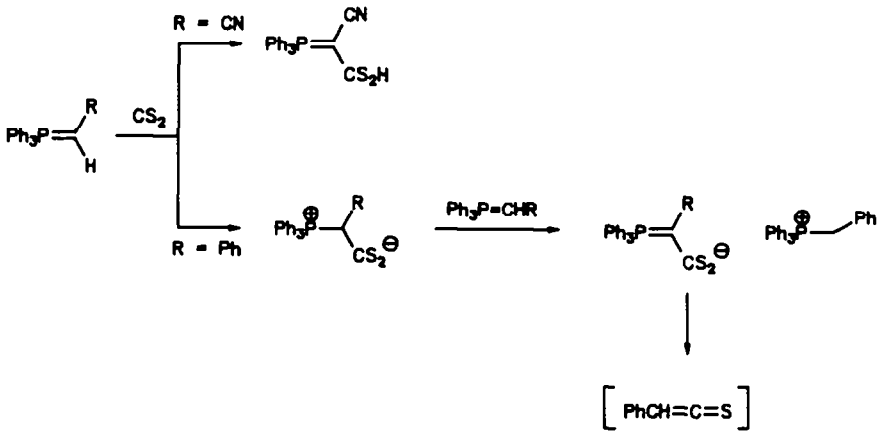
1.5. *Other reactions leading to thioketens*

A number of reactions have been considered for thioketen synthesis, but, so far, have been used for special cases only or proved to be of limited applicability.

A seemingly obvious approach to thioketens is olefination of carbon disulphide in a Wittig reaction. However, the only successful example reported so far is the reaction of a carbodiphosphorane with carbon disulphide to give triphenylphosphoranylidenethioketen.[5] The outcome of the addition of carbon disulphide to other phosphorus ylides strongly depends on the ylide substituents. Monosubstitution of the alkylidenephosphorane by a cyano group leads to 98% of a dithiocarboxylic acid in the reaction with carbon disulphide (Eq. 39).[147] Phenyl substitution allows isolation of a phosphonium salt which, when poured into water, yields dimeric phenylthioketen (75%).[148] Under special conditions, the primary zwitterion is obtained allowing the generation of phenylthioketen.[149]

Diarylmethylenephosphoranes (R^1 = R^2 = aryl in Eq. 41) show a high tendency to undergo a Wittig reaction with carbon disulphide. However, the final outcome is a polymer of diphenylthioketen[150] or the thioketen dimer in the case of a fluorene substituent.[151]

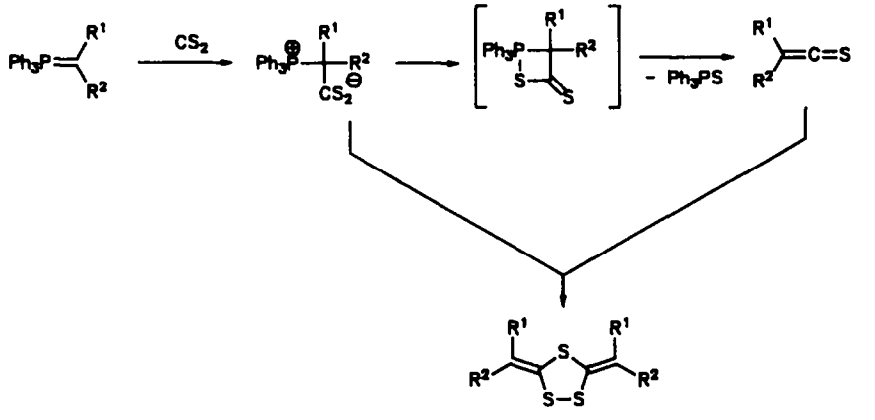
Starting from dialkylmethylenephosphoranes and carbon disulphide in ether, the zwitterionic 1 : 1 adduct precipitates from the reaction mixture.[152–154] With increasing bulk of the alkyl substituents, the



(39)

(40)

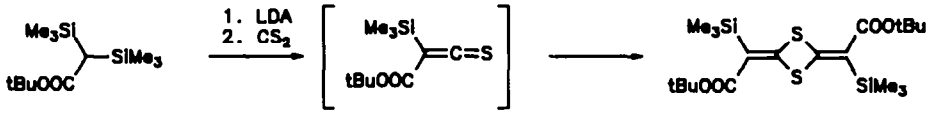
stability of the products is reduced;[154] for methyl/phenyl substitution[154] or a benzo[d]-2H-1,3-dithiol derivative[34] no zwitterion is detected.



(41)

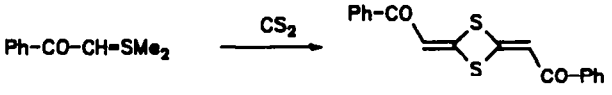
Heating of an isolated zwitterion with a nucleophile allows isolation of products which are formally derived from dialkylthioketens. However, it is not clear whether a true thioketen, the thiaphosphetane or the zwitterion which results from cleavage of the S—CS bond in the thiaphosphetane is the reacting electrophile. In the absence of a suitable trapping agent, 2,5-bis(alkylidene)-1,3,4-trithiolanes are isolated.[155]

Attempts to improve the efficiency of the Wittig route to thioketens by the use of carbonyl sulphide did not meet with success. As with carbon disulphide (Eq. 41), zwitterions are formed[152] which, however, failed to generate thioketens.[156] Similarly, the attempted Horner reaction of phosphonate carbanions with carbon disulphide[50] or carbonyl sulphide[156] does not yield thioketens. However, there is a promising example of thioketen dimer formation (28% yield) in a Peterson olefination of carbon disulphide:[156]



(42)

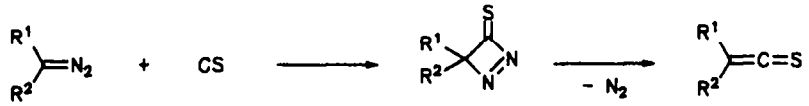
Another case of dimer formation (78% yield) is observed in the reaction of a sulphur ylide with carbon disulphide:[157]



(43)

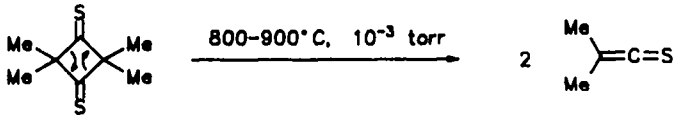
Another application of carbon disulphide, the generation of triphenylphosphoranylidenethioketen, was mentioned earlier (Eq. 10).

Carbon monosulphide can be employed in a successful synthesis of di-tert.butylthioketen and similar sterically hindered thioketens; a diazetinethione is a possible intermediate:[158-160]



(44)

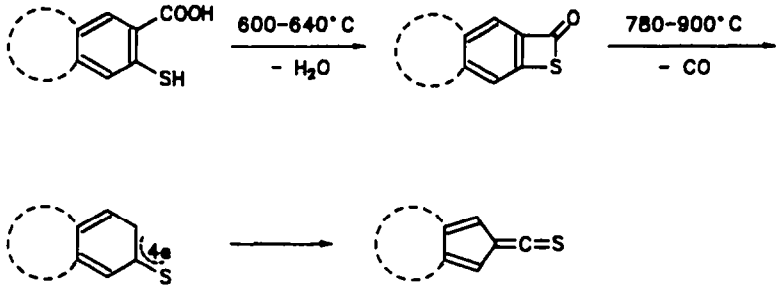
Just as (2+2) cycloreversion of a four-membered ring may represent the key step in Eq. 41, the cleavage of a cyclobutanedithione offers a pyrolytic pathway to dimethylthioketen:[161]



(45)

Similarly, the four-membered ring in a thiocarbonylcyclobutane can be cleaved thermally to give methylene thioketen.[162]

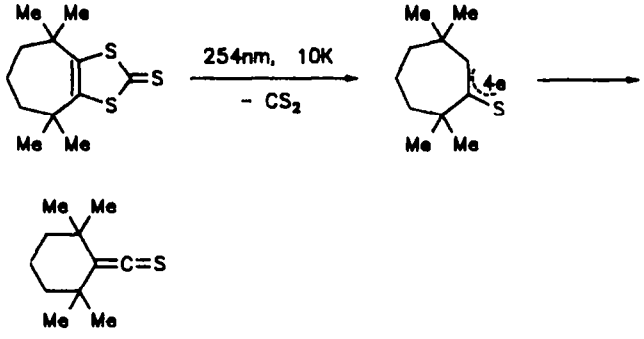
Loss of carbon monoxide from a β-thiolactone provides another route from four-membered rings to thioketens; intermediates of the type indicated in Eq. 24 may be involved;[114,163]



(46)

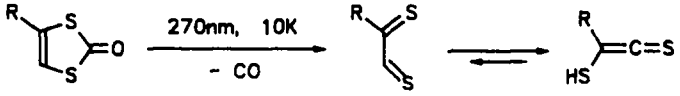
This reaction was originally developed for PES measurements,[114] but could be extended to a preparative scale.[163]

The reactive species of Eq. 24 is also an intermediate in the generation of thioketens from 1,3-dithiol-2-thiones which requires pyrolytic conditions. While the reaction fails for the 4,5-bis(trifluoromethyl) derivative,[87] it works for the parent[87] and, according to IR spectroscopic evidence, for a dialkylthioketen:[63]



(47)

The analogous oxo derivatives are cleaved even more readily though with extrusion of carbon monoxide and formation of a thioketen in a 1,3-hydrogen shift (R = H, Me):[164]

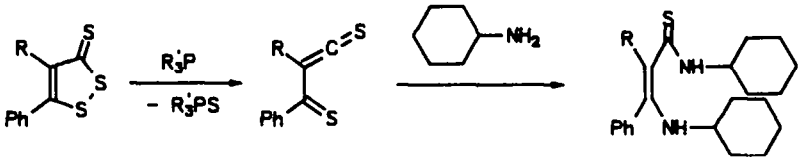


(48)

A similar formation of a diarylthioketen via a 1,5-hydrogen shift has been reported.[165]

Elimination of sulphur from a 1,2-dithiol-3-thione by a phosphorus(III) reagent generates a

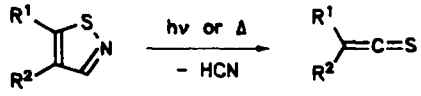
thioacylthioketen as shown by trapping reactions:[166]



(49)

Transient thioketens are invoked for the related, though base-induced, cleavage of 1,2-dithiol-3-ones.[167] Similarly, thioketen dimers are formed on treatment of *N*-alkyl-3-isothiazolones with base, but, based on the failure of trapping reactions, thioketen intermediates were rejected.[168]

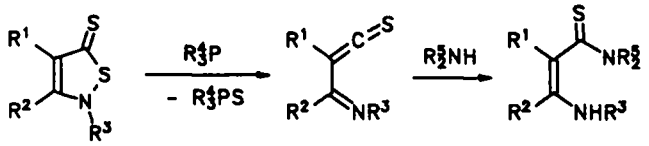
When photolysed, isothiazole itself (R = H in Eq. 50) is a possible precursor of thioketen, albeit compared to the method of Eq. 24, a poor one.[86]



(50)

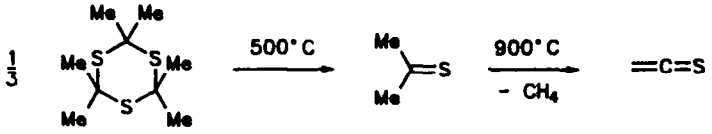
4- or 5-Substituted isothiazoles were pyrolysed at 570–710°C to give aldothioketens (R = Me, NO_2); however, dubious stabilities of the thioketens were reported.[169] In our hands, only traces of the highly unstable methylthioketen could be generated.[64]

The phosphorus-induced desulphurization reaction of Eq. 49 can be applied to isothiazol-5-thiones generating reactive iminothioketens. These thioketens readily dimerize, but can be trapped by amines:[170]



(51)

By analogy with the Schmidlin method of keten generation,[171] thioketen is formed in the pyrolysis of thioacetone and can be studied in the gas phase:[172,173]



(52)

2. TABULAR SURVEY OF SYNTHETICALLY USEFUL THIOKETENS

Table 1. Synthesis and stability of thioketens which can be generated on a preparative scale.

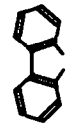
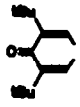
R^1	R^2	Synthesis according to Eq.	Yield[a]	Ref.	Stability	Synthetic uses in Eq.
Aldothioketens						
H	H	15	(35)	45	stable at −80°C	70, 135
		31	?	89, 115, 174		
		34	(40)	117, 125, 128		
Me	H	30	(40)	98		68–70, 87
		33	(40–79)	118, 119, 122		
		34	?	125		
F_3C	H	31	(28)	64, 105	dec. < −78°C	70
Et	H	33	(42–97)	117, 119, 175		68,70
Pr	H	33	(46)	117		68
iPr	H	34	48	127		70
Bu	H	33	(23–88)	117, 123, 175		62, 68, 70
tBu	H	30	(50–79)	97, 98	$t_{1/2}$ = 1 h in	59, 61,
		31	65–75	67, 89	$CFCl_3$ (0.01 M,	69, 70, 80,
		33	(30–99)	117, 119	22°C)	87
		34	(42–61)	127		

[*Table continued overleaf*

Table 1—*continued*

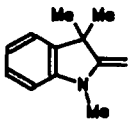
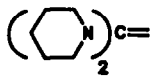
R^1	R^2	Synthesis according to Eq	Yield[a]	Ref.	Stability	Synthetic uses in Eq.
Ph	H	15	(52)	32	partial dec. at	66, 68, 69,
		30	(37–59)	82, 93, 96, 97, 176	−196°C;[104] less stable than	70, 87, 112
		31	70	67	tBuCH=C=S	
		33	(50–85)	119, 121, 122, 126, 127, 177		
		34	?	125, 126		
		40	(75)	148		
4-$MeOC_6H_4$	H	33	(85)	122		70
MeOOC	H	33	(71)	121		66
H_2N—CO	H	33	(59)	121		66
Me_3Si	H	67	?	129		66
O_2N	H	18	(53)	48		70
Ph—SO_2	H	18	(53)	48		70
Dialkylthioketens						
Me	Me	13	(65)	43	$t_{1/2}$ = 3–60 min in	61,70,86,
		41	(10–54)	154	different solvents at	89
		45	(62)	161	−78°C	
Et	Et	41	(27)	154		90
iPr	Me	31	?	64	limited stability at −78°C	
tBu	Me	31	70–80	102	stable in solution at −78°C	86, 90, 120
Bu	H_2C=$CHCH_2$	36	(30–43)	138	70	
tBu	H_2C=$CHCH_2$	36	60–70	140, 141	can be distilled i. vac. + stored at 0°C for 1 week	59, 70, 75 86, 97, 100, 101, 103, 106 114, 119
tBu	iPr	4	57	18	slow dimerization	56, 58, 75
		31	45	102	> 100°C[21]	86, 92–94, 99, 101, 103, 105–109, 114, 116–118 120, 128, 136
tBu	tBu	4	74	17, 18	no dimer known	55, 57, 66, 70
		31	24	64		75, 77–79,
		44	30	158–160		86, 105–107, 114, 116–118, 123, 136–144
tBu	c—C_6H_{11}	4	33	18	stable at 20°C	118, 120, 128 136
$(CH_2)_3$		30	(52)	93		66
$(CH_2)_4$		13	(25)	43	very unstable, dec.	66
		30	(95)	93, 94, 96	at −196°C	
		31	(69)	104, 178		
CMe_2—$(CH_2)_2$—CMe_2		31	95	64		70
$(CH_2)_5$		18	(26)	48		70, 122
		30	(59)	93		
CMe_2—$(CH_2)_3$—CMe_2		4	72	18	slow dim.	56, 58, 66,
		47	?	63	> 200°C[21]	75, 77, 78, 86, 94, 99, 102, 103, 105–108, 114, 116–118, 122, 123, 136–144
CHtBu—$(CH_2)_3$—CHtBu		4	74	19	very stable at 20°C	56, 75, 106, 108, 136
CHtBu—CH_2—CHtBu—CH_2—CHtBu		4	87	19	very stable at 20°C	56
CMe_2—CH_2—S—CH_2—CMe_2		4	54	18	stable at 20°C	57, 58, 114,
		44	42	158–160		118
$(CH_2)_6$		30	(71)	93		
Alkyl(arylthioketens)						
Me	Ph	31	71	67, 102	less stable than Ph_2C=C=S; solution can be handled at −78°C	61, 70, 90, 91, 127

Table 1—*continued.*

R^1	R^2	Synthesis according to Eq.	Yield[a]	Ref.	Stability	Synthetic uses in Eq.
iPr	Ph	31	80	102	stable in solution at −78°C	86, 90, 91, 127
tBu	Ph	31	60–80	102	stability ≈ tBu(Me)C═C═S	86, 90, 91, 100, 101, 108, 120, 127
Diaryl or unsaturated thioketens						
Ph	Ph	15	(83)	32	$t_{1/2}$ = 6 h in CH_2Cl_2	59, 66, 70, 75,
		17	(78)	48	(0.01 M; 30°C)	81, 82, 85, 86,
		22	?	67		91, 98, 100,
		31	73	67		108, 114, 127
4-$MeOC_6H_4$	2-$MeOC_6H_4$	30	(43)	93		
4-ClC_6H_4	4-ClC_6H_4	31	70	67	$t_{1/2}$ = 6h in CH_2Cl_2 (0.01 M; 40°C)	66, 108
		15	(98)	32		108
		46	?	163	stable up to −100°C	66
		46	?	163	stable up to −40°C	66
		15	(30)	32		70
Silylthioketens						
Me_3Si	H_2C═$CHCH_2$	36	(24)	134	can be used immediately at 20°C	
Et_3Si	H_2C═$CHCH_2$	36	89	143	dec. on distillation	
Me_3Si	H_2C═$CHCHMe$	36	57	134, 142	can be distilled	71, 84, 86, 96
Me_3Si	H_2C═$CHCMe_2$	36	80	134, 142	can be distilled	71, 75, 84, 102, 114
Me_3Si	H_2C═$CHCHPh$	36	46	134		71, 84
Me_3Si	H_2C═$C(COOMe)$—CH_2	36	75	143	dec. on distillation	
Me_3Si	Ph	31	(35)	106	stable at 20°C	71
Me_3Si	Me_3Si	35	90	130	can be distilled	66, 71, 79, 134, 138
Me_3Si	Et_3Si	35	36	97, 129, 179		
Me_3Si	$tBuMe_2Si$	35	13	97, 179		
Et_3Si	Et_3Si	35	?	129		
Et_3Si	Et_3Ge	35	?	129		
Functionally substituted thioketens						
F_3C	Ph	31	40	105	stable in solution at 20°C	59
Me—CO	Me	31	?	72, 89	Characterized at 10 K (matrix)	
Et—CO	Ph	18	(25)	45, 47		130
Ph—CO	tBu	15	97	44	dec at 20°C[59]	70, 130
		21	3	59		
Ph—CS	Ph	49	(10–68)	59, 166		131

[*Table continued overleaf*

Table 1—*continued*

R^1	R^2	Synthesis according to Eq.	Yield[a]	Ref.	Stability	Synthetic uses in Eq.
EtOOC	Me	31	?	89	characterized at 10 K (matrix)	
H_2N—CO	Ph	18	(61)	48		70
NC	tBu	5	(21)	20	dec.	70, 86, 88,
		8	?	32	< −78°C	89, 92, 100,
		11	(41)	32		103
		15	(43)	44		
		18	(91)	48		
		21	(51)	31		
		31	4	102		
NC	Ph	15	(90)	32		70
		18	(82)	48		
		31	29	102		
EtS	Ph	31	(?)	104	dec. at −97°C	70
Cl	tBu	31	70	102	stable at −78°C in solution	90, 91, 97, 108, 127
F_3C	F_3C	19	?	55	slow dimerization at	61, 65, 70,
		22	75	15–17	20°C	73, 74, 83, 89, 91, 108, 110, 112, 113, 121, 132, 133, 138
ROOC	NC	21	(56–93)	60		71, 80, 84, 89
		22	(14–33)	180		100, 112, 115
NC	NC	21	(55–78)	60		100, 104, 112, 115, 125, 129
$(EtO)_2PO$	ROOC	21	(25–28)	50		70, 100
Cl	Cl	18	(39)	45, 46, 48		70
Cumulated thioketens						
H_2C=		14	?	43	polymerizes	
		45	?	162	> 120 K	
$tBu(Me_2N)C$=		9	?	3		
		9	30	4		63
		9	10	4		
Ph_3Ph=		7	76	29	stable at 20°C	85, 111, 145
		9	60	35, 36		
		10	?	37		

[a] Numbers in parentheses refer to typical yields in trapping reactions usually with amines or C=N systems.

3. PHYSICAL PROPERTIES AND STRUCTURE OF THIOKETENS

As shown in Table 1, the known thioketens cover the whole range of stabilities from transient species to stable compounds. The stable thioketens have been studied via many physical methods, but data has also been obtained for short-lived thioketens using appropriate techniques. Beyond the experimental evidence, various computations have been carried out to improve our understanding of thioketens.

The *IR spectra* of the parent thioketen in undeuterated and deuterated form could be recorded for argon-matrix isolated material[85,115] or in the gas-phase[174] and, based on a normal coordinate analysis, complete assignment of vibrational frequencies was possible.[115] The striking feature of any thioketen IR spectrum is a strong band around 1750 cm^{-1}; in accordance with the assignment to the antisymmetric vibration of the heteroallene CCS system, the absorption is Raman inactive.[21] As it occurs in an otherwise usually empty region, the CCS band is of high diagnostic value. The influence of substituents on the exact position of the band is obscured by different conditions of

measurement. An obvious explanation for the high wavenumber in thiocarbonylcyclopentane is ring strain in the five-membered ring.[178] Typical values for $R^1R^2C{=}C{=}S$ are shown in Table 2. On the contrary, thioketens of the heterocumulene type (Eq. 2) show a C≡C rather than a CCS vibration around 2000 cm^{-1}.[1,3,29,35,181]

A quality of thioketens which cannot pass unnoticed is their intense *colour*: diarylthioketens are blue,[67] dialkyl derivatives purple or violet,[139] monosilylthioketens red,[134,142] and the parent compound orange–yellow or, in cyclohexane, pink.[125] The colour is due to the excitation of the $n\rightarrow\pi^*$ transition. This assignment is substantiated by the low intensity of this symmetry-forbidden transition. Some quantitative data for this band in thioketens $R^1R^2C{=}C{=}S$ are given in Table 3.

In general, electron-withdrawing substituents (e.g. CF_3) or conjugation apparently result in a bathochromic shift of the $n\rightarrow\pi^*$ transition. As compared to aliphatic thioketones,[184] the visible band of alkyl thioketens is shifted to longer wavelengths and actually occurs in the range of α,β-unsaturated thioketones. Similarly, a bathochromic shift is observed for this transition in arylthioketens as compared to diarylthioketones.[184a] Silyl substitution of the thioketen system leads to a hypsochromic shift.

Besides the transition in the visible range, thioketens show one or two bands in their *UV spectra*. For example, for diphenylthioketen an absorption at 275 nm (log ε 4.5, dichloromethane) is reported,[67] whereas dialkylthioketens[21] or silylthioketens[130,142] exhibit two intense bands around 240 (log ε 3.5) or 260 nm (log ε 3.3), respectively, and 215 nm (log ε 4.0 or higher). By comparison, a cumulated thioketen of the type described by Eq. 2 shows a UV absorption at 380 nm (in chloroform).[3]

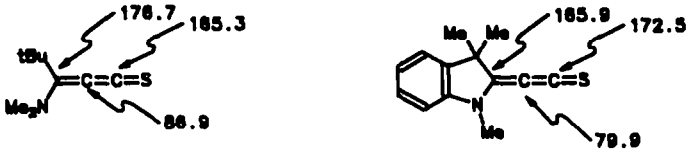
Typical features of the ^{13}C NMR *spectra* of thioketens are an extreme low-field position of the thiocarbonyl carbon and, as a counter point, a resonance of the formally olefinic terminal carbon at relatively high field (Table 4).

Thus, the position of the central carbon ^{13}C resonance covers a range of about 60 ppm. This means that this peak position is far more sensitive toward substituents than the corresponding resonance of cumulenic *sp* central carbons in ketens (range 40 ppm) or allenes (range 10 ppm).[182]

Interestingly, a plot of the wavelengths of the electron transition in the visible range vs ^{13}C chemical shifts of the central thioketen carbon gives a straight line, whereas there is no corresponding correlation for ketens or allenes.[182] The high-field resonance $\delta_{c-\alpha}$ of the terminal carbon has been discussed in terms of a strong contribution by the zwitterionic canonical form in Eq. 1.[21,185] In fact, also according to a restricted Hartree–Fock (RHF) calculation, the terminal carbon bears a considerable negative charge.[23] The shielding effect is qualitatively identical, though less pronounced, to the shift in ketens, where the corresponding peaks appear at even higher field by about 50 ppm.[187] Increased screening is also observed for the α-carbon of the substituents. For tert.butyl-substituted thioketens, this leads to the remarkable effect that the normal positions of quaternary and methyl carbons in the tBu residue are reversed.

Interestingly, the separation of thiocarbonyl and terminal carbon resonances is much less pronounced in dialkylthioketen *S*-oxides.[188] Thus, an upfield shift of the thiocarbonyl signal to δ values around 230 ppm and a downfield shift of the terminal carbon peak to about 160 ppm is detected. At the same time, the inversion of the tert.butyl carbon signals is not observed.

Similarly to thioketens of the heteroallene type (Eq. 1), the peak of C-2 in cumulated thioketens (Eq. 2) occurs at relatively high field; however, the thiocarbonyl carbon gives rise to resonance in an atypical range and, in accord with a partial positive charge, a low-field signal is observed for C-3,[4] as shown in the formulas:



Dipole moment data have been obtained for a few thioketens. For heteroallene-type derivatives $R^1R^2C{=}C{=}S$ (Eq. 1), the dipole moment, if known, is consistently lower than for the corresponding keten $R^1R^2C{=}C{=}O$ (numbers in parentheses in Table 5). On the contrary, an Eq. 2-type thioketen, triphenylphosphoranylidenethioketen, shows a higher dipole moment (8.50 D) than the cor-

Table 2

$\tilde{\nu}_{C=C=X}$ (cm^{-1})	1790	1789	1783	1760, 1763	1758	1757	1755	1753	1750	1737	1725
R^1	$(CH_2)_4$	Me	F_3C	Me	tBu	Me_3Si	H	tBu	HS	tBu	Ph
R^2		Me	F_3C	Me—CO	H	Me_3Si	H	NC	H	tBu	Ph
Ref.	178	161	15, 16	72	67	130	85, 115	63	164	63	67

Table 3

λ_{max} (log ε)	647 (?)	627 (2.3)	624 (2.5)	613 (1.9)	600 (0.8)	596 (?)	592 (0.6)	590 (0 9)	584 (0.3)
Solvent	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	$CFCl_3$	isooctane	CH_2Cl_2	isooctane	isooctane	isooctane
R^1	4-$MeOC_6H_4$	4-ClC_6H_4	Ph	Ph	$CHtBu(CH_2)_3CHtBu$	Ph	$CMe_2(CH_2)_4Me_2C$	tBu	tBu
R^2	4-$MeOC_6H_4$	4-ClC_6H_4	Ph	Me		H		iPr	H_2C=CH—CHMe
Ref.	104	67	67, 182	67, 183	21	67, 183	21	21	140

Table 3 *cont.*

λ_{max}(log ε)	575 (1.0)	575 (0 9)	562 (?)	560 (?)	546 (?)	503 (0.9)	501 (1.5)	413 (1.0)
Solvent	$CFCl_3$	isooctane	Ar matrix	CH_2Cl_2	solid	isooctane	isooctane	hexane
R^1	tBu	tBu	tBu	Ph	Ph—CO	F_3C	Me_3Si	Me_3Si
R^2	H	tBu	NC	CF_3	Ph	F_3C	H_2C=CH—CH_2	Me_3Si
Ref.	67	21	63	105	67	15, 16	142	130

Table 4

$\delta_{C=}$	274.5	272.9	271.2	271 2	271.0	269.1	263.3	252 0	240.3	237.9	225 8	214.4
$\delta_{=C=}$	93 6	98 0	92 3	82.3	85 7	91.2	94.8	88.2	69 0	73 4	82 7	52.0
R^1	Ph	tBu	Ph	Ph	$CH(CH_2)_3CH$ (tBu, tBu)	4-Cl—C_6H_4	Ph	Ph	Me_3Si	Me_3Si	CF_3	Me_3Si
R^2	iPr	iPr	Ph	Me		4-Cl—C_6H_4	tBu	CF_3	Ph	H_2C=CH—CMe_2	CF_3	Me_3Si
Ref.	59	21, 185	104	182	21	67	59	105	106	142	186	130

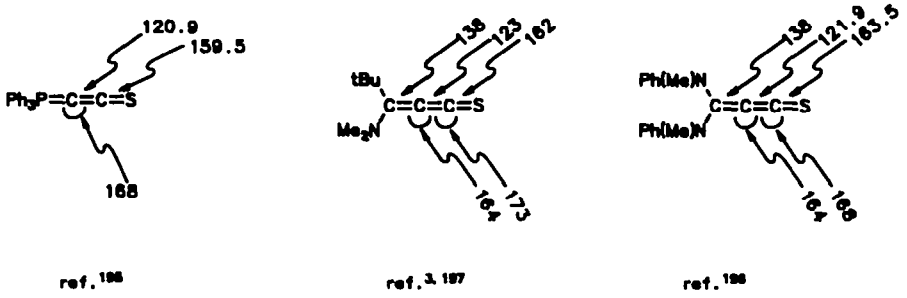
Table 5

μ (D)	1.02–1.07 (1.41) gas phase	1.54 (1.79) gas phase	1.91 (2.04) benzene	1.95 (?) ?
R^1	H	Me	tBu	F_3C
R^2	H	H	tBu	F_3C
Ref.	173, 189 (190)	111 (191)	21	16

responding keten (6.77 D).[192] However, the μ value of propadienone (methylene keten) is slightly higher than for the thione,[162] probably due to the bent structure of the keten.[193]

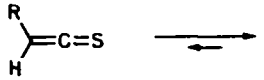
Information on the molecular structure of thioketens has been obtained through *microwave spectra*[110,111,172,173] and *X-ray structural analyses*.[3,19,194–197] As expected, based on the *sp* hybridization of the central carbon, the heteroallene system is almost linear with a CCS angle between 178.1°[19] and 168°.[196] A comparison of keten $R^1R^2C{=}C{=}O$ and thioketen $R^1R^2C{=}C{=}S$ investigations reveals a tendency to a shorter C=C distance in ketens, though ketens would be expected to have a higher contribution of the zwitterionic resonance structure in Eq. 1 and, consequently, a longer C=C bond (keten data in parentheses, Table 6).

This trend is continued with an even longer C=C bond in a thioketen *S*-oxide ($r_{c=c}$ = 129.6 ppm).[19] Not unexpectedly, cumulated thioketens (cf. Eq. 2) show bond data which differ considerably from those given in Table 6 (cf. the data given in the formulas).



ref.[198] ref.[3,197] ref.[196]

As to the question of a *tautomeric equilibrium* in aldothioketens, the structure investigations point toward only a minor concentration of the alkynylthiol form, if any:



(53)

Thus, the microwave spectrum of methylthioketen can be interpreted in terms of the thioketen tautomer, but accompanying weak transitions may be due to the thiol form.[111] Similarly, the ^1H NMR spectrum of tert.butylthioketen shows the thioketen tautomer exclusively.[67] Indirect evidence in favour of the preponderance of the thioketen form was inferred from the ratio of dithietane and dithiafulvene dimers.[148] On the other hand, on irradiation of thioketen itself, a shift of the equilibrium in favour of ethynyl thiol was claimed.[85]

Photoelectron spectra of thioketens $R^1R^2C{=}C{=}S$ reveal that the vertical ionization energies (I. E.) of valence electrons strongly depend on the substituents (Table 7). In general, the first ionization potential is lower than for the corresponding keten due to the smaller effective nuclear charge on sulphur.[62]

Table 6

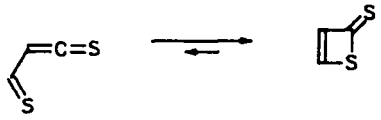
r_{c-s} (ppm) r_{c-c} (ppm)	155.4 131.4 (131.4)	155.2–156.2 131.4–133.2 (130.6)	156.6 128.7 (128.0)
R^1	H	Me	tBuCH—(CH_2)—CHtBu
R^2	H	H	
Ref.	173 (198)	111 (191)	19, 194 (19)

Table 7

1st I. E. (eV)	7.35	7.92	8.52	8.89	9.94	9.96
2nd I. E. (eV)	9 5	10.50	8.67	11.32		12.58
3rd I. E (eV)			11.14	12.14		13.16
R^1	$CHtBu(CH_2)_3tBuCH$	$(CH_2)_4$		H	NC	F_3C
R^2				H	NC	F_3C
Ref.	199	178	114	24	62	200

The *ESCA spectrum* for ionization of S(2*p*) electrons in a dialkylthioketen shows a value of 162.7 eV[194] which seems rather low when compared to a calculated value using the restricted Hartree–Fock (RHF) approach for core ionization energies.[24]

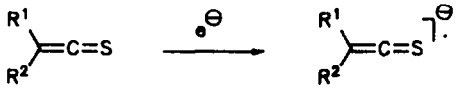
Various computations have been carried out to evaluate the relative stabilities of C_2H_2S isomers, in particular of thioketen, ethynylthiol, and thiirene. SCF or SCF-CI calculations indicate thioketen to be more stable than its alkyne tautomer as supported by experimental data (Eq. 53),[23,24,201] whereas the opposite result was deduced from STO-4G calculations.[76,202] However, in accord with a qualitative view on the stability of antiaromatic compounds, thiirene was unanimously calculated to be much higher in energy.[24] As to the equilibrium between thioformylthioketen and thiet-2-thione, a preference for the cyclic form was claimed[203] and supported by experimental results:[204]



(54)

In addition, data on the heat of formation[205] and an MNDO calculation[200] are available. Along with the calculations on stabilities, geometry optimizations were published.[201–203]

Thermally stable dialkylthioketens can be reduced electrochemically to give radical anions:[206]



(55)

In low-temperature *ESR experiments*, not only the proton hyperfine splittings, but also the ^{13}C satellites could be resolved. The data can be interpreted in terms of a non-planar C_s geometry of the radical anions and give support to their classification as σ radicals.[206]

4. CHEMICAL PROPERTIES OF THIOKETENS

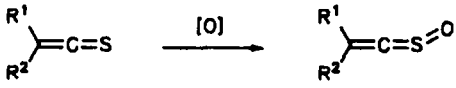
The reactivity of thioketens shows features of the analogous keten chemistry as well as of thioketone chemistry. Thus, thioketens readily add protic nucleophiles to give thiocarboxylic acid derivatives (cf. Section 4.2) or may undergo cycloadditions across the C=C bond (cf. Section 4.3.2) as is also characteristic of ketens. Where data are available, it appears that these reactions are usually a little slower for thioketens than for the corresponding ketens.[21,37]

In addition to keten-type chemistry, the presence of the sulphur atom allows thioketen reactions reminescent of their thiocarbonyl congeners; typical examples are the formation of *S*-oxides (cf. Section 4.1.1), thiophilic attack of organometallics (cf. Section 4.2.3), or cycloadditions across the C=S bond (cf. Sections 4.3.1, 4.3.3 and 4.3.4).

4.1. *Electrophilic attack*

4.1.1. *Oxidation to thioketen* S-*oxides or thiiranones*

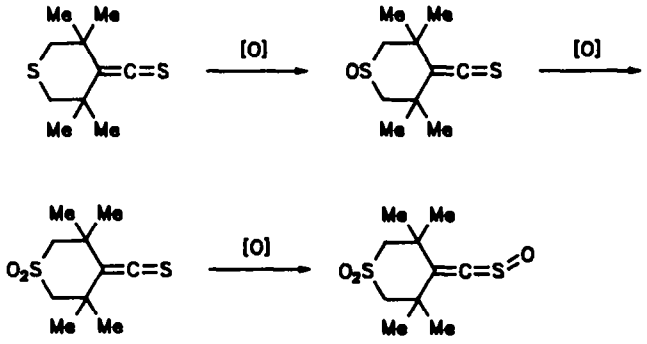
Successful oxidation of thioketens to *S*-oxides is limited to sterically hindered dialkylthioketens; the chemistry of the resulting thioketen *S*-oxides has been reviewed.[207]



(56)

The most convenient reagent for the oxidation is *m*-chloroperbenzoic acid in ether which works instantaneously at room temperature,[188,208] but, alternatively, hydrogen peroxide,[17] monoperphthalic acid,[17] or even ozone[209] may be employed. However, singlet oxygen gives the thioketen *S*-oxide along with other products which seem to stem from attack of the reagent at the thiocarbonyl carbon.[209,210]

In an intramolecular competition experiment, it was shown that the sulphide moiety is oxidized preferentially to the thioketen function:[208]



(57)

This behaviour can be understood in terms of the zwitterionic canonical structure in Eq. 1 which leads to diminished electron density at the thione sulphur and, consequently, encourages attack at the ring sulphur or even at the sulphoxide group rather than at the thioketen.

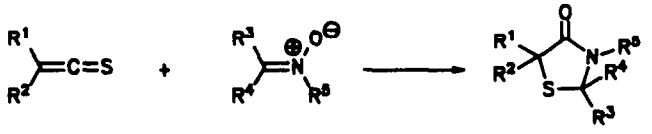
Thioketen *S*-oxides with bulky alkyl substituents are thermally comparatively stable, but less so than the parent thioketens. Gas-phase thermolysis leads to oxygen extrusion along with electrophilic ring-closure to give an alkylidene oxathiirane as primary product.[211] In contrast, on photolysis of thioketen *S*-oxides, deoxygenation occurs in a very clean reaction.[212]

The limit of thioketen *S*-oxide synthesis according to Eq. 56 is marked by tert.butyl-(phenyl)thioketen *S*-oxide which can be isolated on rapid work-up, but decomposes at room-temperature.[59] In other cases, such as diphenylthioketen,[59] allyl(tert.butyl)thioketen, or dimethylallyl(trimethylsilyl)thioketen,[213,214] only secondary products of the *S*-oxides were detected.

A surprising oxidation reaction is observed on addition of *N*-oxides, especially nitrones, to thioketens. Starting from sterically hindered dialkylthioketens, the products are isomers of thioketen *S*-oxides which could be identified as thiiranones (α-thiolactones; yield 36–92%):[208,215]

(58)

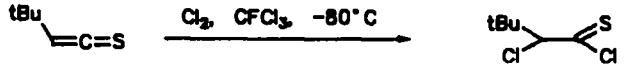
Obviously, primary attack of the nitrone occurs at the thiocarbonyl carbon, though the exact mechanism is not known. The resulting thiiranones are thermally unstable; on gentle heating decarbonylation to thioketones along with some keten formation is observed. Another secondary reaction is *in situ* (3+2) cycloaddition to the parallel product in Eq. 58, the Schiff base. This occurs when only moderately stable thioketens are employed in the reaction of Eq. 58 (yield 30–55%):[104,105,156]



(59)

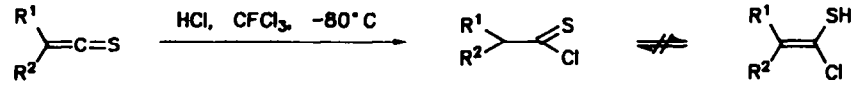
4.1.2. *Other electrophilic additions*

Although thioketens are only moderately reactive toward electrophiles, this mode of addition is encountered in a few examples. Thus, chlorine can be added to tert.butylthioketen to give a quantitative yield of an α-chlorothiocarbonyl chloride which is thermally more stable than the thioketen:[182]



(60)

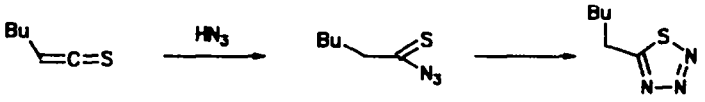
Reactive thioketens add hydrogen chloride at −80°C within seconds to yield yellow–orange thioacyl chlorides (yield ≤49%):[182]



(61)

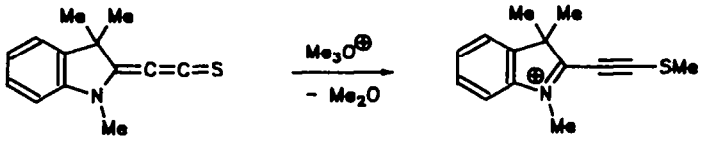
In this reaction, a solution of the thioketen may be employed, or, alternatively, thiadiazole pyrolysis (Eq. 31) be carried out in a stream of hydrogen chloride. The presence of a vinylthiol tautomer could be excluded based on spectroscopic evidence. This result is also in accord with protonation studies in the gas-phase which suggest that the thioacetyl cation is more stable than the tautomeric vinylthiol cation by 14.5 kcal/mol.[205] By analogy with Eq. 61, bis(trifluoromethyl)thioketen adds hydrogen bromide to give a thioacyl bromide (yield 65%).[216]

Hydrazoic acid can be added to butylthioketen as generated according to Eq. 32/33; the resulting thioacyl azide exists in the valencetautomeric cyclic form ("large" yield):[175]



(62)

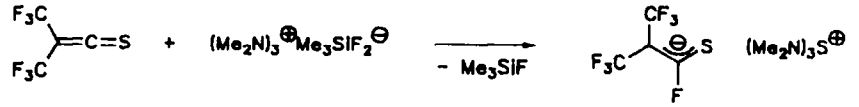
Alkylation of sterically hindered dialkylthioketens fails,[214] but this reaction is feasible for the more nucleophilic sulphur (cf. Eq. 2) in a cumulated thioketen (yield 52%):[4]



(63)

4.2. *Nucleophilic attack*

Attack on the thiocarbonyl carbon by nucleophiles is the most typical reaction of thioketens. Usually, protic nucleophiles are employed (*vide infra*: Sections 4.2.1 and 4.2.2). An example for addition of an aprotic nucleophile is the fluoride ion (yield "nearly quantitative"):[217]

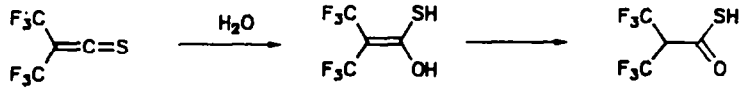


(64)

Contrary to the usual mode of nucleophilic addition, organometallics attack the sulphur in thioketens (cf. Section 4.2.3).

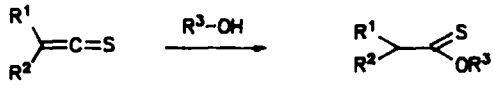
4.2.1. *Addition of water, alcohols, or thiols*

Smooth reaction with water has been reported for bis(trifluoromethyl)thioketen to give a thiocarboxylic acid (yield 67%);[216] as the reactivity resides, in most instances, in the thiocarbonyl group, the addition is believed to proceed through the enethiol and this may also be the general case for the addition of protic nucleophiles to thioketens:



(65)

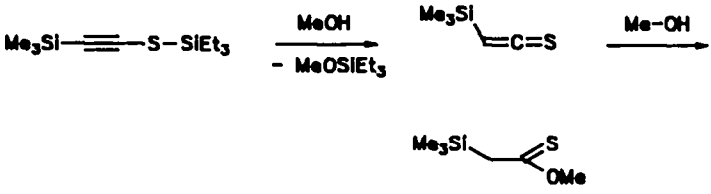
Addition of alcohols to thioketens is a more common reaction. The products are thionocarboxylates.[67,121,163–165] The reaction is of synthetic interest as the reaction conditions are usually very mild so that thermal isomerization to give thiolocarboxylates does not compete.



(66)

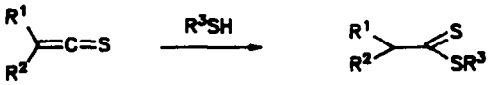
Dialkylthioketens with bulky substituents require acid catalysis for the addition of alcohols;[17] the reaction is also favoured by irradiation (c.f. Section 4.4).[218,219]

Besides trapping the thioketen, the protic alcohol may be used as a reagent in the generation of thioketens from alkynyl silyl sulphides:[129]



(67)

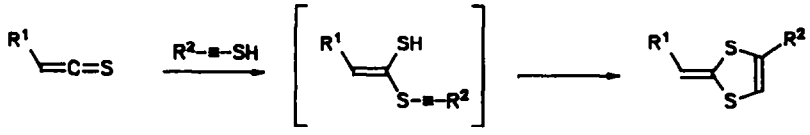
Monodesilylation is also observed in the reaction of bis(trimethylsilyl)thioketen with alcohols.[130] On the other hand, a high-boiling alcohol can be used as a solvent in the thermal generation of thioketens from thiadiazoles (Eq. 30) and serves, at the same time, as a trapping reagent.[82,94] Thioketens add thiols to give dithiocarboxylates (cf. Eq. 66):[117,121,123]



(68)

In the generation of thioketens via protonation of alkynylthiolates (Eq. 33), thiols can be used as a combined proton source and trapping reagent;[117] an alternative mechanism of dithiocarboxylate formation, addition of the thiol to an alkyne intermediate, can be excluded as alkynyl sulphides show the opposite regiochemistry in the addition of thiols.[128]

The usual outcome of the reaction between an aldothioketen and the alkynethiol precursor or tautomer (Eqs 33 and 53) is formation of 1,3-dithiafulvenes (cf. Eqs 20 and 25):[82,119,121,129,133,148,177,220,221]

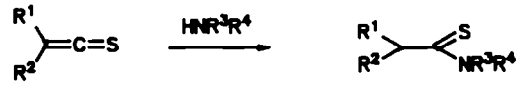


(69)

A related cyclization occurs in the reaction of the parent thioketen and ethyl ethynyl sulphide to give 2-(ethylthio)thiophene (40%).[117,128]

4.2.2. *Addition of amines*

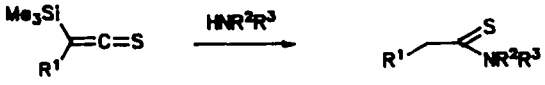
The reaction between a thioketen and a secondary amine is a very efficient process and, consequently, is the best and most frequently applied means of intercepting an unstable thioketen (cf. Section 2).[31,48,50,67,102,118,119,122,124,126,127,138,140,144,145,154,161,170,177,216] Of course, primary amines (R^4 = H)[118,123] or ammonia (R^3 = R^4 = H)[123] can also be employed.



(70)

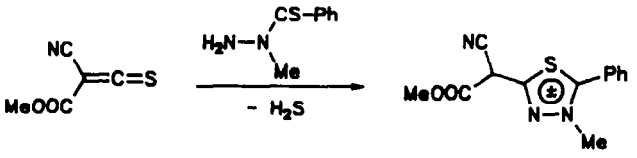
With secondary amines, the reaction appears to be basically quantitative, but often lower yields are obtained for unstable thioketens which tend to dimerize or oligomerize. Thus, assuming a complete conversion of authentic thioketen, the addition of a secondary amine has been used to assess the yield of thioketen in an FVT synthesis (Eq. 31). On the other hand, catalysis by sulphuric acid is required for the addition of amines to sterically extremely hindered dialkylthioketens.[17] Two equivalents of amine have to be used, if the amine also serves as a proton source in the generation of the thioketen (Eq. 33).

Addition of amines to silylthioketens leads to partial (R^1 = Ph, allyl)[97,142] or complete (R^1 = $SiMe_3$) desilylation:[130]



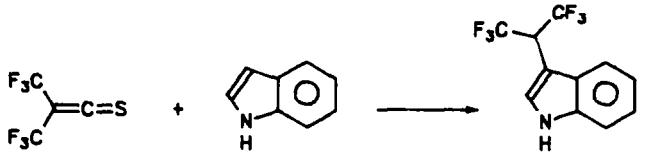
(71)

As with amines, other protic nitrogen nucleophiles will add to thioketens. This is true for hydrazine,[123] many hydrazones (cf. however Eq. 120),[59] or a thiohydrazide which leads to a mesoionic compound (yield 48%):[222]



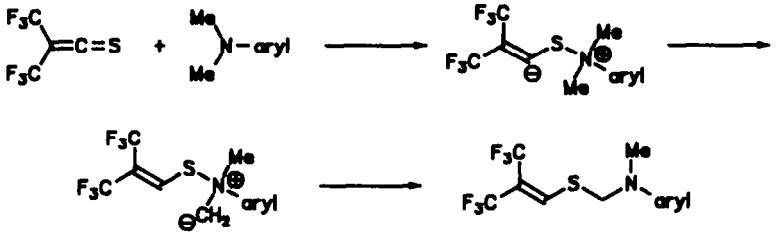
(72)

Indole is C-3 rather than N-thioacylated by bis(trifluoromethyl)thioketen to yield a vinylogous thioamide structure (yield 58%):[216]



(73)

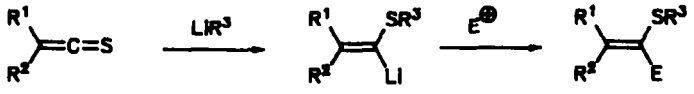
Also *N,N*-dimethylanilines give C-thioacylation with the fluorothioketen (yield 75%); the reaction is rationalized in terms of initial electrophilic attack on nitrogen, followed by proton transfer and finally ylide rearrangement:[216]



(74)

4.2.3. *Addition of organometallic reagents*

Non-cumulated thiocarbonyl compounds such as thioketones, dithiocarboxylates, or trithiocarbonates often add organometallics in an inverse sense, i.e. with nucleophilic attack of the organic residue at sulphur ("thiophilic attack").[223,224] On the contrary, some thiocarbonyl-containing heteroallenes of the type described in Eq. 2 add organometallics in the normal—carbophilic—way, e.g. carbon disulphide[224] and isothiocyanates.[225] Surprisingly, dialkylthioketens[139]or diphenylthioketen[104] are specifically S-attacked by organolithium compounds emphasizing their relationship to thioketones:

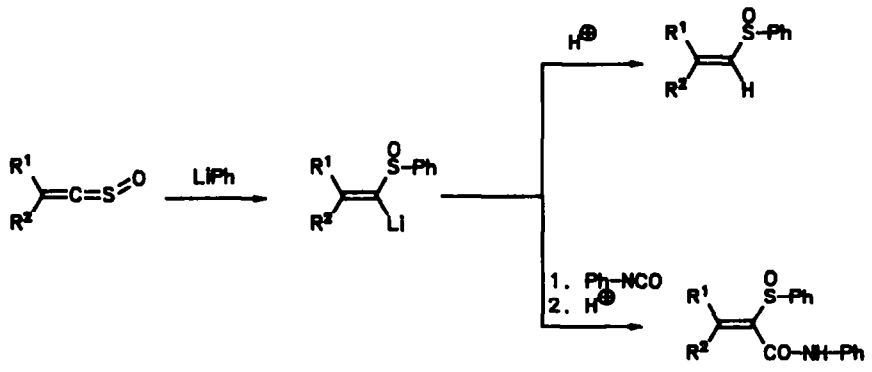


(75)

The reaction is fast even at −78°C and can be carried out like a titration as it leads to decolourization of the thioketen. As to the nucleophilic residue R^3, methyl,[104,139] butyl,[104,214] tert.butyl,[214] benzyl,[214] vinyl,[226] phenyl,[139,226] and even allyl,[226] which gives C-addition with thioketones,[227] show thiophilic attack on thioketens. The primary addition products, which can be looked upon as lithiated vinyl sulphides, smoothly react with various electrophiles E^+. Examples include methyl iodide,[139] benzaldehyde,[226] benzophenone,[226] ethyl cinnamate,[226] benzoyl chloride,[226] benzonitrile,[226] carbon dioxide,[139] and phenyl isocyanate;[214,226] with iodine, oxidative dimerization is achieved.[226]

In the absence of an electrophilic trapping reagent, the intermediate in Eq. 75 tends to eliminate thiolate on warming. The resulting vinylidene carbene then adds to its anionic precursor to give a butatriene derivative or may be trapped by excess R^3Li.[139] For $R^1 = SiMe_3$, the carbene appears to rearrange in a Fritsch–Buttenberg–Wiechell-type reaction to give a 1-(trimethylsilyl)alkyne.[156,214]

Oxidation of the products obtained with electrophiles (Eq. 75) gives the corresponding sulphoxides.[214] Starting from dialkylthioketen *S*-oxides (Eq. 56), the same compounds can be obtained in another example of thiophilic addition:[188]

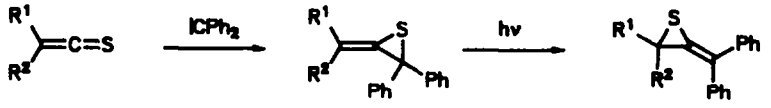


(76)

4.3. *Thermal pericyclic reactions*

4.3.1. (2+1) *Cycloadditions*

Addition of diphenylcarbene as generated via irradiation of diphenylketen[21] or, preferentially, via treatment of diphenyldiazomethane with copper sulphate[213] proceeds across the C=S bond of dialkylthioketens to give alkylidenethiiranes (yield 26–85%). Interestingly, the products of the thermal reaction rearrange on photolysis to provide the isomers with the bulky alkyl groups on the three-membered ring (yield 59–95%):[213]

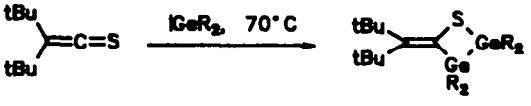


(77)

The same reaction sequence is shown by fluorenylidene[213] and by ethoxycarbonyl carbene as produced from ethyl diazoacetate/copper sulphate (yield 15–39%):[213]

(78)

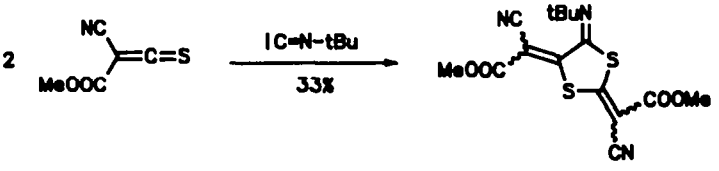
Similar to carbenes, their germanium analogues add to ditert.butylthioketen, apparently in a (2+1+1) cycloaddition:[228]



(79)

However, the germylene desulphurizes bis(trimethylsilyl)thioketen.[228]

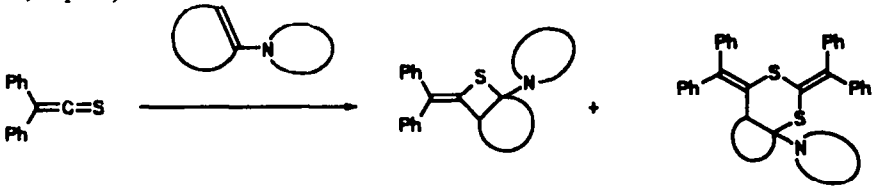
An example of a (2+1+2) cycloaddition was found in the reaction of tert.butylthioketen or dimeric cyano(methoxycarbonyl)thioketen with tert.butylisonitrile:[180]



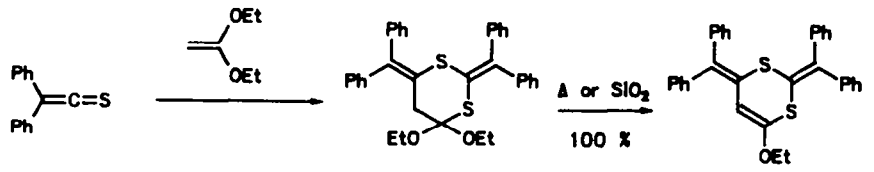
(80)

4.3.2. (2+2) *Cycloadditions*

4.3.2.1. *To* C=C *π systems.* Diphenylthioketen gives a (2+2) cycloaddition with electron-rich C=C systems such as enamines or keten acetals.[104] A mechanism via a zwitterionic intermediate is suggested by the occurrence of 2:1 cycloadducts (yields 0–65% and 8–79%, respectively, Eq. 81; 75%, Eq. 82):[104]



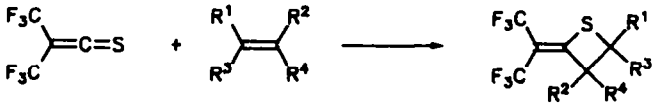
(81)



(82)

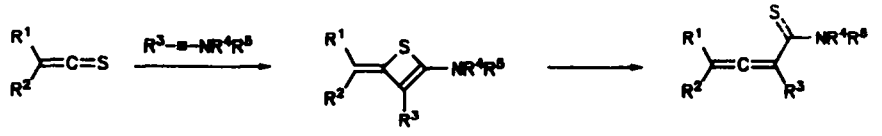
In the enamine reaction (Eq. 81), to obtain the given yields of cycloadducts, the thioketen should be generated in a diethylether rather than in a haloalkane matrix (cf. Eq. 31).[64]

A broad range of C=C systems which includes simple alkenes react with bis(trifluoromethyl)thioketen to give (2+2) cycloadducts across the C=S bond (cf Eq. 81).[16] Remarkably, *cis*-1,2-dimethoxyethylene ($R^1 = R^2 = OMe$; $R^3 = R^4 = H$) reacts with retention of configuration (yield 94%).[16]



(83)

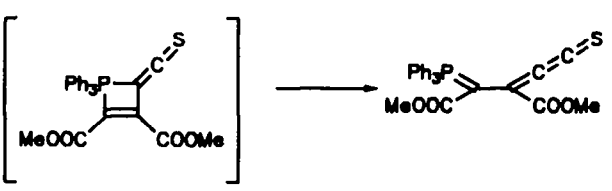
The particularly nucleophilic ynamines are examples of *alkynes* that give a (2+2) cycloaddition with thioketens:



(84)

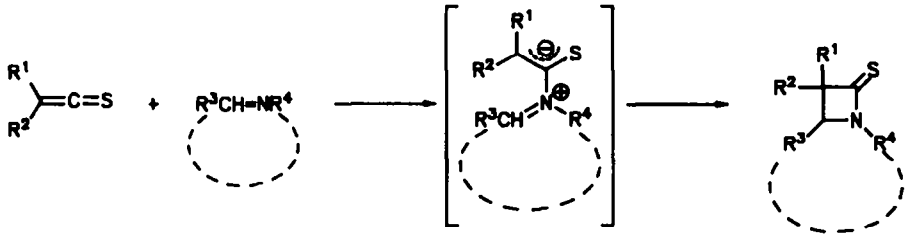
The primary product of the reaction is a thiet,[104,180] which usually undergoes electrocyclic ring-opening to give allene-thiocarboxamides in high yields (15 99%).[106,229]

Reaction with an electron-poor alkyne is observed for triphenylphosphoranylidenethioketen. In a sequence of (2+2) cycloaddition and electrocyclic ring-opening, another cumulated thioketen results (yield 74%):[181]



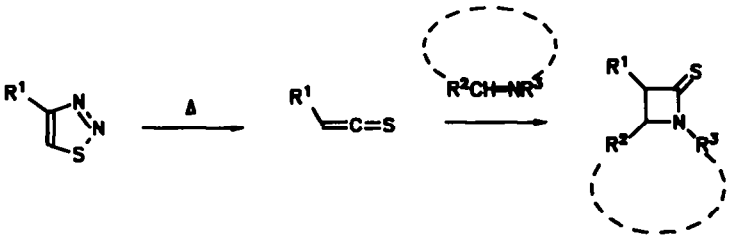
(85)

4.3.2.2. *To* C=N *π systems.* 4.3.2.2.1. *Imines*—Reactions of electrophilic heteroallenes, i.e. of heteroallenes as described by Eq. 1, with C=N systems are particularly popular for the synthesis of a large variety of heterocycles. The polarity of C=N compounds with their strongly nucleophilic nitrogen highly favours cycloadditions and often allows mild conditions. In the reactions with thioketens, addition across the C=C or C=S bond is observed depending on the reaction conditions and the substituents. Thus, sterically hindered dialkylthioketens give a (2+2) cycloaddition with imines which occurs across the C=C bond to give azetidinethiones (β-thiolactams).



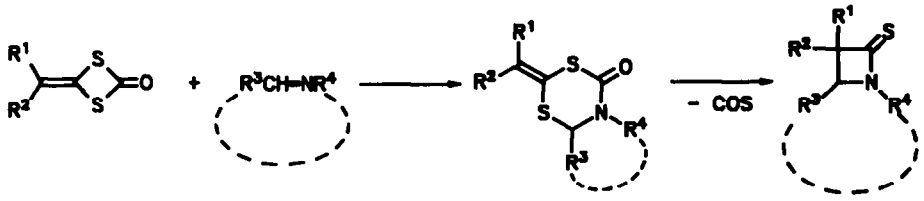
(86)

The best yields are obtained when the C=N group is incorporated in a ring (3,4-dihydroisoquinoline or derivatives, 73–94%), but most *N*-alkylbenzaldimines also give good yields (up to 73%).[98,230] It is certainly surprising that, despite the high reactivity of the C=S bond and despite the inherent steric congestion, dialkylthioketens add imines across the C=C bond. A careful mechanistic investigation revealed that the approach of the two reactants is controlled by the principle of orbital-symmetry conservation and that a zwitterionic species (Eq. 86) is formed only at a later stage of the reaction.[231] β-Thiolactams (Eq. 86) are also formed in the reaction of imines with alkyl(phenyl)thioketens (yield 8%),[98] diphenylthioketen (36–37%),[32,47,98] allylthioketens (7–49%),[98] and allyl(trimethylsilyl) thioketens (up to 70%).[134] Aldothioketens (R^1 = Me, tBu, Ph) lead to β-thiolactams when 4-monosubstituted 1,2,3-thiadiazoles (Eq. 30) are heated in an excess of imine (37–79%):[97,98]



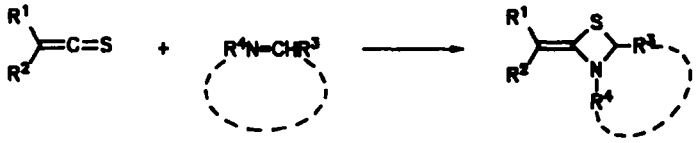
(87)

An indirect route to β-thiolactams is found in the reaction of 4-alkylidene-1,3-dithietane-2-ones with imines. Contrary to the usual cleavage of the four-membered ring to give thioketens (Eq. 21), the imine is inserted into the CO—S bond to give 1,3,5-dithiazine-4-ones (11–57%), which, on heating, lose carbonyl sulphide with concomitant reorganization of the skeleton to provide β-thiolactams in mostly quantitative yield:[31]



(88)

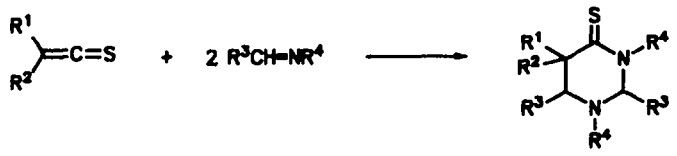
Contrary to the C=C selectivity shown in Eq. 86, thioketens with electron-withdrawing substituents (trifluoromethyl,[232] cyano, or alkoxycarbonyl[180]) show a preference for the addition of imines across the C=S bond (yields 38–79%):



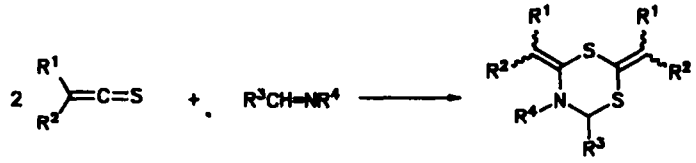
(89)

A borderline case between C=C (Eq. 86) and C=S selectivity (Eq. 89) is tert.butyl(cyano)thioketen. Generation at low temperature according to Eq. 18 appears to lead to the thiazetidine derivative (Eq. 89),[46] whereas liberation of the thioketen at ≥ 0°C (Eq. 11, 15, or 18) gives β-thiolactams (Eq. 86) indicating that, at least in this case, the β-thiolactam is the thermodynamically favoured product.[32,44,46] However, C=S addition is preferred when a cyclic C=N system is used as ring strain in thiazetidines (Eq. 89) is apparently lower than in annulated β-thiolactams.[32,46] Another example of C=S addition to imines is given by the thioketenoid species as generated in the Wittig olefination of carbon disulphide (Eq. 41).[154]

Besides formation of 1 : 1 adducts (Eqs 86, 87 and 89), reactive thioketens may give 1 : 2 or 2 : 1 adducts with imines, for which a hexahydropyrimidine-4-thione ("δ-thiolactam", Eq. 90) and a 4H-1,3,5-dithiazine structure, respectively, were established.[98,154] Usually, the method of mixing and the ratio of reactants determines which product is formed preferentially. But for bis(trifluoromethyl)thioketen only 2 : 1 adducts with imines are known (Eq. 91),[232] whereas silylthioketens only give desilylated 1 : 2 adducts (Eq. 90):[134]

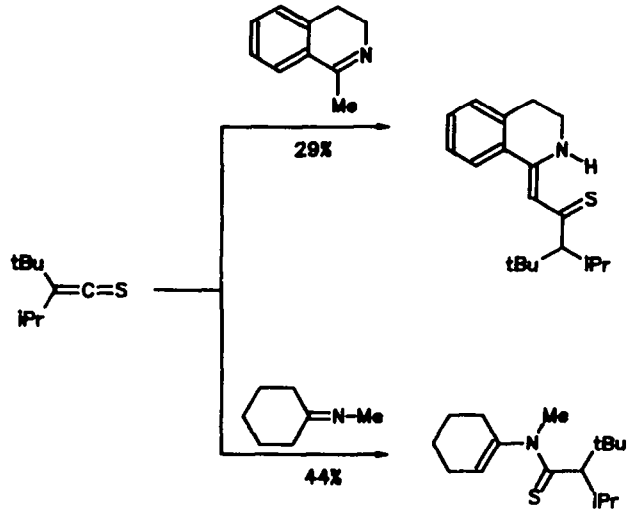


(90)



(91)

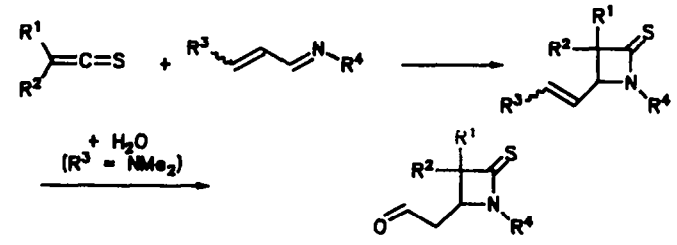
CH-acidic imines show addition to thioketens rather than cycloaddition, as seen for tert.butyl (isopropyl)thioketen:[230]



(92)

(93)

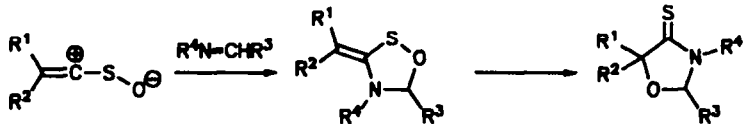
The reaction of thioketens with α,β-unsaturated imines raises a problem of electroselectivity.[233] At least for dialkylthioketens, a strong preference for (2+2) rather than (2+4) cycloaddition is observed and, by analogy to Eq. 86, β-thiolactams are isolated (R^3 = Ph, NMe_2, R^4 = Me, Ph; 15–90%; cf., however, Eq. 128):[59]



(94)

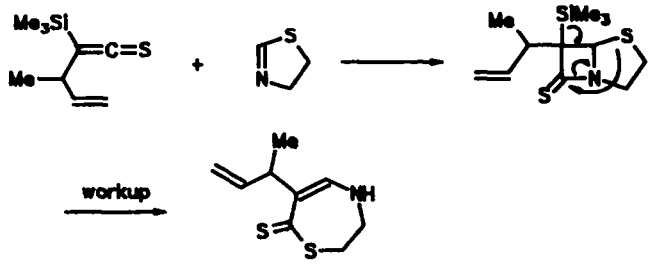
Bis(trifluoromethyl)thioketen gives a smooth reaction with one C=N bond in azines[234] or carbodiimides[16,234] showing the typical C=S selectivity of this thioketen (Eq. 89). In the same manner, diphenylthioketen adds to dicyclohexylcarbodiimide (yield 66%).[104] In their reaction with imines, acylthioketens exhibit the (4+2) rather than the (2+2) cycloaddition mode (cf. Section 4.3.4, Eq. 130).

The reaction of thioketen *S*-oxides with imines is in sharp contrast to the corresponding reaction of their thioketen congeners. Surprisingly, thioketen *S*-oxides behave as 1,3-dipoles to give five-membered sultenes which slowly rearrange to oxazolidinethiones (48–72%):[235]



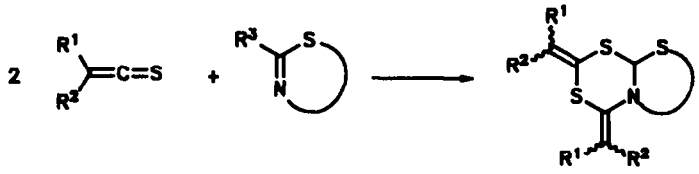
(95)

4.3.2.2.2. *Thioimidates*—Reactions of thioketens with cyclic thioimidates (2-thiazolines, 5,6-dihydro-4H-1,3-thiazines) have been looked at with the idea to synthesize β-thiolactam analogues of penam or cepham systems. In fact, 1 : 1 adducts could be obtained from silylthioketens and 2-thiazolines, but these products proved to be thiazepine derivatives which result from rearrangement of an intermediate thiopenam system (yield 52%):[236]



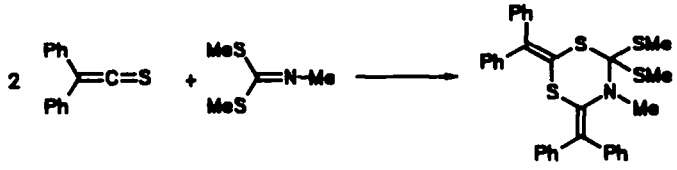
(96)

The reaction of (2-cyanoalkylidene)-1,3-dithietane-2-ones with 2-thiazolines stops at the stage of the dithiazine derivative (Eq. 89: $R^3+R^4 = SCMe_2CH_2$ or SCH_2CH_2; yield 12–17%).[31] Other reactive thioketens show a strong preference for the formation of 2 : 1 adducts with cyclic thioimidates, even if care is taken to maintain an excess of the C=N component in the reaction mixture (R^3 = H, Ph; yield 8–57%):[22,156]



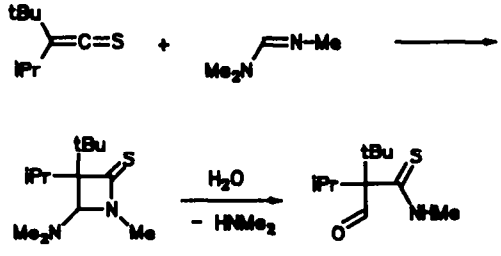
(97)

In a related reaction, diphenylthioketen gives a 1 : 2 cycloadduct of the dithiazine type with dimethyl *N*-methylimidodithiocarbonate (86%):[104]



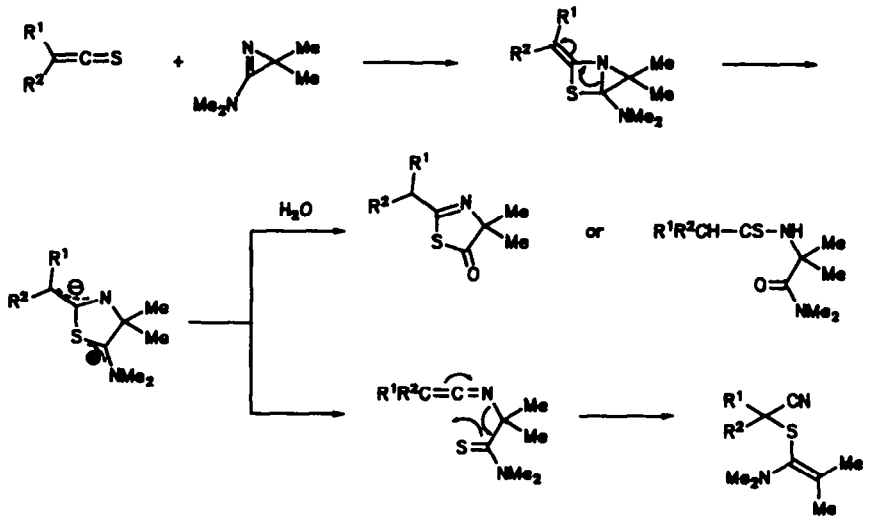
(98)

4.3.2.2.3. *Amidines*—The example in Eq. 99 shows that the reaction of thioketens with simple amidines provides products which, by analogy with Eq. 86, are derived from cycloaddition across the C=C bond of the thioketen (yield 30%):[237]



(99)

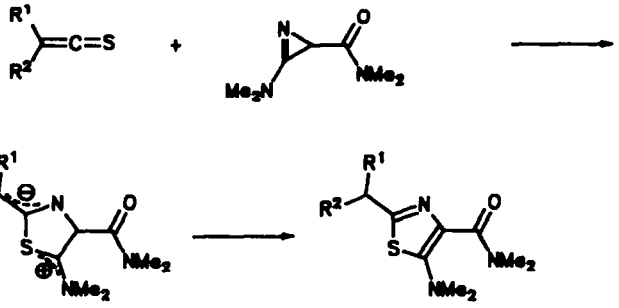
However, addition across the C=S bond of the thioketen is observed when the amidine system is incorporated into a three-membered ring. Thus, 3-dimethylamino-2,2-dimethyl-2H-azirine adds thioketens to give a strained bicyclic system which cleaves to zwitterionic thiazolidine (R^1, R^2 = cyano, methoxycarbonyl, diethoxyphosphoryl; yield 12–93%) or ketenimine derivatives (R^1, R^2 = alkyl, allyl, phenyl). The latter may rearrange thermally in a [3.3] sigmatropic shift (Eq. 101, yield 19–65%), while the zwitterions readily hydrolyse to give cyclic or acyclic products (Eq. 100, yield 10–37%):[31,238]



(100)

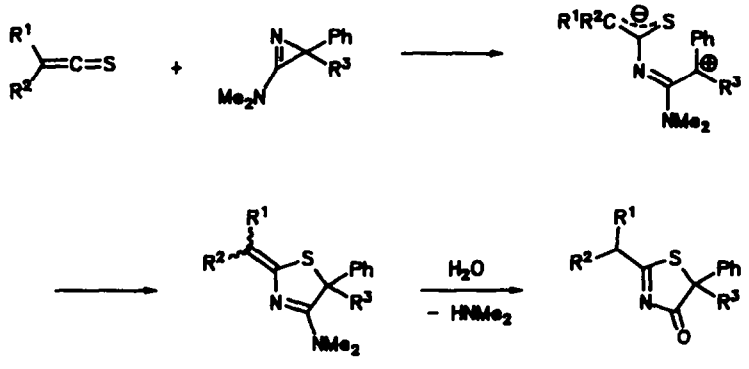
(101)

Starting from a 2-monosubstituted azirine, the zwitterionic intermediate in Eq. 100 undergoes a hydrogen shift to furnish thiazoles (41–92%):[238]



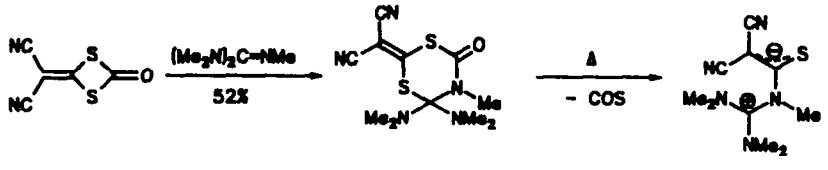
(102)

Contrary to Eqs 100–102, a 2-phenyl substituent on the azirine system encourages cleavage of the 1,2 σ bond in the reaction with thioketens,. The resulting 3-thiazolines hydrolyse fairly easily (yields 8–28%):[31,238]



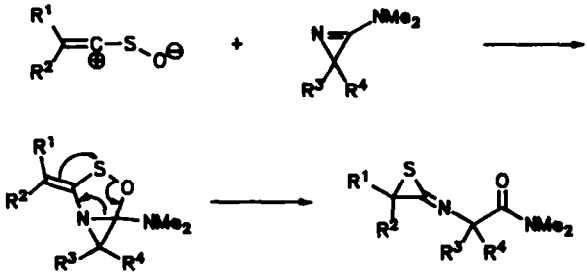
(103)

A precursor of dicyanothioketen (cf. Eq. 21) reacts with pentamethylguanidine, i.e. the amidine of carbamic acid, initially analogous to imines (cf. Eq. 88). However, the efficient charge stabilization allows isolation of a zwitterion rather than the cyclic 1 : 1 adduct (Eq. 86 or 89).[31,239]



(104)

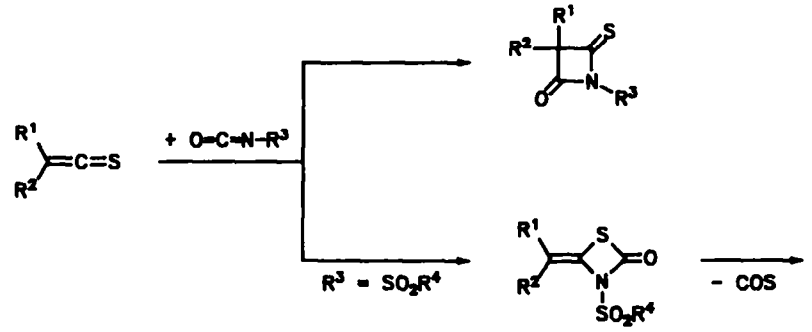
By analogy with Eq. 99, thioketen *S*-oxides give a (3+2) cycloaddition to the C=N bond in azirines instead of a (2+2) cycloaddition. The strained primary adducts rearrange to give thiiranimines (yields 11–96%):[240,241]



(105)

4.3.2.2.4. *Isocyanates*—Contrary to the reactions with the C=N systems discussed above (Sections 4.3.2.2.1–4.3.2.2.3) thioketens play the part of the nucleophile in the reaction with isocyanates. Thus, the yields of 1:1 adducts decrease with decreasing electrophilicity of the isocyanate:[21,242] $ClSO_2NCO$ > $PhOSO_2NCO$ > TosNCO > $MeSO_2NCO$ > 4-O_2N—C_6H_4—NCO.

However, as is the case in the cycloadditions with nucleophilic C=N components, the C=C bond in dialkylthioketens is the preferred reaction site to give 4-thioxo-2-azetidinones (Eq. 106; yield up to 85%). Some contribution of C=S addition is indicated by the isolation of *N*-sulphonylamides (up to 13%), i.e. the hydrolysis products of *N*-sulphonylketenimines as formed in the (2+2) cycloreversion[61] of the alternative (2+2) cycloadducts (Eq. 107):[21,242,243] The latter pathway seems to prevail in the reaction of bis(carbamoyl)thioketen with aryl isocyanates.[42]



(106)

(107)

Starting from fluoro- or chlorosulphonyl isocyanate and using reductive work-up (Zn/methanol), dialkylthioketens yield N-unsubstituted 4-thioxo-2-azetidinones (Eq. 106, R^3 = H; 28–85%).[243]

4.3.2.3. *To* C=S *systems*. The most common example of (2+2) cycloadditions between thioketens and C=S compounds is dimerization of thioketens to give 2,4-bis(alkylidene)-1,3-dithietanes, i.e. the reverse of Eq. 22:

(108)

Such dimers have been known for more than 100 years. Based on the yellow colour of the derivative with R^1 = Ph, R^2 = PhCO, the name "desaurins" [*des*oxybenzoin and *aur*eus (L., golden)] was introduced for these compounds.[52] However, it should be noted that in many cases 2,4-bis(alkylidene)-1,3-dithietanes do not result from dimerization of authentic thioketens, but from alkene-1,1-dithiolates (cf. Eq. 20) and thioketens with elimination of a sulphide ion.[51,52]

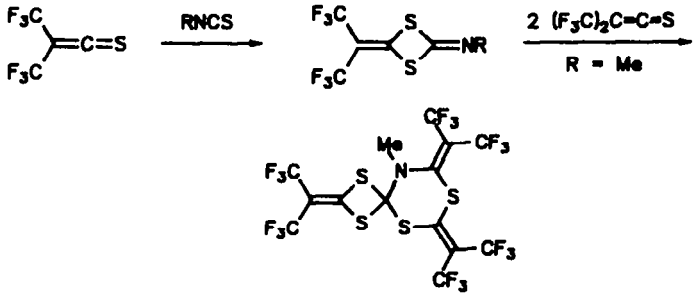
The dimerization of thioketens (Eq. 108) can be induced by heat or Lewis bases[15,16,66] and is thermodynamically strongly favoured.[203] However, no dimer is known for di-tert.butylthioketen

and aldothioketens lead to dithiafulvenes (Eq. 69) rather than dithietane derivatives. Reactive thioketens may oligomerize to give products of unknown structure. Thus, dimers of allylthioketens, as formed according to Eq. 36, have not yet been detected.

Reaction across the C=S bond of the thioketen as seen in Eq. 108 is also observed with other types of C=S compounds. Thus, tert.butyl(isopropyl)thioketen yields a 1,3-dithietane derivative on heating with thiobenzophenone (yield 41%):[21,230]

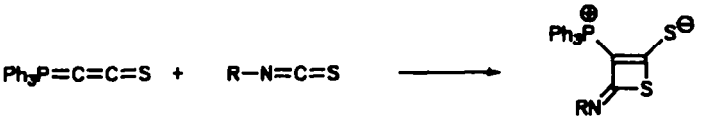
(109)

Bis(trifluoromethyl)thioketen and arylisothiocyanates react to give 1 : 1 adducts (yields 45–73%).[16] With methylisothiocyanate, consecutive steps provide a 3 : 1 adduct incorporating all four participating heteroallene molecules across their C=S bonds (yield 52%):[16]



(110)

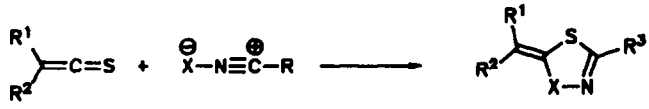
A different behaviour toward isothiocyanates is shown by triphenylphosphoranylidenethioketen:[2]



(111)

4.3.3. (2+3) *Cycloadditions*

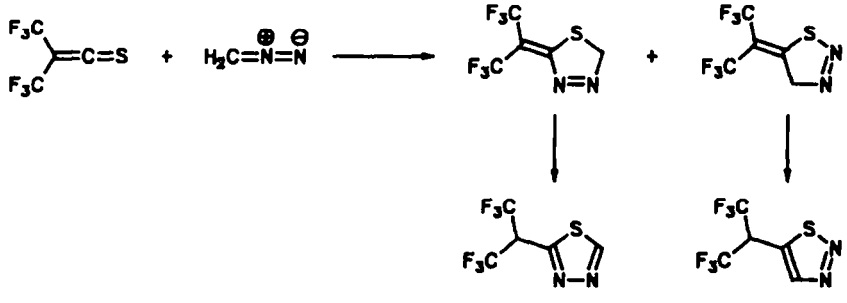
Thioketens represent a class of fairly good 1,3-dipolarophiles. Striking exceptions are provided by nitrones, which except for bis(trifluormethyl)thioketen,[16,24] oxidize thioketens to α-thiolactones (Eq. 58) and by ozone, which leads to thioketen *S*-oxides (Eq. 56). In successful cycloadditions, usually 1,3-dipoles with octet stabilization are employed. Thus, nitrile oxides (Eq. 112, X = O) and nitrile imines (Eq. 112, X = NR), examples of the linear allenyl-propargyl type, form five-membered rings with electron-deficient thioketens (R^1, R^2 = cyano, alkoxycarbonyl; 55–87%)[60] or arylthioketens (R^2 = H; 27–38%):[149]



(112)

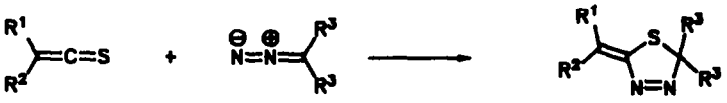
The same type of reaction was reported for bis(trifluoromethyl)thioketen and benzonitrile oxide (68%).[16]

Another linear 1,3-dipole, diazomethane, readily adds to bis(trifluoromethyl)thioketen in both directions without loss of nitrogen. The presumed intermediates undergo a hydrogen shift to form the more stable thiadiazoles (yields 59 and 41%, respectively):[16]



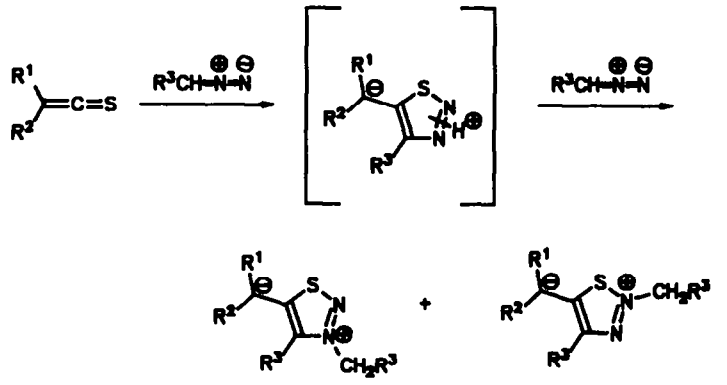
(113)

The first-mentioned addition mode is the exclusive process in the reaction between various keto-thioketens and 2-diazopropane (Eq. 114, $R^3 = Me$) or di-tert.butyldiazomethane (Eq. 114, $R^3 = tBu$), though, naturally with no subsequent hydrogen shift (yields 24–85%):[136]



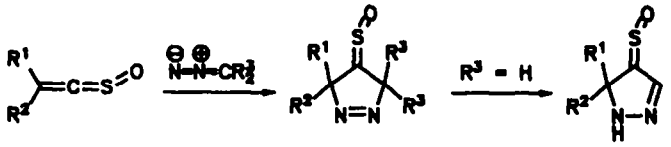
(114)

By comparison, electron-deficient thioketens obviously react with diazomethane or phenyldiazomethane (Eq. 114, $R^3 = Ph$) by analogy with the second-mentioned product in Eq. 113 to give, eventually, mesoionic products (yields 3–40%):[65]



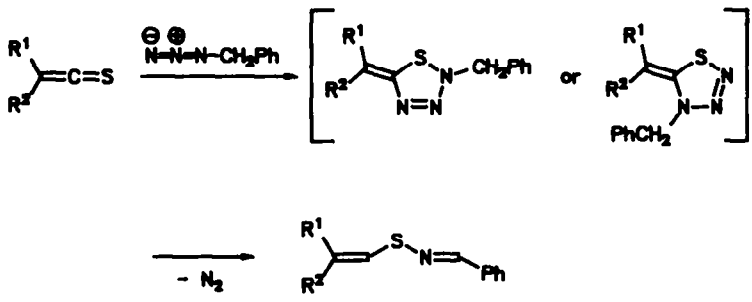
(115)

It should be noted that, while the C=S bond participates in the above-mentioned additions of thioketens to diazo compounds, the C=C bond is the reactive site in the analogous reaction with thioketen *S*-oxides (yields 13–95%):[244]



(116)

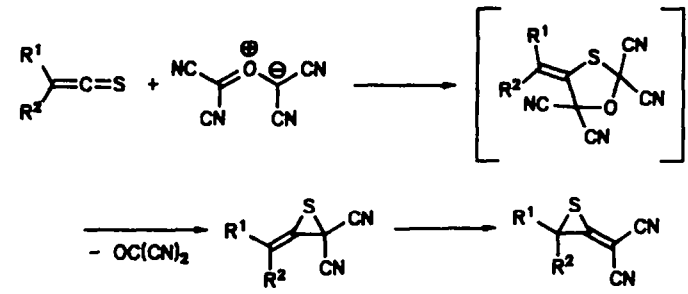
Whereas bis(trifluoromethyl)thioketen smoothly reacts with hydrazoic acid[16] (cf. also Eq. 62) or aryl azides[232] to give cycloadducts, dialkylthioketens do not react with most azides (methyl, phenyl, tosyl, trimethylsilyl azide).[213] However, on heating, a reaction occurs with benzyl azide in which the initially formed cycloadduct loses nitrogen and gives a subsequent hydrogen shift to furnish *S*-alkylidene thiooximes (yields 80–95%):[213]



(117)

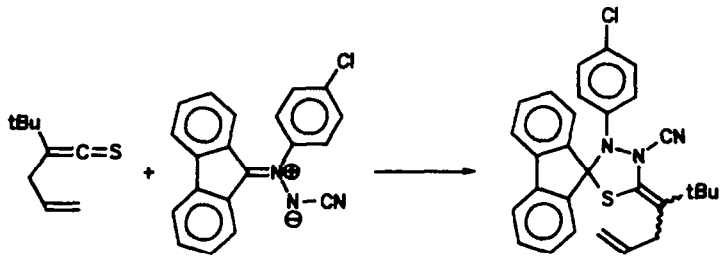
However, an alternative mechanism involving a benzylnitrene intermediate cannot be excluded.

Relatively few examples have been studied for the reaction of thioketens with 1,3-dipoles of the allyl anion type. Thus, a smooth and clean cycloaddition is observed even for sterically hindered thioketens in the reaction with tetracyanocarbonyl oxide as generated from the corresponding oxirane.[245] Along with some thioketen *S*-oxide, dicyanothiiranes are isolated which show a tendency to rearrange to the isomer with the bulky alkyl groups on the ring (yields 15–63%; cf. Eq. 77):[246]



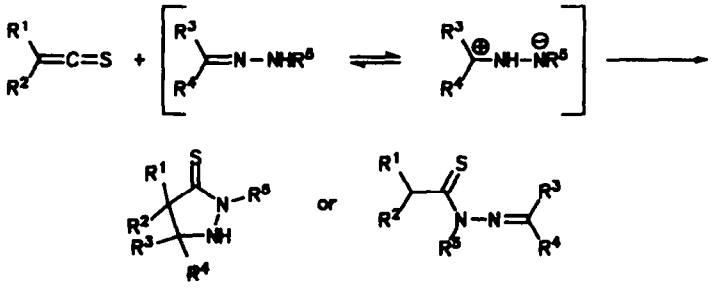
(118)

A stable five-membered ring is formed in the reaction of a thioketen with an azomethine imine (yield 30%):[156]



(119)

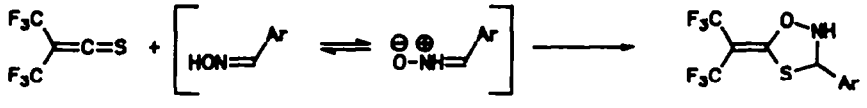
In this example as in the reactions of Eqs 112–115, 117 and 118, the alternative site selectivity in the cycloaddition, i.e. reaction across the C=C bond of the thioketen, can be excluded based on the spectroscopic evidence. Here, the lack of a C=S resonance in the ^{13}C NMR spectrum is of particular diagnostic value. However, in the cycloaddition between a sterically hindered thioketen (R^1 = tBu, R^2 = iPr) and benzaldehyde hydrazones (R^3 = Ph, R^4 = H, R^5 = Me, Ph), which may react in a tautomeric 1,3-dipolar form,[247,248] the C=C bond is the reactive site (yields 31–62%):[59]



(120)

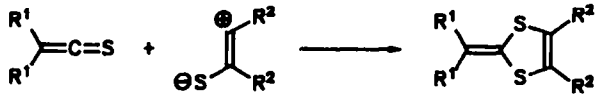
In a competing reaction, N-thioacylation of the hydrazone may occur (58–98%).

Similar to hydrazones (Eq. 120), oximes may exhibit 1,3-dipolar reactivity through a tautomeric form.[248] However, contrary to Eq. 120, in the cycloaddition between arylaldoximes and bis(trifluoromethyl)thioketen the C=S bond is the site of reaction (yields 31–78%):[16]



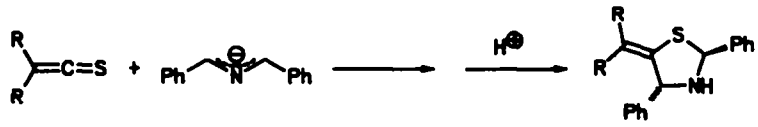
(121)

The only example of a 1,3-dipole without octet-stabilization which has been studied in its reaction with thioketens is the fragment which results from 1,2,3-thiadiazoles by loss of nitrogen (Eq. 24).[73] Trapping of this fragment with alkynes gives thiophenes and this result has been interpreted as evidence for the putative thiirene species.[83,95] However, interception of a formal 1,3-dipole by thioketens is possible (R^1–R^1 = $(CH_2)_5$; Me_2C—$(CH_2)_3$—CMe_2; R^2 = Ph, R^2–R^2 = $(CH_2)_4$; yields 6–66%):[21,94]



(122)

In additional examples of (2+3) cycloadditions to thioketens, 1,3-anionic species are employed. Thus, a 2-azaallyl anion as generated from an aziridine and butyl lithium[249] adds to sterically hindered thioketens to give thiazolidines (yields 18–83%):[250]

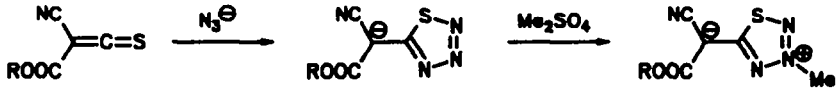


(123)

The analogous reaction of thioketen *S*-oxides takes a more complicated course which involves a "second-generation"[251] Pummerer reaction (yields 11–18%);[250]

(124)

Another example of a 1,3-anionic cycloaddition can be seen in the reaction of an electron-deficient thioketen with azide anion to give, after methylation, mesoionic products (yield 16%):[180]



(125)

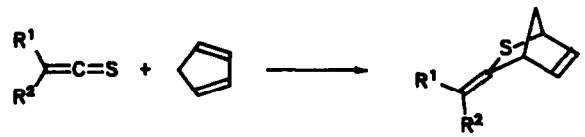
4.3.4. (2+4) *Cycloadditions*

A striking feature of keten chemistry is, except for exceptional cases,[252] the specific (2+2) cycloaddition to dienes rather than formation of Diels–Alder adducts. In contrast, thioketens usually give (2+4) cycloadditions with dienes. This is true for bis(trifluoromethyl)thioketen,[232,253,254] e.g. (yield 84%):[16]

(126)

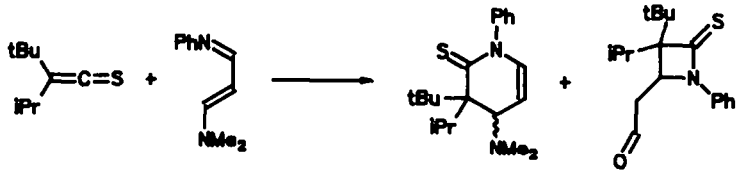
The product shows antiarthritic effects in rats.[253]

For other thioketens, so far only cyclopentadiene has been shown to be sufficiently reactive to give Diels–Alder adducts with thioketens (yields 36–100%):[64,104,108]



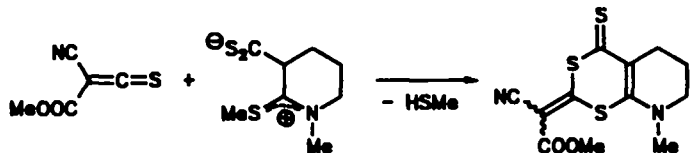
(127)

Contrary to Eq. 127, azadienes usually give (2+2) rather than (4+2) cycloadditions with thioketens (Eq. 94). However, as with diphenylketen,[255] charge control in the intermediate zwitterion may allow competing formation of some Diels–Alder product [25% along with 26% of (2+2) cycloadduct where the enamine function has been hydrolysed]:[59]



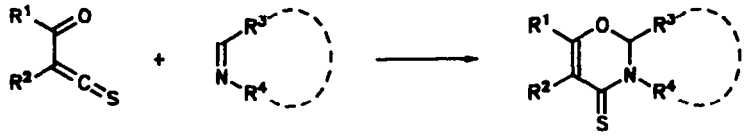
(128)

Another example of charge control leading to a six-membered ring is the reaction of a thioketen with the 1,4-dipole which is formed from a cyclic keten *S,N*-acetal and carbon disulphide:[255,256]



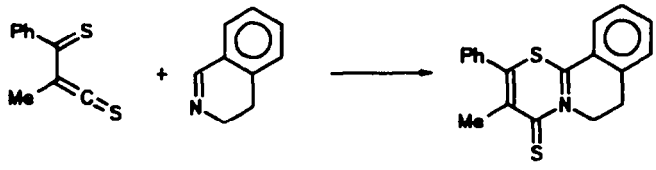
(129)

On the other hand, (thio)acyl thioketens may serve as 4π electron components in Diels–Alder reactions. Thus, the reaction of acyl thioketens (R^1 = Et, Ph; R^2 = Ph, tBu) with C=N systems opens up an efficient route to 1,3-oxazinethione derivatives (yields 25–97%):[32,45]



(130)

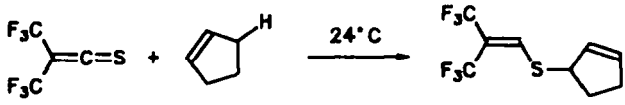
Similarly, a thioacyl thioketen may be trapped in a (4+2) cycloaddition, though the process is less efficient (yield 10%):[59,257]



(131)

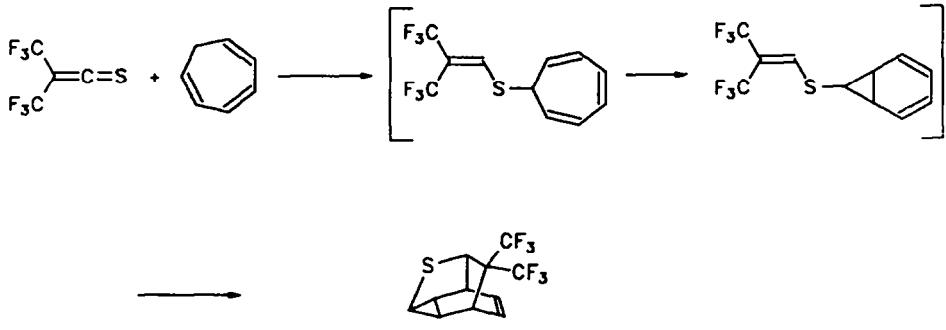
4.3.5. *Other pericyclic reactions*

Bis(trifluoromethyl)thioketen readily undergoes an ene reaction with a range of olefinic substances and with dimethyl or ethyl(butyl)keten,[216] e.g. (yield 89%):



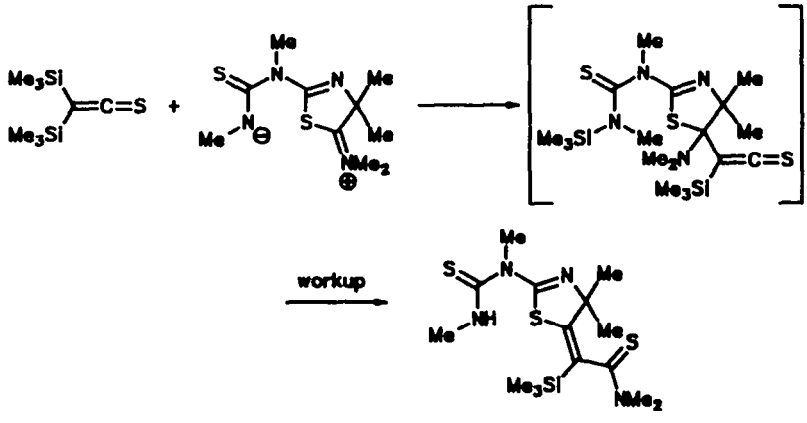
(132)

On addition of cycloheptatriene to the thioketen, a sequence of ene reaction, bond rearrangement to a norcaradiene, and intramolecular Diels–Alder reaction of the side chain to the norcaradiene to form a polycyclic compound has been observed (yield 51%):[216]



(133)

An unusual reaction was found on addition of bis(trimethylsilyl)thioketen to a 1,6-dipole; formation of the product (yield 51%) involves a 1,3-shift of the dimethylamino group:[258]



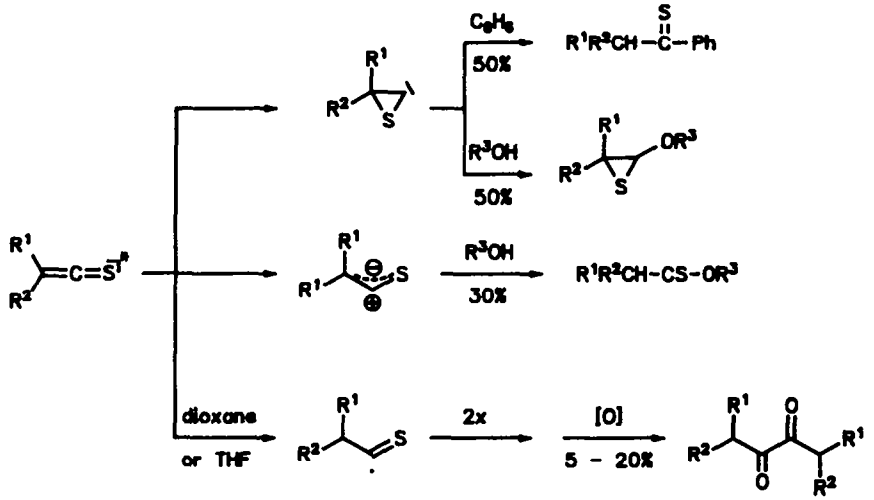
(134)

4.4. *Photochemistry of thioketens*

Recently, thiocarbonyl compounds have emerged as particularly intriguing and variable chromophores in photochemistry.[259] However, thioketens have received only relatively scant attention. Some information on the photostability of simple representatives was obtained in conjunction with the photochemical decomposition of 1,2,3-thiadiazoles (Eq. 24). Thus, the matrix-isolated parent thioketen proved to be not photoreactive at wavelengths above 280 nm, but slowly rearranges to ethynylthiol on prolonged irradiation at wavelengths between 220 and 250 nm.[76,85] Under the same conditions, the two carbons change their positions. This photoisomerization may be interpreted in terms of a thiirene intermediate:[85]

(135)

The stability of sterically hindered dialkylthioketens (Section 1.1) allowed a more comprehensive study of thioketen photochemistry.[209,218,219,260,261] The compounds proved unreactive upon excitation to S_1 (wavelengths > 480 nm) possibly due to self-quenching[212] but, upon irradiation to S_2, they produce thiiranyliden carbenes and zwitterionic intermediates. The products depend on the solvents used:[219]



(136)

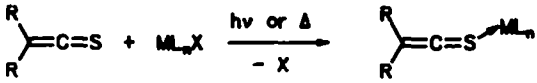
Interestingly, the typical photoreaction of ketens, cleavage of the C=C bond to give a carbene,[262] is not observed for thioketens.

The prevailing reaction pathway on irradiation of thioketen *S*-oxides is photodeoxygenation to provide the parent thioketens.[212]

4.5. *Co-ordination chemistry of thioketens*

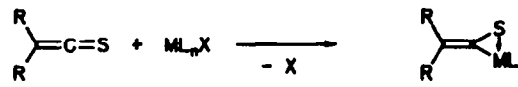
With the background of carbon dioxide fixation, the co-ordination of transition metals to analogues of carbon dioxide, especially carbon disulphide,[263] has been the subject of intensive studies. Very recently, thioketens have been included in these investigations. Here, the use of stable dialkylthioketens (Section 1.1) proved particularly helpful.

The most simple way to co-ordinate a thioketen to a metal is an η^1 (S) bond (ML_n = $Cr(CO)_5$,[264,265] $W(CO)_5$,[265] $MnCp(CO)_2$,[265] 1/2 $PdCl_2$[266]):



(137)

Frequently, a dihapto co-ordination of the metal across the CS bond [η^2 (CS)] is found (ML_n = $TiCp_2$,[267] VCp_2,[268,269] $FeCp(CO)_2Fe(CO)Cp$,[266] $CoCp(CO)$,[270] $CoCp(PMe_3)$,[271,272] $RhCp(PMe_3)$,[271,272] $Ir(CO)Cl(PR_3)$,[273] $Pt(PPh_3)_2$[266,273]):



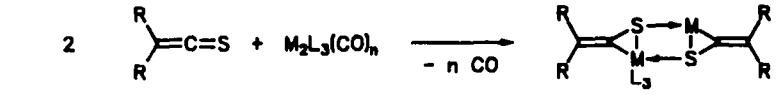
(138)

Here, besides dialkyl derivatives, examples include bis(trimethylsilyl)thioketen[269] and bis(trifluoromethyl)thioketen as generated from perfluoroisopropylidene-substituted polysulphur heterocycles.[273]

An alternative route to co-ordination compounds of the type depicted in Eq. 138 employs the addition of sulphur to vinylidene precursors (M = Rh, R = H;[274] M = Os, R = Ph[275]):

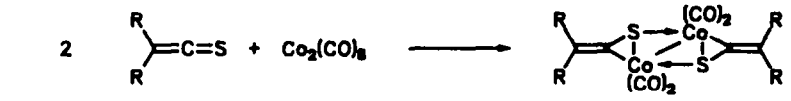
(139)

Examples of simultaneous η^1 (S) and η^2 (CS) bonding are dimeric iron and cobalt co-ordination compounds (ML_3 = $Fe(CO)_3$,[276] $CoCp$[270]):



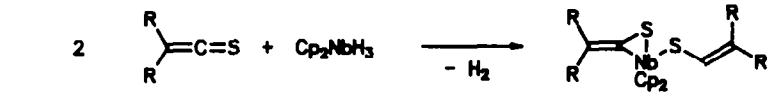
(140)

or[270]



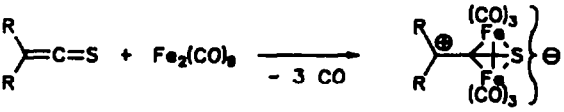
(141)

Another way of η^2 (CS) and η^1 (S) bonding, i.e. co-ordination to a thioketen and an enethiolate ligand, is encountered in a niobium derivative:[277]



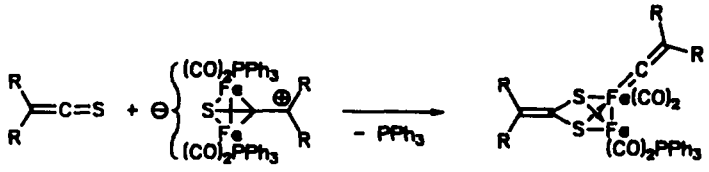
(142)

A particularly interesting bonding situation is found in an η^6 co-ordination compound with iron; the positive charge is stabilized by the substituents and the negative charge is delocalized within the tetrahedral $CSFe_2$ cluster:[278]



(143)

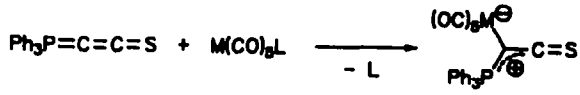
The product of Eq. 143 serves as starting material for some remarkable transformations. Thus, after partial exchange of carbon monoxide for a phosphane and with additional thioketen, the compound reacts to give a product with simultaneous dithiolato and vinylidene co-ordination of the original thioketen:[279]



(144)

With carbon monoxide, a phosphane, arsane, or stibane one of the carbon–iron bonds in the product of Eq. 143 is cleaved;[280] with hydride, a thioacyl complex results.[281]

As usual, triphenylphosphoranylidenethioketen shows a behaviour toward co-ordination compounds that is different from thioketens of the heteroallene type as depicted in Eq. 1 (M = Cr, Mo, W; L = CO, MeCN):[282]



(145)

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