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The 1,3-Anionic Cycloaddition Reactions of αβ-Unsaturated Thiolates and Their Analogues

M.L.Petrov and A.A.Petrov

The reactions of αβ-unsaturated alkali metal thiolates and the analogous salts of selenols and tellurols involving the 1,3-anionic cycloaddition mechanism are examined. The principal factors determining the capacity of the unsaturated triad anions for 1,3-anionic cycloaddition are identified and surveyed, which makes it possible to predict the mode of the reactions of these compounds.
The bibliography includes 93 references.

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I. INTRODUCTION

The reactions involving the cycloaddition of neutral 1,3-dipoles to unsaturated compounds have now been thoroughly investigated in relation to many examples. Huisgen formulated the main principles governing the structure of the 1,3-dipolar system and proposed a synchronous cycloaddition mechanism. As a result of these studies, 1,3-dipolar cycloaddition has become an important method of synthesis of heterocyclic compounds.[1]

The αβ-unsaturated compounds of sulphur and its analogues (selenium and tellurium) usually participate in 1,3-dipolar cycloaddition reactions as fairly reactive dipolarophiles and, due to the specific influence of the sulphur atom, the product is a regioisomer of the cyclic adduct different from that obtained in the case of αβ-unsaturated oxygen-containing compounds. However, the multiple bond remains the reaction site.[2]

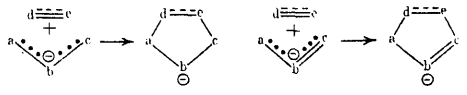
The reactions of αβ-unsaturated sulphur compounds in which they participate as 1,3-dipoles and not as dipolarophiles have also been discovered recently. Thus a group of Soviet and foreign chemists have been actively investigating the interaction of 1,2-dithiole-3-thiones, which are stable quasi-aromatic compounds, with dipolarophiles.[2,3] Drozd and co-workers extended the above reaction to allylic and propargyl derivatives of dithiocarboxylic acid esters.[4,5] In all these cases the cyclisation is accompanied by a sigmatropic shift.

Other instances of the 1,3-dipolar reactivity of sulphur compounds, for example, the adducts of carbon disulphide with phosphines or diamines, are also known.[2]

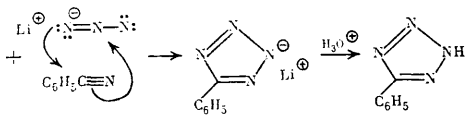
Nitrile sulphides, whose structure and reactivity are analogus to the classical 1,3-dipolar nitrile oxide systems, have been obtained recently.[6]

Thus the capacity for 1,3-dipolar cycloaddition, known previously only for oxygen and nitrogen compounds, has been recently demonstrated also for sulphur compounds.

Within the framework of the principle of the conservation of orbital symmetry in a chemical reaction, 1,3-dipolar cycloaddition is a special case of the symmetry-allowed $[{}_{\pi}4_{s} + {}_{\pi}2_{s}]$cycloaddition of allyl anions to unsaturated compounds.[7] For this reason, the allyl and propargyl anions have been used as the basis of the classification of the octet-stabilised 1,3-dipoles:[8]



The possibility of the involvement of such anions in cycloaddition reactions analogous to that of the "classical" 1,3-dipoles was predicted by Woodward and Hoffmann.[7] These reactions with participation of αβ-unsaturated anions have been called "1,3-anionic cycloaddition" (1,3-AC) on Kauffmann's suggestion.[9] The reactions involving the cycloaddition of inorganic azides (anionic 1,3-dipoles) to multiple bonds, known for a long time, can also be included among them:[1]

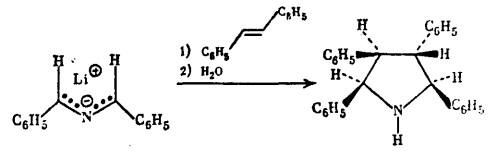


The 1,3-AC reaction of the unsubstituted allyl anion has not so far been achieved. However, allyl anions having substituents in the 2-position capable of stabilising the charge on the central atom of the triad do undergo the 1,3-AC reaction with activated alkenes. Thus 2-cyano-1,3-diphenylallyl-lithium reacts with *trans*-stilbene in a rigorously stereospecific manner with formation of the corresponding cyclopentantes. *cis*-Stilbene does not react with the salt, which confirms the concerted mechanism of the formation of new bonds.[10]

The participation of propargyl anions in 1,3-AC reactions has not been investigated, although it has been suggested that the dimerisation of 1,3-diphenylpropyne under the influence of lithium diisopropylamide proceeds via the 1,3-AC of the 1,3-diphenylpropargyl anion.[9]

The study of this key reaction, predicted by the theory, developed only after 1974 as a result of the studies by Kauffmann and co-workers devoted to the nitrogen-containing allyl anions.[9] This group of chemists demonstrated that 1,3-diphenyl-2-aza-allyl-lithium is the most reactive in 1,3-AC reactions with participation of a wide variety of unsaturated compounds ("anionophiles" according to Kauffmann's terminology).

The study of the 1,3-AC reactions of 2-aza-allyl-lithium compounds with simple alkenes demonstrated their great similarity to the reactions of 1,3-dipoles of the allylic type.[8] Thus simple unsubstituted alkenes do not react with 2-aza-allyl-lithium compounds, as in the case of the usual 1,3-dipoles. Only the introduction of phenyl substituents (styrene, stilbenes) into the dipolarophile or an increase in the strain in the multiple bond (norbornene, acenaphthylene) leads to 1,3-AC. Such reactions proceed exclusively regioselectively, as for the usual 1,3-dipoles. *trans*-Stilbene is more reactive in 1,3-AC reactions than *cis*-stilbene. In most cases the 1,3-AC proceeds stereospecifically: *trans*-stilbene reacts with *cis*-1,3-diphenyl-2-aza-allyl-lithium to form only one conformer of tetraphenylpyrrolidine:



These data indicate a concerted mechanism of 1,3-AC. Apart from the alkenes enumerated above, alkadienes and, as shown recently, arylallenes are fairly reactive in the 1,3-AC reactions with 2-aza-allyl-lithium compounds.[11] The introduction of organoelemental substituents, incorporating Group IV–VI elements in the Third and Fourth Periods such as sulphur, selenium, phosphorus, arsenic, silicon, and germanium, into alkenes favours the 1,3-AC reactions.[12]

The 1,3-AC reactions of 2-aza-allyl-lithium compounds with alkynes and nitriles frequently lead to heteroaromatic products, since they are accompanied by the elimination of hydrogen.

The nature of the multiple bond in the anionophile has a particularly pronounced influence on the 1,3-AC reactions. As in the reactions with the usual 1,3-dipoles, the oxygen-containing anionophiles are less reactive in cycloaddition to 2-aza-allyl-lithium anions than the sulphur and nitrogen compounds. Aldehydes, ketones, and carbon dioxide react with 2-aza-allyl-lithium compounds to form only linear adducts. Carbon disulphide is uniquely reactive in 1,3-AC reactions.[9]

Thus 1,3-AC reactions have been relatively thoroughly investigated only for nitrogen-containing allyl anions. The results of these studies have been summarised in a review[9] and have been included in a reference publication on general organic chemistry.[13]

Yet another type of 1,3-AC reactions involving sulphur compounds, namely αβ-unsaturated thiolates and their Group VIA analogues has been investigated in very recent years. These reactions make available new groups of sulphur-containing hereocycles and extended thereby greatly the scope of 1,3-AC in organic synthesis. The present review is devoted to a survey of the results of the authors of the review and other chemists in the study of the reactivities of αβ-unsaturated thiolates in 1,3-AC reactions.

αβ-Unsaturated thiolates are generally related to thioaldehydes, thioketones, and thioketens and the investigation of their reactivity therefore helps to extend the applications of various thiono-compounds in organic synthesis.

Ethylenic thiolates, which are salts of enethiols—a tautomeric form of thiono-compounds—have been known for a comparatively long time, while the salts of acetylenic thiols—the "enol" form of thioketens—were first obtained only in 1962.[14] The electrophilic substitution reactions of αβ-unsaturated thiolates have been most thoroughly investigated. In contrast to the enolates, which react both via the oxygen and carbon centres, unsaturated thiolates interact with electrophiles only via the thiol reaction centre.[15] Ethylenic selenolates and even more so the tellurolates were until recently difficult to obtain or were unknown owing to the instability of the initial >C=Se and >C=Te compounds.[16] As a result of studies mainly by Arens and his school,[14] the salts of αβ-acetylenic selenols and partly tellurols are readily available.

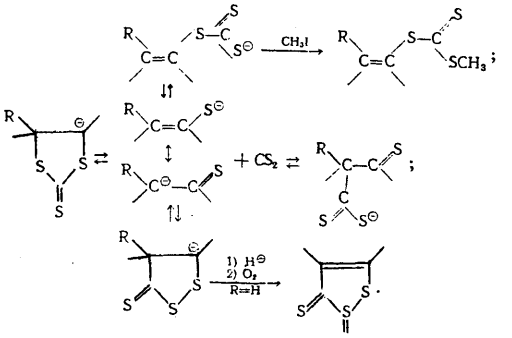
The nucleophilic character of the heteroatom in αβ-unsaturated thiolates and their analogues as well as the available data on the reactivity of 1,3-dipoles of the "allylic type"[8] have determined the choice, as objects of study, of anionophiles such as heterocumulenes and activated acetylenes, in the first place carbon disulphide, whose unique reactivity in 1,3-dipolar cycloaddition reactions is well known.[1] Furthermore, αβ-unsaturated thiolates can be successfully introduced into "mixed" dimerisation reactions with Huisgen's classical 1,3-dipoles. Such reactions have been fairly thoroughly investigated for the αβ-unsaturated compounds of tervalent phosphorus.[2] The latter are regarded as 1,3-dipolar systems with the negative charge on the phosphorus atom and the positive charge on the extreme carbon atom involved in the multiple bond.

II. INTERACTION WITH HETEROCUMULENES

1. αβ-Ethylenic Thiolates

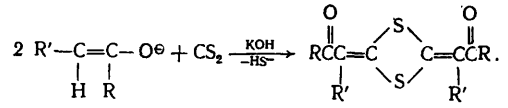
2-Alkyl(aryl)ethylenethiolates are usually obtained as mixtures of the *Z*- and *E*-isomers on treatment of the corresponding ethylthioethylenes with alkali metals in liquid ammonia.[17,18]

Despite the fact that carbon disulphide exhibits a unique reactivity in both 1,3-dipolar cycloaddition and 1,3-AC reactions, 2-alkyl(aryl)ethylenethiolates enter into the 1,3-AC reaction with the above anionophile with difficulty. The formation of cyclic adducts is not then the only reaction pathway. The unsubstituted ethylenethiolate does not form cyclic adducts with carbon disulphide, like the allyl anion:[19,20]



The reactions of alkali metal 2-alkyl(aryl)ethylenethiolates with carbon disulphide lead to the corresponding 1,2-dithiole-3-thione in a low yield after neutralisation and oxidation with atmospheric oxygen. The addition is preferentially to the thiol reaction centre. Treatment of the reaction mixture with methyl iodide results in the formation of methylalk-1-enyl trithiocarbonates. On the other hand, when iodine is added to the reaction mixture as the oxidant, only dialk-1-enyl disulphide is obtained.[20] In contrast to the thiolate anions, the enolate anions react with carbon disulphide to

form *C*-adducts and not cyclic adducts:[21]



In order to elucidate the causes of this difference between the behaviour of enolates and αβ-unsaturated thiolates in the reaction with carbon disulphide, the charge distribution in the C(2)=C(1)–X (X = S or O) systems was estimated from ^{13}C NMR spectra and from quantum-chemical calculations.[22] It was established that the maximum negative charge is located in both cases on the heteroatom, but the nono-uniformity in charge distribution is more striking for enethiolates than enolates. In the case of enethiolates one may speak of the strong nucleophilic centre on sulphur and the weak centre on the C(2) atom, while in the enolate anion there are two nucleophilic centres of approximately equal strength [O and C(2)].

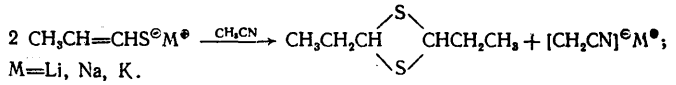
These data agree with the mode of nucleophilic addition of alkenethiolates to the electrophilic carbon atom of carbon disulphide. However, the question of the mode of addition of enolates and the mechanism of the [3 + 2]cycloaddition of alkenethiolates to carbon disulphide remains open.

The possibility that the reaction proceeds not only via the concerted mechanism but also via a stepwise mechanism is real for 1,3-AC reactions to an even greater extent than for 1,3-dipole cycloaddition.[8,9] One can assume accordingly that the reactions of an enolate with carbon disulphide belong, like the reactions of alkenethiolates, to the [$_{\pi}4_S$ + $_{\pi}2_S$] cycloaddition type, but the suggested cyclic adduct is unstable owing to the instability of the O–S bond. A similar hypothesis has been put forward in the literature for the reactions of enolates with carbonyl compounds.[23]

In order to confirm this hypothesis and to explain the causes of the observed high regioselectivity of the reaction, the results of quantum-chemical calculations for the enolate and enethiolate ions and carbon disulphide were analysed with the aid of the rules established by the molecular orbital perturbation theory in the 1,3-dipolar cycloaddition reaction.[22] Such analysis is entirely justified, since 1,3-AC also belongs to the class of [$_{\pi}4_S$ + $_{\pi}2_S$]cycloaddition reactions.

The calculations have shown that the distribution of the energy levels of the frontier orbitals in the reactions of both enethiolates and enolates with carbon disulphide belongs to Sustmann's type I. However, the estimation of the regiospecificity of the cycloaddition of enethiolates and enolates to carbon disulphide by the energy stabilisation method yields a different result for these interactions. The observed regioisomer of the cyclic anion (1,2-dithiole-3-thione and not 1,3-dithiole-2-thione) was accurately predicted in the case of enethiolates, while for the enolates the stabilisation energies of different regioisomers of the cyclic adduct are approximately the same. The reaction of the enolate with carbon disulphide is not cycloaddition. On the other hand, the same method predicts correctly the experimentally observed mode of nucleophilic addition of enethiolates and enoaltes to carbon disulphide.[22] Thus it has been suggested that the formation of 1,2-dithiole-3-thiones in the reactions of alkenethiolates with carbon disulphide proceeds via a concerted mechanism with the immediate formation of a cyclic anion and not the nucleophilic addition product, which cyclises under the influence of the oxidant after neutralisation.[20,22]

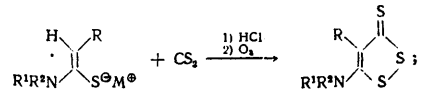
A mixture of the *Z*- and *E*-isomers of 2,4-diethyl-1,3-dithietan (the propenethiol dimer), whose formation is promoted by the presence of weak proton donors, has also been discovered in the products of the reaction of propene-1-thiolate with carbon disulphide:[19,20]



A similar dimerisation has been observed also for thioketones in the presence of bases.[24]

Heterosubstituted ethylenethiolates are much more reactive in the 1,3-AC reactions with carbon disulphide. In view of the fact that the capacity of the 1,3-dipole for cycloaddition reactions is directly related to the ability of substituents to destabilise the dipole and to stabilise the transition state,[8] the ease of the 1,3-AC should diminish in the following sequence of heteroatoms in the 1-position in the ethylenethiolate: N > O > S.

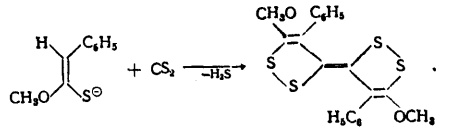
Substituted 1-aminoethylenethiolates do indeed react with carbon disulphide even at –55 °C to produce a high yield of only substituted 5-amino-1,2-dithiole-3-thiones:[25–27]



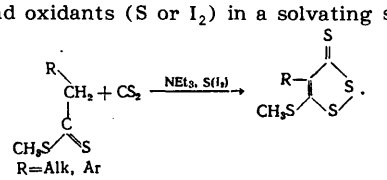
M=K, Na; R=H, Alk, Ar; R¹,R²=Alk, Ar.

Here it is essential to note that substituted 1-aminoethylenethiolates, obtained by the reaction of thioamides with potassium or sodium amides in liquid ammonia, exist exclusively in the form of the *Z*-isomers.[28]

On the other hand, 1-methoxy-2-phenylethylenethiolate reacts with carbon disulphide only at room temperature, and more effectively on heating, the product of the oxidative dimerisation of the intermediate cyclic anion, namely 5,5'-dimethoxy-4,4'-diphenyl-1,1',2,2'-tetrathiofulvalene, being formed unexpectedly:[29]



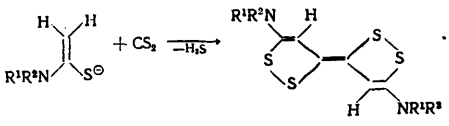
The reactions of 1-methylthioethylenethiolates with carbon disulphide give rise to only traces of 1,2-dithiole-3-thiones. Cyclic adducts were obtained only by the reaction of the dithioesters with carbon disulphide in the presence of triethylamine and oxidants (S or I_2) in a solvating solvent:[25]



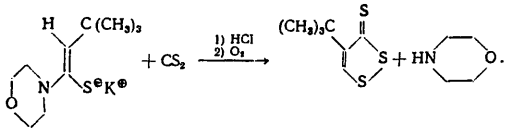
NN-Disubstituted 1-aminopropene-1-thiolates react vigorously with carbon disulphide regardless of the structure of the substituents at the nitrogen atom with formation of only the *NN*-disubstituted 5-amino-4-methyl-1,2-dithiole-3-thiones.[26]

The nature of the substituent in the β-position in *N*-substituted α-aminoethylenethiolates has a much more significant influence on the reaction with carbon disulphide.[27]

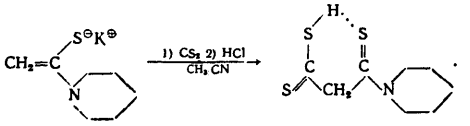
Thus, in the absence of a β-substituent, the products of the competing oxidative dimerisation, namely substituted 5,5'-diamino-1,1'-2,2'-tetrathiafulvalene, are formed apart from the usual 1,3-AC products:[27,29]



The introduction of a bulky substituent in the β-position in ethylenethiolate results in the reaction with carbon disulphide being accompanied by the elimination of an amine molecule and the formation of 4-t-butyl-1,2-dithiole-3-thione:[27]

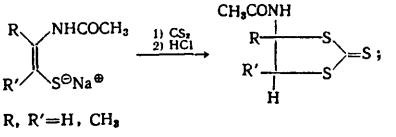


The cyclic structure of the intermediate is confirmed by the formation of a monopiperidide of trithiomalonic acid on interaction of potassium 1-piperidinoethylenethiolate with carbon disulphide in the presence of acetonitrile:



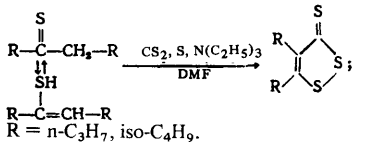
The compound isolated is not oxidised by atmospheric oxygen to the corresponding 1,2-dithiole-3-thione.[27]

Only one example of the formation of 1,3-dithiolan-2-thiones, and not 1,2-dithioles, in the reactions of alkene-1-thiolates with carbon disulphide is known in the literature, namely on interaction of 2-acetamidoethylenethiolate with carbon disulphide:[30]



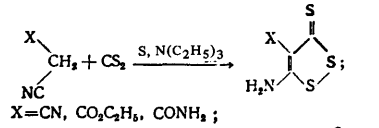
R, R'=H, CH_3

The formation of alkene-1-thiolates may be postulated as an intermediate stage in certain methods of synthesis of 1,2-dithiole-3-thiones, in the first place in the reaction of thioketones with carbon disulphide in the presence of a base (triethylamine) and an oxidant (sulphur):[24]

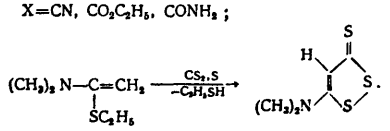


R = n-C_3H_7, iso-C_4H_9.

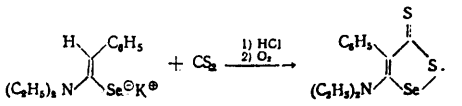
This can also occur on interaction of alkyl-substituted enamines with a mixture of sulphur and carbon disulphide[31] and also in the reactions of nitriles having mobile hydrogen atoms in the α-position with carbon disulphide and sulphur in the presence of bases[32,33] and in the exothermic reaction of keten *NS*-acetals with carbon disulphide and sulphur in dimethylformamide (DMF):[34]



X=CN, $CO_2C_2H_5$, $CONH_2$;



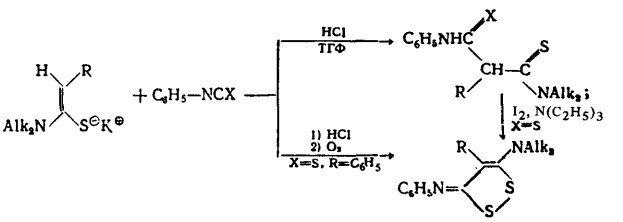
The αβ-ethylenic selenolates, which are isoelectronic analogues of alkene-1-thiolates having the amino-group in the α-position and which have been obtained recently, are also capable of entering into the 1,3-AC reaction:



The reaction is accompanied by the formation, together with a thiaselenole, also of compounds with the dithiole structure, because selenium is replaced by sulphur in the selenolate anion.[35]

Like carbon disulphide, phenyl isothiocyanate is an active dipolarophile and anionophile in 1,3-dipolar cycloaddition and 1,3-AC reactions.[1,9] In contrast to carbon disulphide, its molecule is asymmetric and, as shown in relation to the 1,3-dipolar cycloaddition reactions, it is capable of interacting via the C=S and C=N bonds.[1] However, in 1,3-AC reactions involving 2-aza-allyl anions, phenyl isothiocyanate reacts only via the C=N bonds.[9]

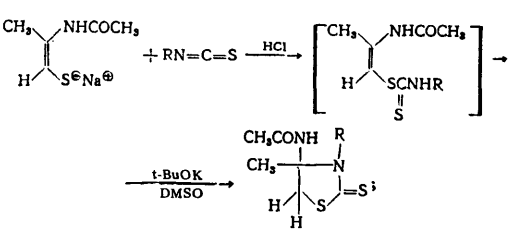
NN-Disubstituted 1-aminoethylenethiolates, which are the most reactive in the 1,3-AC reactions with carbon disulphide, combine with phenyl isothiocyanate and phenyl isocyanate via the carbon reaction centre with formation of derivatives of dithio- and mono-malonic acids respectively:[36]



R=Alk, Ar; X=O, S.

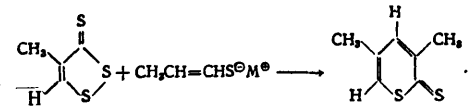
The products of the reactions of ethylenethiolates with phenyl isothiocyanates are oxidised by iodine to the corresponding 3-phenylimino-1,2-dithioles. The unusual site of nucleophilic addition (at the carbon centre of ethylene-1-thiolate) and the formation of a cyclic adduct in the reaction of 2-phenyl-1-piperidinoethylenethiolate with phenyl isothiocyanate suggest a concerted mechanism of the addition reaction. Derivatives of thiomalonic acid are formed as a consequence of the high instability of the corresponding cyclic anions. The phenyl substituent increases somewhat the stability of the cyclic anion, which is oxidised to a 1,2-dithiole after neutralisation.[28,36]

Sodium 2-acetamidoalkenethiolates react with isothiocyanates, forming, after neutralisation, linear nucleophilic addition products, which are tentatively identified as substituted dithiocarbamates. The latter cyclise to thiazolidine-2-thiones on heating in dimethyl sulphoxide (DMSO) in the presence of t-C_4H_9OK:[30]

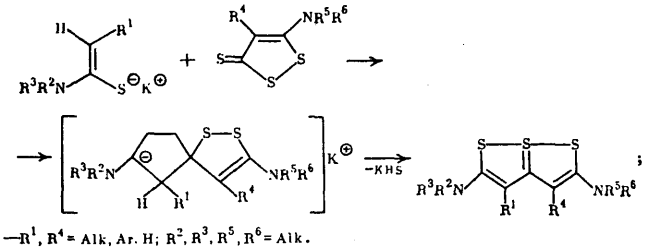


R=Alk, Ar.

Ethylenethiolates can react even with 1,2-dithiole-3-thiones. Thus the condensation of 4-methyl-1,2-dithiole-3-thione with sodium or potassium propene-1-thiolate results in the formation of 3,5-dimethylthiapyran-2-thione:[20]

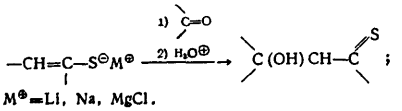


On the other hand, the interaction of *NN*-disubstituted 5-amino-1,2-dithiole-3-thiones with an excess of *NN*-disubstituted potassium 1-aminoethylenethiolate leads to derivatives of 1,6,6a-*S*(IV)-trithiapentalene:[37]



—R^1, R^4 = Alk, Ar, H; R^2, R^3, R^5, R^6 = Alk.

It has been shown for aza-allyl anions that the nature of the double bond involving a heteroatom has a marked influence on the 1,3-AC reaction. Thus aldehydes, ketones, and carbon dioxide react with 2-aza-allyl-lithium derivatives to form only linear products.[9] Alkene-1-thiolates react analogously with carbonyl compounds:[38–40]



$M^{\oplus}$ = Li, Na, MgCl.

2. αβ-Acetylenic Thiolates

αβ-Acetylenic thiolates are isoelectronic analogues of 1,3-dipolar systems of the propargyl type such as nitrileimides, nitrileimines, and diazonium betaines.[8,41] Instead of the nitrogen atom, the role of the centre at which the charge is stabilised is assumed by the *sp*-hybridised carbon atom having a higher electronegativity than the sulphur atom.[42]

The cyclic anions formed on the 1,3-AC of αβ-acetylenic thiolates are more stable than in the case of αβ-ethylenic thiolates, since they have the character of the cyclopentenyl and cyclopentadienyl anions.[43] However, both the cyclopentadienyl anion and its hetero-analogues readily undergo cycloelimination for an "inexplicable" reason (in Huisgen's words[41]). Probably, the 1,3-AC reactions of αβ-acetylenic thiolates can take place only in the presence of stabilising substituents such as aromatic groups. The activating influence of such substituents has been noted for 2-aza-allyl anions[9] and for αβ-ethylenic thiolates.[19,20,25,27]

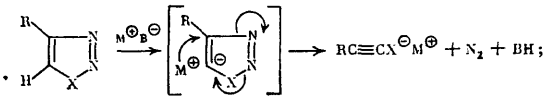
αβ-Acetylenic thiols and their analogues are unknown and are believed to be extremely unstable.[44] In the form of alkali metal salts, they are nevertheless readily available. The method of synthesis of αβ-acetylenic thiolates, selenolates, and tellurolates on interaction of acetylides with chalcogens in liquid ammonia was proposed as early as 1962:[45]

$$RC{\equiv}C^{\ominus}Na^{\oplus} + X_8 \rightarrow RC{\equiv}CXX_7^{\ominus}Na^{\oplus};$$

$$RC{\equiv}CXX_7^{\ominus}Na^{\oplus} + RC{\equiv}C^{\ominus}Na^{\oplus} \rightarrow RC{\equiv}CX^{\ominus}Na^{\oplus} + RC{\equiv}CXX_8^{\ominus}Na^{\oplus} \ldots \text{ etc.};$$

R = Alk, Ar; X = S, Se, Te.

The main deficiency of this method is the synthesis of salts with impurities comprising polyelement derivatives. The most convenient method of preparation of the salts of αβ-acetylenic thiols and selenols is the decomposition of 4-substituted 1,2,3-thia- and 1,2,3-selena-diazoles by strong bases (alkali metal amides and hydrides and alkyl-lithium):[46–49]

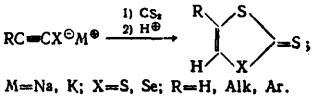


X = S, Se; R = Alk, Ar.

There also exists a convenient preparative version of the method of synthesis of an important group of thiolates and selenolates—potassium 2-arylethylenethiolates and 2-arylethyleneselenolates—by treating the corresponding thia- and selena-diazoles with KOH.[49,50]

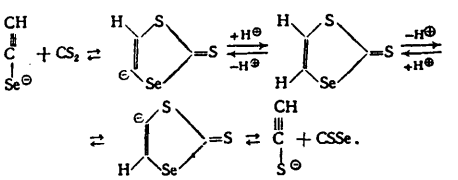
The synthesis of potassium 2-phenylethylenethiolates and 2-phenylethyleneselenolates in a pure form made it possible to investigate them by infrared and ^{13}C NMR spectroscopy. Analysis of the spectroscopic data and the results of quantum-chemical calculations demonstrated a significant non-uniformity in the charge distribution in the C≡C–X (X = S or Se) system. In the selenolate anion, this non-uniformity is more pronounced than in the thiolate anion.[51] The presence of a strong nucleophilic centre at the heteroatom in the molecules of αβ-acetylenic thiolates and selenolates agrees well with the mode of the alkylation and acylation reactions.[44,51] The non-uniformity in the charge distribution in these anions predetermines the possibility of their involvement in 1,3-AC reactions.

Compared with αβ-ethylenic thiolates, their acetylenic analogues react more vigorously with heterocumulenes containing the C=S bonds. Thus it has been established that both αβ-acetylenic thiolates[52–57] and the analogous selenolates[49,57–60] interact with carbon disulphide to form only 1,3-dithiole-2-thiones and 1,3-thiaselenole-2-thiones respectively:



M = Na, K; X = S, Se; R = H, Alk, Ar.

Some workers suggested an unusual nucleophilic addition mechanism for this reaction (the formation of a salt of trithiocarbonic acid) with subsequent intermolecular addition of the anion to the triple bond.[52] A similar reaction mechanism has been invoked to account for the results of the interaction of sodium acetylide in succession with selenium and carbon disulphide; in addition to the expected 1,3-thiaselenole-2-thione, 1,3-dithiole-2-thione, 1,3-dithiole-2-selenone, 1,3-thiaselenole-2-selenone, and 1,3-diselenole-2-thione are also formed:[60]

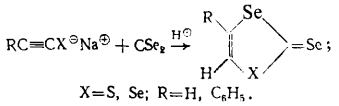


Anothe reaction mechanism is more probable. The 1,3-thiaselenole-2-thione formed in the course of the concerted 1,3-AC of ethyleneselenolate to carbon disulphide undergoes 1,3-anionic cycloelimination[61] to form ethylenthiolate and CSSe. The latter reacts further analogously to carbon disulphide.

The introduction of substituents increasing the stability of the cyclic anion prevents the 1,3-anionic cycloelimination. For this reason, only 5-aryl-1,3-thiaselenole-2-thiones are formed in the 1,3-AC of 2-arylethyleneselenolates to carbon disulphide.[49,50]

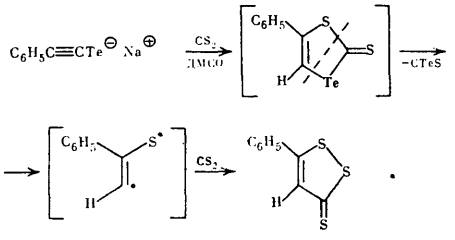
The influence of substituents on the 1,3-AC has been investigated by the method of competing reactions in relation to the interaction of potassium 2-(*p*-R-phenyl)ethyleneselenolates with carbon disulphide. It has been observed that the introduction of electron-donating substituents promotes and that of the electron-accepting substituents hinders cycloaddition. As was to be expected, electron-accepting substituents stabilise the heteropropargyl system C≡CSe, while electron-donating substituents actually destabilise it.[49]

Acetylenic thiolates and their analogues react analogously also with CSe_2:[60,62]

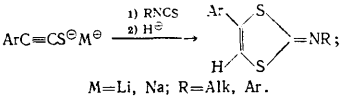


X=S, Se; R=H, C_6H_5.

The interaction of sodium 2-phenylethylenetellurolate with carbon disulphide leads to the formation of 5-phenyl-1,2-dithiole-3-thione, which confirms the intial formation of 5-phenyl-1,3-thiatellurole-2-thione. 5-Phenyl-1,2-dithiole-3-thione could have been formed only from its decomposition products by interaction with a new carbon disulphide molecule:[63]

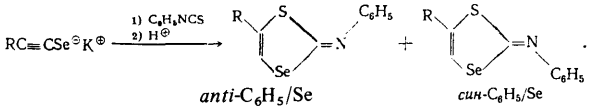


In contrast to αβ-ethylenic thiolates, the 1,3-AC reactions of αβ-acetylenic thiolates with isothiocyanates lead only to *N*-substituted 4-aryl-1,3-dithiole-2-imines:[64,65]



M=Li, Na; R=Alk, Ar.

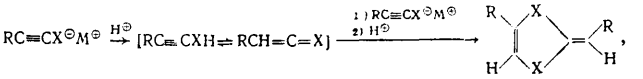
On reaction with phenyl isothiocyanate, potassium 2-aryl-(alkyl)ethyleneselenolates produce 5-aryl)alkyl)-1,3-thiaselenole-2-phenylimines in the form of mixtures of the *syn*- and *anti*-isomers, differing in the position of the benzene ring at the nitrogen atom relative to the selenium atom, in 60–80% yield:[49,64,66]



anti-C_6H_5/Se *син*-C_6H_5/Se

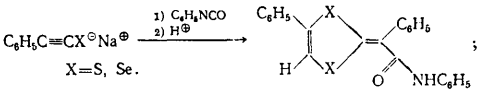
In the case of aryl-substituted selenolates, the *anti*-isomers are formed as the main product, while alkyl-substituted selenolates give rise to the *syn*-isomers.[49]

In the absence of heterocumulenes and when proton donors with pK_a < 18 (water, methanol, acids) are used, αβ-acetylenic thiolates and selenolates "dimerise" to *cis*-2,ω-diaryl-(alkyl-1,4-dithiafulvenes or their selenium analogues:[53,57,67–69]



M=Li, Na, K; X=S, Se; R=$(CH_3)_3C$, $(CH_3)_2CH$, Ar.

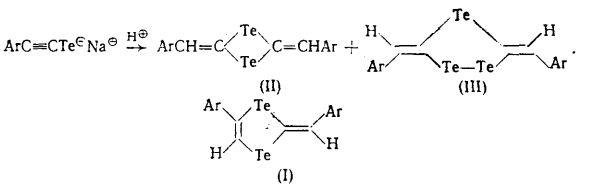
The stereoslectivity of this reaction[68,69] and its kinetics[70] confirm the occurrence of the concerted 1,3-AC of 2-aryl-substituted ethylenethiolates and ethyleneselenolates to the thio- or seleno-ketens formed from them as intermediates. This mechanism has also been confirmed by the unusual character of the interaction of sodium 2-phenylethylenethiolate or 2-phenylethyleneselenolate with phenyl isocyanate:[64]



X=S, Se.

The formation of "1,4-dichalcogenfulvenes" agrees well with the much greater reactivity of thiono-compounds compared with carbon compounds in 1,3-AC and 1,3-dipolar cycloaddition reactions.[1,9]

When the salts of 2-arylethylenetellurol are neutralised with an ethereal solution of HCl in DMSO and other similar solvents, they give rise to mixtures of *cis*- and *trans*-2,4-diarylidene-1,3-ditelluretans (II) in a satisfactory yield[63,71] and not to ditellurafulvenes (I), as expected by analogy with sulphur and selenium compounds:



(II) (III)

(I)

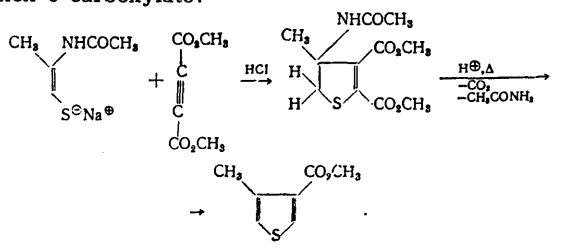
cis-3,5-Dibenzylidene-1,2,4-tritellurole (III) was isolated in an insignificant yield as an impurity.[72] The neutralisation of tellurolates with trifluoroacetic acid nevertheless leads to ditellurafulvenes (I).[73] The role of DMSO is extremely significant.[63] When diethyl ether is incompletely replaced by DMSO,[71–73] the yield of 1,3-ditelluretan (II) falls sharply.

III. INTERACTION WITH ACETYLENIC COMPOUNDS

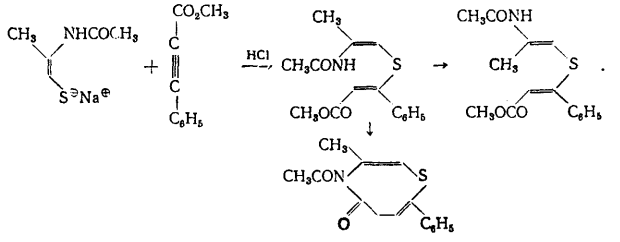
Like heterocumulenes, acetylenecarboxylate esters are active electron-accepting dipolarophiles or anionophiles in 1,3-dipolar cycloaddition or 1,3-AC reactions.[1,9] However, it has been shown that, under the conditions of the reaction of *N*-substituted 1-aminoethylenethiolates with acetylenecarboxylate esters, the latter polymerise readily.[74]

On the other hand, the interaction of sodium 2-acetamidopropene-1-thiolate with dimethyl acetylenedicarboxylate leads to a high yield of the cyclic [3 + 2]adduct—the dimethyl ester

of 2-acetamido-4-methyl-4,5-dihydrothiophen-2,3-dicarboxylic acid and the product of its further reaction—methyl 4-methylthiophen-3-carboxylate: [75]

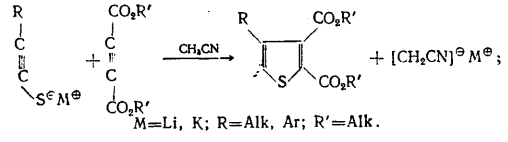


The study of the interaction of 2-acetamidopropene-1-thiolate with other anionophiles containing a triple bond (methyl ester or nitrile of phenylpropiolic acid) showed that only linear adducts—substituted divinyl sulphides—and also the products of their subsequent reaction are formed in both cases, [74] for example:



In contrast to αβ-ethylenic thiolates, the 1,3-AC reactions of αβ-acetylenic thiolates with a triple bond are energetically more favourable, since the charge redistribution takes place more readily: a more stable cyclic anion with a thiophen structure is formed.

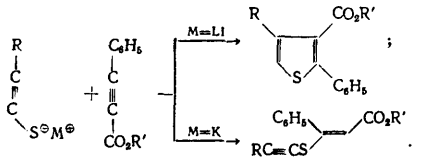
Thus it has been established that αβ-acetylenic thiolates react with acetylenedicarboxylate esters via the [3 + 2]-cycloaddition mechanism with formation of derivatives of thiophen-2,3-dicarboxylic acid: [50,67]



M=Li, K; R=Alk, Ar; R'=Alk.

The reaction proceeds most effectively in aprotic non-polar or weakly polar solvents (benzene, THF) in the presence of proton donors with pK_a = 20–25 (acetone, acetonitrile). Under these conditions, a solution of potassium 2-phenylethylenethiolate in a mixture of THF and acetonitrile contains only ion pairs, which has been demonstrated by the study of the electrical conductivities of these solutions. [77] The role of the solvents as the proton donor for the cyclic anion has been confirmed by carrying out the reaction of potassium 2-phenylethylenethiolate with dimethyl acetylenedicarboxylate in the presence of deuterioacetone. This resulted in the formation of dimethyl 4-phenyl-5-deuteriothiophen-2,3-dicarboxylate. When the reaction is carried out without a proton donor, or with proton donors having pK_a < 18, or in the presence of the "mild" proton donor $(CH_3)_3CBr$, the "dimerisation" of acetylenethiols to *cis*-2,ω-diaryl-1,4-dithiafulvenes takes place instead of cyclisation. [50]

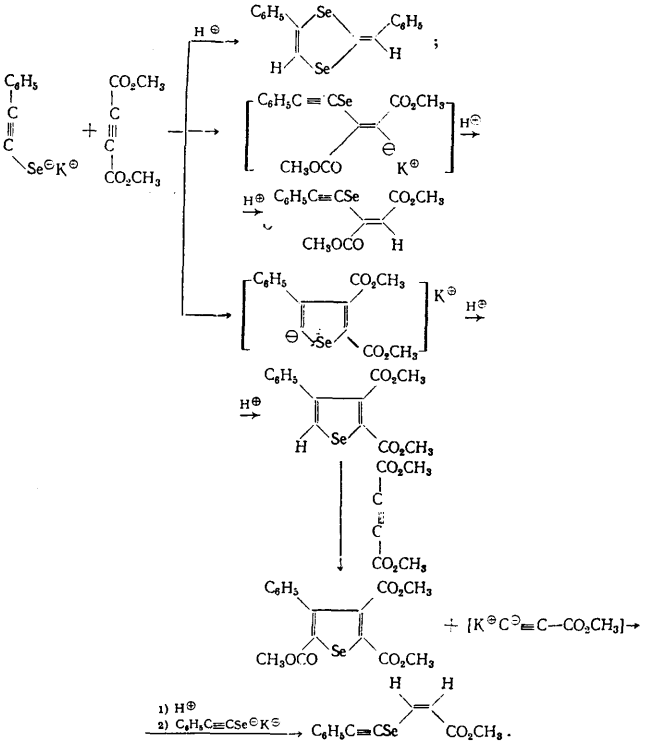
The study of the interaction of 2-arylethylenethiolates with asymmetric dipolarophiles—phenylpropiolic acid—demonstrated a significant dependence of the mode of reaction on the nature of the cation. Thus only one of the possible regioisomers of the cyclic adduct, namely alkyl 4-aryl-2-phenylthiophen-3-carboxylate, is formed in 65–82% yield from lithium 2-arylethylenethiolates. Under the same conditions, potassium 2-arylethylenethiolates gives rise to the *E*-isomers of the products of nucleophilic addition to the triple bond in phenylpropiolate esters and not to cyclic adducts: [78]



The absence of products of nucleophilic addition to acetylenedicarboxylate esters can be accounted for by the more effective stabilisation of the cyclic anion under the influence of two carboxy-groups.

In order to investigate the reactivity of acetylenic selenolates in 1,3-AC reactions wth acetylenic compounds and to determine the influence of the nature of the heteroatom, a study was made of the reactions of 2-phenylethyleneselenolate with an active anionophile—dimethyl acetylenedicarboxylate: [79]

Scheme



Careful analysis of the reaction products revealed the presence, together with the usual 1,3-AC products, namely dimethyl 4-phenylselenophen-2,3-dicarboxylate, [80,81] also of the nucleophilic addition product, i.e. dimethyl *Z*-(2-phenylethynylseleno)butenedioate, and trimethyl 4-phenylselenophen-2,3,5-tricarboxylate. The formation of derivatives of selenophentricarboxylic acid can be regarded as the result of the carboxymethylation of the selenophen anion by dimethyl acetylenedicarboxylate. The resulting methyl propiolate combines with the initial selenolate to form the ester of *Z*-3-(2-phenylethynylseleno)propenoic acid. As usual, 2,ω-diphenyl-1,4-diselenafulvene is formed as a side product. [53] The formation

of these reaction products supports the intermediate existence of the anion of the substituted selenophen formed in the course of the concerted 1,3-AC reaction.

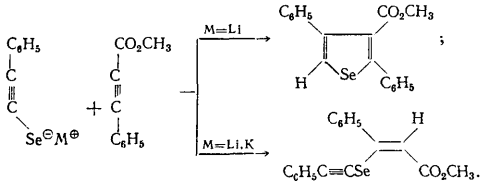
On passing from acetylenic thiolates to selenolates, the negative charge on the heteroatom increases,[51] which should promote nucleophilic addition to the heteroanion. Indeed, the products of nucleophilic addition to the triple bond of the ester were not detected in the reactions of acetylenic thiolates with dimethyl acetylenedicarboxylate.[50] Acetylenic selenolates give rise to small amounts of nucleophilic addition products, but 1,3-AC products are mainly produced.[79]

In order to investigate the influence of the cation on the selectivity of the 1,3-AC reactions of acetylenic selenolates, a study was made of the interaction of lithium 2-phenylethyleneselenolate with the same anionophile—the ester of acetylenedicarboxylic acid. The nucleophilic addition product was not then detected, the 1,3-AC product being formed with a significant increase of the yeild of the dimerisation product.[79]

All these data suggest that the influence of the cation on the mode of the reactions of selenolates with acetylenecarboxylic acid esters is due to the different states of the selenolate in the reaction medium, i.e. the different amounts of ionic character of the selenium–methyl bond.

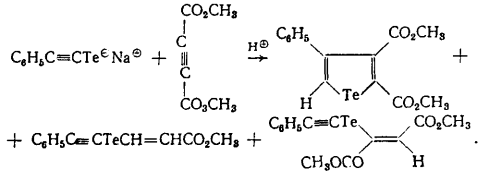
Since it is known that crown-ethers alter significantly the state of salts in solutions as a result of their coordination to the cation, the interaction of the potassium salt of 2-phenylethyleneselenol with the same anionophile was investigated in the presence of dibenzo-18-crown-6 ether. Only the cyclic adduct was then obtained in a satisfactory yield.[79]

The 1,3-dipolar cycloaddition reactions are usually highly regiospecific.[1] In order to determine the regiospecificity of the reactions investigated, a study was made of the interaction of 2-phenylethyleneselenolates with asymmetric anionophiles—phenylpropiolic acid esters.[79,82] It was then observed that the lithium salt produces only one of the possible regioisomers—methyl 2,4-diphenylselenophen-3-carboxylate, together with the product of the nucleophilic addition of the initial selenolate to the triple bond of the anionophile—methyl *Z*-3-(2-phenylethynylseleno)-3-phenylpropenoic acid:



On the other hand, the poassium salt of 2-phenylethyleneselenol (which is more nucleophilic than the lithium salt) reacts with the same anionophile to form only the nucleophilic addition product having the same *Z*-configuration.

The interaction of sodium 2-phenylethylenetellurolate with dimethyl acetylenedicarboxylate led to the dimethyl ester of 4-phenyltellurophen-2,3-dicarboxylic acid. As for selenolates, the cyclisation is accompanied by nucleophilic addition to the triple bond of the ester:[63]

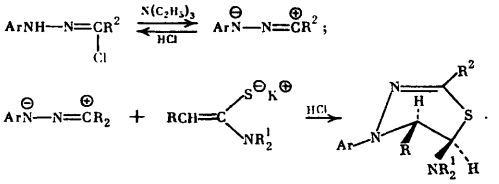


The yield of the tellurophen is appreciably lower than that of the thiophen[50] or selenophen[79] in the analogous reactions.

IV. "MIXED" DIMERISATION WITH HUISGEN'S 1,3-DIPOLES

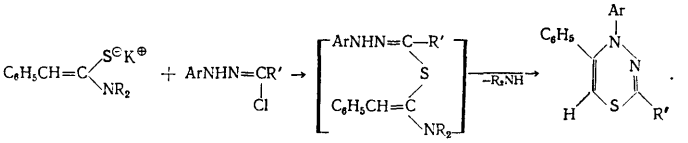
Ethylenethiolates enter into "mixed" dimerisation reactions[2] with 1,3-dipolar systems of the kind formed when HCl is eliminated on treatment with bases.[1] The hydrochloride of the base formed in the reaction reacts as a proton donor in the neutralisation of the cyclic anion.

Thus, when the *C*-chlorohydrazone is converted by treatment with triethylamine into a nitrileimine and the latter is made to react, without being isolated, with *N*-substituted 1-aminoalkenethiolates, then [3 + 3]cycloaddition products, namely 5,6-dihydro-4*H*-1,3,4-thiadiazines, are mainly obtained:[83]



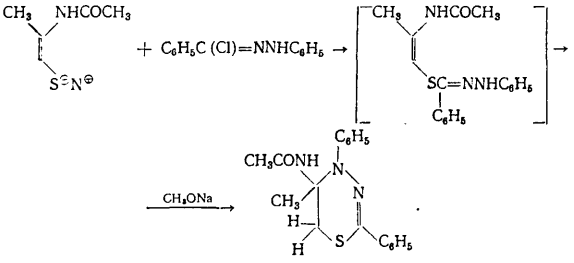
Although the formation of both "half-chair" and "half-boat" conformers with any relative disposition of the substituents is sterically feasible, nevertheless, judging from the ^{1}H NMR spectrum, only the "half-chair" conformer is actually formed.[83]

On the other hand, 1-*NN*-dialkylamino-2-phenylethylenethiolates react with *C*-chloro-*N*-phenylhydrazones under conditions which rule out the generation of nitrileimine, with formation of only 4*H*-1,3,4-thiadiazines,[83,84] i.e. the reaction is accompanied by the elimination of an amine:

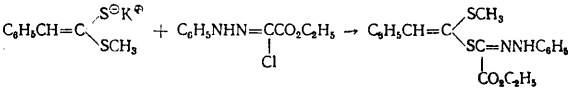


Under the reaction conditions, 5,6-dihydro-4*H*-1,3,4-thiadiazine is not converted into 4*H*-1,3,4-thiadiazine, but it does readily eliminate an amine molecule in the presence of an equimolar amount of acid or on the surface of silica gel.[83]

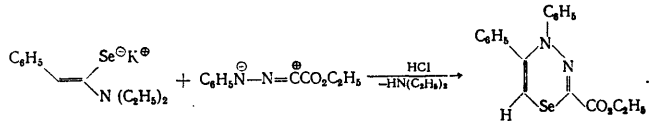
Sodium 2-acetoamidoethylenethiolate reacts with *N*-phenylmethylenehydrazonoyl chloride to form 5-acetamido-5,6-dihydro-1,3,4-thiadiazine. The product of the nucleophilic substitution of the halogen in the *C*-chlorohydrazone by the thiolate is suggested as an intermediate:[85]



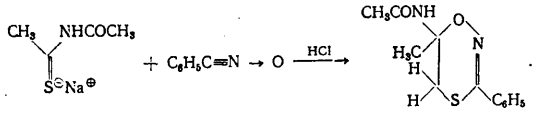
The less reactive potassium 1-methylthio-2-phenylethylenethiolate reacts with the *C*-chloro-*N*-phenylhydrazone of ethyl glyoxylate to form only the linear product of the nucleophilic substitution of chlorine:[83]



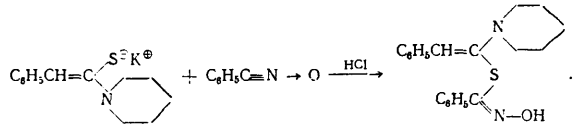
However, potassium 1-diethylamino-2-phenylethyleneselenolate readily enters into the [3 + 3]cycloaddition reaction with nitrileimines obtained from the same *C*-chlorohydrazones. forming 2-ethoxycarbonyl-4,5-diphenyl-4*H*-1,3,4-selenadiazine:[86]



Sodium 2-acetamidoethylenethiolates react also with another widely used 1,3-dipole—benzonitrile oxide,[1] forming 6-acetamido-5,6-dihydro-1,4,2-oxathiazines:

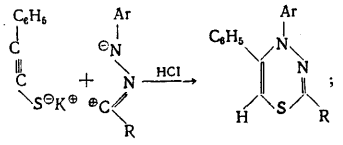


Here too it is assumed that the reaction proceeds via a two-stage mechanism.[85] On the other hand, the interaction of potassium 2-phenyl-1-piperidinoethylenethiolate with benzonitrile oxide yielded only benzohydroximoyl-2-phenyl-1-piperidinovinyl sulphide:[87]



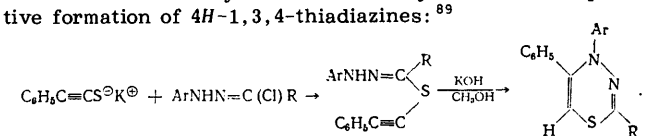
Acetylenic analogues of ethylenethiolates and ethyleneselenolates are also capable of undergoing the [3 + 3]cycloaddition reaction with the usual dipoles—nitrileimines.

Thus potassium 2-phenylacetylenethiolate reacts with nitrileimines, generated from *C*-chloro-*N*-arylhydrazones by treatment with bases, via the [3 + 3]cycloaddition mechanism with formation of 2,4,5-trisubstituted 4*H*-1,3,4-thiadiazines in a satisfactory yield:[88,89]



R=Ar, $CO_2C_2H_5$.

When the reaction of potassium 2-phenylacetylenethiolate with *C*-chloro-*N*-arylhydrazones is carried out in the absence of a base, the products of the nucleophilic substitution of the hydrogen atom—the corresponding (*C*-2-phenylethynyl sulphido)-*N*-arylhdrazones—are formed in a quantitative yield.[89] Their treatment with strong bases (KOH in methanol) results in their ready intramolecular cyclisation with quantitative formation of 4*H*-1,3,4-thiadiazines:[89]



(C-2-phenylethynyl mercapto)-N-arylhydrazones

However, under the influence of triethylamine the intramolecular cyclisation does not occur, which permits the unambiguous assumption that the interaction of 2-phenylacetylenethiolate with nitrileimine proceeds only via a two-stage mechanism.

V. CONCLUSION

Among the αβ-unsaturated heteroanions of Group VIa elements, only sulphur and selenium derivatives, in which the electronegativities of the heteroatom and the extreme C(2) atom of the anion are comparable, exhibit a distinct capacity for 1,3-AC. It has been shown for αβ-ethylenic thiolates that the introduction into the anion of substituents equalising the charge distribution and the p,π-electron density at C(2) and S has the greatest influence on the reactivity of unsaturated sulphur and selenium anions in cyclisation reactions.[21,28]

The influence of the heteroatom is no less significant. Thus the basicity of the heteroatom increases in the series of αβ-acetylenic thiolates, selenolates, and tellurolates, which promotes the occurrence of reactions involving the nucleophilic addition of the anion to the multiple bond of the anionophile.[50,63,79]

On the other hand, enolates have a fairly uniform charge and p,π-electron density distribution over the C(2) and O atoms of the triad,[21,28] but cyclic adducts are not formed. It may be that, as a consequence of the weak transmission properties of the oxygen bridge,[90] charge redistribution on formation of the cyclic anion is difficult.

The majority of the features of the 1,3-AC reactions investigated for αβ-unsaturated heteroanions can be readily accounted for from a standpoint of the concerted cycloaddition mechanism. The αβ-unsaturated heteroanions of the sulphur subgroup behave like Sustmann's type (I) 1,3-dipolar system or as electron-donating 1,3-dipoles.[21,28,51,74] The introduction of electron-donating substituents promotes and that of electron-accepting substituents hinders the 1,3-AC reactions of the anion, destabilising or stabilising its charge respectively. The stability of the intermediate cyclic anions, which increases under the influence of substituents, particularly aromatic substituents, plays an important role in 1,3-AC reactions.[40] The structure of the anionophile influences the reactivity of the unsaturated anions analogous to 1,3-dipolar cycloaddition reactions.[1] Only electron-accepting anionophiles with substituents capable of stabilising the charge give rise to stable cyclic adducts with αβ-unsaturated heteroanions.[51]

The accumulated data concerning the effect of the character and positions of substituents on the reactivity of heteropropargyl and heteroallyl anions and also the available literature data on the 1,3-AC reactions of aza-allyl anions[9] and allyl anions[10] make it possible to formulate general postulates on the basis of which a particular unsaturated triatomic anion can be assigned to systems capable of entering into 1,3-AC reactions.

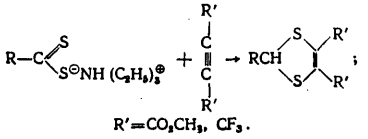
1. A uniform distribution of the p,π-electron density at the extreme atoms of the triad is necessary. It can be achieved either as a result of their approximately equal electronegativities or by introducing the appropriate substituents.

2. Since the reactions involving the 1,3-AC of αβ-unsaturated anions to anionophiles are accompanied by a cyclic charge shift on formation of the cyclic anion, the bonds and atoms entering into the composition of the αβ-unsaturated anions must have satisfactory transmission properties. The bonds both in the anion and in the anionophile must have high polarisabilities.

3. The cyclic anion formed as an intermediate must be stabilised either by the increased electronegativity of the central atom of the triad, or by conjugation with a substituent, or by the removal of the anionic group. Otherwise the reaction proceeds with formation of linear products of addition to the multiple bonds with retention of the same regioselectivity as in the cycloaddition.

Using these principles, it is possible to predict the reactivities in the 1,3-AC reactions of heteroallyl anions containing Group V and VI elements which have not been investigated in this respect. Thus the $R_2C{=}N{-}X^{\ominus}$ or $R{-}C(X)(X^{\ominus})$ (X = S or Se) systems having substituents such as aryl, heteroaryl, CH=CHR, or C≡CR at the central atom should be reactive in 1,3-AC reactions.

Indeed it has been found recently that the trialkylammonium salts of aromatic and heteroaromatic dithiocarboxylic acid[91-93] interact with active anionophiles, forming the corresponding 1,3-dithioles:



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