Russian Chemical Reviews **70** (8) 655 – 672 (2001) © 2001 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2001v070n08ABEH000645

Sulfur ylides in the synthesis of heterocyclic and carbocyclic compounds

S N Lakeev, I O Maydanova, F Z Galin, G A Tolstikov

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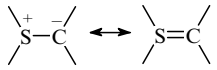
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Abstract. Data on the use of sulfonium ylides in the synthesis of carbocyclic and heterocyclic compounds published over the last 15 years are analysed, systematised and generalised. The bibliography includes 139 references.

I. Introduction

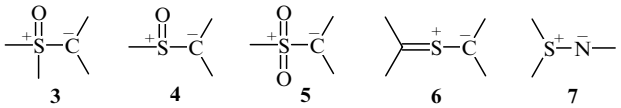
The chemistry of ylides attracted considerable interest in the early 1950s after Wittig has discovered the reaction of phosphonium ylides with carbonyl compounds giving rise to alkenes.[1] Investigations carried out by Corey[2] and Franzen[3,4] extended the Wittig reaction to sulfur ylides and initiated extensive studies of sulfonium ylides. The further development of the chemistry of these compounds demonstrated that they could be widely used in organic synthesis.

Sulfur ylides contain a negatively charged carbon atom directly bound to a positively charged sulfur atom. In the general form, these compounds can be represented by two resonance structures, *viz*., ylide **1** and ylene **2**.[5]



1 **2**

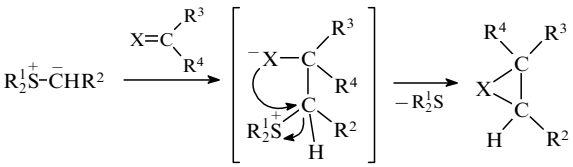
Sulfonium (**1**) and sulfoxonium (**3**) ylides containing two organic substituents at the sulfur atoms are most often used in organic synthesis.[6–9] Sulfinyl ylides (**4**), sulfonyl ylides (**5**), thiocarbonyl ylides (**6**) and iminosulfuranes (**7**) are also known.[8]



3 **4** **5** **6** **7**

Sulfur ylides act as nucleophilic reagents, their reactivities being inversely proportional to their stability. Ylides are stabilised through the electron density delocalisation under the action of electron-withdrawing substituents at the carbanionic centre. The properties of stabilised sulfur ylides are summarised and compared with the properties of non-stabilised ylides in reviews.[6,10,11]

The reactions of sulfur ylides with compounds containing C=X bonds (X = O, C or N) gained wide acceptance in organic synthesis. These reactions proceed as the nucleophilic addition followed by 1,3-elimination of a sulfur-containing group to form epoxide, cyclopropane or aziridine, respectively.[6]

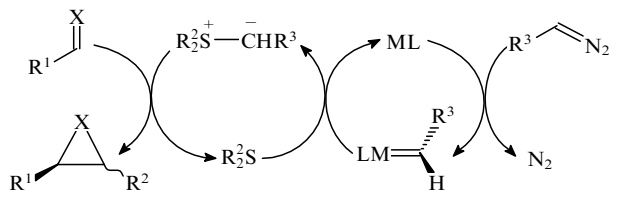


X = O, C, N.

The data on these reactions were surveyed in detail in the monograph[6] and in a series of studies.[7,12–16] Due to their zwitterionic character, sulfonium ylides are also widely used in rearrangements generating new C–C bonds (often with high stereo- and regioselectivity).[16–20] In the last decade, interest in sulfur ylides was quickened owing to their successful use in asymmetric synthesis.[16] A one-stage procedure, which has been developed recently for the synthesis of optically active epoxides and aziridines,[21,22] represents a considerable achievement in this field. Optically pure sulfur ylides, which are generated *in situ* in reactions of catalytic amounts of chiral sulfides with diazo compounds in the presence of dirhodium tetraacetate or copper acetylacetonate, react with aldehydes or imines to give epoxides or aziridines, respectively, and the sulfide is recovered and recycled to the catalytic cycle. This procedure was used for the syntheses of various substituted epoxides and aziridines in good yields and with high enantioselectivity.[16,23–25]

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Received 21 December 2000
Uspekhi Khimii **70** (8) 744 – 762 (2001); translated by T N Safonova



X = $Me_3Si(CH_2)_2SO_2N$, O; ML = $Rh_2(OAc)_4$, $Cu(acac)_2$.

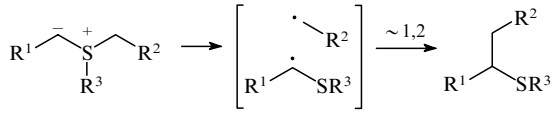
Sulfur ylides also find wide application in the synthesis of other cyclic compounds as well as of hetero-, macro- and polycyclic structures, including natural compounds and their analogues. Special-purpose reviews devoted to this aspect are lacking. The only study dealing with this problem [13] has covered the results published up to 1986 inclusive. The present review surveys the data on the use of sulfur ylides in syntheses of complex cyclic, heterocyclic and natural compounds published over the last 15 years. Systematisation and analysis of the available data will help in evaluating the possibilities of the use of sulfur ylides in the synthesis of complex structures and give a deeper insight into prospects of the further development of this line of investigation. Reactions of ylides giving rise to three-membered carbo- and heterocycles are beyond the scope of the present review.

II. Rearrangements of cyclic sulfur ylides

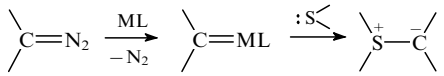
Sigmatropic rearrangements of cyclic sulfur ylides were investigated in most detail. In these studies, sulfur ylides were used in the synthesis of various carbo- and heterocyclic compounds. The reactions are carried out with the use of either ylides generated *in situ* or individual compounds prepared in advance. The 1,2-Stevens rearrangements [18, 20] and 2,3-sigmatropic rearrangements of sulfur ylides find most extensive synthetic applications.[16–20, 26]

1. 1,2-Stevens rearrangements

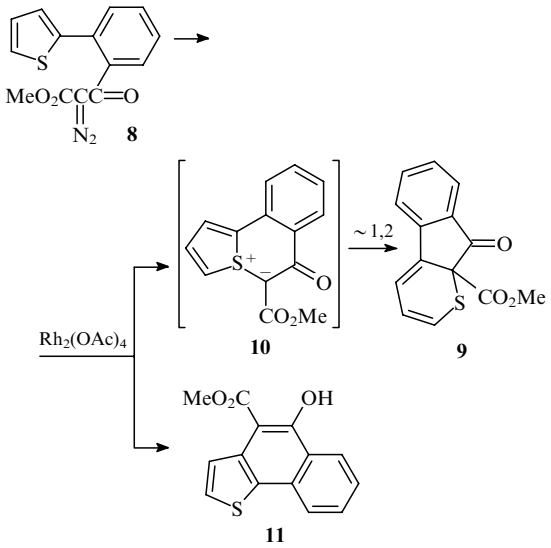
The 1,2-Stevens rearrangements of sulfur and nitrogen ylides were discovered in 1928.[27] According to orbital symmetry rules, the concerted mechanism of this thermal rearrangement is forbidden.[28] Hence, the most probable mechanism involves the dissociation–recombination process. It was demonstrated [29, 30] that the rearrangements proceed through the formation of a radical pair, the rate of radical recombination being higher than the rate of their diffusion into a solvent.



The employment of rearrangements of sulfur ylides in the synthesis of cyclic compounds appeared to be particularly promising in connection with the development of the carbene method for the generation of cyclic sulfur ylides.[20, 31–34] Ylides are formed through the electrophilic addition of a carbenoid species, which is generated from the diazo group under the action of transition metal (predominantly, Rh or Cu) compounds, to the sulfur atom.[34] These reactions are most often performed with stable diazoesters or diazoketones. Recently,[35, 36] it was demonstrated that trimethylsilyldiazomethane can also be successfully used for the generation of sulfur ylides.

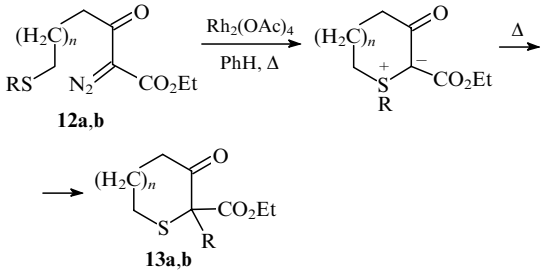


Sometimes the process is complicated by a side reaction of insertion of the carbene formed into the C–H bond. Thus intramolecular cyclisation of diazosulfide **8** afforded not only the major reaction product **9**, generated through the 1,2-rearrangement of intermediate unstable tricyclic thiophenium ylide **10**, but also a product of insertion into the C–H bond (**11**).[37]

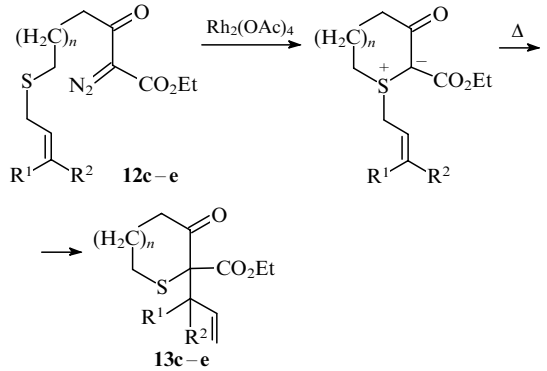


New stable four-to-seven-membered cyclic ylides were synthesised by intramolecular cyclisation of diazosulfides and their thermal rearrangements giving rise to heterocyclic compounds were carried out virtually simultaneously by two independent research groups.[38–40] It was demonstrated [38, 39] that six- and seven-membered cyclic ylides **12a**,**b** underwent the 1,2-Stevens rearrangement on heating to give the corresponding substituted cyclic thioesters **13a**,**b** in 40%–60% yields.

Decomposition of the diazoallyl sulfide **12b** catalysed by $Rh_2(OAc)_4$ afforded directly the rearranged thiepane **13b** (the yield was 59%); intermediate cyclic sulfonium ylide was not detected. The fact that the thiepane **13b** was formed through the 2,3-rearrangement rather than through the [1,2]-shift was exemplified by the reactions of diazosulfides **12c–e** containing the prenyl, cinnamyl or crotyl substituent at the sulfur atom, which were accompanied by the allylic inversion.



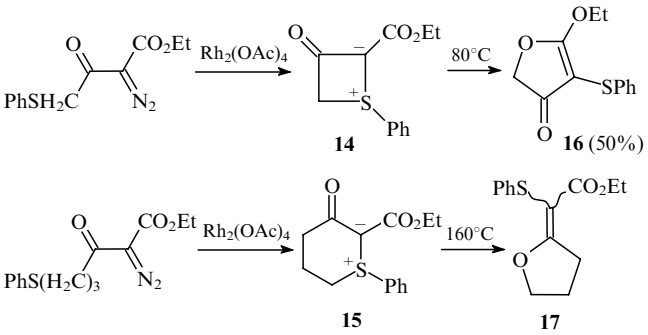
R = Bn, n = 1 (**a**); R = $H_2C{=}CHCH_2$, n = 2 (**b**).



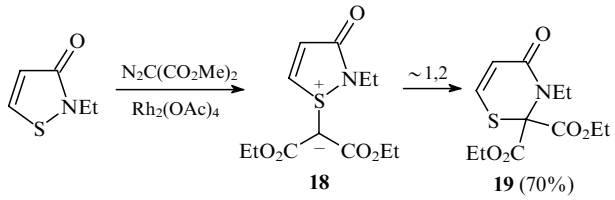
R^1 = R^2 = Me, n = 1 (**c**); R^1 = Ph, R^2 = H, n = 2 (**d**); R^1 = Me, R^2 = H, n = 2 (**e**).

On heating, four- (**14**) and six-membered *S*-phenyl-substituted (**15**) sulfur ylides underwent the 1,4-rearrangement to form derivatives of dihydro- (**16**) and tetrahydrofuran (**17**), respec-

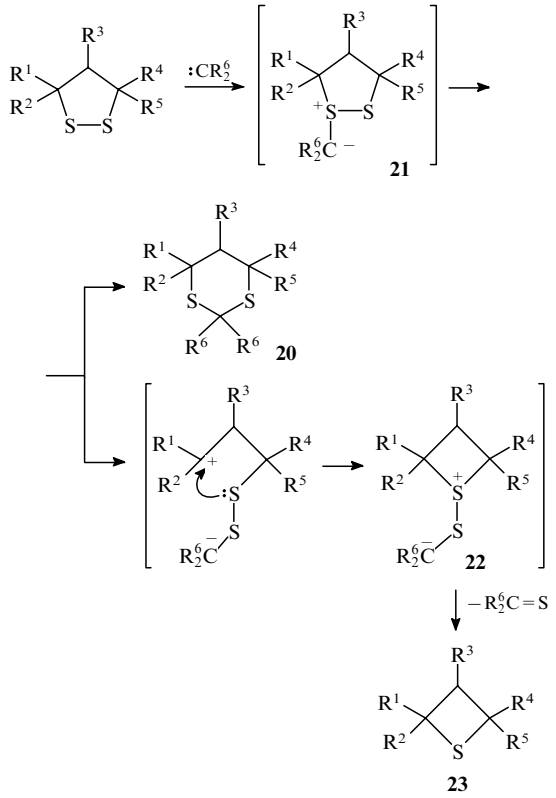
tively.[40] Seven-membered and some six-membered cyclic ylides decompose giving rise to unsaturated sulfur-free compounds.[40]



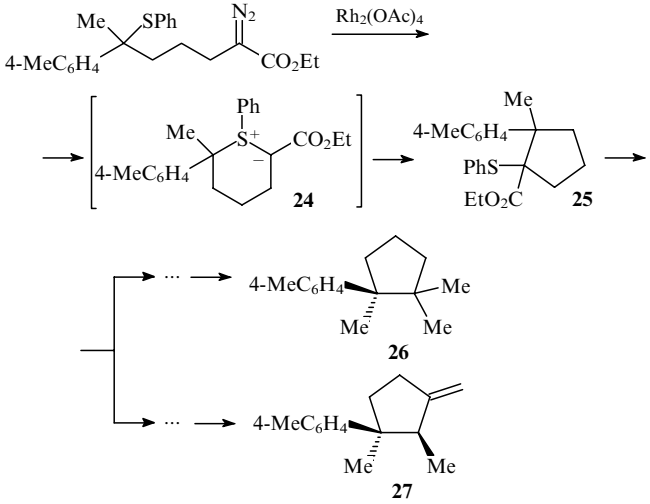
The 1,2-rearrangement of cyclic ylide **18** stabilised by two ethoxycarbonyl groups, which was formed in the reaction of 2,3-dihydroisothiazol-3-one with diazomalonic ester, was accompanied by insertion of carbene into the S–N bond to form 3,4-dihydro-1,3-thiazin-4(2*H*)-one **19**.[41]



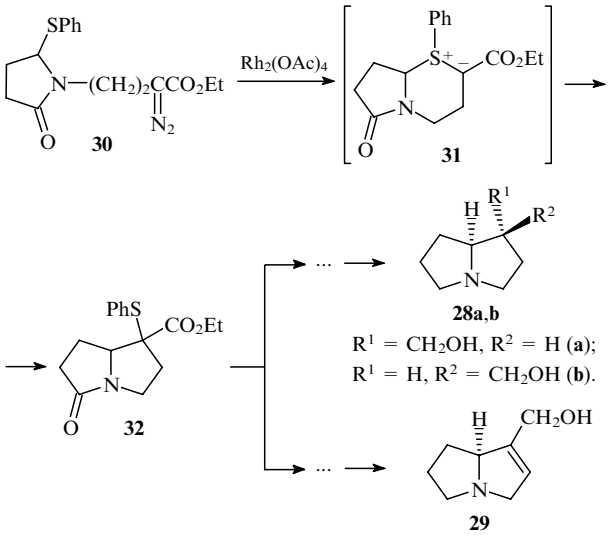
Substituted 1,3-dithianes **20** were synthesised by the 1,2-rearrangement proceeding with the cleavage of the S–S bond of intermediate 1,2-dithiolane ylides **21**.[42] The ylides **21** were generated by the reactions of cyclic disulfides with carbenes, which were prepared from diazo compounds under conditions of catalytic or photochemical reactions. If cyclic disulfides contain more than four substituents, the C–S bond in the ylides **21** can be cleaved. Subsequent desulfation of intermediates **22** afforded thietanes **23**.



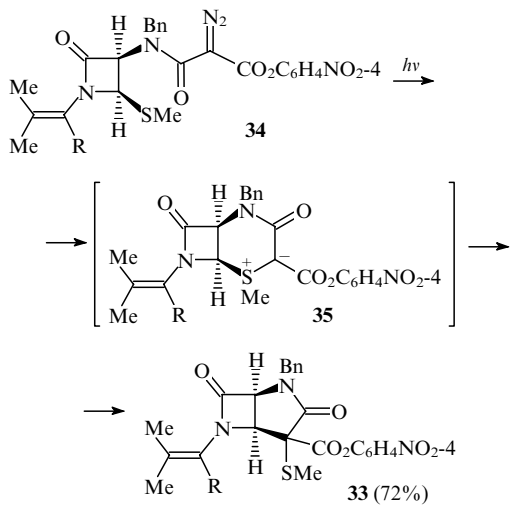
The generation of cyclic ylides by intramolecular reactions of sulfur-containing compounds with carbenes followed by their thermal rearrangements was successfully used in the synthesis of carbocyclic natural compounds. Thus the 1,2-rearrangement of ylide **24** proceeded with ring contraction to give substituted cyclopentane **25**. The latter served as the key compound in the synthesis of sesquiterpenes (±)-cuparene (**26**) and (±)-laurene (**27**).[43,44]



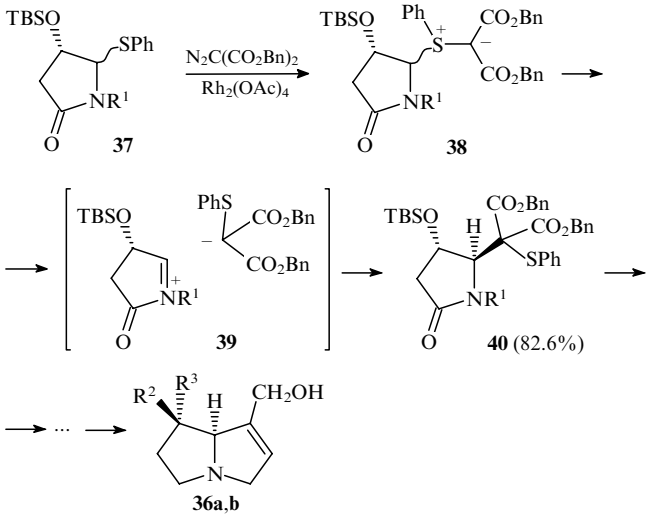
An analogous strategy was applied to the synthesis of pyrrolizidine alkaloids, *viz*., (±)-trachelanthamidine (**28a**), (±)-isoretronecanol (**28b**) and (±)-supinidine (**29**).[45,46] Diazoketone **30** was converted under the action of a rhodium catalyst into bicyclic sulfonium ylide **31** whose subsequent rearrangement afforded a compound of the pyrrolizidine series (**32**). The latter was used for the synthesis of the alkaloids **28a**,**b** and **29**.



1,2-Rearrangements proceed with high stereoselectivity, particularly, at low temperature and in viscous solvents. These reactions involving chiral sulfides can be employed in asymmetric synthesis.[18] In particular, the Stevens rearrangement allows one to solve the key problem in the synthesis of natural nitrogen-containing compounds consisting in the stereoselective formation of new C–C bonds at the α position with respect to the nitrogen atom. Thus a new approach to 6-amidocarbopenicillan antibiotics was exemplified by the synthesis of bicyclic β-lactam **33**.[47] Photolysis of diazoketone **34** afforded ylide **35**, which was rearranged to give the compound **33**, the new C–C bond being formed stereoselectively.



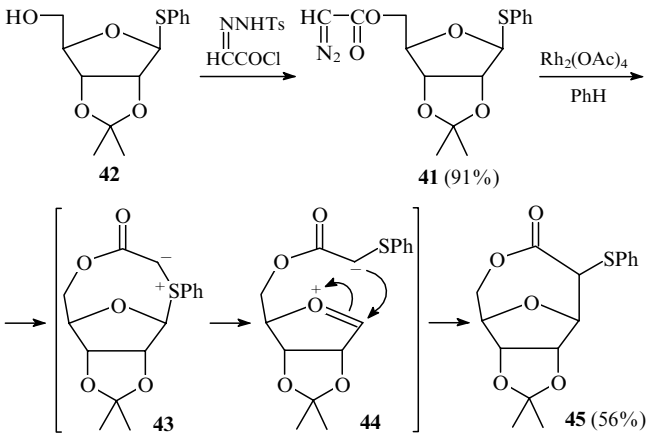
This synthetic approach was further developed in the stereoselective synthesis of alkaloids (+)-heliotridine (**36a**) and (+)-retronecine (**36b**).[48]



TBS is Bu^tMe_2Si;
36a: $R^1 = (CH_2)_2OC(O)Bu^t$, $R^2 = H$, $R^3 = OH$;
36b: $R^1 = (CH_2)_2OC(O)Bu^t$, $R^2 = OH$, $R^3 = H$.

The catalytic reaction of optically active sulfide **37**, which can be readily derived from (*S*)-malic acid, with dibenzyl diazomalonate afforded ylide **38** whose 1,2-rearrangement proceeded with high stereoselectivity. It is believed that the first stage of this reaction involved the cleavage of the C–S bond to produce salt **39**. The attack of the carbanion on the C=N bond proceeded predominantly from the less shielded side to form 2,3-*trans*-pyrrolidone derivative **40**, which was used as the starting compound in the synthesis of the alkaloids **36a**,**b**.

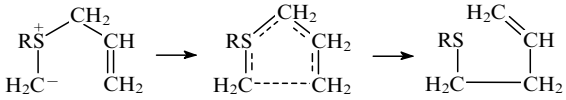
The application of the intramolecular rearrangement of cyclic sulfonium ylides allowed the development of a new method for the preparation of lactones,[49] which were used in the synthesis of C-nucleosides. Diazoacetyl thioglycoside **41** was prepared from precursor **42** according to the modified Corey method.[50] When refluxed in benzene with a catalytic amount of rhodium acetate, the compound **41** was converted into lactone **45** through sulfur ylide **43** and oxonium intermediate **44**. The lactone **45** served as the key compound in the synthesis of nucleoside antibiotic (+)-showdomycin.



2. 2,3-Sigmatropic rearrangements

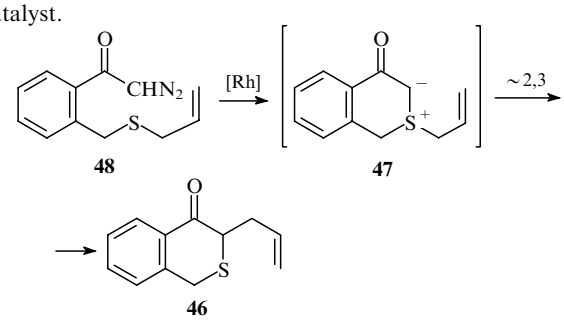
In the last two decades, the synthesis of cyclic compounds made wide use of 2,3-sigmatropic rearrangements of allylic and benzyl sulfur ylides. Baldwin was the first to carry out these studies [51–53] as early as 1968. Since then the 2,3-sigmatropic rearrangements of ylides have found many applications.

The rearrangement of allylic ylides into homoallylic sulfides can be represented in general form as follows:



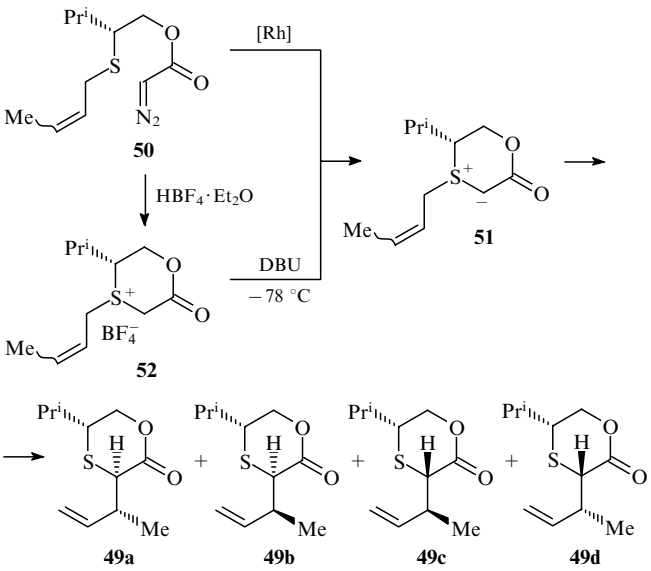
According to the orbital symmetry rules, 2,3-sigmatropic rearrangements are allowed [28] and they proceed either on heating or photolysis of ylides with complete inversion of the allylic substituent.[54,55] Since these reactions proceed by a concerted mechanism, high regio-, diastereo- and enantioselectivity are achieved, which is of particular interest from the standpoint of their application in asymmetric synthesis.

A gentle and efficient procedure for the synthesis of 3-allylisothiochroman-4-one (**46**)[56] involves the 2,3-sigmatropic rearrangement of cyclic sulfur ylide **47** formed by intramolecular cyclisation of diazosulfide **48** under the action of a rhodium catalyst.



The use of chiral allylic sulfides in 2,3-sigmatropic rearrangements offers considerable possibilities for enantioselective syntheses of cyclic compounds, including analogues of natural compounds.

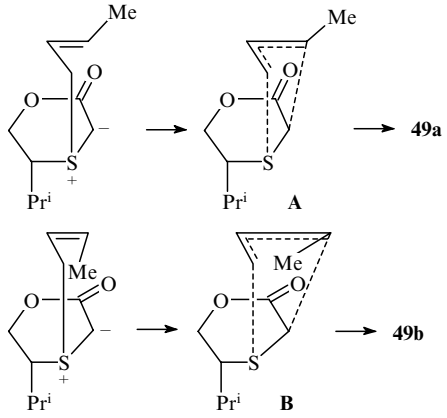
Thus the synthesis of optically active thioxanones **49a**–**d** was based on the 2,3-sigmatropic rearrangement of optically pure cyclic sulfur ylide **51**, which proceeded with high asymmetric induction.[57,58] Crotyl thiodiazoester **50** derived from L-valine was converted into the corresponding cyclic allylic sulfur ylide by either rhodium-catalysed intramolecular cyclisation or deprotonation of sulfonium salt **52** derived from the compound **50**. The rearrangement of the ylide **51** afforded four isomeric thioxanones **49a**–**d**. The best yield and diastereoselectivity were achieved on deprotonation of the sulfonium salt **52**.



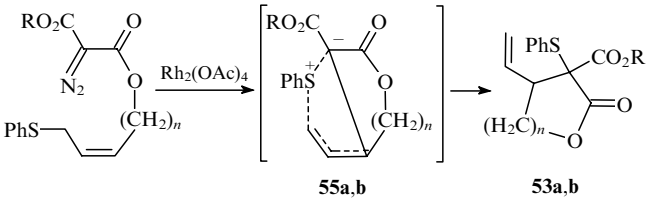
DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene.

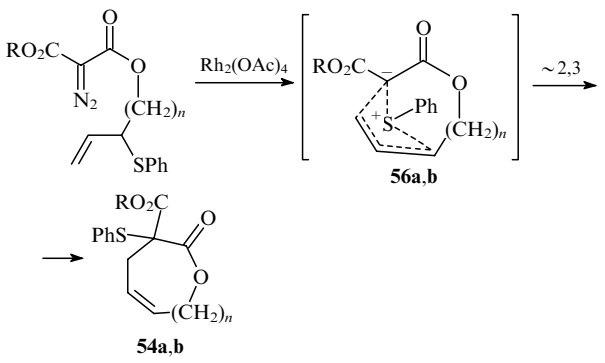
Starting compound	Reagent	Total yield (%)	Isomer ratio			
			49a	**49b**	**49c**	**49d**
(*Z*)-**50**	[Rh]	35	84	8	7	1
(*E*)-**50**	[Rh]	28	10	83	2	5
(*Z*)-**52**	DBU	66	94	4	2	traces
(*E*)-**52**	DBU	64	4	93	1	2

The reactions involving the *Z*-isomers of the compounds **50** and **52** yielded the thioxanone **49a** as the major product, whereas the reactions with the participation of the *E*-isomers gave rise to the thioxanone **49b**. This stereoselectivity was attributed [59] to the *endo* conformation of the allyl-containing five-membered ring in the prevailing transition states **A** or **B**.



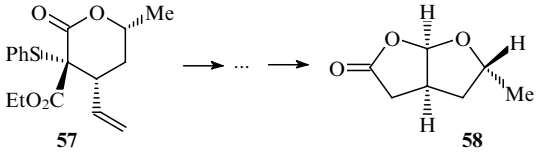
Substituted five-to-eight-membered lactones **53a**,**b** and **54a**,**b** were prepared by the 2,3-sigmatropic rearrangements of allylic sulfonium ylides **55a**,**b** and **56a**,**b** generated from the corresponding diazoesters under the action of dirhodium tetraacetate.[60–63]



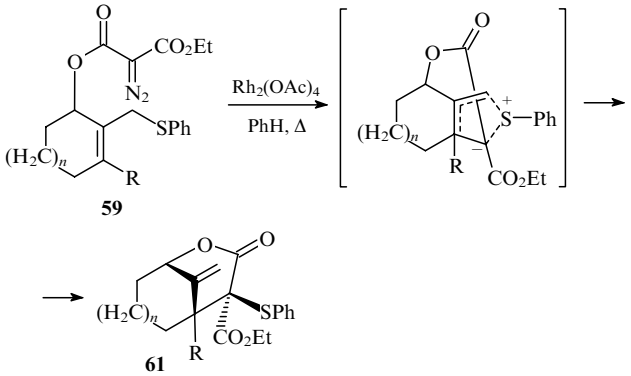


R = Me, Et; *n* = 1, 2.

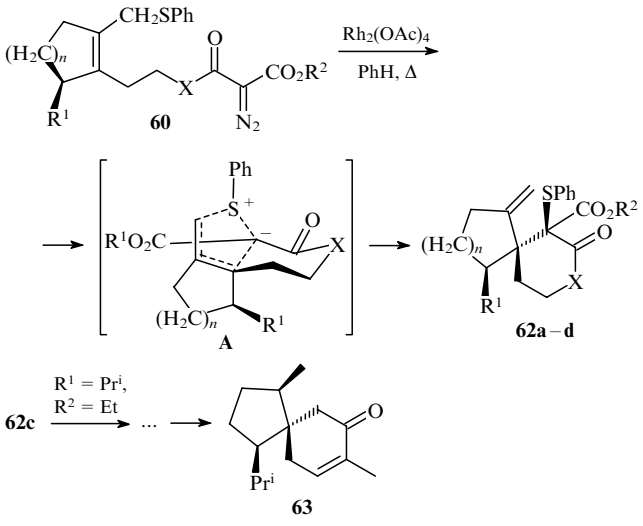
Lactone **57** was prepared according to an analogous procedure and was used in the stereoselective synthesis of perhydro[2,3-*b*]furanone derivative **58**.[62]



The rearrangement of sulfur ylides, which were prepared by treatment of sulfur-containing diazoketones **59** and **60** with dirhodium tetraacetate in boiling benzene, was used in a new approach to the synthesis of bridging δ-lactones **61** [64] as well as of spiro-fused five- and six-membered lactones **62a**,**b** [65] and spirocarbocyclic compounds **62c**,**d**.[66]



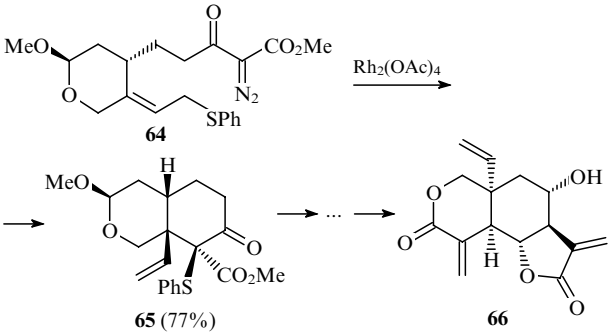
R = H, Me; *n* = 1, 2.



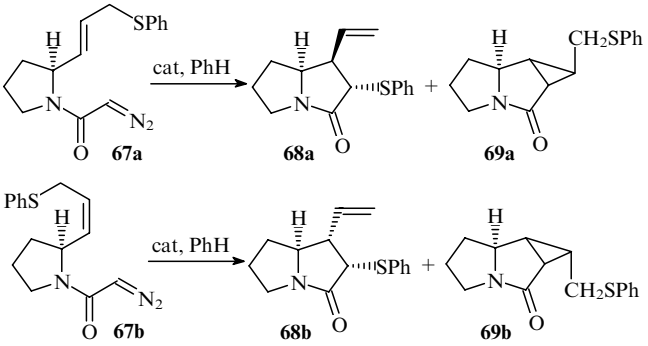
R^1, R^2 = Alk; X = O, *n* = 1 (**a**), 2 (**b**); X = CH_2, *n* = 1 (**c**), 2 (**d**).

Spiroannelation using the [2,3]-sigmatropic rearrangement *via* cyclic allylic sulfonium ylide was applied in the enantioselective synthesis of sesquiterpene (+)-acorenone B (**63**).[66] High stereoselectivity of the sigmatropic rearrangement is attributed to the fact that the less sterically hindered side opposite to the isopropyl group is favourable for the attack of the carbanion on the sulfonium reaction centre (transition state **A**).

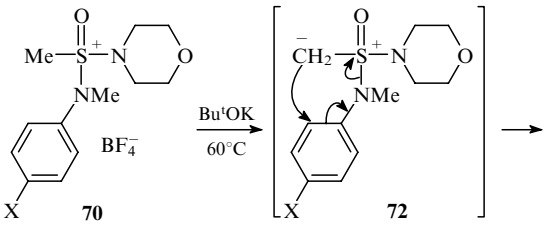
Rhodium-catalysed stereoselective cyclisation of diazosulfide **64** followed by the 2,3-rearrangement of the resulting ylide afforded *cis*-2-oxa-9-vinyldecalin derivative **65**, which served as the starting compound in the synthesis of vernolepin (**66**).[67]

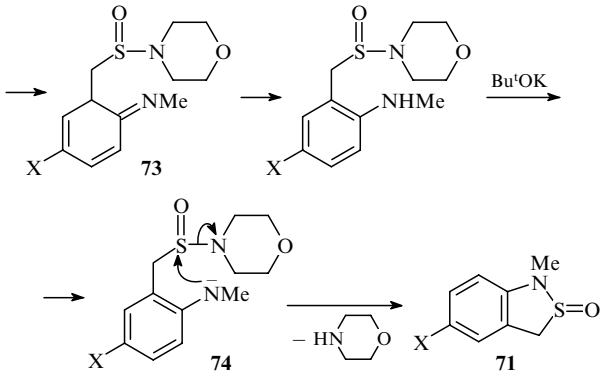


The rhodium-, copper- and palladium-catalysed stereoselective reactions of diazosulfides **67a** and **67b** were studied.[68] Depending on conditions, these reactions can afford either sulfonium ylides, which undergo the 2,3-sigmatropic rearrangement to form bicyclic compounds **68a** and **68b**, or tricyclic cyclopropane derivatives **69a** and **69b**. The latter are products of intramolecular cyclopropanation. Decomposition of the diazoamides **67a**,**b** in the presence of the rhodium complex with caprolactam gave rise predominantly to the azabicyclooctanes **68a**,**b**, whereas cyclopropane derivatives were selectively formed as the major products in the presence of catalysts containing electron-withdrawing ligands [$Rh_2(OAc)_4$, $Cu(acac)_2$, $Cu(OTf)_2$ or $Pd(OAc)_2$].



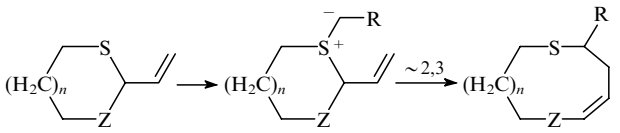
The rearrangements of diaminosulfoxonium salts of type **70** to form dihydro-2,1-benzoisothiazole derivatives **71** were described.[69] Treatment of the salts **70**, which were prepared by alkylation of sulfonimidoamides, with Bu^{t}OK resulted in the 2,3-sigmatropic rearrangement of intermediate ylides **72** to produce cyclohexadieneimine derivatives **73** in the first stage. The transfer of the hydrogen atom in the latter compounds was accompanied by rearomatisation. Cyclisation of intermediates **74** afforded the final products **71**.





X = Me, Cl.

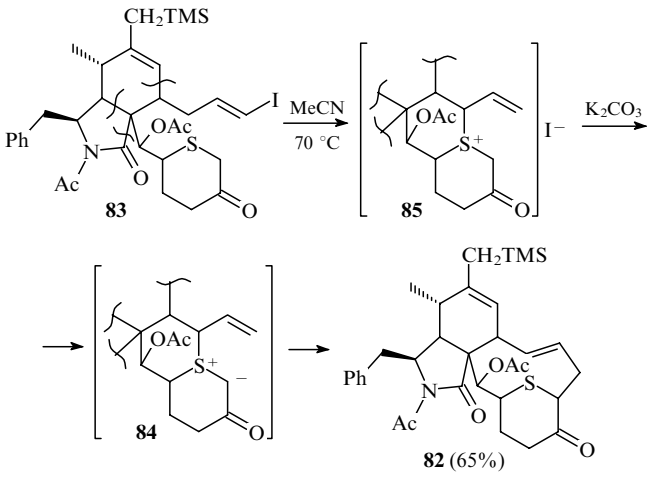
Yet another promising synthetic application of sulfur ylides is based on the 2,3-sigmatropic rearrangements of cyclic allylic sulfonium ylides proceeding with ring expansion.[17,70]



Z is the carbon atom or a heteroatom.

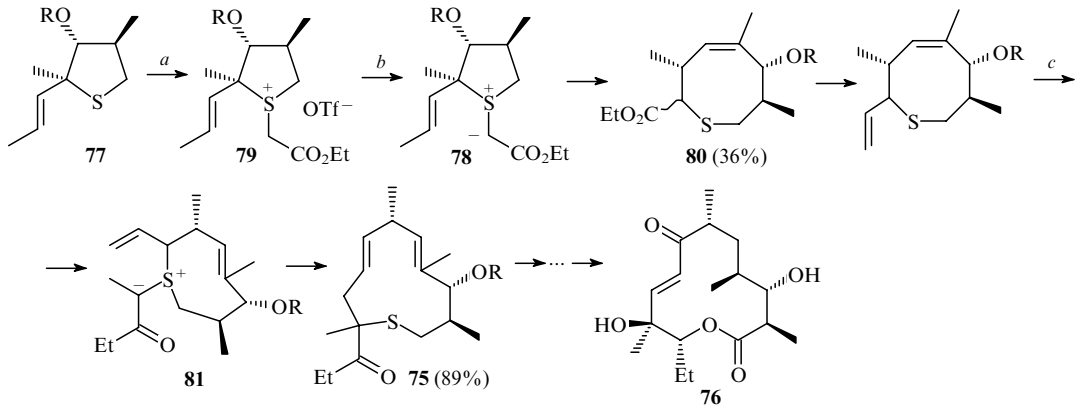
Ylides can be generated by reactions of cyclic α-vinyl sulfides with diazo compounds in the presence of copper [17,70] or rhodium catalysts [71] or by reactions of bases [17,70] with sulfonium salts. These procedures were used for the preparation of various macrocyclic compounds. For example, the synthesis of thiacycloundeca-4,7-diene derivative **75**, which is a precursor of aglycon of macrolide antibiotic methymycin, *viz*., methyneolide **76**, was carried out starting from tetrasubstituted thiolane **77**.[72–74] The rearrangement of ylide **78** derived from salt **79** afforded thiacyclooctene **80** from which ylide **81** was synthesised in several steps. The subsequent stereoselective 2,3-sigmatropic rearrangement of the ylide **81** gave rise to thiacycloundecadiene **75** (Scheme 1).

The 2,3-sigmatropic rearrangements of bicyclic allylic sulfonium ylides, which gave rise to compound **82** containing the thiabicyclo[6.3.1]undec-3-ene fragment, was used in the total synthesis of cytochalasines.[75,76] In this synthesis, vinyl iodide **83** served as the starting compound. The key stage of this synthesis involved the rearrangement of ylide **84** generated from sulfonium salt **85** under the action of potassium carbonate.



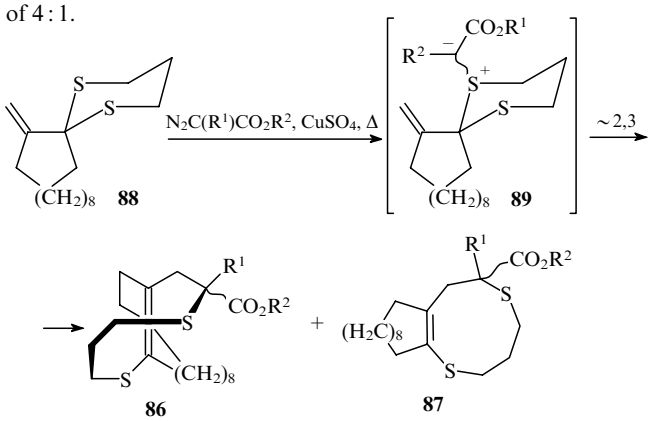
Difficultly accessible bicyclic unsaturated disulfides **86** (the so-called betweenanene structures) and **87** were synthesised.[77,78] Heating of dithioketal **88** with diazoacetate in the presence of $CuSO_4$ afforded ylide **89**, which underwent the 2,3-sigmatropic

Scheme 1

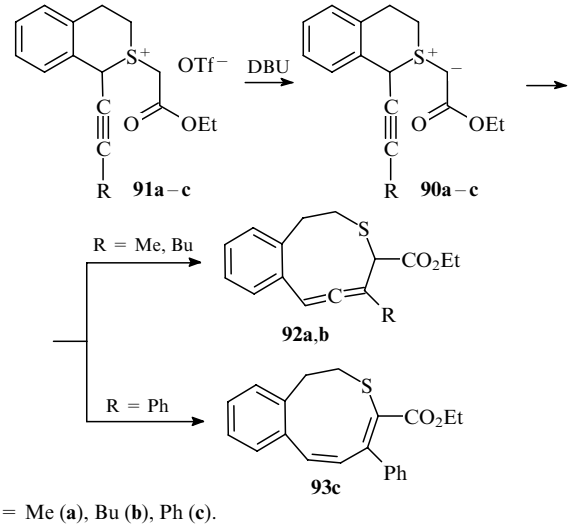


Tf = F_3CSO_2; (*a*) $TfOCH_2CO_2Et$; (*b*) K_2CO_3; (*c*) $TfOCHMeCOEt$, K_2CO_3.

rearrangement to give two geometric isomers **86** and **87** in a ratio of 4 : 1.

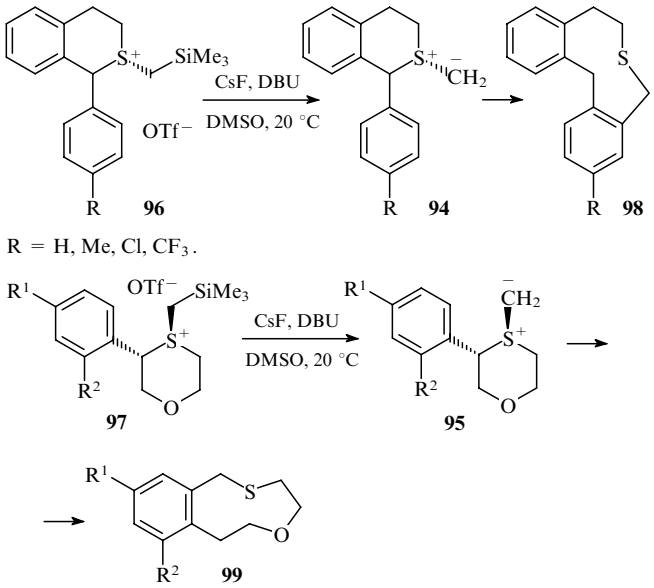


The structures of the 2,3-sigmatropic rearrangement products of acetylenic ylides **90a**–**c** derived from the corresponding sulfonium salts **91a**–**c** depend on the nature of the substituent at the triple bond. Thus the ylides containing alkyl substituents were converted into allenic sulfides **92a**,**b**, whereas the phenyl substituent promoted isomerisation into 1,3-diene **93c**.[79]



R = Me (**a**), Bu (**b**), Ph (**c**).

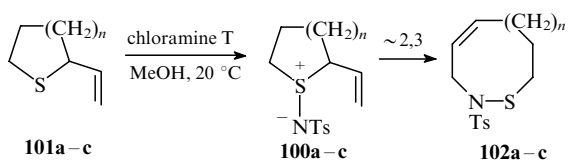
Aryl-substituted ylides **94** and **95**, which were formed on desilylation of salts **96** and **97**, underwent the Sommelet–Hauser rearrangement giving rise predominantly to substituted 2,5,8,9-tetrahydrodibenzo[*c*,*f*]thionines **98**[80] and 3,4,6,7-tetrahdydro-1*H*-5,2-benzooxathionines **99**, respectively.[81]



R = H, Me, Cl, CF_3.

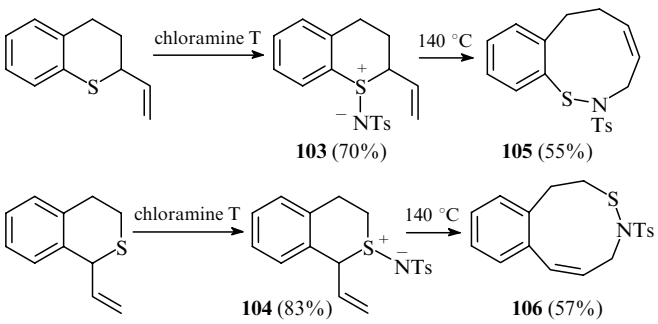
R^1, R^2 = H, Me, OMe, CF_3.

Analogous thermal 2,3-sigmatropic rearrangements accompanied by ring expansion proceeded in the case of α-vinyl iminosulfurane ylides **100a**–**c**, which were prepared by treatment of sulfides **101a**–**c** with chloramine T in methanol at ~20 °C.[82] The rearrangements of the ylides **100a**–**c** afforded azathiacyclenes **102a**–**c**. It should be noted that treatment of 2-vinylthiepane **101c** with chloramine T gave rise to the final product **102c** even at room temperature. Attempts to isolate the intermediate ylide **100c** failed.

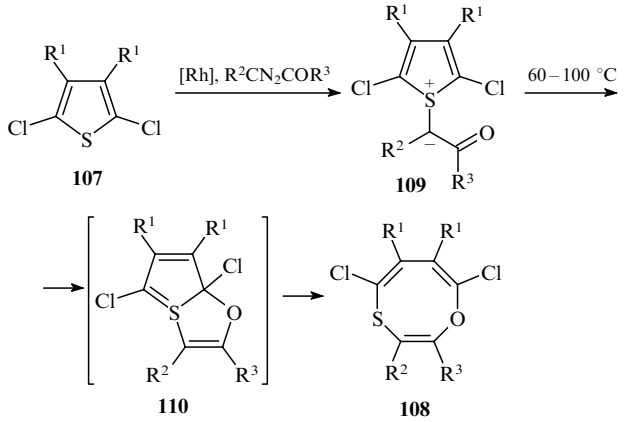


Compound **101**	*n*	Yield of **100** (%)	Temperature of the rearrangement /°C	Yield of **102** (%)
a	1	70	140	55
b	2	61	140	54
c	3	–	~20	61

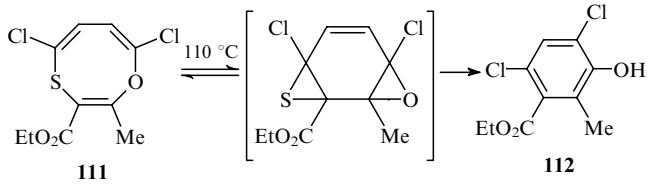
Under the same conditions, benzoiminosulfuranes **103** and **104** produced 1,2- (**105**) and 3,4-benzothiazonines (**106**), respectively.[82]



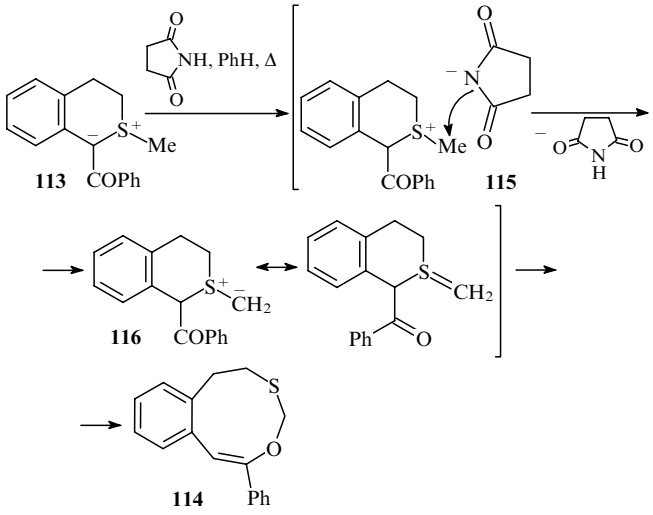
The reactions of 3,4-disubstituted 2,5-dichlorothiophenes **107** with diazoketones in the presence of rhodium catalysts afforded derivatives of a new heterocyclic system, *viz*., of 1,4-oxathiocine **108**.[83,84] The reaction scheme involves the formation of sulfur ylides **109** and their subsequent thermal 2,3-sigmatropic rearrangement proceeding through intermediates **110**. Heating of oxathiocine **111** at 110 °C gave rise to benzene derivative **112** due to elimination of the sulfur atom and 1,2-shift of the chlorine atom. It should be noted that the reactions of diazoketones with thiophenes, which do not contain chlorine atoms at positions 3 and 5, do not yield oxathiocine derivatives.



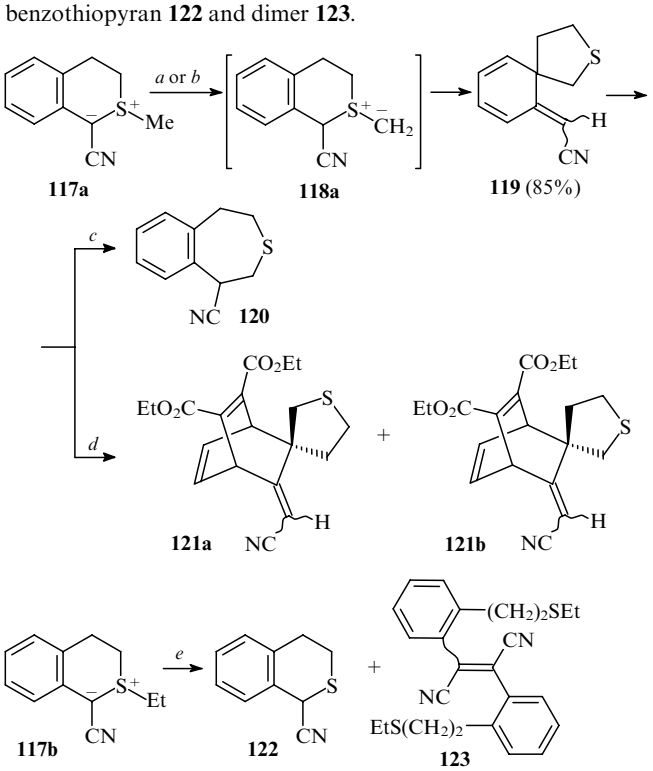
R^1 = H, Cl; R^2 = CO_2Et, CO_2Bu^t, Ts; R^3 = Me;
R^2-R^3 = $COCH_2CMe_2CH_2$.

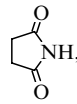


The 2,3-sigmatropic rearrangements of bi- and tricyclic sulfur ylides derived from substituted thiaphenanthrenes and isothiochromans, respectively, afforded both ring expansion products and spirane compounds.[85–88] The direction of the reaction and the structures of the final products depend essentially on the nature of the substituents at the sulfur atom and at position 1 of the initial ylide. For example, the reaction of stabilised ylide **113** with succinimide gave rise to the ring expansion product, *viz*., 2-phenyl-4,5-dihydro-3,5-benzooxathionine **114**, in high yield. The reaction mechanism involves deprotonation of intermediate **115** with the imide anion to form exocyclic methylide **116** whose 2,3-sigmatropic rearrangement yielded the target product **114**.[85] The reaction of the ylide **113** with phthalimide proceeded analogously.

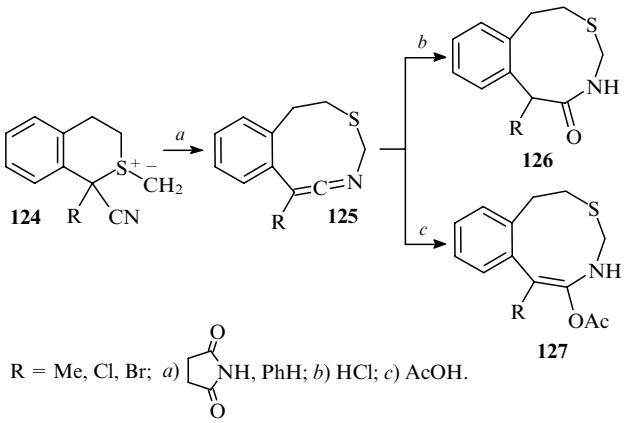


The reaction of 1-cyanoisothiochroman ylide **117a** proceeded by the same mechanism; however, due to the presence of the cyano group, the 2,3-sigmatropic rearrangement of intermediate exomethylide **118a** proceeded differently to form spirocyclic compound **119**.[86] On thermolysis, the compound **119** was isomerised to tetrahydrothiepin **120**, whereas its reactions with acetylenedicarboxylic esters afforded cycloadducts **121a**,**b**. The course of the reaction is substantially affected by the substituent at the sulfur atom. Thus the bulkier ethyl substituent in the ylide **117b** hinders the 2,3-rearrangement and the reaction gave rise to a mixture of benzothiopyran **122** and dimer **123**.



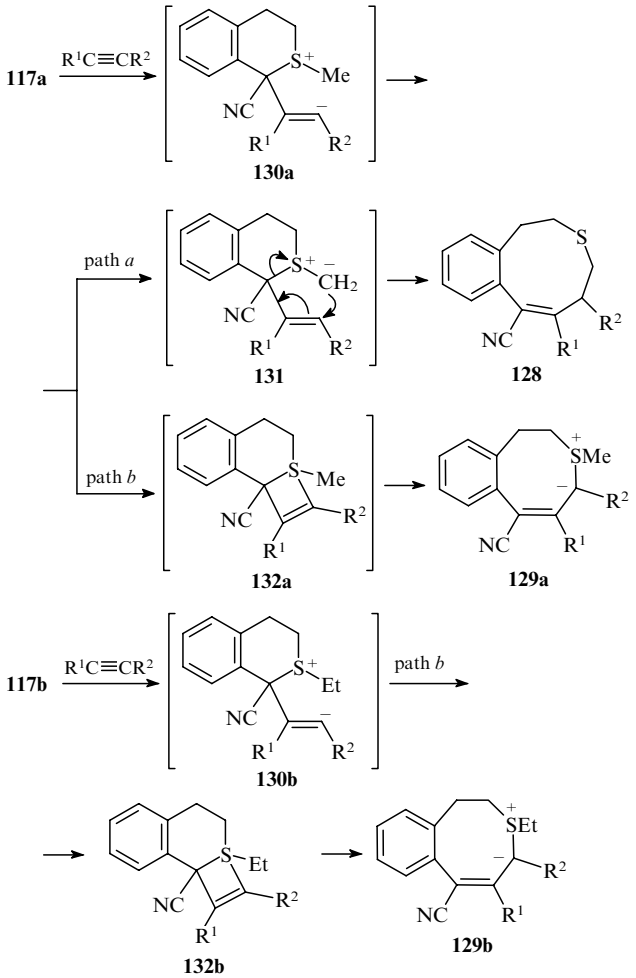
(*a*) EtOH or MeOH, Δ; (*b*) ; (*c*) 205 °C;
(*d*) $EtO_2CC{\equiv}CCO_2Et$; (*e*) EtOH, Δ.

Due to the presence of one more substituent (Cl, Br or Me) at position 1 in ylides **124**, their reactions proceeded through the 2,3-sigmatropic rearrangement involving the S–N bond. The reactions of the ylides **124** with succinimide afforded ketenimines **125**, which gave amides **126** or enol acetates **127** upon acid hydrolysis.[86]



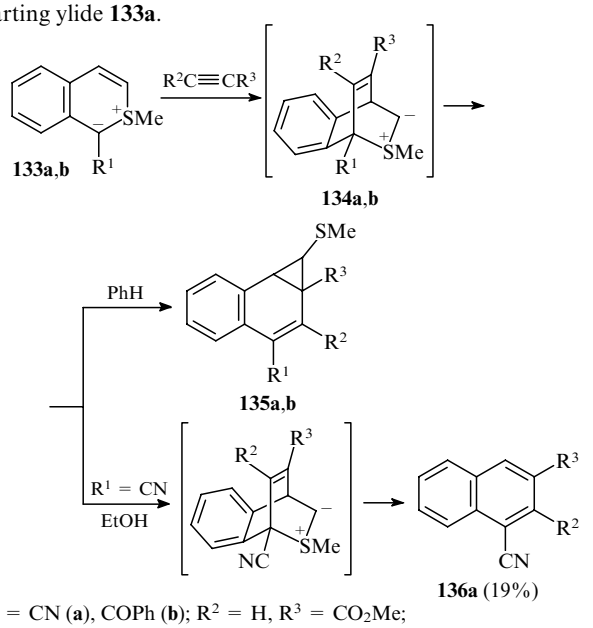
R = Me, Cl, Br; *a*) ; *b*) HCl; *c*) AcOH.

The reactions of the 1-cyano ylides **117a**,**b** with activated acetylenes (dimethyl acetylenedicarboxylate or methyl propiolate) afforded fused compounds **128** and **129a**,**b**.[86] The methyl derivative **117a** gave a mixture of the compounds **128** and **129a** (~1 : 1) in 75% total yield. The reaction mechanism involves the intermediate formation of zwitterions **130a**,**b** whose isomerisation can take two different pathways (path *a* and path *b*). Intramolecular deprotonation of the *S*-methyl group (path *a*) gave rise to ylide **131** whose 2,3-sigmatropic rearrangement afforded the compound **128**. The nucleophilic attack of the vinyl anion on the positively charged sulfur atom produced unstable σ-sulfurane intermediate **132a**, which was converted into the ylide **129a**. The ethyl derivative **117b** gave only the doubly stabilised ylide **129b** in 31% yield.

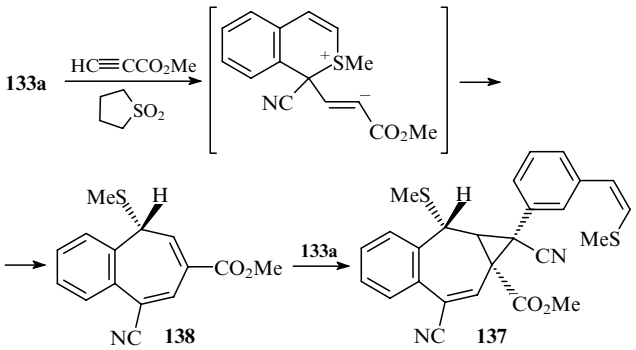


R^1 = H, R^2 = CO_2Me (**129a**); R^1 = R^2 = CO_2Me (**129b**).

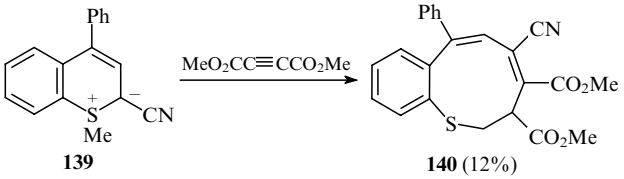
The reactions of stabilised isothiochromene sulfonium ylides **133a**,**b** with acetylenic dienophiles proceeded differently.[87] These compounds reacted as heterodiene systems and the reactions proceeded as [4 + 2]-cycloaddition to yield intermediates **134a**,**b**. Depending on the solvent, subsequent conversions of these intermediates afforded either dihydrocyclopropa[*a*]naphthalene derivatives **135a**,**b** (in aprotic solvents) or naphthalene derivative **136a** (in protic solvents). It should be noted that only [2 + 1]-adduct **137** was formed in high yield in the reaction of the compound **133a** with methyl propiolate in sulfolane. This adduct was generated by the interaction of intermediate **138** with the starting ylide **133a**.



R^1 = CN (**a**), COPh (**b**); R^2 = H, R^3 = CO_2Me;
R^2 = R^3 = CO_2Me, CO_2Et.

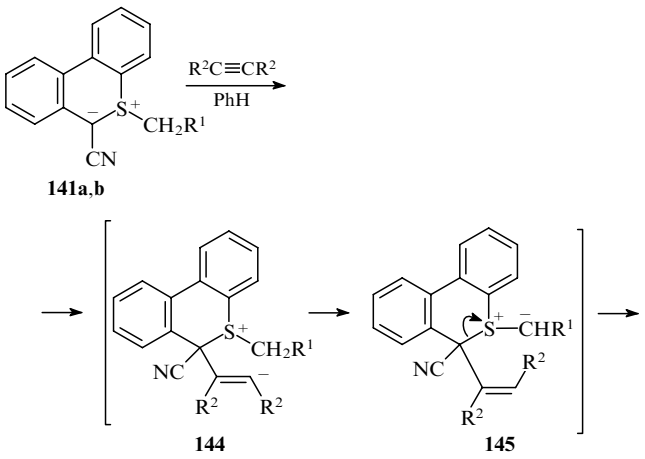


The reaction of 2-cyano-α-thiochromene ylide **139** with dimethyl acethylenedicarboxylate afforded the ring expansion product **140** in low yield.



The reactions of tricyclic sulfur ylide **141a** stabilised by the adjacent cyano group (the thiaphenathrene derivative) with activated acetylenes produced spirocyclic compounds **142** (the yields were up to 31%), which underwent the 1,5-rearrangement upon heating to give dibenzothionine derivatives **143** in yields of up to 95%.[88] It is assumed that the reaction mechanism involves the formation of zwitterionic intermediates **144**, which are rearranged to exocyclic sulfonium ylides **145**. The ylides **145** can undergo the

Sommelet–Hauser rearrangement to produce the compounds **142**. In the case of the ethyl-substituted ylide **141b**, spirocyclic compounds were not formed; instead, the reaction afforded dibenzothiepin derivatives **146** as the major products (the yields were up to 38%). Since the ethyl substituent at the sulfur atom in the compound **141b** causes steric hindrances to the Sommelet–Hauser, this compound underwent the 1,2-Stevens rearrangement to form the ring expansion product **146**. The rearrangements of the zwitterions **144** afforded dibenzothiocine derivatives (in the yields of up to 22%) along with the compounds **146** (see the scheme for the formation of the compound **129a**).[86]

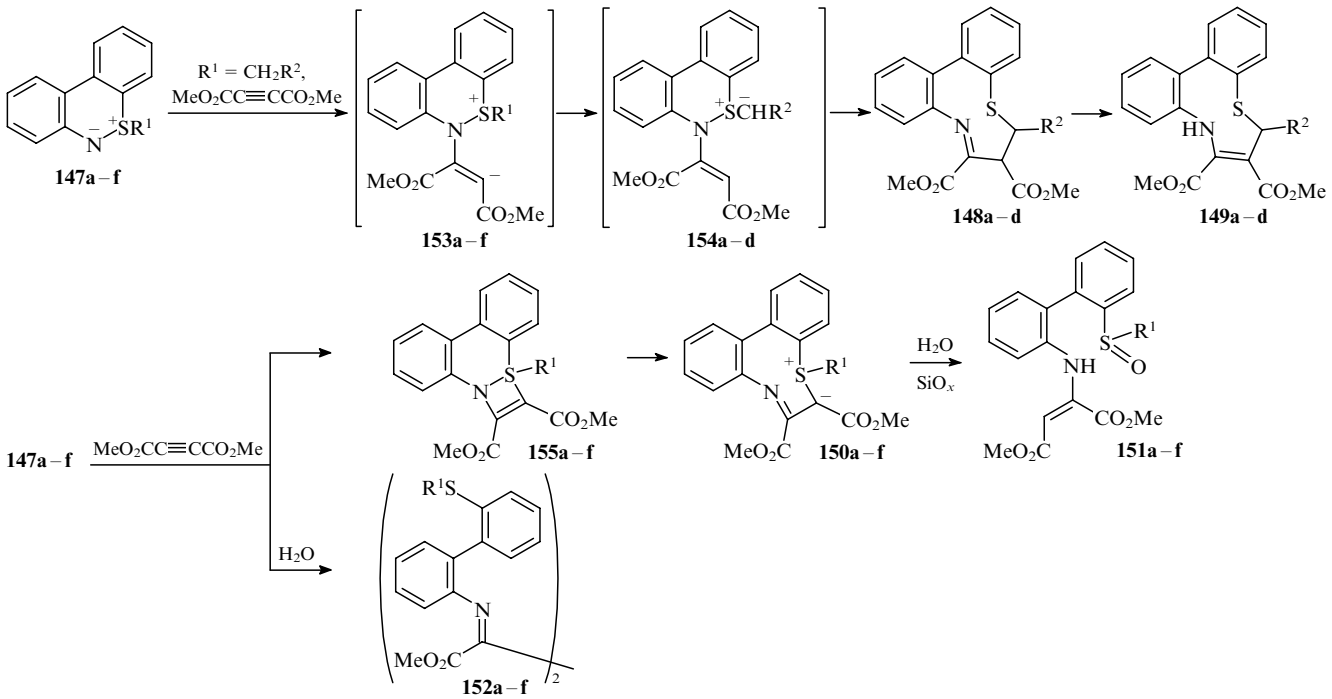


R^1 = H (**a**), Me (**b**); R^2 = CO_2Me, CO_2Et.

The reactions of sulfur ylides **147a–f**, *viz*., 9-alkyl-9-thia-10-azaphenanthrenes, with dimethyl acetylenedicarboxylate gave rise to dibenzothiazonium derivatives (compounds **148** and **149**), dibenzothiazocine derivatives (compounds **150**), 2-alkylsulfinyl-2′-vinylamionbiphenyls **151** and bis(biphenylylimino)ethane derivatives **152** (Scheme 2).[89]

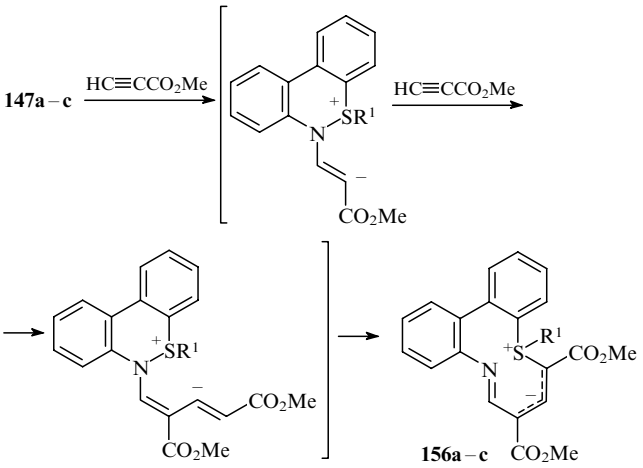
The composition of the reaction products depends substantially on the substituent at the sulfur atom. Thus the compound **147a** produced predominantly dibenzothiazonine derivatives **149a** and **148a**, whereas the ylides **147b**,**c**,**d** gave predominantly dibenzothiazocine derivatives **150** and biphenyls **151**. The ylides **147e**,**f**

Scheme 2

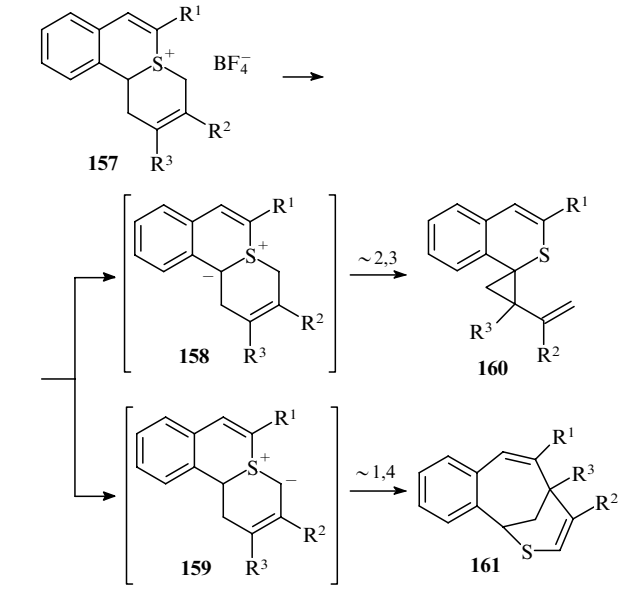


R^1 = CH_2R^2 (R^2 = H (**a**), Me (**b**), Et (**c**), C_5H_{11} (**d**)); R^1 = Ph (**e**), CH=CPh_2 (**f**).

containing the phenyl or vinyl substituent at the sulfur atom produced only dibenzothiazocine derivatives **150e**,**f**. The reaction mechanism involves the formation of zwitterions **153** and **154**. The exocyclic ylide **154** was isomerised to form the compounds **148** and **149**. The zwitterion **153** can produce intermediate **155** from which the derivatives **150** and **151** are generated or can react with water giving rise to the dimers **152**. The reactions of 9-alkylthiaazaphenanthrenes **147a – c** with methyl propiolate afforded 1 : 2 adducts, which are dibenzothiazocine derivatives **156a – c**.[89]

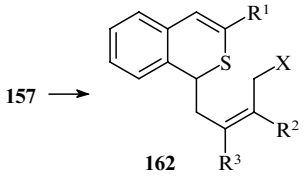


The rearrangements of tricyclic sulfonium salts **157** under the action of various bases have been studied thoroughly.[90] Thus treatment with strong bases [lithium diisopropylamide(LDA), NaH or K_2CO_3] afforded ylides **158** and **159**, which underwent the 2,3- and 1,4-sigmatropic rearrangements to form spirovinylcyclopropane derivatives **160** or tricyclic compounds **161**. The ratio of the reaction products depends on both the base used and the nature of the substituents.



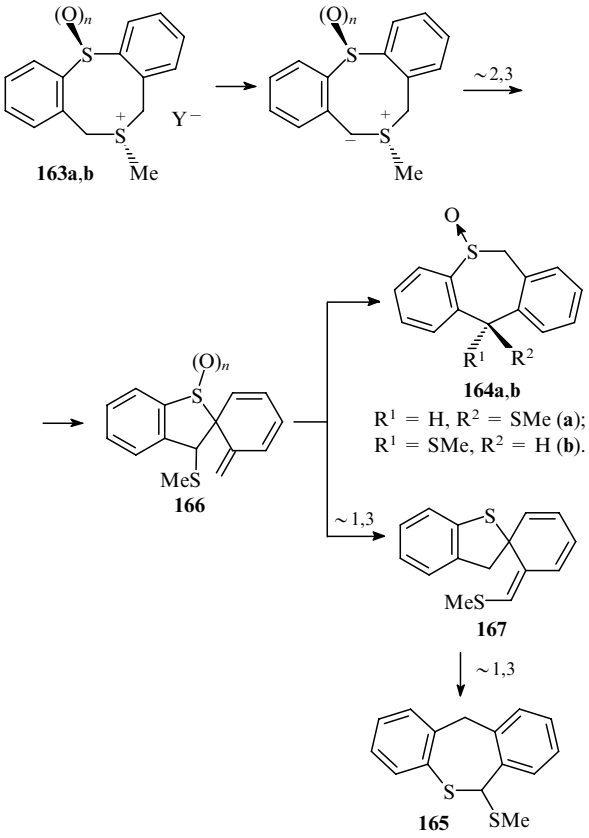
R^1	R^2	R^3	Base	Yield (%)	
				160	**161**
H	Me	Me	LDA	35	52
Bz	Me	Me	LDA	57	7
H	Me	Me	NaH	28	70
Bz	Me	Me	NaH	75	0
H	H	Me	NaH	44	45
Me	Me	Me	NaH	46	46
H	Me	Me	K_2CO_3	21	22
Bz	Me	Me	K_2CO_3	64	0

In the reactions with the salts **157**, weak bases, such as Et_3N, Et_2NH, $BuNH_2$ or AcOK, act as nucleophilic reagents and attack the CH_2 group adjacent to an electron-deficient centre to yield ring expansion products **162** in high yields.



X = NEt_3BF_4, NEt_2, OAc, NHBu.

Interesting results were obtained in studies of the rearrangements of dibenzothiocine salts **163a**,**b**, which took place under the action of a KOH solution in methanol.[91] Thus the sulfoxide **163a** was converted into a mixture of enantiomers of dibenzothiepin derivative **164a**,**b** (in a ratio of ~2 : 1). Under the same conditions, the sulfide **163b** unexpectedly gave compound **165**. The assumed reaction mechanism involves the tandem of the 2,3- and 1,3-sigmatropic rearrangements with the intermediate formation of spirocyclic intermediates **166** and **167**.

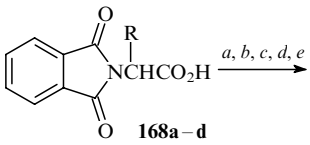


n = 1, Y = $SbCl_6$ (**a**); *n* = 0, Y = BF_4 (**b**).

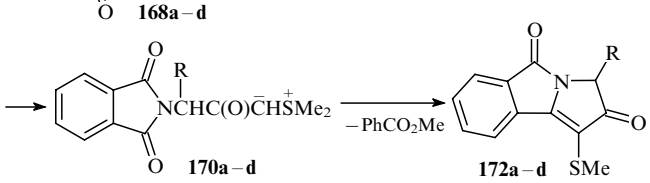
III. Intramolecular cyclisation of sulfur ylides

A promising approach to the synthesis of nitrogen-containing heterocycles, including analogues of alkaloids, is based on intramolecular cyclisation of phthalimido-substituted sulfur ylides stabilised by the carbonyl group.[92–98] Under the conditions of the Arndt – Eistert reaction,[99] *N*-phthaloyl-α- (**168**) and -β-amino acids (**169**) generated bromo ketones, which were converted into the corresponding sulfonium salts. Deprotonation of these salts afforded stabilised ylides **170** and **171**, respectively, which underwent intramolecular cyclisation on heating in toluene with an equimolar amount of benzoic acid[96] to give methylthio-substituted pyrrolizidine- (**172**) and indolizidinediones **173** and **174**. It is significant that racemisation does not take place in the reactions

involving optically active ylides. Longer-chain sulfur ylides derived from γ- and δ-amino acids did not undergo cyclisation; instead, alkyl thioketones and oxobenzoates were formed as the major products.[96] The effect of the substituents in the phthalimide fragment on the regioselectivity of the reaction and the yields of the products was also studied.[97]

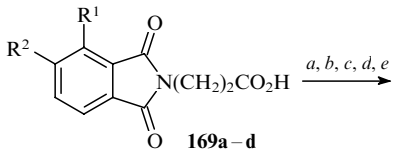


168a–d

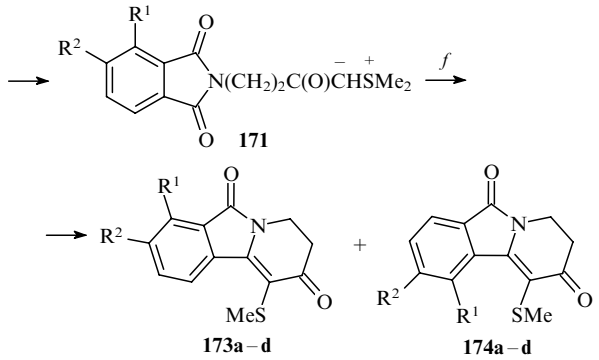


170a–d **172a–d**

Compound **172**	R	Yield (%)
a	H	86
b	Me	85
c	Pr^i	84
d	Bn	83



169a–d

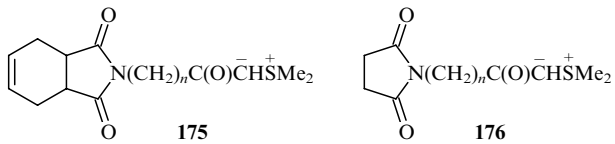


171 **173a–d** **174a–d**

Compound **169**	R^1	R^2	Yield (%)	
			173	**174**
a	H	H	86	
b	NO_2	H	52	
c	Cl	H	75	
d	H	NO_2	38	35

(*a*) $SOCl_2$; (*b*) CH_2N_2; (*c*) HBr; (*d*) Me_2S; (*e*) NaOH – K_2CO_3; (*f*) $PhCO_2H$, 110 °C.

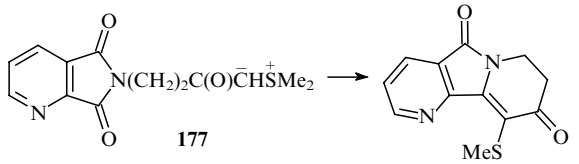
Ylides **175** and **176** containing the tetrahydrophthalimide or succinimide fragment, respectively, instead of the phthalimide fragment did not undergo cyclisation.[97]



175 **176**

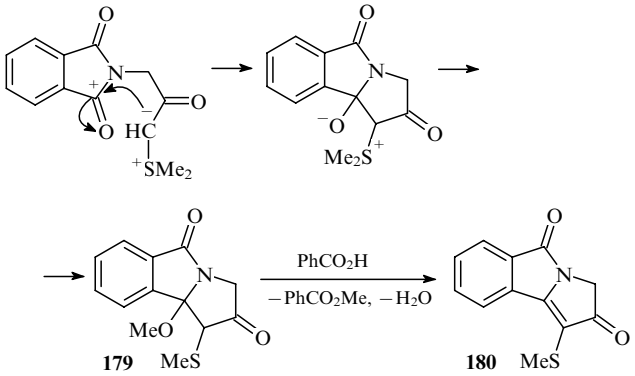
n = 1, 2.

Under the conditions of cyclisation, ylide **177**, which was synthesised from β-alanine and pyridine-2,3-dicarboxylic anhydride, selectively formed a tricyclic compound, *viz*., 5-methylthio-7,8-dihydro-4,8*a*-diazafluorene-6,9-dione (**178**).[98]



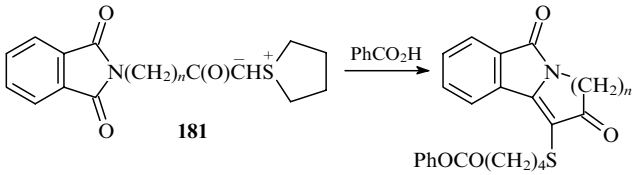
177 **178** (58%)

The assumed mechanism of a new type of intramolecular cyclisation, which is not quite typical of sulfonium ylides, involves, apparently, the attack of the anionic centre on one of the carbonyl groups of the phthalimide fragment followed by migration of the methyl group.[100, 101] The reaction ends in elimination of the methanol fragments from intermediate **179** under the action of benzoic acid to form rearrangement product **180**, methyl benzoate and water.



179 **180**

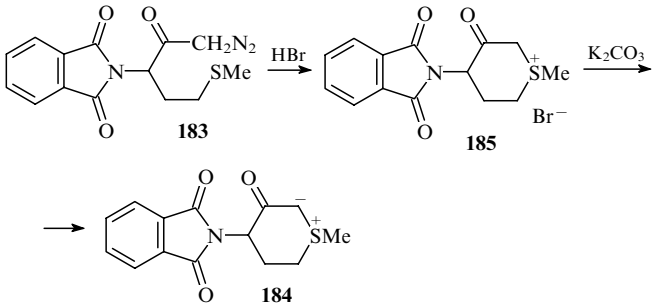
Intramolecular cyclisation of ylides **181** containing the sulfur atom in the ring gave rise to benzoates **182**.



181 **182**

n = 1, 2.

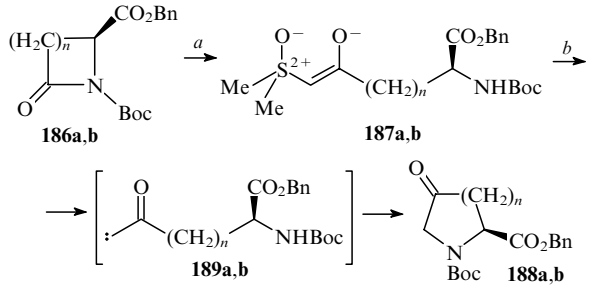
Diazosulfides (*R*)- or (*S*)-**183** generated from D- or L-methionine, respectively, underwent cyclisation under the action of HBr to form optically active sulfonium salts (*R*)- or (*S*)-**185** (the yields were 54 and 62%, respectively). Subsequent treatment of these salts with potassium carbonate afforded cyclic ylides (*R*)- or (*S*)-**184** stabilised by the carbonyl group (the yields were 75% and 90%, respectively).[102]



183 **185** **184**

A new approach to the stereoselective synthesis of amino acids from chiral lactams through intermediate formation of β-ketosulfoxonium ylides was developed.[103, 104] Previously,[105, 106] it was found that these ylides were converted into intermediates of the carbene type on photolysis or under the action of transition metals. The reactions of activated chiral lactams **186a**,**b** with dimethylsulfoxonium methylide were demonstrated to produce ylides **187a**,**b** in high yields.[103, 104] Under the action of rhodium

catalysts, the reactions of the ylides **187a**,**b** proceeded stereoselectively giving rise to derivatives of 4-oxopyrrolidine **188a** or 5-oxopiperidine **188b** formed as a result of cyclisation of intermediate carbenes **189a**,**b**. The compounds **188a**,**b** were used in the synthesis of optically active α-amino acids.[107]

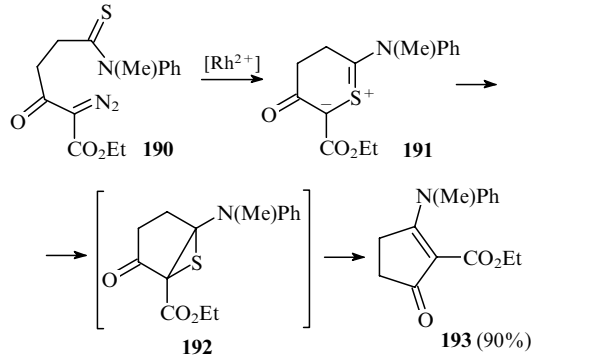


Boc = Bu^{t}OCO; n = 1 (**a**), 2 (**b**);

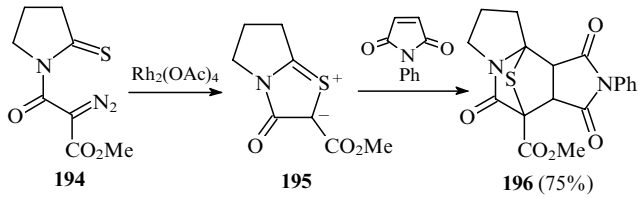
(*a*) $Me_2\overset{+}{S}(O)CH_2^-$, DMSO, 20 °C; (*b*) [$Rh^{2+}$].

IV. Reactions of thiocarbonyl ylides

Considerable recent attention has been given to thiocarbonyl ylides, which are readily accessible and highly reactive intermediates. Several procedures were developed for the preparation of thiocarbonyl ylides among which are the 1,3-dipolar cycloaddition of diazo compounds to thioketones to form 1,3,4-thiadiazolines followed by nitrogen elimination,[108] the addition of thioketones to oxiranes[109] or photoisomerisation of aryl vinyl sulfides.[110] Thiocarbonyl ylides readily undergo rearrangements. These compounds are involved in cycloaddition with dipolarophiles and in 1,3- and 1,5-electrocyclisations, which often proceed with high regio- and stereoselectivity. The reactions of thiocarbonyl ylides with compounds of the RXH type (X = N, O or S) giving rise to 1 : 1 adducts were also studied.[111–113] Recently, cyclisation of carbenes generated by catalytic decomposition of diazothioamides has gained wide acceptance for the preparation of thiocarbonyl ylides.[114] Thus diazothioamide **190** gave cyclic thiocarbonyl ylide **191** under the action of a rhodium catalyst. The ylide **191** was converted into enaminoketone **193** due to elimination of sulfur from intermediate episulfide **192**.[115]

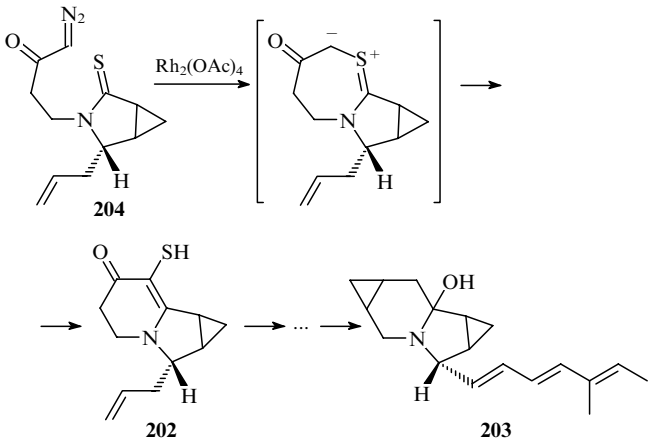


Intramolecular cyclisation of diazothioamide **194** catalysed by dirhodium tetraacetate afforded thiocarbonyl ylide **195** stabilised through the aromatic mesoionic structure. The ylide **195** reacted with *N*-phenylmaleimide according to the scheme of the diene synthesis to give adduct **196**.[115]



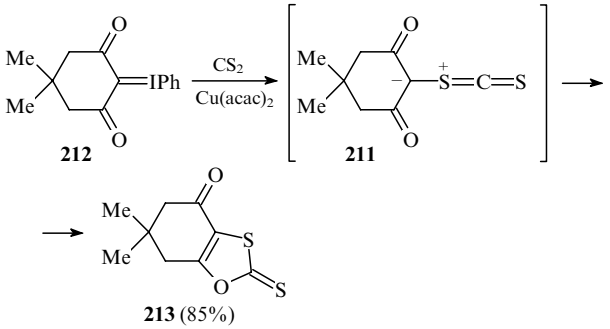
Thiocarbonyl ylides were successfully used in the synthesis of natural alkaloids.[116–120] Thus non-stabilised ylide **198** was generated from diazothioamide **197** under the action of rhodium acetate followed by the rearrangement of the latter into episulfide **199**. Isomerisation of the compound **199** afforded thioketone **200**, which underwent desulfurisation under the action of Raney nickel to yield dihydropyridone **201**.[116]

This procedure was used for the synthesis of dihydropyridone **202**, which was the key intermediate in the total synthesis of antibiotic indolisomycin **203**.[117, 118] Diazothioamide **204** was used as the starting compound.

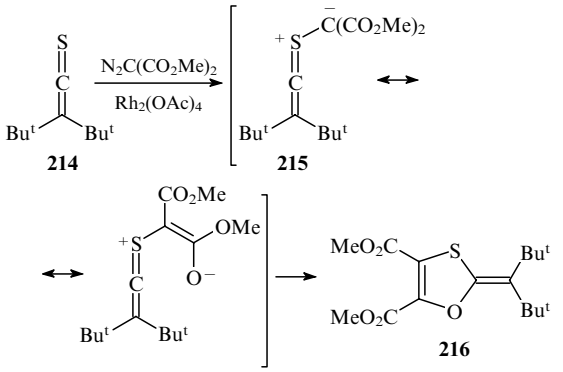


Alkaloids helenine (**205**)[119] and cephalotaxine (**206**)[120] were synthesised using compounds **207** and **208**, respectively. The latter were prepared by cyclisation of hydrazones **209** and **210**, which were synthesised from substituted benzaldehydes and *N*-amino-1,2-diphenylaziridine, in the presence of dirhodium tetraacetate. The reactions proceeded through the corresponding carbenoids and cyclic thiocarbonyl ylides (Scheme 3).

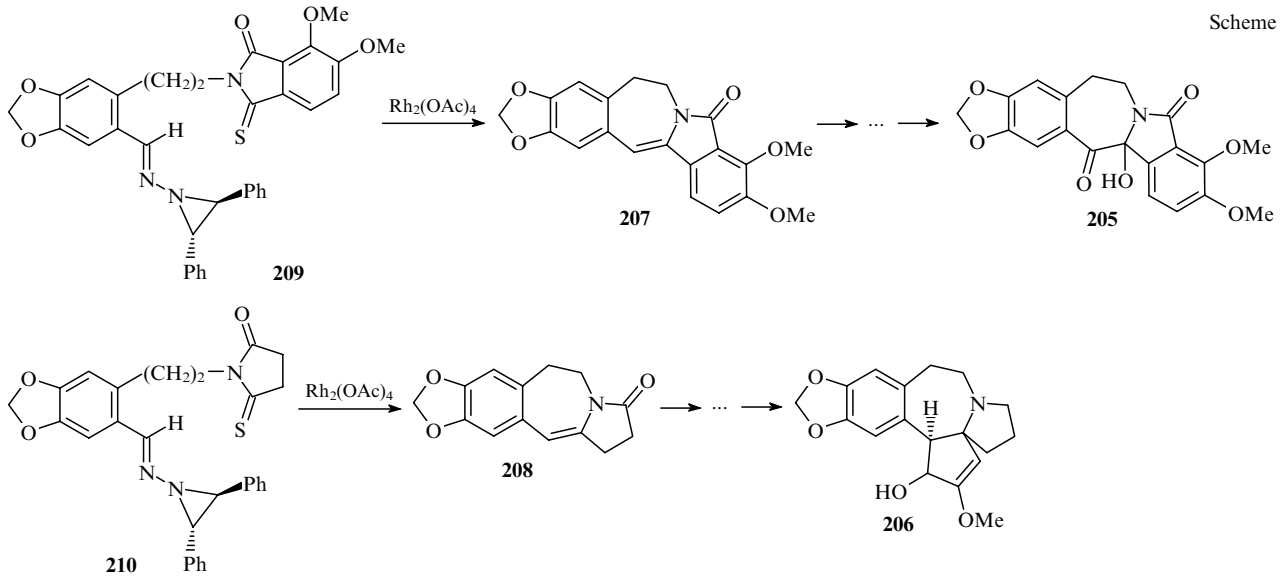
Thiocarbonyl ylide **211**, which was generated *in situ* on heating of a suspension of iodonium compound **212** in carbon disulfide in the presence of copper acetylacetonate, underwent cyclisation to yield oxathiol heterocycle **213**.[121]



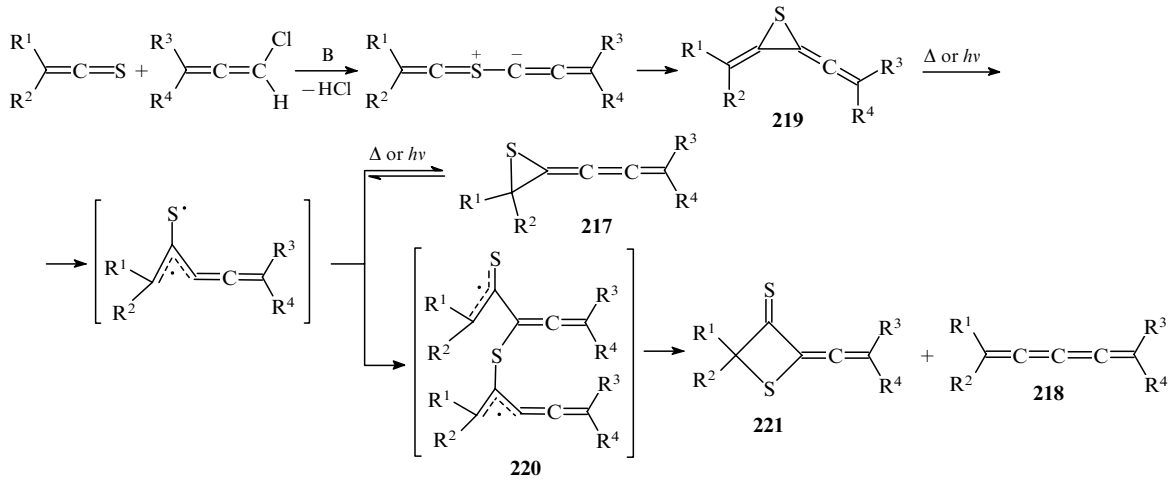
The reaction of di-*tert*-butylthioketene (**214**) with diazomalonate afforded thioketene ylide **215**, which underwent cyclisation to give 2-alkylidene-1,3-oxathiol **216**.[122]



Scheme 3



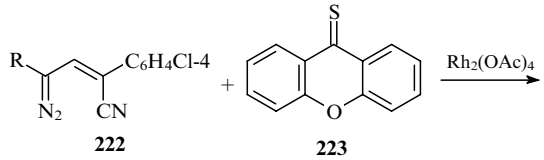
Scheme 4

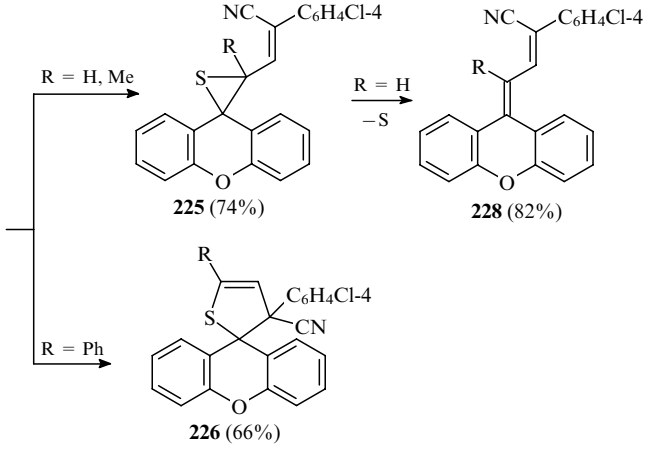


$R^1 = R^2 = R^3 = R^4 = Bu^t$; $R^1 - R^2 = CMe_2(CH_2)_3CMe_2$, $R^3 = R^4 = Bu^t$; B is a base.

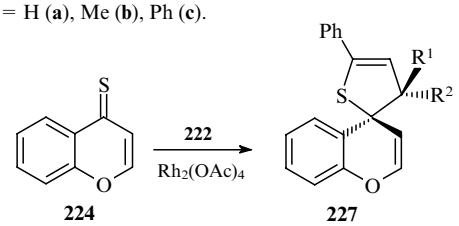
Various cumulenes and cumulene episulfides were prepared by the addition of alkenylidene dicarbenes to thioketenes.[123] Episulfides **217** were isolated as stable crystal compounds, which underwent predominantly desulfurisation on heating or photolysis to give tetraenes **218** in yields from 50% to 69% and were also partially isomerised to episulfides **219**. Substituted thietanethiones **221** were obtained as by-products (9% – 20%) due to the intermolecular transfer of the sulfur atom through biradical intermediate **220** (Scheme 4).

Vinylthiocarbonyl ylides generated from vinyldiazoalkanes **222** and thiochromones **223** or **224** gave 1,3- (**225**) or 1,5-electrocyclisation (**226** or **227**) products depending on the nature of substituents in the ylide.[124] Unstable thiirane **225** (R = H) was immediately converted into diene derivative **228** with elimination of sulfur. The reactions of diazo compounds **222a**,**b** with thiochromone **224** proceeded through the formation of analogous dienes. Diazo compound **222c** containing the bulkier phenyl substituent was involved in 1,5-electrocyclisation with the thiochromones **223** and **224** to give dihydrothiophene derivatives **226** and **227**, respectively.



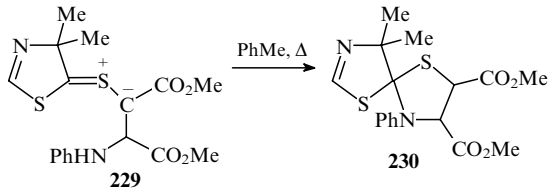


R = H (**a**), Me (**b**), Ph (**c**).



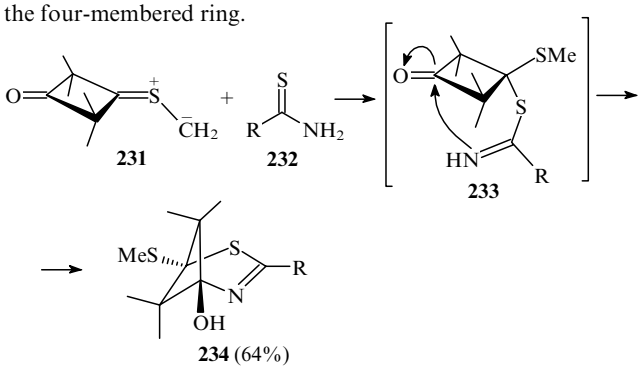
R^1 = CN, R^2 = C_6H_4Cl-4 (55%); R^1 = C_6H_4Cl-4, R^2 = CN (28%).

Amino-substituted thiocarbonyl ylide **229** underwent intramolecular condensation of a new type providing an approach to 1,6-dithia-3,9-diazaspiro[4.4]non-2-enes **230**.[125]



229 **230**

The reactions of thiocarbonyl ylide **231** with thioamides **232** were accompanied by unusual intramolecular cyclisation.[108] Adduct **233** generated initially underwent cyclisation to give 2-thia-4-azabicyclo[3.1.1]hept-2-ene derivative **234**. This is the first example of the nucleophilic addition of a cyclobutanone derivative to the carbonyl group proceeding without opening of the four-membered ring.

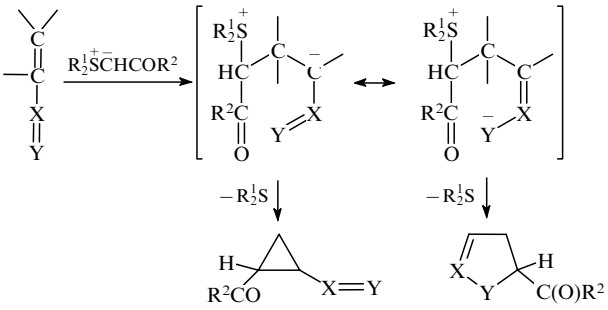


231 **232** **233** **234** (64%)

R = Me, Ph.

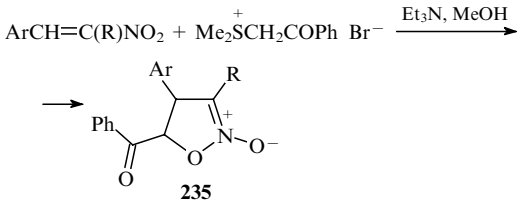
V. Cycloaddition of ylides to alkenes

The reactions of stabilised sulfonium ylides with electron-deficient alkenes of the C=C–X=Y type generally afford cyclopropanes (the $Ad_N-E_{1,3}$ mechanism);[6] however, five-membered heterocycles can also be formed due to the involvement of the activating X=Y group, where X=Y = NO_2, N=O or N=NAr (the $Ad_N-E_{1,5}$ mechanism).[10, 13]



These reactions were considered in sufficient detail in the review,[13] which surveyed the data available up to 1986. Hence, we dwell only on the recent most interesting results published in the literature.

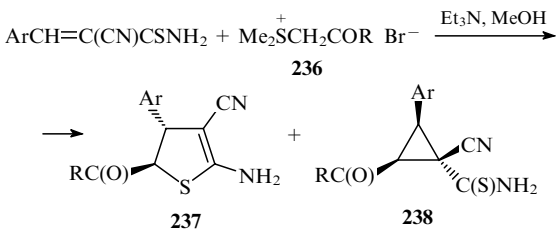
The reactions of nitroalkenes with stabilised sulfonium ylides were demonstrated [126, 127] to proceed stereoselectively to give both *trans*-4,5-dihydroisoxazole *N*-oxides **235** and substituted cyclopropanes, the ratio of the reaction products being essentially dependent on the α-alkyl substituent in nitroalkenes. In the case of bulkier substituents R, heterocyclic adducts are formed in substantially higher yields.



235

Ar = 3-$NO_2C_6H_4$, R = CO_2Et (85%); Ar = Ph, R = Me (41%).

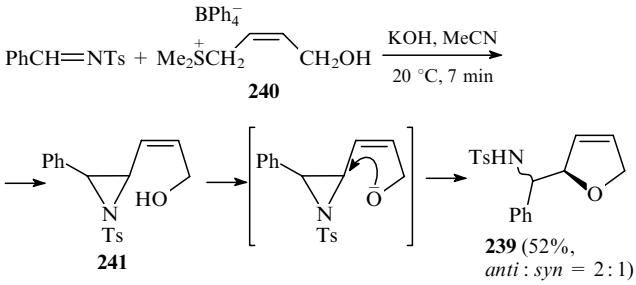
The reactions of arylmethylenecyanothioacetamides with stabilised sulfur ylides **236** proceeded stereoselectively to give mixtures of 2-amino-4,5-dihydrothiophenes **237** and cyclopropanethiocarboxamides **238**.[128] In most cases, the dihydrothiophenes **237** were obtained as the major reaction products. For R = cyclo-C_3H_5, cyclopropane derivatives did not form at all.



236 **237** **238**

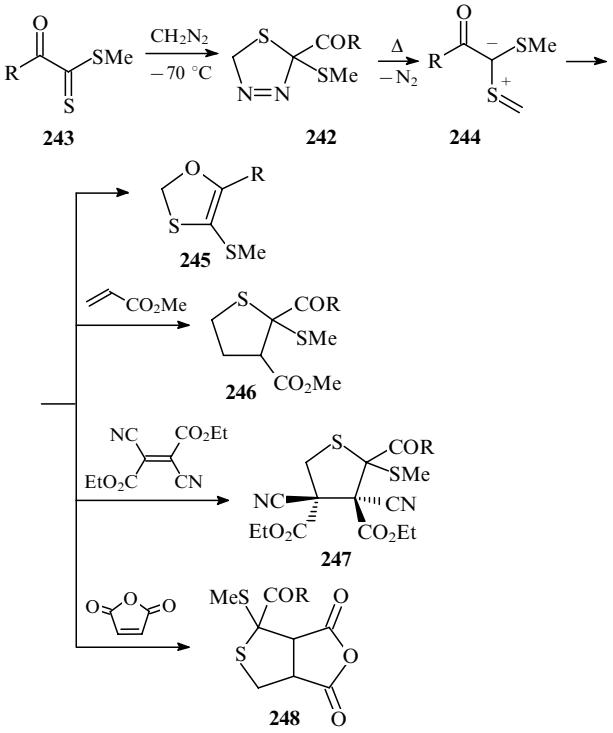
Ar = 2-MeC_6H_4, 2-$NO_2C_6H_4$, 4-$MeOC_6H_4$, 3-pyridyl, 2-thienyl;
R = Ph, 2-thienyl, cyclo-C_3H_5.

A simple and efficient procedure for the preparation of 2,5-dihydrofurans **239** containing the *N*-tosylamino substituent is based on the reaction of *N*-sulfonylimines with sulfur ylides generated from *cis*-4-hydroxybut-2-enyldimethylsulfonium salts **240**.[129] The assumed mechanism involves the formation of aziridine derivative **241**, ring opening through the attack of the internal nucleophile and subsequent cyclisation to form 2,5-dihydrofuran. The reaction involving the *trans*-isomer of the sulfonium salt **240** afforded only the aziridine derivative.

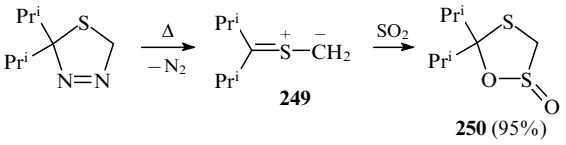


240 **241** **239** (52%, *anti* : *syn* = 2 : 1)

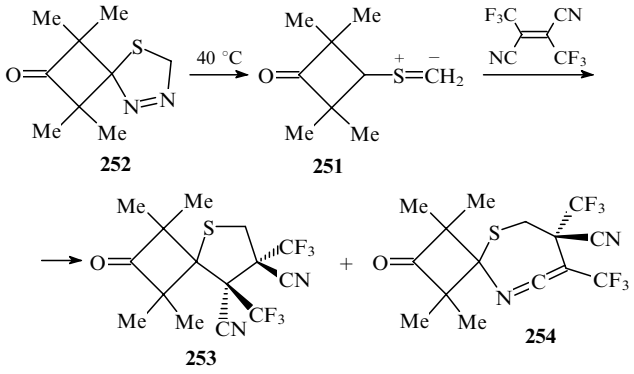
As mentioned above, thiocarbonyl ylides are readily involved in 1,3-dipolar cycloaddition to give the corresponding cycloadducts in high yields and with high regioselectively. Thus when heated, dihydrothiadiazoles **242**, which were formed in the reactions of diazomethane with derivatives of oxodithiocarboxylic acids **243**, gave intermediate **244**, which reacted with dienophiles to yield substituted thiolanes **246**–**248**.[130] In the absence of dienophile, the ylide **244** produced intramolecular cyclisation product **245**.



1,3-Dipolar cycloaddition of thiocarbonyl ylide **249** to sulfur dioxide gave rise to 1,2,4-oxadithiolane 2-oxide **250**.[131]

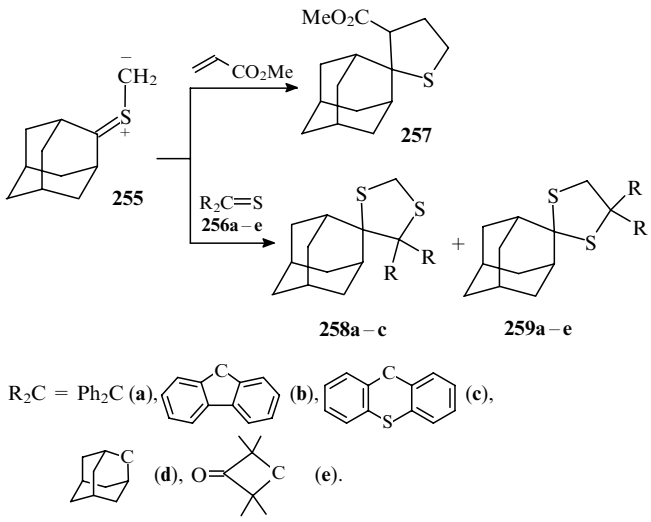


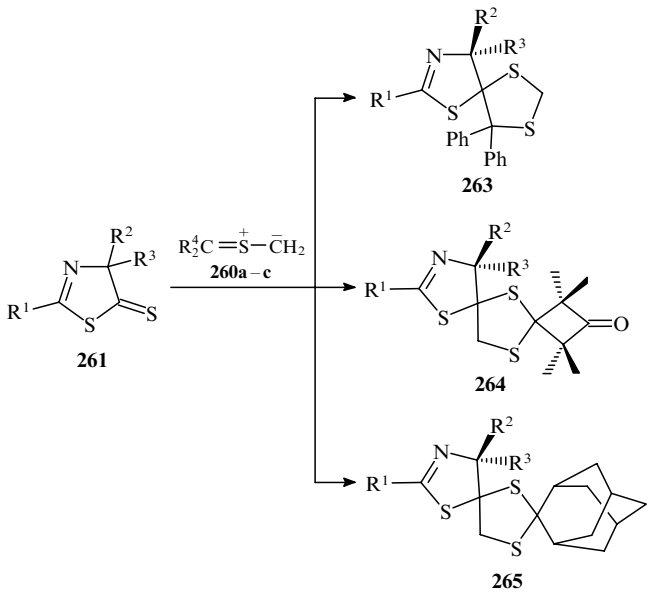
The reaction of thiocarbonyl ylide **251**, which was generated *in situ* from oxospiro[cyclobutanedihydrothiadiazole] **252**, with *trans*-1,2-bis(trifluoromethyl)-1,2-dicyanoethylene afforded thiolane **253** and stable strained cyclic ketenimine **254** in a ratio of ~1 : 4.[132]

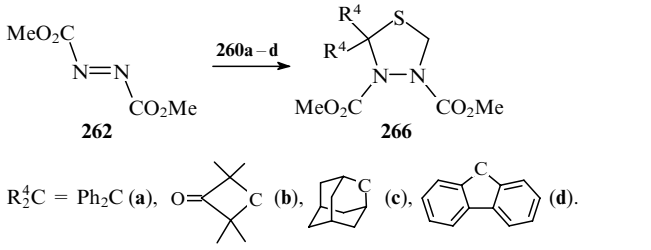


Adamantanethione-*S*-methylide (**255**) reacted with methyl acrylate to form substituted thiolane **257**, whereas its reactions with thioketones **256** gave rise to 1,3-dithiolanes **258a–c** and **259a–e**. The reactions involving thiobenzophenone (**256a**), thiofluorenone (**256b**) or thioxanthione (**256c**) produced two regioisomers.[133]

1,3-Dipolar cycloaddition of thiocarbonyl ylides **260** to thiazole-5(4*H*)-thiones **261**[134] or azodimethyl carboxylate **262**[135] proceeded with high regioselectivity to give the corresponding spirocyclic adducts **263–266** in high yields.







Cycloaddition of the thiocarbonyl ylides **251** and **260a** to *N*-sulfinylaniline and *N*-sulfinyltosylamide gave rise to both substituted 1,3,4-dithiazolidine 3-oxides (adducts at the N=S bond) and 1,2,4-oxadithiolane-2-tosylimides (adducts at the S=O bond).[136] The reactions of thioketones with diazoacetates performed on heating in THF[137,138] afforded acyl-substituted thiocarbonyl ylides as the initial reaction products, which either underwent 1,3- or 1,5-dipolar electrocyclisation or reacted with the second thioketone molecule to give a 1,3-dipolar cycloaddition product. The first example of 1,3-dipolar cycloaddition of thiocarbonyl ylide $CH_2=S-CH_2$ to fullerene C_{60} giving rise to a tetrahydrothiophene derivative was reported.[139] This product is a convenient starting compound for subsequent functionalisation.

* * *

As evident form the published data, the recent investigations dealt with more and more complex conversions involving sulfur ylides. We believe that the synthesis of heterocyclic compounds with unique structures and the total synthesis of natural products and biologically active synthetic analogues will be the major field of application of ylides in the coming years. The reactions of ylides producing alkaloids and alkaloid-like compounds are worthy of particular attention because they have an increasingly important place among drugs used in oncology and cardiology. There is no doubt that new biologically active compounds will be discovered among organosulfur heterocyclic compounds prepared by ylide procedures.

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