USE OF SULFONIUM YLIDES IN THE SYNTHESIS OF HETEROCYCLIC SYSTEMS (REVIEW)

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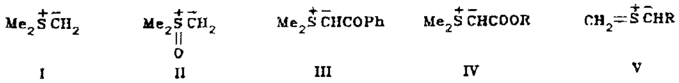
UDC 547.379.2

The literature on the use of sulfur ylides in the synthesis of heterocyclic systems of varied structure is reviewed. The possible preparative value of these reactions is discussed.

The sulfur ylides so far employed in the synthesis of heterocyclic systems are for the most part reactive methylides of the following types:



$$\overset{+}{S}\text{Me}_2\overset{-}{\text{C}}\text{H}_2 \quad \text{Me}_2\overset{+}{\underset{\|O}{S}}\overset{-}{\text{C}}\text{H}_2 \quad \text{Me}_2\overset{+}{S}\overset{-}{\text{C}}\text{HCOPh} \quad \text{Me}_2\overset{+}{S}\overset{-}{\text{C}}\text{HCOOR} \quad \text{CH}_2{=}\overset{+}{S}\overset{-}{\text{C}}\text{HR}$$

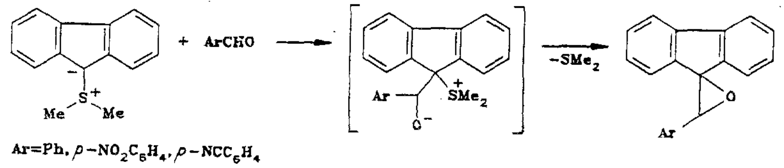
I II III IV V

Of the reactions of sulfonium ylides, those receiving most attention have been with electrophilic reagents, which usually afford carbo- and heterocyclic systems. The reactivity of the sulfonium ylides in these reactions is determined by their nucleophilicity. The reactions normally occur under relatively mild conditions, and are frequently superior to classical methods for the synthesis of heterocycles from the preparative point of view. We here review the literature on the reactions of monostabilized sulfonium ylides, classified according to the type of heterocycle formed, viz., three-, four-, five-, or six-membered ring, or a condensed heterocycle.

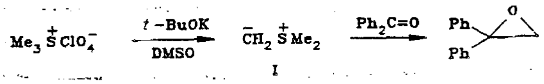
1. SYNTHESIS OF O-, S-, and N-HETEROCYCLES

1.1. Synthesis of Oxiranes

The reactions of sulfonium ylides with carbonyl compounds are currently used extensively for the synthesis of oxiranes. The first reactions of this type to be studied were the reactions of the fluorenylide with aromatic aldehydes containing electron-acceptor substituents [1, 2].



Dimethylsulfonium methylide (I), generated by treating trimethylsulfonium bromide or perchlorate with potassium tert-butoxide in DMSO, reacts with both aldehydes and ketones (benzaldehyde and cyclohexanone) to give the oxiranes in 43-82% yields [3].



The behavior of dimethylsulfonium and dimethylsulfoxonium methylides (I, II) in their reactions with carbonyl compounds (benzophenone, cycloheptanone, and carvone) to give quantitative yields of the oxiranes have been examined [4, 5]. Differences between the sulfonium and sulfoxonium ylides become apparent in their reactions with α,β-unsaturated aldehydes and ketones, the sulfonium ylide (I) giving oxiranes selectively, and the sulfoxonium ylide (II) the Michael addition products (substituted cyclopropanes) [5-7].

M. V. Lomonosov State University, Moscow 119899. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 147-173, February, 1990. Original article submitted April 2, 1986; revision submitted June 12, 1989.

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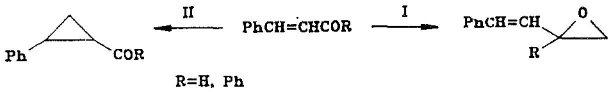
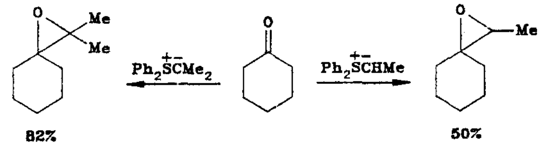
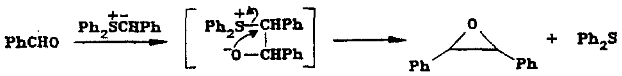


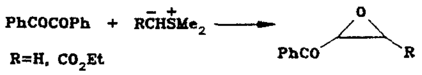
Taking the reaction of diphenylsulfonium methylides with cyclohexanone as an example, it was shown that sulfonium ylides bearing two alkyl groups on the carbanionic carbon atom are less stable, and correspondingly more reactive, than ylides containing a single alkyl group [8-10].



It was shown that the reaction of sulfonium ylides with carbonyl compounds is stereospecific, giving the trans-oxiranes exclusively [8]. Epoxidation of carbonyl compounds by sulfonium ylides involves reversible attack of the carbanionic carbon of the ylide on the electrophilic carbonyl carbon to give an unstable betaine, followed by S_N2 replacement of the sulfonium group by the oxy-anion.

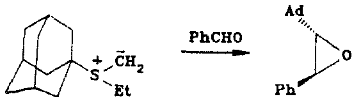


The reactivity of ylides towards electrophiles is known to decrease as the extent of delocalization of the negative charge is increased [11]. In their reactions with electrophilic substrates, therefore, both sulfur β-ketoylides and sulfoxonium ylides add to chalcones to give cyclopropanes [12-15]. Reaction of sulfonium ylides with α-diketones occurs at one carbonyl group only, and provides a preparative method for obtaining functionalized oxiranes (epoxyketones and esters). Chloral has also been epoxidized, albeit in low yields [16, 17].

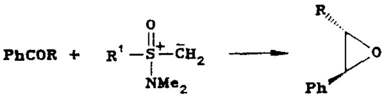


Sulfonium ylides react with γ-diketones and 1,4-diacylbenzenes at both carbonyl groups to give two oxirane rings [18].

Sulfonium ylides can be employed in the synthesis of oxiranes with an asymmetric center. It has been found that, although optically active sulfonium salts can be obtained [19, 20], they undergo extremely rapid racemization in solution, even at ambient temperatures, as a result of the low inversion barrier. Hence, transfer of chirality from the sulfur in the ylide to carbon has been examined in the reaction of adamantylethylsulfonium methylide with benzaldehyde [21].

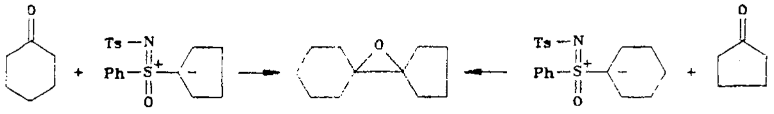


For the asymmetric synthesis of oxiranes with an optical purity of 20-75%, frequent use is made of the optically active sulfonium ylides (dialkylamino)methyl- and (dialkylamino)-arylsulfoxoniiomethylides, generated from the tetrafluoroborates. The best results were obtained using a 50-100% excess of the ylide [22-27].

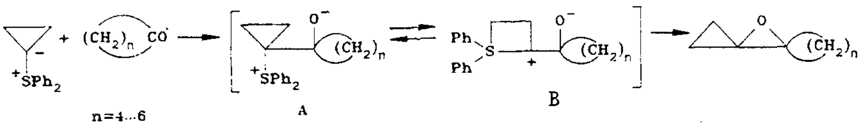


R=H, Me; R'=Me, Ph, $4\text{-}MeC_6H_4$

By using sulfoximinomethylides, oxiranes containing ω-sulfinamido-groups have been obtained [28], together with the difficulty-accessible dispirooxiranes [29].

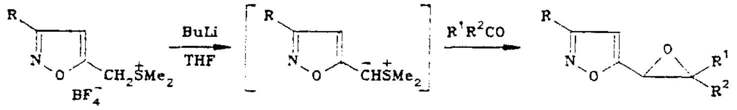


Reaction of carbonyl compounds with the ylide generated from cyclopropyldiphenylsulfonium tetrafluoroborate affords high yields of oxaspiropentanes, which had previously been regarded as unstable intermediates [30]. Two possible pathways for the reactions of sulfur diphenylcyclopropylides with carbonyl compounds are known [30]:



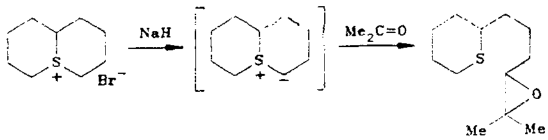
Closure of the oxaspirane ring either involves intramolecular nucleophilic displacement of diphenyl sulfide by the oxide anion in the intermediate betaine (A), or via the four-membered intermediate state (B).

Epoxidation with sulfonium ylides also provides a convenient method for the synthesis of oxiranes with heterocyclic substituents [31, 32].

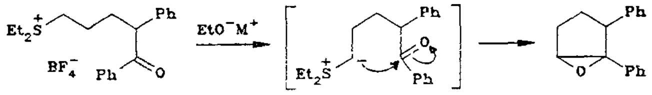


R=Me, Ph; R^1=Alk, Ar, R^2=H; R^1=R^2=Ph

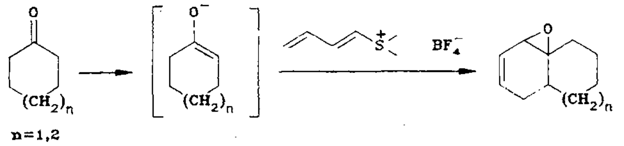
Reaction of a bicyclic sulfonium ylide with acetone involves both formation of the oxirane, and cleavage of the ring in the original ylide [33].



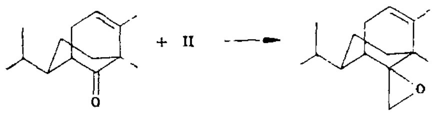
All these methods of synthesis of oxiranes involve the reaction of sulfonium ylides with carbonyl compounds. In recent years, however, methods have been proposed and successfully developed which consist in the intramolecular cyclization of ketosulfonium ylides, generated from the appropriate conjugated acids [34, 35]. These epoxycyclizations usually afford qualitative yields.



Epoxidation of cycloalkanone enolates with simultaneous cyclization involving the diene system of the ylide, generated by treatment of the sulfonium fluoroborate with base, is a promising method for the synthesis of unsaturated epoxy-compounds. The base used in this reaction may be either lithium diiodopropylamide, or methyllithium in THF at −78°C [36]. However, the reaction fails with acyclic ketones [36].

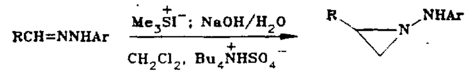


An important area of use of sulfur ylides is in the synthesis of polycyclic and steroidal compounds containing the oxirane moiety [37-39].



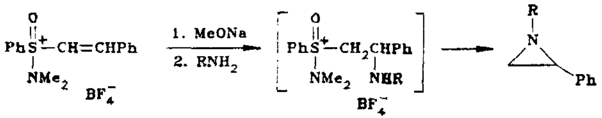
1.2. Preparation of Aziridines and Thiiranes

Substituted aziridines (the nitrogen analogs of oxiranes) are obtained in good yields by reacting dimethylsulfonium methylide (I) with benzalanilines [3, 7]. Sulfoxonium methylide gives a mixture of diphenylaziridine and acetophenone anil [5] in a ratio of 2:1. Sulfoxaminomethylides are much less reactive (the yields of aziridines are no greater than 23%). An interesting modification of this method has been proposed [40]. Dimethylsulfonium methylide, generated by phase-transfer catalysis, reacts with arylbenzaldimines or benzaldehyde arylhydrazones to give the substituted aziridines in quantitative yields, which constitutes a convenient synthetic method.



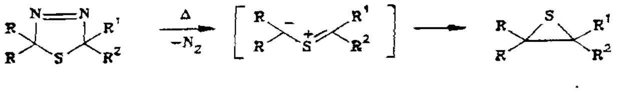
R=Me, Ph, 4-ClC_6H_4; Ar=Ph, 4-$MeOC_6H_4$, 2,4-$(NO_2)_2C_6H_3$

A fundamentally novel method of synthesis of aziridines is by the reaction between phenylstyryl(dimethylamino)sulfoxonium fluoroborate and primary amines in the presence of sodium methoxide [26, 41].



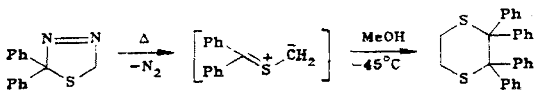
R=Me, *t*-Bu

In contrast to the oxiranes, only a few examples of the synthesis of thiiranes have been reported, viz., a) by reaction of thiobenzophenone with dimethylsulfoxonium methylide; b) by closure of the thiirane ring in the thiocarbonylylide obtained by pyrolysis of 2,5-disubstituted Δ^3-1,3,4-thiadiazolyls [42, 43].



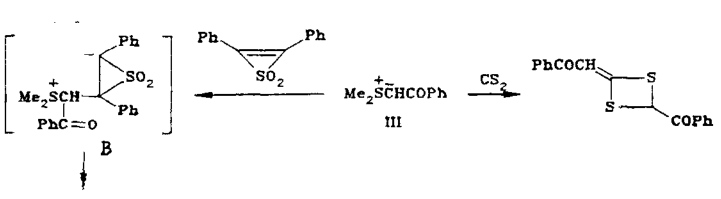
R=R^1=R^2=$(CH_2)_5$, Ph, CF_3; R=R^1=Ph, R^2=H

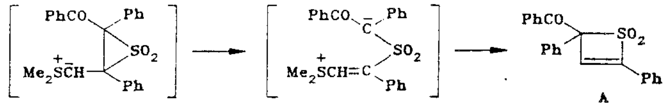
2,2-Diphenyl-1,3,4-thiadiazoline, obtained by reacting thiobenzophenone with diazomethane, on elimination of nitrogen in methanol at −45°C gives the thiocarbonylylide, converted in high yields into the dithiane [44].



2. SYNTHESIS OF FOUR-MEMBERED O-, S-, AND N-HETEROCYCLES

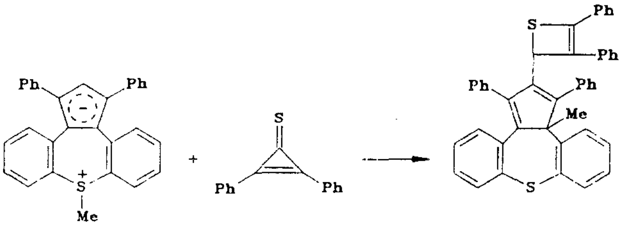
The synthesis of four-membered heterocycles from sulfonium ylides has received little attention. For example, dithietanes have been obtained by the reaction between dimethylbenzoylsulfonium methylide (III) and carbon disulfide [45], and a thietene dioxide by reaction of (III) with diphenylthiirene dioxide [46].



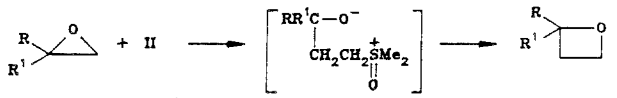

A

The formation of the thietene dioxide (A) results from the addition of the ylide to the activated double bond of the starting sulfone to give the betaine (B), followed by migration of the benzoyl group in the betaine, cleavage of the three-membered ring and closure of the four-membered ring with the elimination of dimethyl sulfoxide.

Reaction of a stable thiaazulene ylide with diphenylcyclopropenethione affords a polycyclic compound containing the thietene grouping [47].



An interesting property of sulfoxonium ylides is their ability to add to oxiranes and aziridines followed by opening of the three-membered ring and the formation of substituted oxetanes [48] or azetidines [49, 50].


R=H, Me, Ph; R^1=Me, Ph

A convenient single-stage method for the synthesis of azetidines was reported in 1983 [51]. The yields obtained in this reaction are higher than in any of the previously known methods of preparation of such azetidines. Another advantage of this method is the accessibility of the starting materials. However, the method has the considerable drawback that only N-arenesulfonylimines undergo this reaction (the reaction did not occur with N-benzylideneaniline).


Ar=Ph, 4-ClC$_6$H$_4$; Ar$'$=Ph, 4-MeC$_6$H$_4$

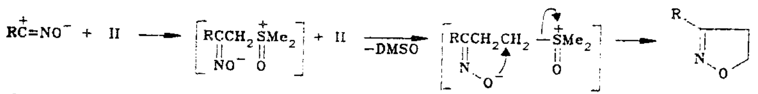
3. SYNTHESIS OF FIVE-MEMBERED HETEROCYCLES

The reactions of sulfonium ylides to give heterocycles have been employed most extensively for the synthesis of five-membered heterocycles. Formally speaking, nearly all reactions of this type may be regarded as either 1,3- (the majority), or 1,4-dipolar additions. In 1,3-dipolar additions, ylides may function either as dipolarophiles, or as 1,3-dipoles.

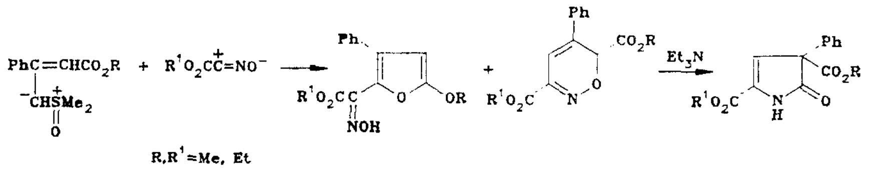
3.1. Reactions of Sulfonium Ylides with 1,3-Dipoles

The 1,3-dipoles most frequently used in reactions with ylides are nitrile oxides, nitrilimines, diazo-compounds, and azides. It is noteworthy that these reactions are often complicated by the insertion of carbene (from the sulfonium ylide) into substrate C—C bonds, and by reaction of the ylide with the solvent, for example DMSO.

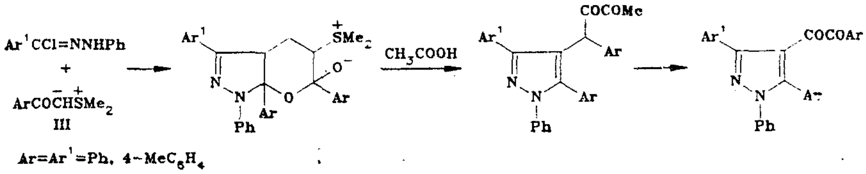
Some workers have examined the reactions of dimethylsulfoxonium methylide (II) with nitrile oxides [52-55]. The predominant reaction was found to result in the formation of oximes, only 5-10% of the isoxazolines being obtained, together with small amounts of diphenyloxadiazole, diphenyloxazole, and diphenylfuroxan.


R=Me, CMe$_3$, Ph, 4-NO$_2$C$_6$H$_4$

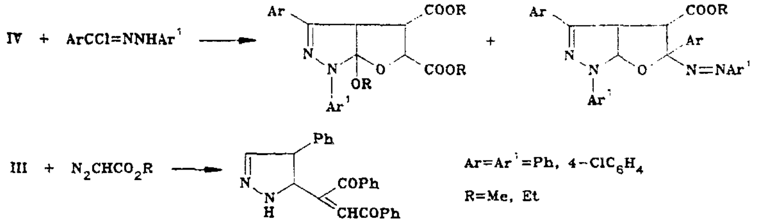
Nitrile oxides react with allyl ylides to give substituted furans and small amounts of oxazines, which result from [3+3]-cycloaddition of the ylide. The latter can be converted into the pyrrolidones by treatment with triethylamine [56].



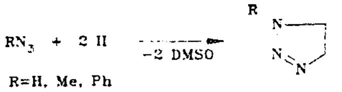
Unlike nitrile oxides, other 1,3-dipoles (nitrilimines) react cleanly with sulfur ylides to give the pyrazolines [55, 57]. The use of carbonyl-stabilized ylides in reactions with nitrilimines, generated from N-(α-chlorobenzylidene)-N'-phenylhydrazines, affords quantitative yields of α-diketones containing the pyrazoline ring [58].



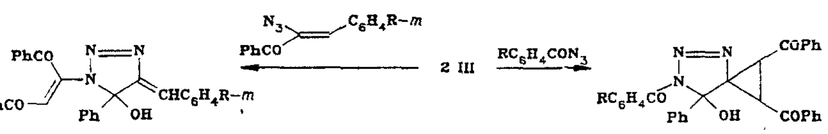
Mixtures of furopyrazolines were obtained on reacting similar nitrilimines with dimethyl (alkoxycarbonyl) methylides such as (IV). The product ratios and yields were dependent on the molar ratios of the reactants, an increase in the molar proportion of the nitrilimine favoring the formation of aryl-substituted product. Substituted pyrazolines are formed when the sulfonium benzoylmethylide (III) reacts with benzoyldiazomethane or diazoacetic ester [59].



The use of azides as 1,3-dipoles, with two molecules of dimethylsulfoxonium methylide, enables difficulty-accessible triazolines to be obtained [57, 59-61], but with dimethylbenzoylmethylide (III) acylic enamines are formed in preference to triazolines [59, 61]. Ethyl azidoformate, however, also reacts with benzoylmethylides to give triazolines [62].

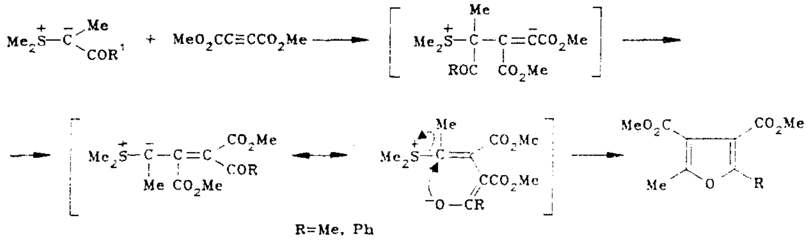


Benzoyl azides behave somewhat differently, reacting with the ylide (III) to give spirocyclopropyltriazolines [62]. A final example of the reactions of ylides with azides is the reaction of the ylide (III) with α- and β-azidovinyl ketones [63]:

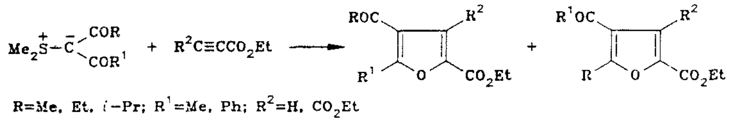


3.2. Reactions of Sulfonium Ylides with 1,3-Dipolarophiles

The 1,3-dipolarophiles used in reactions with sulfonium ylides are frequently activated acetylenes. The vigorous development of this area results from the high reactivity of the triple bond towards nucleophilic addition. For example, a method has been described for the synthesis of 3,4-di-(alkoxycarbonyl)furans by the reaction between sulfur acylmethylides and acetylenedicarboxylate esters [64]:

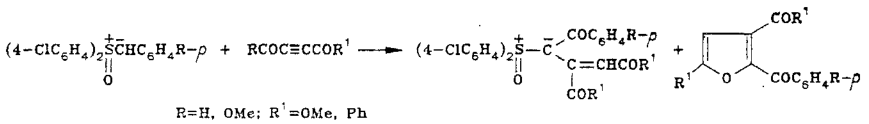


This reaction involves the initial formation of a 1,4-betaine, which is converted by 1,3-acyl migration of the acyl group into a new ylide, intramolecular cyclization of which results in closure of the furan ring. Diacylmethylides react similarly to acylmethylides with acetylenedicarboxylate esters, but the acyl group does not migrate [65, 66]. Ylides with different acyl groups ($R \neq R^1$) give mixtures of isomeric furans.

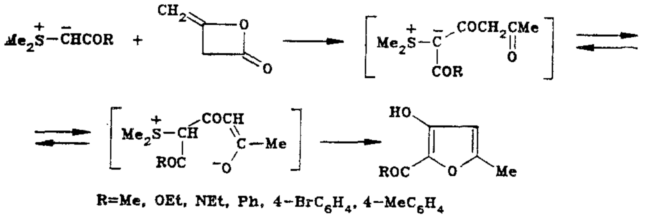


The ester carbonyl group of the ylide when R = OEt does not participate in cyclization. The formation of the two furans is assumed to occur via the intermediate formation of a betaine following attack of the carbanionic carbon on the triple bond. With a symmetrical acetylene, however (R = COOEt), the authors have put forward another mechanism in which the intermediate betaine is formed by attack of the oxygen of the carbonyl group in the acylmethylide on the acetylene.

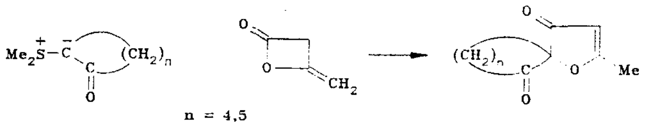
A similar reaction occurs with benzoylacetylenes. However, on reacting phenacylides with dibenzoylacetylenes, in addition to 2,3-diacylfurans, the sulfoxonium ylide is formed. When the reaction is carried out in the presence of catalytic amounts of copper acetylacetonate, only the diacylfuran is obtained, formation of the ylide being totally suppressed.



Ketene and phenyl isocyanate dimers are also active dipoles. Ketene dimers react readily with sulfonium ylides to give acylhydroxyfurans [68].

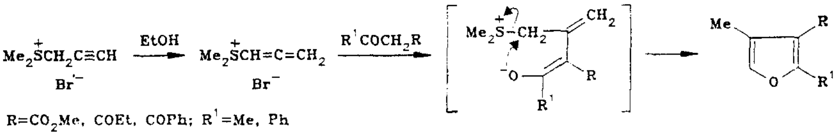


Sulfonium ylides react similarly with ketene dimer to give spiro-derivatives of oxodihydrofuran [69].



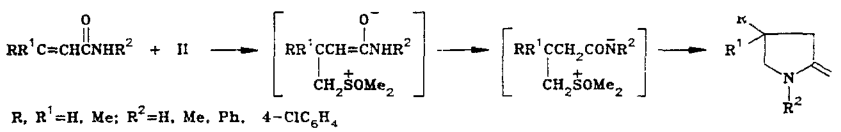
The reaction between dimethylsulfonium methylide (I) and phenyl isocyanate dimer affords 1,3-diphenylhydantoin, although in low yield [70]. The use of carbonyl-stabilized ylides also enables substituted hydantoins to be obtained [70].

A method has been reported for the synthesis of furans by the reaction between β-ketoester, β-ketosulfone, or diketone enolate anions and allenic sulfonium salts formed by rapid isomerization of an acetylenic sulfonium salt in ethanol solution [71]

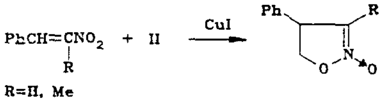

R=CO$_2$Me, COEt, COPh; R^1=Me, Ph

3.3. [1+4]-Cycloaddition

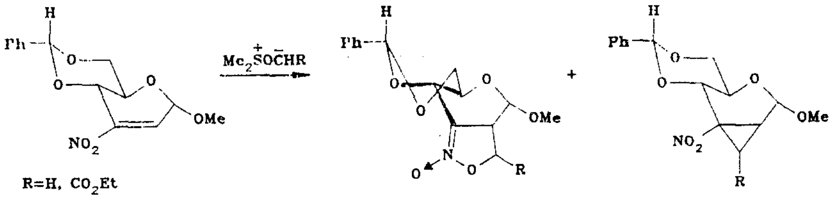
The most convenient and synthetically flexible method for the preparation of five-membered heterocycles is by [1+4]-addition of sulfonium ylides to compounds containing conjugated multiple bonds. For instance, cycloaddition of dimethylsulfoxonium methylide (II) to α,β-unsaturated carboxamides affords high yields of pyrrolidones [72].


R, R^1=H, Me; R^2=H, Me, Ph, 4-ClC$_6$H$_4$

When dimethylsulfoxonium methylide reacts with nitroolefins, catalyzed by CuI, isoxazoline N-oxides are formed [73]. It was assumed that Cu$^+$ coordinates with the betaine formed, facilitating the formation of the isoxazoline N-oxide.

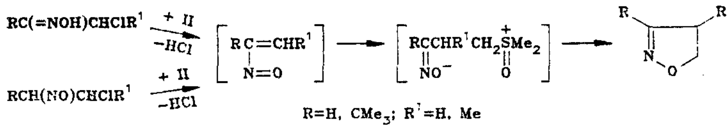

R=H, Me

The noncatalyzed addition of a sulfoxonium ylide to conjugated nitroolefins to give isoxazoline N-oxides has been studied with nitrosugars [74-76]:


R=H, CO$_2$Et

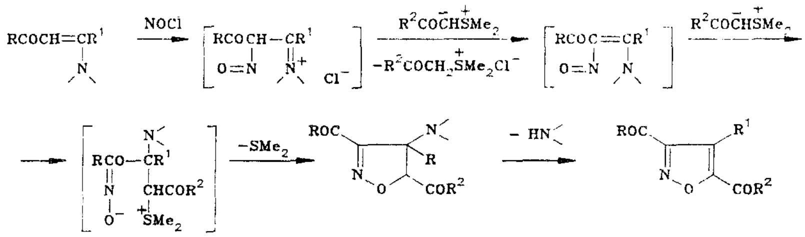
The reaction does not proceed cleanly, giving products of both [1+4]- and [1+2]-cycloaddition depending on the mode of attack of the ylide. Axial attack is preferred to equatorial attack, giving the [1+4]-cycloaddition product, whereas equatorial attack gives the nitrocyclopropane, i.e., the [1+2]-cycloaddition product.

The reaction of sulfonium ylides with chlorooximes, the precursors of conjugated nitrosocompounds, which can, like nitroolefins, function as electrophiles in these reactions has been studied [77-80]. It was found that the reaction between α-chlorooximes or α-nitrosyl chlorides and dimethylsulfoxonium methylide (II) affords, under certain conditions, the Δ^2-isoxazoline [77, 78].


R=H, CMe$_3$; R^1=H, Me

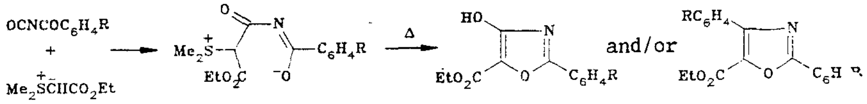
The behavior of keto-stabilized sulfonium ylides towards α-chlorooximes and nitrosyl chlorides has been examined [79]. Two reaction pathways are possible. Initial attack of the ylide on the chlorooxime or nitrosyl chloride affords a betaine, which may then either undergo β-elimination to give the α-methylenoxime, or intramolecular cyclization to give the Δ^2-isoxazoline. The factor governing the fate of the betaine is the basicity of the ylide. The mode of reaction of the betaine is also influenced by the configuration of the oximate anion, and the volume of the substituent on the α-carbon atom of the chlorooxime.

Unstable, highly reactive α-alkoxy-α-chloronitrosoethers and -esters, generated in situ by chloronitrosation of unsaturated ethers and esters, react with phenacylide to give isoxazolines, which on losing a molecule of alcohol are converted into the isoxazoles [79]. An interesting method for the synthesis of isoxazoles from enamines, nitrosyl chloride, and sulfonium ylides has been described [80]. It was found that the monoenamines of β-dicarbonyl compounds react with nitrosyl chloride to give α-nitrosochlorimines, which then react with the ylide, to give, after hydrolysis of the reaction mixture, the isoxazoles:



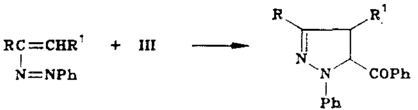
R=Me, OMe, Ph; R^1=H, Me; R^2=Ph, 4-MeC_6H_4

Oxazoles may be obtained by reacting sulfonium ylides with benzoyl isocyanate [81]. Dimethylsulfonium benzoylmethylide reacts similarly with thiobenzoyl isocyanate to give thiazoles. No intermediate was isolated in this case.



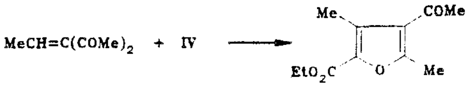
IV R=H, 4-Cl, 4-NO_2

The [1+4]-cycloaddition of sulfur ylides to unsaturated azo-compounds has been reported [82].



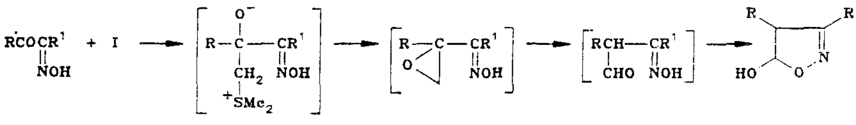
R, R^1=$(CH_2)_4$; R=Me, Ph; R^1=H,Ph

Payne [83] has reported an interesting [1+4]-cycloaddition to give the dihydrofuran on reacting (ethoxycarbonyl)dimethylsulfonium methylide (IV) with olefins containing two reactive groups, although it had previously been found that reactions of this type resulted in the formation of cyclopropanes. Further development of the method enabled other acetylacetone derivatives to be employed [84].



3.4. Other Reactions of Sulfonium Ylides Giving Five-Membered Heterocycles

Isoxazolines may be obtained either by [1+4]-cycloaddition, or by the reaction between sulfonium methylides and α-ketoximes [85].

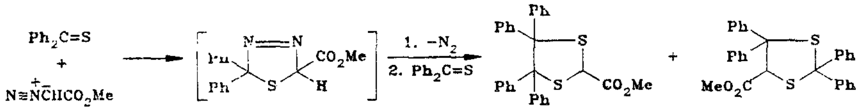


R=Me, Ph, 4-$MeOC_6H_4$; R^1=H, Me, Ph

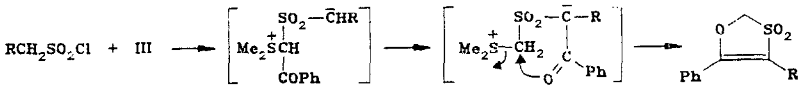
Instead of the expected 4-hydroxyoxazoline, the 5-hydroxyoxazoline was obtained. This is possible if the reaction proceeds via an intermediate epoxide, which in alkaline media is converted into the aldehyde. Cyclization of the latter gives the 5-hydroxyisoxazoline. Such rearrangements are known to occur in the presence of strong bases, but have never been reported in the synthesis of epoxides from ylides. It is likely that in this case there is assistance by the oximate anion. In some instances, isoxazolines are accompanied by isoxazoles.

An interesting property of dimethylsulfonium methylide is its ability to react with aromatic carbonium ions. For example, 1,2,3-trimethyl- and 1,2,3-triphenylcyclopropyl cations afford the 2,3,4-trisubstituted thiophenes, the sulfur atom of the ylide being incorporated in the heterocycle [86]. This is the first instance of the use of sulfur ylides as donors of the C—S fragment.

Another example of the formation of the C—S bond in heterocyclic systems is the reaction of diazoacetate with thiobenzophenone, which affords isomeric 1,3-dithiolanes in a ratio of 1:1 [87].

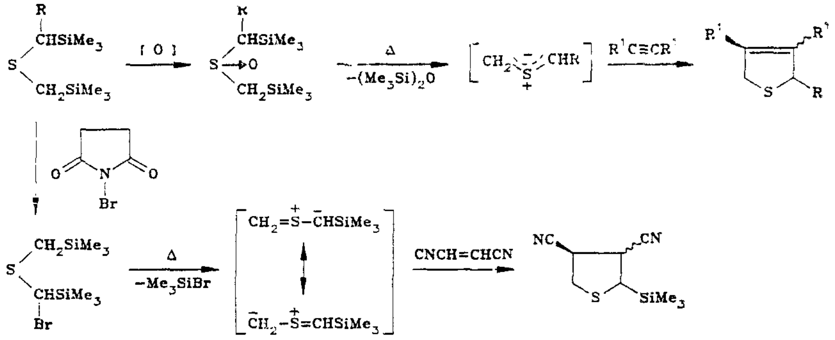


An unusual method of preparation of sulfur heterocycles is by addition of carbonyl-stabilized sulfur ylides to sulfonyl chlorides, followed by isomerization and ring closure of the intermediate betaine [88].



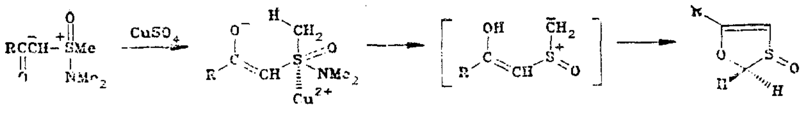
R=Me, Ph

A study has been made of the cycloaddition of thiocarbonyl ylides, readily obtained from bis(trimethylsilyl)-α-bromosulfides or sulfoxides followed by elimination of trimethylbromosilane or trimethyldisiloxane, to conjugated dipolarophiles (acetylenedicarboxylate, ethyl acrylate, diethyl fumarate, and N-phenylmaleimide), to give 3,4-disubstituted tetrahydrothiophenes and 2,5-dihydrothiophenes [89, 90].



R=H, Ph, CH_2Ph; $R^1=CO_2Et$

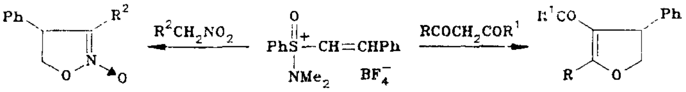
The reaction of keto-stabilized dimethylaminomethylsulfoxonium methylides with two equivalents of anhydrous copper sulfate in cyclohexane or benzene gives high yields of the 1,3-oxathiole 3-oxides [91].



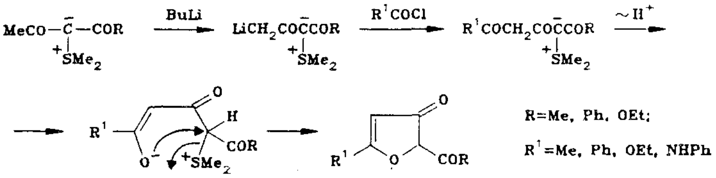
R=Me, Ph, CH_2Ph, $4-ClC_6H_4$, $4-NO_2C_6H_4$

The Cu^{2+} ion coordinates with the dimethylamino-group of the ylide, thereby promoting its elimination. The reaction proceeds via an S-stabilized carbonium ion, which then undergoes cyclization.

A convenient method for the preparation of five-membered heterocycles (dihydrofurans and isoxazoline N-oxides) is from vinylsulfoxonium salts and C-nucleophiles in the presence of base (sodium methoxide or triethylamine) [92].

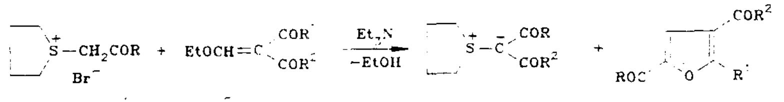

R=Me, R'=OEt; R=Ph, R'=OEt; R²=Me, Et, CO₂Me

Acylation of biscarbonyl-stabilized ylides, generated from the lithium derivatives of diketo-stabilized sulfur ylides, affords disubstituted furanones in near-quantitative yields [93].

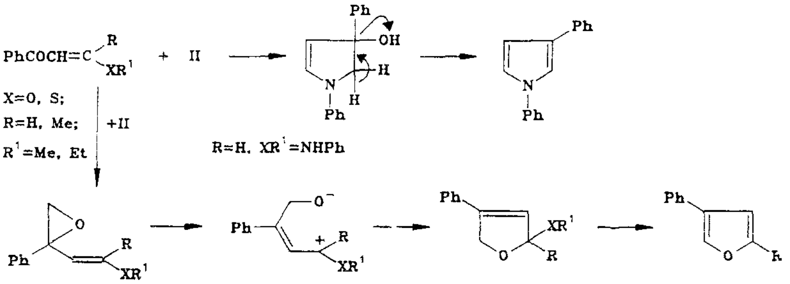

R=Me, Ph, OEt;
R'=Me, Ph, OEt, NHPh

The mechanism of this reaction involves the initial transfer of a proton from the methylene group to the ylide carbon atom, followed by ring-closure of the enolate anion and elimination of dimethyl sulfide.

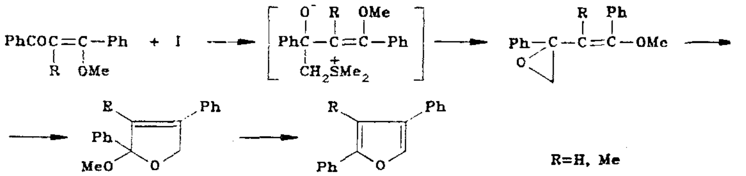
Noteworthy amongst the range of methods of synthesis of furans from sulfonium ylides is that involving the reaction of cyclic sulfonium ylides with ethoxydiacylethylenes in the presence of triethylamine to give 3,5-diacylfurans [94]. Thermolysis or photolysis of the intermediate vinylsulfonium ylides gives the acylfurans.


R=Me, OEt; R'=Me, Ph; R²=Me, OEt

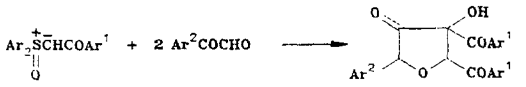
β-Heteroatomically substituted α,β-unsaturated ketones react with dimethylsulfoxonium methylide (II) to give substituted furans and pyrroles, albeit in low yields [95].


X=O, S;
R=H, Me;
R'=Me, Et
R=H, XR'=NHPh

The intermediate vinyl epoxide undergoes intramolecular ring fission to give the substituted furan or pyrrole, if the starting material is a β-aminovinyl ketone. Sulfonium methylides (I) react with enol ethers of β-diketones to give 2,4-disubstituted furans [96] via the intermediate epoxy compounds, which rearrange with elimination of methanol to give the furans. In some cases, instead of the furan, thiabenzene oxide was formed. The enol ethers of β-diketones such as acetylacetone, benzoylacetone, and dibenzoylmethane gave only C-methylated products, which considerably restricts the scope of this reaction.

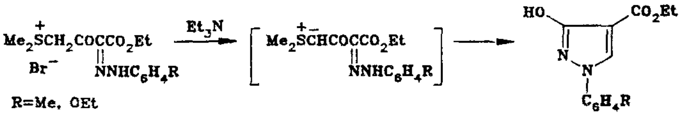

R=H, Me

Worthy of note is the method of preparation of tetrahydrofurans by the reaction of β-ketosulfoxonium ylides with glyoxals in the presence of catalytic amounts of copper acetylacetonate (II) [97].

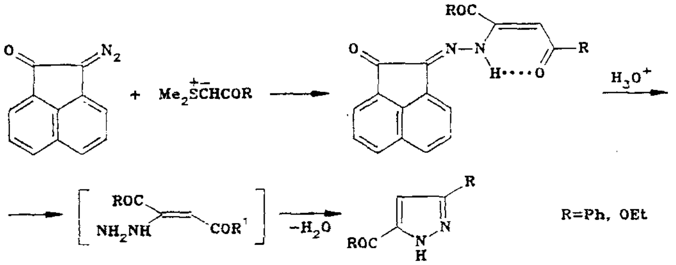


Ar = Ph, 4-ClC$_6$H$_4$; Ar^1 = Ph, 4-MeOC$_6$H$_4$; Ar^2 = Ph, 4-MeC$_6$H$_4$

The ylides obtained from the previously unknown arylhydrazono-substituted sulfonium salts are converted by intramolecular cyclization into 4-hydroxypyrazoles [98].



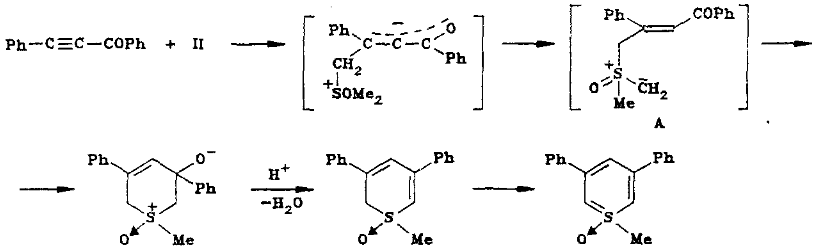
Carbonyl-stabilized ylides react with diazoacenaphthenes to give an adduct which on hydrolysis gives 3,5-disubstituted pyrazoles, although in low yields [99].



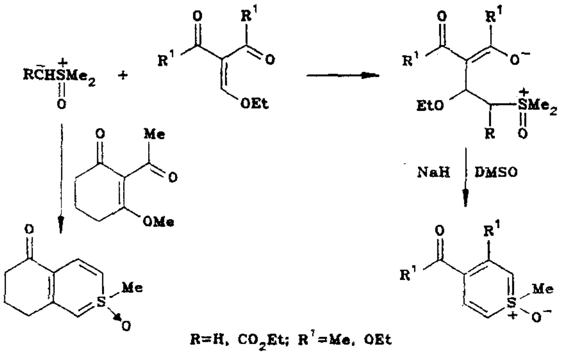
4. SYNTHESIS OF SIX-MEMBERED HETEROCYCLES AND MACROCYCLES

The use of sulfonium ylides has enabled six-membered heterocycles to be obtained which are difficult, or even impossible, to synthesize by other methods.

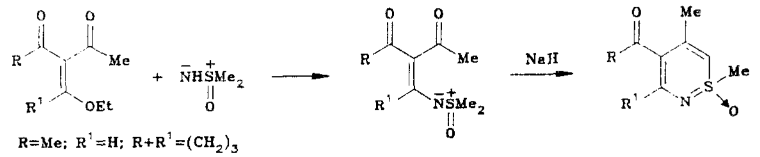
The greatest number of reports concern the synthesis of thiabenzene oxides. 3,5-Diphenylthiabenzene oxide has been obtained by the reaction of dimethylsulfoxonium methylide with phenylbenzoylacetylene [100]. Subsequently, alkyl- and arylacetylenes were employed successfully in this reaction [101].



Functionally substituted thiabenzene oxides can be obtained by using two equivalents of ylide [102]. In some instances, it was possible to isolate an intermediate stable allyl ylide (A), which on treatment with sodium hydride on DMSO was converted into the thiabenzene oxide [102]. Condensed thiabenzene oxides have been obtained by using cyclic β-diketones [84].

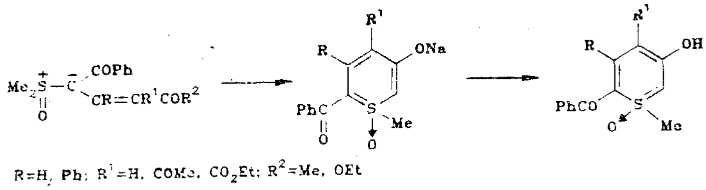


The same method may be used to synthesize six-membered heterocyclic systems with two heteroatoms, by using a sulfoxonium azomethinylide [102]:



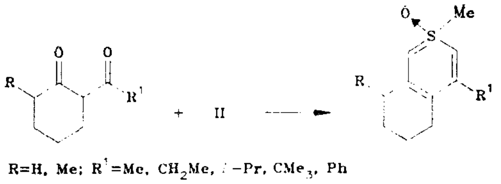
$R=Me; R^1=H; R+R^1=(CH_2)_3$

Thiabenzene oxides have also been obtained by cyclization of allylsulfonium salts by treatment with sodium methoxide in methanol [103, 104].



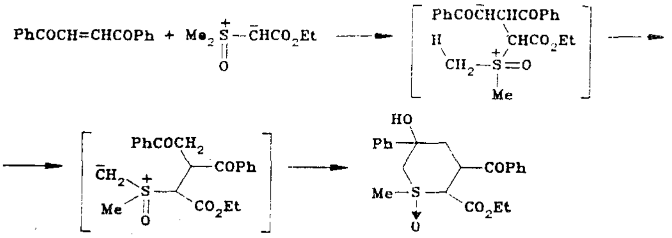
$R=H, Ph; R^1=H, COMe, CO_2Et; R^2=Me, OEt$

The reaction of β-diketones with a sulfoxonium methylide affords a bicyclic thiabenzene oxide [105]:

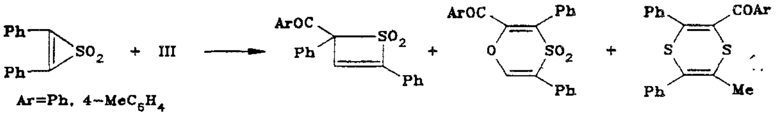


$R=H, Me; R^1=Me, CH_2Me, i-Pr, CMe_3, Ph$

A synthesis of an alicyclic sulfoxide has been reported which involves the reaction of dimethylsulfoxonium ethoxycarbonylmethylide with dibenzoylethylene [106]. This is, so far, the only example of the synthesis of an acyclic sulfoxide from a sulfonium ylide.



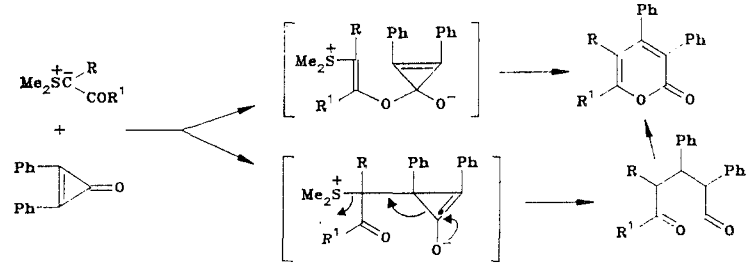
The reaction between diphenylthiirene dioxide and dimethylsulfonium benzoylmethylide (III) affords, in addition to thietane dioxide, two sulfur-containing six-membered heterocycles, an oxathiine dioxide and a dithiine [46].



$Ar=Ph, 4-MeC_6H_4$

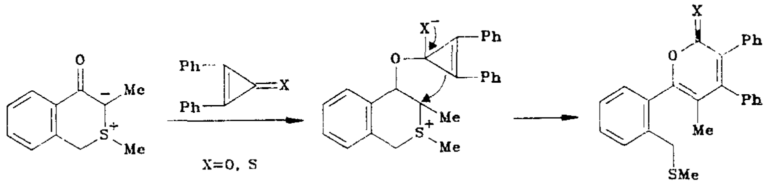
Many workers have employed diphenylcyclopropenone as the reactive electrophile, and have examined its behavior in reactions with relatively unreactive carbonyl-stabilized sulfonium ylides [107, 108] (see top of following page).

Hayashi and Nozaki [107] have discussed two possible mechanisms for the formation of pyrones. The first pathway consists in nucleophilic addition of the ylide to the cyclopropenone carbonyl group to give a betaine, followed by ring closure with elimination of dimethyl sulfide, and the second pathway postulates the formation of a 1,5-diketone as a possible intermediate. The formation of pyrones is unaffected by the extent of substitution of the ylide carbon atom, the disubstituted ylides (III) (R ≠ H) reacting with diphenylcyclopropene at ambient temperatures to give the pyrones.

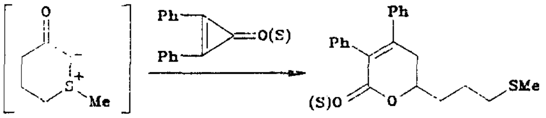


R=H, Me, Ph, Br; R^1=Me, OMe, Ph, 4-MeC$_6$H$_4$

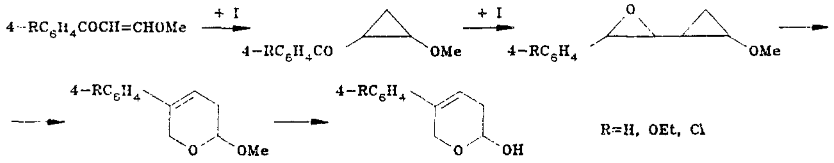
Up to the present time, the behavior of sulfonium ylides has mainly been considered in respect of acyclic ylides, the reactions of electrophiles with cyclic ylides forming the subject of only a few reports in view of the high lability of the latter compounds. The reactions of both diphenylcyclopropenones and cyclopropenethiones with cyclic sulfonium ylides have been reported. These reactions give rise to pyranone or pyranthione derivatives, respectively [109].



The unstable thiacyclohexanone ylide undergoes ring opening during the course of the reaction.



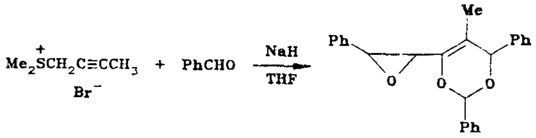
Sulfonium ylides are known to react with enones to give furans. In some instances, however, hydroxydihydropyrans are formed [96].



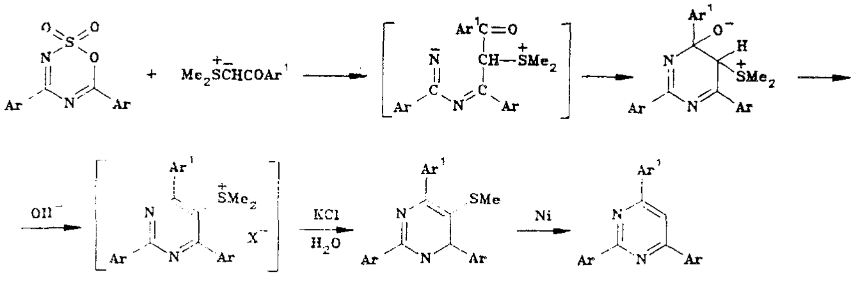
R=H, OEt, Cl

Initial attack of the ylide occurs at the β-position to give the cyclopropyl ketone, the second attack (at the carbonyl group) affording the cyclopropyl epoxide, which rapidly rearranges to the acetal. Hydrolysis of the latter affords the hydroxydihydropyran.

A reaction of ylides which has received considerable attention is that with aldehydes to give oxirans. Yoshimoto and Kishida, however, obtained an unexpected result [110], the reaction between dimethylsulfonium propynylmethylide and benzaldehyde affording a dioxen in addition to the oxiran.

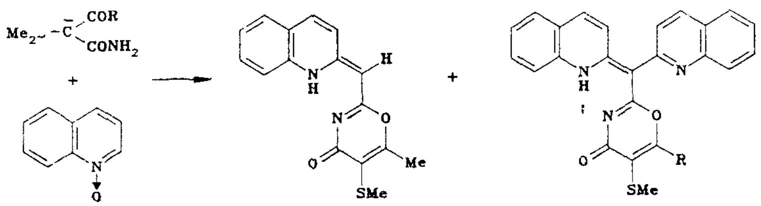


Carbonyl-stabilized ylides have been used with success for the synthesis of pyrimidines [111].



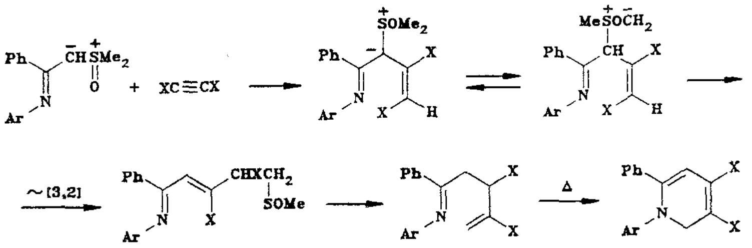
Ar=Ph, 4-MeC$_6$H$_4$; Ar^1=Ph, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-MeC$_6$H$_4$

An interesting reaction has been reported by Kinoshita et al. [112], the reaction between a sulfonium ylide and quinoline 1-oxide in the presence of acetyl chloride giving a mixture of products with one and two quinoline rings. The oxazine ring is formed by reaction of the reactive C$_2$ carbon atom of the quinoline oxide with the terminal methyl carbon of the acetyl group in the ylide. This method could prove extremely useful for the synthesis of biologically active compounds and drugs.



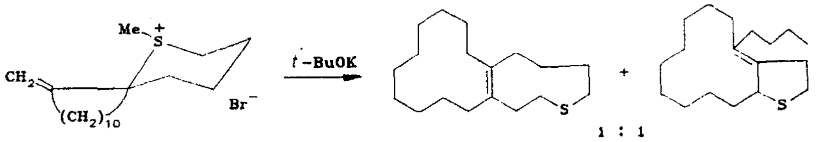
R=Me, Ph

The [2,3]-sigmatropic rearrangement of allylsulfoxonium ylides has been used to form new C—C bonds. Such rearrangements have been utilized successfully for the construction of the six-membered heterocycle dihydropyridine [113].

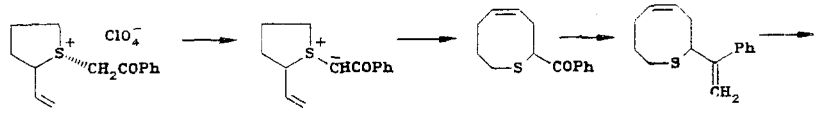


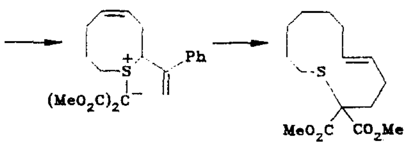
X=COPh, CO$_2$Et: Ar=Ph, 4-NO$_2$C$_6$H$_4$

[2,3]-Sigmatropic rearrangements are efficient methods for the synthesis of macrocyclic systems. For example, the stereospecific [2,3]-sigmatropic rearrangement of the ylide of a spirosulfonium salt by treatment with potassium tert-butoxide afforded thiabicyclononadecenes [114]. This is the first example of the use of a novel method of synthesis of difficulty-accessible cis-trans-(polymethylene)ethylenes with a bridging double bond.

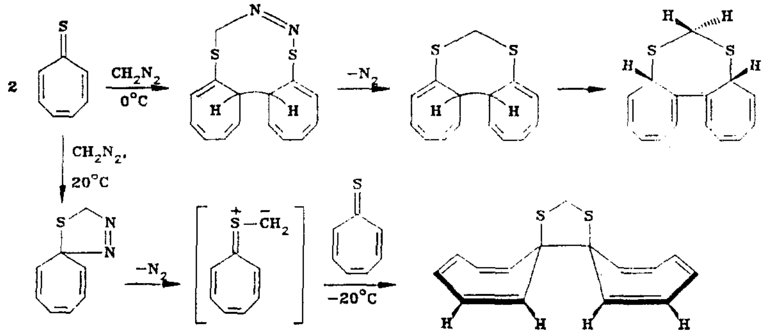


A modification of this method is the synthesis of sulfur macrocycles by successive [2,3]-sigmatropic shifts [115]:

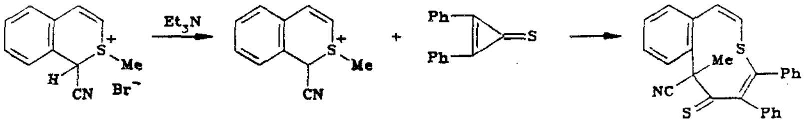




The reaction between tropothione and diazomethane in a ratio of 2:1 at 0°C results in the formation of a condensed heterocyclic system with two atoms of sulfur. When this reaction is carried out at 20°C, a thiadiazoline is first formed, which on losing nitrogen is converted into the ylide. The latter undergoes 1,3-dipolar cycloaddition to another molecule of thiotropolone to give the dispiro-1,3-dithiolane [42].

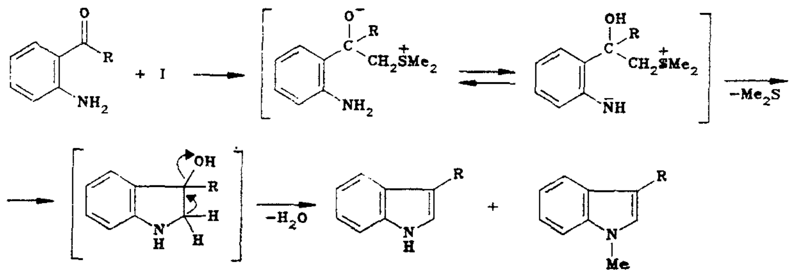


The reaction between cyclic sulfur ylides and diphenylcyclopropenethione results in ring enlargement [116]:



5. METHODS OF SYNTHESIS OF CONDENSED HETEROCYCLIC SYSTEMS

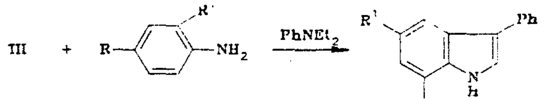
One of the earliest methods of synthesis of condensed heterocycles was the preparation of indoles by the reaction between dimethylsulfonium (I) or dimethylsulfoxonium methylide (II) and o-acylanilines [117, 118].



R=H, Me, Ph, COOH

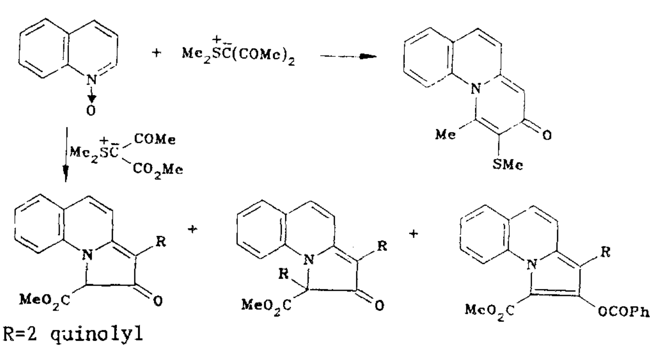
In addition to the indole, the N-methylindole is formed, apparently by N-methylation of the indole by the ylide (I).

There have been reports of the synthesis of substituted indoles by the reaction between aromatic amines and the ylide (III) [119-121]. Good yields are obtained.

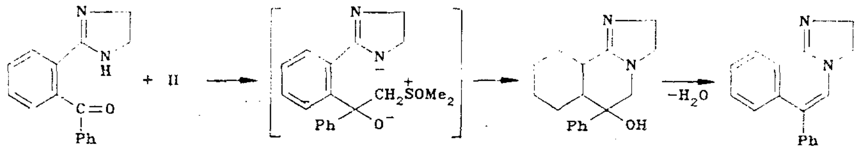


R=H, Me; R'=H, Me, F

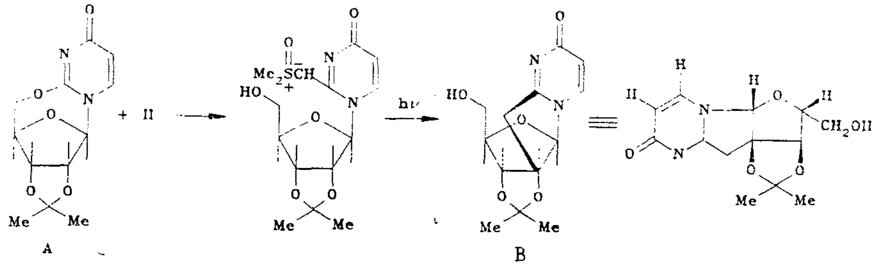
The reaction of carbonyl-stabilized ylides with quinoline 1-oxide in the presence of phenacyl chloride follows a different course, depending on the second substituent on the ylide carbon atom [122]. Thus, when R = COOMe, a mixture of isomeric ketoindolizines is formed, whereas with diacetylmethylide and quinoline oxide the products are totally different:



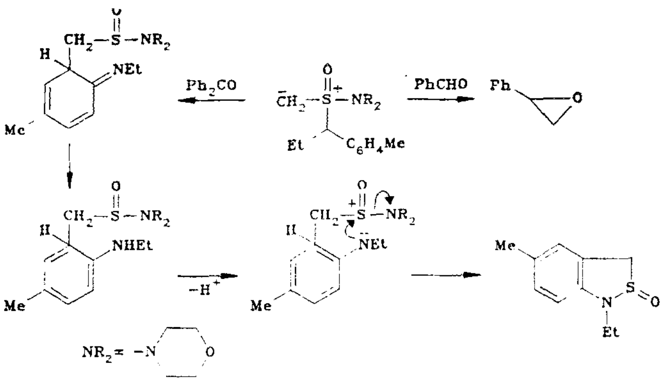
It has been shown that in some instances the imidazoline grouping may function as an amino-group, participating in ring closure on reaction with dimethylsulfoxonium methylide [123].



The reactions of sulfonium ylides have been successfully extended to naturally occurring compounds. For example, the nucleoside (A) on treatment with dimethylsulfoxonium methylide (II) is converted into a new ylide in quantitative yield. Photolysis of the latter gives the nucleoside (B) [124]:

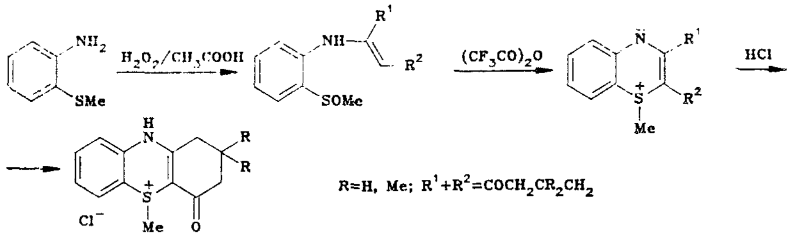


An unusual reaction of diaminosulfoxonium methylide with benzophenone has been reported [125]. Although the reaction of this ylide with benzaldehyde proceeds normally to give the phenyloxirane, with benzophenone the isothiazole is formed by intramolecular cyclization of the ylide with the benzophenone, in quantitative yield.

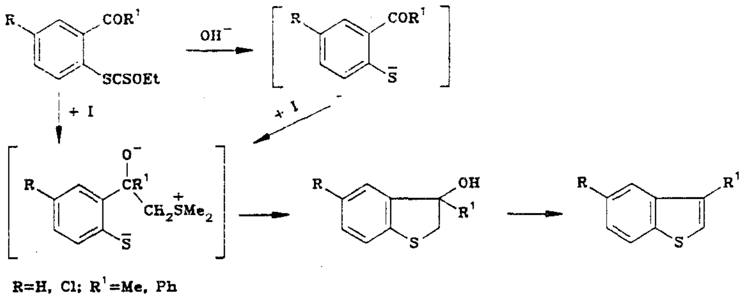


A possible mode of formation of the dihydrobenzisothiazole is as follows: a) intramolecular rearrangement of the ylide; b) proton transfer, accompanied by aromatization; and c) formation of the isothiazole in the presence of base. This mechanism was confirmed by Johnson and by Gassman. Johnson showed [24] that sulfoximinoylides react with carbonyl compounds to form the oxiranes, products of the attack of the N-alkyl group on the sulfur atom never being found. Gassman, however, found that [2,3]-sigmatropic rearrangement was the only reaction when N-phenylaminosulfonium salts were treated with base, no cyclization products of the ylide being obtained [126]. This reaction provides a promising route to dihydrobenzothiazoles.

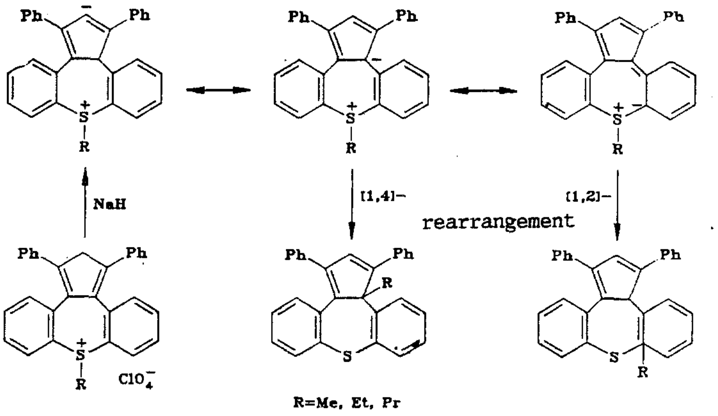
The synthesis of 1H-1,4-benzothiazines from cyclic ylides has been accomplished by cyclodehydration of sulfoxides [127].



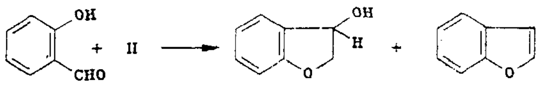
A novel method for the synthesis of benzothiophenes is similar to the synthesis of indoles, namely by reaction of aromatic o-ketothiophenols or their xanthates with dimethylsulfoxonium methylide [128]. Mercaptoketones give higher yields of the benzothiophene than the mercaptoxanthates.



A considerable advance in the chemistry of ylides was provided by the synthesis of the first stable ylide with the thiaazulene system, by deprotonation of thiaazulenium salts. An interesting property of the ylide is its ability to form thiaazulenium compounds by rearrangement [129]. The mode of rearrangement is governed by the volume of the substituent on the ylide sulfur atom. When R = Me, the reaction gives only the [1,4]-rearrangement product. Replacement of the methyl by more bulky substituents results in the additional formation of [1,2]-rearrangement products of the ylide, the proportion of this product increasing with the bulk of the substituent R. This reaction therefore provides an interesting preparative method for the introduction of alkyl groups into thiaazulenes.

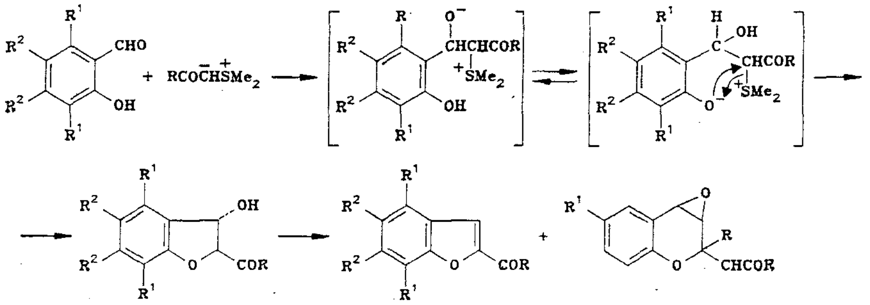


There have been many reports of the synthesis of benzofurans. Sulfonium ylides have been shown to react readily with aldehydes possessing a nucleophilic center close to the carbonyl group. For example, the ylide (II) reacts with salicylaldehyde to give a mixture of 3-hydroxy-2,3-dihydrobenzofuran and benzofuran [130].



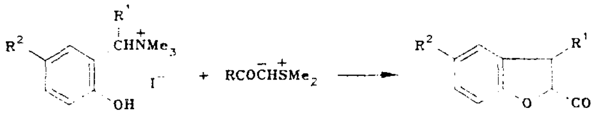
It was previously believed that the hydroxy compound was extremely labile, undergoing facile dehydration to benzofuran. It has, however, been shown [130] that the dihydrofuran is stable over a period of months at ambient temperatures. On distillation, or on heating an aqueous solution containing an acid catalyst, the dihydrofuran is readily converted into the furan. It was shown that o-hydroxyacetophenone reacts similarly.

A further development of this method consists in the preparative synthesis of acylbenzofurans from carbonyl-stabilized ylides. In some instances, in addition to benzofurans there were also formed small amounts of epoxychromans, which are the products of the addition of two molecules of the ylide to the aldehyde molecule [131].



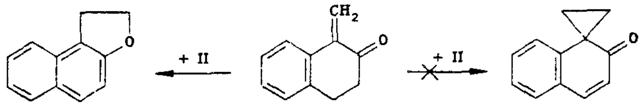
R=Ph, 4-MeC_6H_4; R^1=H, Me; R^2=H, Me, OH

A reaction with a similar mechanism to the above is that between carbonyl-stabilized sulfonium ylides and ammonium salts. When the starting material is an ammonium salt of β-naphthol, this reaction affords substituted dihydrobenzo- or dihydronaphthofurans [132].

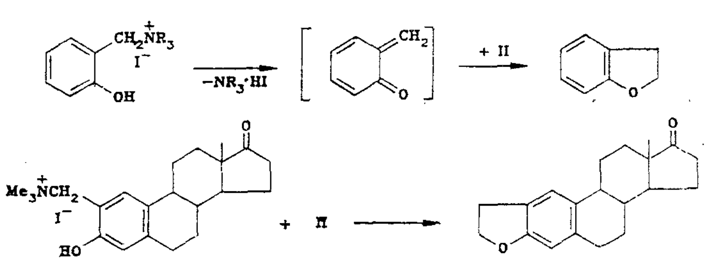


R=Me, OEt, Ph, 4-$NO_2C_6H_4$, 4-HOC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$; $R^1=R^2$=H, Me; R^1=Ph, R^2=Me; R^1=Me, R^2=H

The reaction between a sulfonium ylide and an α,β-unsaturated ketone containing a semicyclic double bond has given good yields of the dihydronaphthofuran, but no spiran ketone was found [133]. No reason for this behavior was given, but it may be that the decisive step in this reaction is the conversion of the intermediate betaine into the energetically more favored aromatic system.

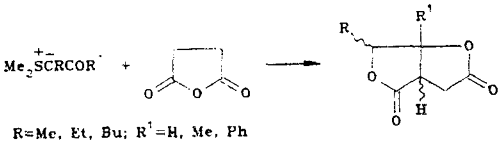


A dihydrofuran is also formed when the ylide (II) reacts with α,β-unsaturated ketones, generated in situ from the ammonium salts [134]. This method has been used to obtain steroids containing the dihydrofuran ring [134].

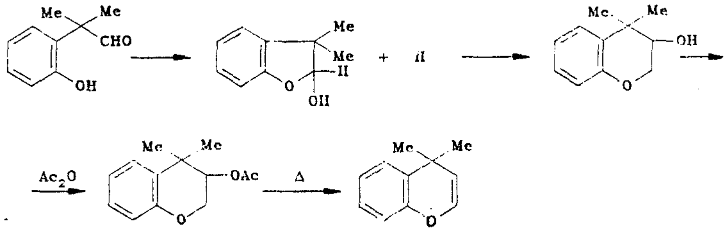


In contrast to the highly stable benzofurans, epoxybenzopyrenes undergo further reactions with cleavage of the oxirane fragment to give 6-substituted benzo[a]pyrenes [135].

It has been found that substitution of the α-hydrogen atom in the ylide results in a radical change in its reactivity [136]. For instance, the reaction between unsubstituted carbonyl-stabilized ylides and succinic anhydride affords new ylides, whereas α-substituted ylides give furofurans [136].



As already pointed out, the reaction between ylides and o-hydroxybenzaldehydes sometimes affords epoxychromans [131]. Using sulfur methylides, a synthesis of dimethylchromene has been developed [137].



As will be apparent from this review, sulfur ylides are highly efficient nucleophilic reagents which have been successfully employed in organic syntheses, especially those of heterocyclic systems, enabling otherwise difficulty-accessible, or even otherwise inaccessible, heterocyclic compounds with one, two, or three heteroatoms in the ring to be obtained. The reactions of sulfonium ylides with natural compounds (epoxidation, formation of isoxazoline N-oxides, dihydrofurans, etc.) are worthy of note, as are the numerous reactions of sulfur ylides resulting in the formation of heterocyclic systems which are stereoselective and sterically controlled.

The chemistry of sulfonium ylides has been investigated extensively, and is now of independent interest. The chemistry of sulfur ylides has formed the subject of several reviews [138-140], chapters in the monograph of Johnson [141] and in the book General Organic Chemistry [142], as well as in the monograph of Trost and Melvin [143], in which some theoretical aspects of the formation of the ylide bond and their experimental confirmation are discussed. Also given are the principal methods for the synthesis of sulfur ylides, together with their physicochemical characteristics, reactions, and applications in organic synthesis.

There is, as yet, no generally accepted nomenclature for the ylides of groups V and VI elements of the periodic system. That most frequently used is based on the methylide, with all the substituting groups indicated, for example dimethylsulfonium methylide $\mathrm{Me_2\overset{+}{S}\overset{-}{C}H_2}$ (I), dimethylsulfoxonium methylide $\mathrm{Me_2\overset{+}{S}O\overset{-}{C}H_2}$ (II), dimethylsulfonium benzoylmethylide $\mathrm{Me\overset{+}{S}\overset{-}{C}HCOPh}$ (III), etc.

The potentialities of sulfur ylides both from the theoretical and practical points of view are far from exhausted, and further studies in this area hold promise.

LITERATURE CITED

1. A. W. Johnson and R. B. La Count, Chem. Ind., No. 4, 1440 (1958).
2. A. W. Johnson and R. B. La Count, J. Am. Chem. Soc., 83, 417 (1961).
3. V. Franzen, and H.-E. Driessen, Tetrahedron Lett., No. 15, 661 (1962).
4. E. D. Corey and M. Chaykowsky, J. Am. Chem. Soc., 84, 867 (1962).
5. E. D. Corey and M. Chaykowsky, J. Am. Chem. Soc., 84, 3782 (1962).
6. E. D. Corey and M. Chaykowsky, J. Am. Chem. Soc., 87, 1353 (1965).
7. V. Franzen and H.-E. Driessen, Chem. Ber., 96, 1881 (1963).
8. A. W. Johnson, V. J. Hruby, and J. S. Williams, J. Am. Chem. Soc., 86, 917 (1964).
9. E. D. Corey and W. Oppolzer, J. Am. Chem. Soc., 86, 1899 (1964).

10. E. D. Corey, M. Jautelat, and W. Oppolzer, Tetrahedron Lett., No. 24, 2325 (1967).
11. K. W. Ratts and A. N. Yao, J. Org. Chem., 31, 1185 (1966).
12. B. M. Trost, J. Am. Chem. Soc., 89, 138 (1967).
13. M. Takaku, Y. Hayashi, and H. Nozaki, Tetrahedron, 26, 1243 (1970).
14. A. W. Johnson and R. T. Amel, Tetrahedron Lett., No. 8, 819 (1966).
15. A. W. Johnson and R. T. Amel, J. Org. Chem., 34, 1240 (1969).
16. J. L. Pierre, R. Guidotty, and P. Arnaud, Bull. Soc. Chim. France, No. 4, 1439 (1967).
17. G. B. Payne, J. Org. Chem., 33, 3517 (1968).
18. C. W. Schimelpfenig and J. A. Ruder, Chem. Eng. Data, 14, 133 (1969).
19. K. K. Andersen, J. Chem. Soc. Chem. Commun., No. 18, 1051 (1971).
20. K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, J. Org. Chem., 35, 706 (1970).
21. B. M. Trost and R. F. Hammen, J. Am. Chem. Soc., 95, 962 (1973).
22. C. R. Johnson, E. R. Janiga, and M. Haake, J. Am. Chem. Soc., 90, 3890 (1968).
23. C. R. Johnson, M. Haake, and C. W. Schroeck, J. Am. Chem. Soc., 92, 6594 (1970).
24. C. R. Johnson and P. R. Rogers, J. Org. Chem., 38, 1793 (1973).
25. C. R. Johnson and C. W. Schroeck, J. Am. Chem. Soc., 95, 7418 (1973).
26. C. R. Johnson, C. W. Schroeck, and J. R. Shanklin, J. Am. Chem. Soc., 95, 7424 (1973).
27. C. R. Johnson and C. W. Schroeck, J. Am. Chem. Soc., 90, 6852 (1968).
28. C. R. Johnson and L. J. Pepoy, J. Org. Chem., 37, 671 (1972).
29. C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, J. Am. Chem. Soc., 93, 3771 (1971).
30. M. J. Bogdanovizc and B. M. Trost, Tetrahedron Lett., No. 10, 887 (1972).
31. P. Bravo and G. Gaviraghi, Gazz. Chim. Ital., 104, 1307 (1974).
32. P. Bravo and G. Gaviraghi, J. Heterocycl. Chem., 14, 37 (1977).
33. K. Tokuno, F. Miyoshi, J. Arata, J. Itatani, J. Arakawa, and T. Ohashi, Yakugaku Zasshi, 98, 1005 (1978); Chem. Abstr., 90, 6195 (1978).
34. P. Cazeau and B. Muckensturm, Tetrahedron Lett., No. 17, 1493 (1977).
35. M. E. Garst and A. T. Johnson, Tetrahedron Lett., 21, 4811 (1980).
36. M. E. Garst, J. Org. Chem., 44, 1578 (1979).
37. O. Tsuge and I. Shinkai, Bull. Chem. Soc. Jpn., 43, 3514 (1970).
38. E. D. Corey and S. Nozoe, J. Am. Chem. Soc., 85, 3527 (1963).
39. G. Drefahl, K. Ponsold, and H. Schick, Chem. Ber., 97, 3529 (1964).
40. R. S. Tewari, A. K. Awasthi, and A. Awasthi, Synthesis, No. 4, 330 (1983).
41. C. R. Johnson and J. P. Lockard, Tetrahedron Lett., No. 48, 4589 (1971).
42. R. Huisgen, C. Fulka, I. Kalwinsch, Xingua Li, G. Mloston, J. Morgan, and A. Probste, Bull. Soc. Chim. Belges, 93, 511 (1984).
43. R. M. Kellog, M. Noteboom, and J. K. Kaiser, J. Org. Chem., 40, 2573 (1975).
44. Xigya Li and R. Huisgen, Tetrahedron Lett., No. 23, 4181 (1983).
45. Y. Hayashi, T. Akazama, K. Yamamoto, and R. Oda, Tetrahedron Lett., No. 21, 1781 (1971).
46. Y. Hayashi, H. Nakamura, and H. Nozaki, Bull. Chem. Soc. Jpn., 46, 667 (1973).
47. M. Hory, T. Kataoka, H. Shimizu, and M. Okitsu, Heterocycles, 16, 721 (1981).
48. K. Okuma, J. Tanaka, S. Kaji, and H. Ohta, J. Org. Chem., 48, 5133 (1983).
49. M. Vaultier, R. Danion-Bougot, D. Danion, J. Hamelin, and R. Carrie, Tetrahedron Lett., No. 22, 1923 (1973).
50. M. Vaultier, R. Danion-Bougot, D. Danion, J. Hamelin, and R. Carrie, J. Org. Chem., 40, 2990 (1975).
51. U. K. Nadir and V. K. Koul, Synthesis, No. 7, 554 (1983).
52. A. Umani-Ronchi, P. Bravo, and G. Gaudiano, Tetrahedron Lett., No. 29, 3477 (1966).
53. P. Bravo, G. Gaudiano, and A. Umani-Ronchi, Chim. Ind., 49, 286 (1967).
54. P. Bravo, G. Gaudiano, and A. Umani-Ronchi, Gazz. Chim. Ital., 97, 1664 (1967).
55. G. Gaudiano, P. P. Ponti, and A. Umani-Ronchi, Gazz. Chim. Ital., 98, 48 (1968).
56. Y. Nakada, T. Hata, C. Tamura, T. Iwaoka, M. Kondo, and J. Ide, Tetrahedron Lett., 22, 473 (1981).
57. G. Gaudiano, A. Umani-Ronchi, P. Bravo, and M. Acampora, Tetrahedron Lett., No. 2, 107 (1967).
58. Y. Hayashi and R. Oda, Tetrahedron Lett., No. 11, 853 (1969).
59. Y. Hayashi, T. Watanabe, and R. Oda, Tetrahedron Lett., No. 8, 606 (1970).
60. G. Gaudiano, C. Ticozzi, A. Umani-Ronchi, and P. Bravo, Gazz. Chim. Ital., 97, 1411 (1967).
61. E. Van Loock, G. L'abbe, and G. Smets, J. Org. Chem., 36, 2520 (1971).
62. E. Van Loock, G. L'abbe, and G. Smets, Tetrahedron, 28, 3061 (1972).
63. G. L'abbe, G. Mathys, and S. Toppet, Chem. Ind., No. 6, 278 (1975).

64. M. Higo and T. Mukaiyama, Tetrahedron Lett., No. 29, 2565 (1970).
65. M. Takaku, Y. Hayashi, and H. Nozaki, Tetrahedron Lett., No. 25, 2053 (1969).
66. H. Hayashi, M. Kobayashi, and H. Nozaki, Tetrahedron, 26, 4353 (1970).
67. M. Takebayashi, T. Kitashoju, F. Nagaoka, and H. Ueda, Kinki Daigaku Rikogabubu Kenkyu Hikoku, No. 16, 25 (1981); Chem. Abstr., 96, 203646 (1981).
68. H. Takei and T. Mukaiyama, Bull. Chem. Soc. Jpn., 43, 3607 (1970).
69. T. Mukaiyama, M. Higo, and T. Sacashita, Tetrahedron Lett., No. 40, 3697 (1971).
70. T. Mukaiyama, M. Higo, and H. Takei, Bull. Chem. Soc. Jpn., 43, 2566 (1970).
71. J. K. Batty, P. D. Howes, and C. J. M. Stirling, J. Chem. Soc., Chem. Commun., No. 11, 534 (1971).
72. H. König, H. Metzger, and K. Sulert, Chem. Ber., 98, 3712 (1965).
73. M. Clagett, A. Gooch, P. Graham, N. Holy, B. Mains, and J. Strunk, J. Org. Chem., 41, 4043 (1976).
74. T. Sakakibara and R. Sudoh, J. Chem. Soc. Chem. Commun., No. 1, 7 (1977).
75. T. Sakakibara, R. Sudoh, and T. Nakagawa, Bull. Chem. Soc. Jpn., 51, 1189 (1978).
76. T. Sakakibara and R. Sudoh, Bull. Chem. Soc. Jpn., 51, 1193 (1978).
77. P. Bravo, G. Gaudiano, C. Ticozzi, and A. Umani-Ronchi, J. Chem. Soc. Chem. Commun., No. 21, 1311 (1968).
78. P. Bravo, G. Gaudiano, C. Ticozzi, and A. Umani-Ronchi, Gazz. Chim. Ital., 99, 549 (1969).
79. P. Bravo, G. Gaudiano, P. P. Ponti, and C. Ticozzi, Tetrahedron, 28, 3485 (1972).
80. P. Bravo and C. Ticozzi, Gazz. Chim. Ital., 105, 91 (1975).
81. O. Tsuge, A. Sakai, and M. Tashiro, Tetrahedron, 29, 1983 (1973).
82. P. Dalla Croce, Ann. Chim., 63, 895 (1973).
83. G. B. Payne, J. Org. Chem., 32, 3351 (1967).
84. Y. Tamura, H. Taniguchi, T. Miyamoto, N. Tsunekawa, and M. Ikeda, J. Org. Chem., 39, 3519 (1974).
85. P. Bravo, G. Gaudiano, and C. Ticozzi, Gazz. Chim. Ital., 102, 395 (1972).
86. B. M. Trost, R. C. Atkins, and L. Hoffmann, J. Am. Chem. Soc., 95, 1285 (1973).
87. I. Kalvinsch and R. Huisgen, Tetrahedron Lett., No. 40, 3941 (1981).
88. H. Nozaki, M. Takaku, Y. Hayashi, and K. Kondo, Tetrahedron, 24, 6563 (1968).
89. J. Terao, M. Tanaka, M. Imai, and K. Achiva, Tetrahedron Lett., No. 25, 3011 (1985).
90. M. Aono, C. Hyodo, J. Terao, and K. Achiva, Tetrahedron Lett., No. 34, 4039 (1986).
91. C. R. Johnson and P. E. Rogers, J. Org. Chem., 38, 1798 (1973).
92. C. R. Johnson, J. Lockard, and E. Kennedy, J. Org. Chem., 45, 264 (1980).
93. M. Yamamoto, J. Chem. Soc., Perkin Trans. 1, No. 16, 1688 (1976).
94. M. Watanabe, M. Baba, T. Kinoshita, and S. Furukawa, Chem. Pharm. Bull., 24, 2421 (1976).
95. T. Nishio, M. Sugawara, and J. Omore, J. Heterocycl. Chem., 16, 815 (1979).
96. C. M. Harris, J. C. Cleary, and T. M. Harris, J. Org. Chem., 39, 72 (1974).
97. M. Takebayashi, H. Matsuji, and J. Hirata, Kinki Daigaku Rikogabubu Kenkyu Hikoku, No. 17, 33 (1982); Chem. Abstr., 97, 181389 (1982).
98. M. O. Lozinskii, S. N. Kukota, V. N. Bondar, and P. S. Pel'kis, Zh. Org. Khim., 9, 216 (1973).
99. O. Tsuge and M. Koga, Org. Prep. Proc. Int., 7, 173 (1975).
100. A. B. Hortmann, J. Am. Chem. Soc., 87, 4972 (1965).
101. A. B. Hortmann and R. L. Harris, J. Am. Chem. Soc., 93, 2471 (1971).
102. Y. Tamura, T. Miyamoto, H. Taniguchi, M. Tsunekawa, and M. Ikeda, J. Org. Chem., 39, 3519 (1974).
103. M. Watanabe, T. Kinoshita, and S. Furukawa, Chem. Pharm. Bull., 23, 258 (1975).
104. Y. Kishida and J. Ide, Chem. Pharm. Bull., 15, 360 (1967).
105. B. Holt, J. Howard, and P. A. Lowe, Tetrahedron Lett., No. 56, 4937 (1969).
106. H. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, Tetrahedron, 23, 545 (1967).
107. Y. Hayashi and H. Nozaki, Tetrahedron, 27, 3085 (1971).
108. T. Eicher, E. Angerer, and A.-M. Hansen, Liebigs Ann., 746, 102 (1971).
109. K. Tanaka, Y. Hayashi, and A. Kaji, Phosph. Sulf., 16, 201 (1983).
110. M. Yoshimoto and Y. Kishida, Chem. Pharm. Bull., 18, 2518 (1970).
111. S. Ueda, Y. Hayashi, and R. Oda, Tetrahedron Lett., No. 56, 4967 (1969).
112. T. Kinoshita, T. Onoue, M. Watanabe, and S. Furukawa, Chem. Pharm. Bull., 28, 795 (1980).
113. R. Faragher, T. L. Gilchrist, and I. W. Southon, Tetrahedron Lett., No. 42, 4113 (1979).
114. V. Cere, C. Paolucci, E. Sandri, and A. Fava, J. Chem. Soc., Chem. Commun., No. 16, 755 (1980).

115. E. Vedejs and J. P. Hagen, J. Am. Chem. Soc., 97, 6878 (1965).
116. M. Hory, T. Kataoka, H. Simizu, K. Marita, S. Ohno, and H. Aoki, Chem. Lett., No. 9, 1109 (1974).
117. P. Bravo, G. Gaudiano, and A. Umani-Ronchi, Tetrahedron Lett., No. 9, 679 (1969).
118. P. Bravo, G. Gaudiano, and A. Umani-Ronchi, Gazz. Chim. Ital., 100, 652 (1970).
119. H. Junjappa, Synthesis, No. 12, 799 (1975).
120. P. G. Gassman, T. J. Van Bergen, D. P. Gilbert, and B. W. Cue, J. Am. Chem. Soc., 96, 5495 (1974).
121. P. G. Gassman and T. J. Van Bergen, J. Am. Chem. Soc., 96, 5508 (1974).
122. M. Watanabe, M. Kodera, T. Kinoshita, and S. Furukawa, Chem. Pharm. Bull., 23, 2598 (1975).
123. M. Chaykovsky, L. Benjamin, R. I. Fryer, and W. Metlesics, J. Org. Chem., 35, 1178 (1970).
124. T. Kunieda and B. Witkop, J. Am. Chem. Soc., 91, 7752 (1969).
125. K. Okuma, N. Higuchi, H. Ohta, and M. Kobayashi, Chem. Lett., No. 12, 1503 (1980).
126. P. G. Gassmann and G. D. Gruetzmacher, J. Am. Chem. Soc., 96, 5487 (1974).
127. T. L. Gilchrist and G. M. Iskander, J. Chem. Soc. Perkin Trans. 1, No. 3, 831 (1982).
128. P. Bravo, G. Gaudiano, and M. G. Zubiani, J. Heterocycl. Chem., 7, 967 (1970).
129. M. Nori, T. Kataoka, H. Shimizu, and M. Okitsu, Tetrahedron Lett., 21, 4287 (1980).
130. B. Holt and P. A. Lowe, Tetrahedron Lett., No. 7, 683 (1966).
131. P. Bravo, G. Gaudiano, and C. Ticozzi, Gazz. Chim. Ital., 103, 95 (1973).
132. L. Cadona and P. Dalla Croce, Synthesis, No. 12, 800 (1976).
133. E. Breuer and D. Melumad, Tetrahedron Lett., No. 23, 1875 (1969).
134. H.-G. Lehmann, Tetrahedron Lett., No. 5, 607 (1968).
135. M. S. Newman and Lee Len-Fang, J. Org. Chem., 39, 1446 (1974).
136. T. Mukaiyama, K. Hagio, H. Takei, and K. Saigo, Bull. Chem. Soc. Jpn., 44, 161 (1971).
137. M. C. Sacquet, B. Graffe, and P. Maitte, Tetrahedron Lett., 43, 4453 (1972).
138. E. Block and M. Haake, Organic Compounds of S, Se, Te, 4, 78 (1977).
139. R. Huisgen, C. Fulka, and Y. Kalwinsch, Bull. Soc. Chim. Belges, 93, 511 (1984).
140. Yu. G. Gololobow, A. N. Nesmejanov, V. P. Lysenko, and I. E. Boldeskul, Tetrahedron, 43, 2609 (1987).
141. A. Johnson, The Chemistry of Ylides [Russian translation], Mir, Moscow (1969), pp. 324-391.
142. K. R. Johnson, in: General Organic Chemistry [D. Barton and U. D. Ollis (eds.)] [Russian translation], Khimiya, Moscow (1983), Vol. 5, pp. 403-417.
143. B. M. Trost and L. S. Melvin, Sulfur Ylides, Acad. Press, New York (1975).