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The Chemistry of Stabilised Sulphonium Ylides

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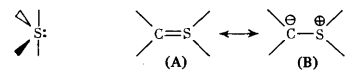
The review is devoted to the chemistry of stabilised sulphonium ylides, i.e. ylides with substituents at the carbanionic carbon atom capable of delocalising its negative charge. The physical properties of compounds of this class are examined and the methods of synthesis of stabilised sulphonium ylides, their rearrangements, and their reactions with electrophiles and nucleophiles are described. The structures and reactivities of the complexes of stabilised sulphonium ylides with transition metals and their organometallic derivatives are considered. The practical applications of the stabilised sulphonium ylides are indicated.
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I. INTRODUCTION

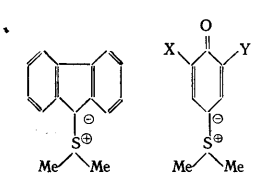
The organic chemistry of sulphur ylides is one of the most vigorously developing branches of organic chemistry. Ylides are compounds in which a negatively charged carbon atom is linked directly to a heteroatom carrying a positive charge[1]. There is at present no systematic nomenclature of sulphur ylides, but the majority of investigators regard them, on Johnson's suggestion[1], as derivatives of the hypothetical sulphurane SH_4. Hence one can consider two classes of sulphuranes: σ-sulphuranes with four σ-bonds and an unshared electron pair, and π-sulphuranes (ylides) having two σ-bonds, one π-bond, and an unshared electron pair. The structure of π-sulphuranes can be described in terms of resonance between ylene (A) and ylide (B) structures:



σ-sulphurane π-sulphurane

In order to avoid ambiguity in the names of σ- and π-sulphuranes, in the present review we shall use the suffix "yl" in the names of the former and the suffix "ylidene" in those of the latter. Thus a substituent containing tetracoordinate sulphur will be referred to as sulphuranyl and one with tricoorindate sulphur will be called sulphuranylidene.

The first representatives of stable σ-sulphuranes having electronegative substituents at the sulphur atom have been obtained recently by Martin and coworkers[2-4]. The first stable π-sulphurane is believed to be dimethylsulphuranylidenefluorene (I),[1,5] which was synthesised[6] approximately 50 years ago. However, there is no doubt that the thioniaquinones (II), synthesised much earlier, belong to this class[7,8]:



(I) (II)

X = Br or NO_2; Y = Br, NO_2, or Me.

Up to the beginning of the 1960's, the chemistry of π-sulphuranes was hardly investigated and this class of compounds became the subject of continued attention by investigators only after the brilliant research of Corey[9] and Franzen[10,11] undertaken in an endeavour to extent the Wittig reaction to sulphur ylides.

At the present time there are a series of reviews in the literature on the chemistry of sulphur ylides[1,4,5,12-25], among which only one has been translated into Russian[1]. However, they are devoted not only to sulphonium ylides, among which attention is concentrated on the non-stabilised ylides, but also to many related compounds, for example sulphoxides, sulphilimines, oxosulphonium ylides, sulphenes, sulphines, etc., which made it impossible to cover sufficiently fully the chemistry of sulphonium ylides.

This review is devoted to the chemistry of stabilised sulphonium ylides, i.e. ylides containing electronegative substituents at the carbanionic carbon atom capable of delocalising its negative charge. The decrease of the nucleophilicity of the carbanionic carbon atom in ylides leads to an appreciable alteration of their chemical properties compared with unstabilised sulphonium ylides, which makes it possible to regard the chemistry of stabilised sulphonium ylides as an entirely independent branch of organic chemistry.

II. PHYSICAL PROPERTIES

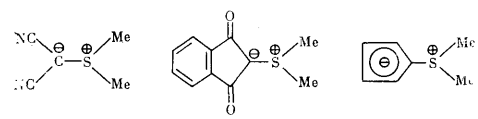
The main question to which investigators turned their attention in the study of the physical properties of sulphonium ylides was that of the nature of the ylide linkage. Initially the majority of investigators assumed that the *d* orbitals of sulphur are effectively involved in the stabilisation of the negative charge on the carbanion via $p_\pi-d_\pi$ bonding[1,18,19] and it was believed that the $p_\pi-d_\pi$ bonding is favoured by the presence of a positive charge on the sulphur atom of the ylide or of strongly electron-accepting substituents linked to the sulphur atom or the α-carbon atom[26-28]. In relation to the simplest sulphonium ylide SH_2CH_2, the problem of the involvement of the 3*d* orbital of sulphur in the formation of the C–S ylide linkage has been recently examined. Using the Hartree–Fock molecular orbital method, it was

concluded that the use of *d* orbitals for the formation of the highest occupied molecular orbital of the ylide results in an appreciable energy gain. Furthermore, the involvement of the *d* orbitals in the formation of the C–S ylide linkage is confirmed, according to the authors[29], by the distribution of charges in the ylide molecule. These data are analogous to those obtained earlier for phosphorus ylides[30].

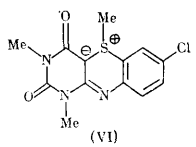
Studies[5,31–34] in which the involvement of the *d* orbitals of Third Period elements (P, S, and Si) is questioned or rejected have been published in recent years. The differences between the properties of the phosphorus, sulphur, and silicon compounds, on the one hand, and those of their analogues in the Second Period, on the other, are explained by the difference between the effective dimensions of their *s* and *p* orbitals[31], the accessibility of the low-lying π^* orbitals of the phosphonium and sulphonium cations[32], or the possibility of the expansion of the valence shell of the heteroatom only as a result of the combination of *s*- and *p*-type orbitals [33,34].

Thus the question of the involvement of the *d* orbitals of the Third Period heteroatoms in the formation of bonds and in particular of the C–S ylide linkage remains open at present.

The physical properties of stabilised sulphonium ylides have been studied very thoroughly. Thus the molecular structure of dimethylsulphuranylidenedicyanomethane (III), [35,36] 2-dimethylsulphuranylideneindan-1,3-dione (IV),[37] dimethylsulphuranylidenecyclopentadiene (V),[38] and 7-chloro-1,3,5-trimethyl-5*H*-pyrimido(5,4-*b*[[1,4]benzothiazine-2,4-[1*H*,3*H*]dione (VI) [39] have been established on the basis of X-ray diffraction data:



(III) (IV) (V)



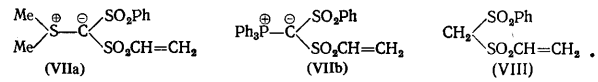
(VI)

The sulphur atom in ylides is pyramidal and the length of the C–S ylide bond (1.71–1.72 Å) is smaller than that of a single C–S bond (1.809 Å) [19] and close to that of the C–S bond in ethylenethiourea (1.708 Å), in which the amount of double bond character has been estimated as approximately 20%.[39] It is noteworthy that in sulphonium salts, where the negative charge is concentrated on the anion, the lengths of all the C–S bonds are close to that of a standard single bond[38]. The bonds between the carbanionic carbon atom and the neighbouring carbon atoms are shortened (1.40–1.43 Å) and the C–O bonds of the carbonyl groups attached to the carbanionic carbon are lengthened (1.23–1.24 Å), compared with the usual values for the C–C and C–O bonds[19,39,40]. In the case of the ylide (V) the distribution of bond lengths in the cyclopentadiene ring approaches the equalised distribution and resembles that in the structure of the analogous phosphorus ylide, for which the proportions of the ylide (~80%) and ylene (~20%) structures have been estimated[38]. The ratio of the latter in the sulphonium ylide is approximately the same, which has been confirmed by ^{13}C NMR spectra obtained recently for the corresponding sulphonium and phosphonium ylides[41].

It follows from X-ray diffraction data that the sulphonium and electron-accepting groups at the carbanionic carbon atom are involved in the delocalisation of its negative charge.

This is also reflected in the infrared spectra of the sulphonium ylides, where in the case of the carbonyl-,[35,42,43] cyano-,[35,44] sulphonyl-,[45] phosphoryl-,[46] and nitro-stabilised[47] sulphonium ylides the stretching vibration bands in these groups are displaced towards lower frequencies compared with the corresponding sulphonium salts[35,42,44,45] and other carbonyl, nitryl, sulphonyl, phosphoryl, and nitro-compounds[48], which is similar to the situation observed for phosphorus ylides[1].

The ultraviolet spectra of the dimethylsulphuranylidene derivatives (VIIa) and the triphenylphosphoranylidene derivatives (VIIb) of benzenesulphonylethylenesulphonylmethane[44] show a broadening of the phenyl band of the ylides and a smoothing of its fine structure compared with the initial methylene compound (VIII):



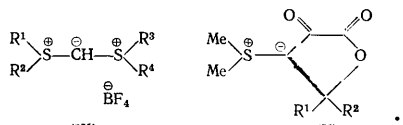
(VIIa) (VIIb) (VIII)

This is evidence for a relatively high electron density on the carbanion in ylides, i.e. ylides exist predominantly in the ylide form (B). Analysis of the ultraviolet spectrum and calculation of the energies of the transitions of dimethylsulphuranylidenecyclopentadiene (V) showed[49,50] that the ylide structure (B) makes an 83% contribution to the ground state and that the latter is stabilised relative to the ylene structure (A) by 1.038 eV (24 kcal). Analogous data were obtained in other studies[51–53]. The ultraviolet spectra of carbonyl-stabilised sulphonium ylides exhibit an absorption which is similar, in terms of the intensity and position of the bands, to that of the enolic form of the corresponding methylene compound but differs appreciably from the absorption of the corresponding sodium salts of the enolic forms[43].

The charge distribution in sulphonium ylides can be inferred from data obtained by the dipole moment method, which are available for the sulphuranylidene derivatives of dicyanomethane[35,54], indan-1,3-dione[54], fluorene[1], and cyclopentadiene derivatives[53,55]. The high dipole moment (4–8 D) shows that the charges in the sulphonium ylides are appreciably separated. However, the dipole moments of ylides are smaller than the value calculated for the ylide structure (B),[1] i.e. the ylene structure (A) makes an appreciable contribution to the ylide–ylene resonance. The dipole moment of the ylide depends on the nature of the substituent at the sulphur atom. Thus replacement of an alkyl group at the sulphur atom by the phenyl group increases the dipole moment of the ylide by 0.4–0.8 D.[54] The introcution of a methoxy-group in the *para*-position of the *S*-phenyl group of the methylphenylsulphuranylidene derivatives of indan-1,3-dione and dicyanomethane increases the dipole moment of the ylide relative to that of the unsubstituted analogue and the introduction of a halogen or the acetyl group lowers the dipole moment of the ylide[54], which indicates the polarity of and ready polarisability of the ylide linkage. In contrast to the data presented above, in their study of the dipole moments of sulphonium, phosphonium, and arsonium ylides derived from cyclopentadienes, Lumbroso et al.[55] concluded that the ylene structure (A) predominates in these compounds.

NMR data are important for the understanding of the geometry and electronic interactions in sulphonium ylides. The positive charge on the sulphur atom leads to the deshielding of the substituent linked to it[42,43,56–58]. The asymmetry of the tetrahedral sulphur atom is responsible for the non-equivalence of the methylene protons of the benzyl or ethyl substituents, which depends on the nature of the solvent[43,59–61], as has been noted for sulphonium salts

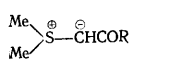
and many other sulphur compounds[62]. In the dimethylsulphuranylidene derivatives of acetophenone and β-dicarbonyl compounds the non-equivalence of the protons of the *S*-methyl groups is not observed even at −60 °C,[59] which can probably be accounted for by the ease of inversion at the sulphur atom. Hindrance of the pyramidal inversion at the sulphur atom should lead to the non-equivalence of the *S*-methyl groups, which has been demonstrated recently for a series of 1,3-bis-sulphonium ylides (IX) in the temperature range 40–80 °C.[63] It was established that the activation energy for this process at 80 °C is 19.8 kcal mol^{-1} and that the barrier to inversion is reduced by approximately 5 kcal mol^{-1} on passing from the salt to the ylide. The non-equivalence of the protons of the *S*-methyl groups can be due to the presence of a chiral centre as the carbanionic carbon atom, which has been observed for the derivatives of 4-dimethylsulphuranylidene-2,3-dioxotetrahydrofuran (X) ($\Delta\delta \cong 0.16$ p.p.m.) and the non-equivalence does not disappear in the temperature range 30–100 °C:[64]



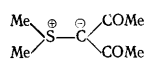
(IX)

(X)

As shown in the study of the molecular structures of the stabilised sulphonium ylides (see above), the bonds between the carbanionic carbon atom and the neighbouring substituents are shortened, so that the existence of rotational isomers may be expected for the stabilised sulphonium ylides. This possibility was demonstrated in an ^{1}H NMR study on dimethylsulphuranylidenemethyl carboxylate (XIa) [58] and dimethylsulphuranylideneacetylacetone (XII),[59] where the non-equivalence of the protons of the methylidyne and *C*-methyl groups was observed as the temperature was altered. The presence of such isomers of dimethylsulphuranylideneacetophenone (XIb) was demonstrated chemically, since its methylation with trimethyloxonium tetrafluoroborate led to the formation of a mixture of the *cis*- and *trans*-vinyl ethers in proportions of 94 : 6:[65]



(XI) (a) R=OMe; (b) R=Ph



(XII)

^{13}C NMR spectra yield extremely valuable information about the reactivities of stabilised sulphonium ylides, their study permitting infereneces about the electronic structure of the carbon atoms in the ylide molecule[41,66–69]. The spin–spin coupling constant of the carbanionic carbon atom with the methylidyne proton in the ylide (XIb) ($J_{^{13}C-H_2} = 179.7$ Hz) confirms that this atom is sp^2-hybridised. The upfield shift of the signal due to the nucleus of the carbonyl carbon atom in carbonyl-stabilised sulphonium ylides relative to the signal of this carbon atom in the corresponding sulphonium salts (−9.5–11.8 p.p.m.) permits the conclusion that the contribution of the ylide structure (B) to the ylene–ylide resonance is important[66]. The substitution of the methylidyne hydrogen atom in the ylide by an electron-accepting substitutent results in a downfield shift of the signal of the carbanionic carbon atom and a reduction of the nucleophilicity of such ylides[66,67].

Important data on the electronic interactions in sulphonium ylides can be obtained by studying the basicity of the latter or the acidity of the corresponding sulphonium salts. Thus the basicity of the sulphuranylidene derivatives of acetophenone decreases after the introduction of electron-accepting substituents in the *para*-position of the S-phenyl or phenacyl group[70,71]. Similar data have been obtained for the phosphonium analogues[72]. The basicity of the sulphonium ylides diminishes in the following sequence of substituents at the sulphur atom: Me > Et > iso-Pr > Ph, i.e. the dialkylsulphonium group is less involved in the delocalisation of the negative charge in the carbanion than the dephenylsulphonium group[73–75]. Thus the introduction of groups stabilising the ylide leads to a decrease of its basicity owing to the greater delocalisation of the negative charge on the carbanion.

The basicity of sulphonium ylides is lower than that of the corresponding phosphonium and ammonium analogues and increases in the sequence S < P < N,[70,71] which depends on the degree of involvement of onium groups in the stabilisation of the carbanionic system of the ylide. The dependence of the stabilising effect of the onium group on the nature of the heteroatom (S ≅ Se ≫ P > As > Sb) has been determined in a study of the ^{1}H NMR and ultraviolet spectra and of the basicities of the corresponding cyclopentadiene ylides[55,75–77]; the analogous series S > P > As > N has been obtained in a study of the rates of isotope exchange of onium salts with D_2O.[78] These data are frequently quoted as evidence for the delocalisation of the negative charge of the carbanion over the *d* orbitals of sulphur[1,55,70], but Kissel et al.[71] regard this as doubtful, since the properties of the ylides examined above can be accounted for also without invoking the "concept of *d* orbitals".

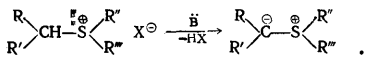
The synthesis of optically active stabilised sulphonium ylides is of great interest. The first attempt at their synthesis was unsuccessful[59], evidently owing to the ease of their racemisation. Theoretical calculation of the barriers to pyramidal inversion and the internal rotation relative to the formally double C=S ylide bond showed that the automerisation of ylides proceeds as a two-stage process[79]. The inversion of the sulphur pyramid is preceded by the rotation about the C–S ylide bond and the *gauche*-conformation constitutes a transition state. The calculated barrier to the inversion of the pyramid at the sulphur atom (35.3 kcal mol^{-1}) corresponds to the condition for its configurational stability; the barrier to rotation about the C–S ylide bond is 8.7 kcal mol^{-1}.[79] Optically active (−)-ethylmethylsulphuranylideneacetophenone has been obtained[80] and it has been shown that it racemises at 90 °C 200 times faster than the corresponding sulphonium salt and approximately 10^{11} times faster than methyl *p*-tolyl sulphoxide. The enthalpy of activation of the ylide is 23.3 kcal, while for sulphonium salts it is 25 to 29 kcal and for sulphoxides 35–43 kcal.[80,81] The greater ease of racemisation of the ylide can be explained by the fact that the interaction of the sulphonium centre with the carbanionic component of the ylide stabilises the transition state for its inversion[80,81]. The fact that the racemisation of the ylide proceeds via the pyramidal inversion mechanism has been confirmed[82]. It was found that the activation volume for this process is close to zero ($\Delta V^{\neq} \cong 0$) in contrast to the t-butylethylmethylsulphonium ion ($\Delta V^{\neq} = +6.4$), whose activation volume corresponds more closely to a transition state involving partial dissociation. A number of optically active sulphonium ylides stabilised by two carbonyl groups were later obtained[83,84].

Thus, stabilised sulphonium ylides are an extremely **unusual class** of organic compounds. They are highly polar **and their stability** is due to the degree of delocalisation of **the electron** density in the molecule.

III. METHODS OF SYNTHESIS

Several method of synthesising stabilised sulphonium ylides are now known: the "salt method", the "iodonium method", the reaction of sulphides with diazo-compounds, and other less general methods.

The salt method consists in the deprotonation of sulphonium salts already prepared or synthesised *in situ* by means of a suitable base:

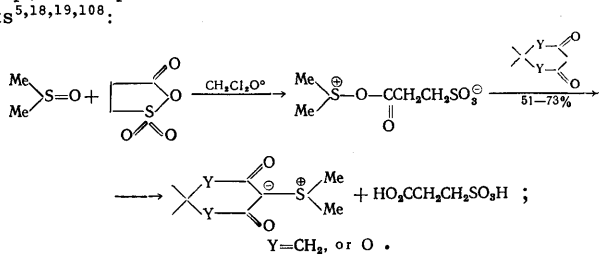


The choice of the base, which can be potassium carbonate, amines, alkoxides, sodium hydride in DMSO, etc.[5,85], is determined by the acidity of the proton at the α-carbon atom of the salt. This method has been used successfully to synthesise a number of carbonyl-stabilised sulphonium ylides[42,86–89]. The applicability of the "salt method" to the synthesis of stabilised sulphonium ylides is limited by the availability of the sulphonium salts and the occurrence of side reactions involving β-elimination and the formation of σ-sulphuranes[5].

The method based on the substitution of the proton at the carbanionic carbon atom of the ylide is a variety of the "salt method". The attempts to alkylate the sulphuranylidene derivatives of acetophenone by methyl iodide, benzyl bromide[42,56,57], and α-halogenoketones[90,91] were unsuccessful, since the reactions were accompanied by the dealkylation of the sulphonium salt formed. The reactions of similar ylides with picryl chloride[92], aromatic amine oxides (*C*-arylation),[93] vinyl ethers (*C*-alkenylation),[94] benzenesulphenyl chloride[95], and *N*,*N*-diethylbenzenesulphenamide[96] (sulphenylation), which led to new stabilised sulphonium ylides, proved more successful.

Carbonyl-stabilised sulphonium ylides can be obtained by acylating ylides with a proton at the carbanionic carbon atom. Acid anhydrides[42,97–99], isocyanates[59,90,99,100], acid azides[101,102], aldehydes, α-diketones, α-ketoacid esters[63], and acyl halides[42,64,95,98,99,103–107] can be used as acylating agents. The employment of acyl halides for the acylation of monocarbonyl-stabilised sulphonium ylides is limited by the formation of *O*-acylation side products, which is evidently associated with the enolate stabilisation of ylides[42].

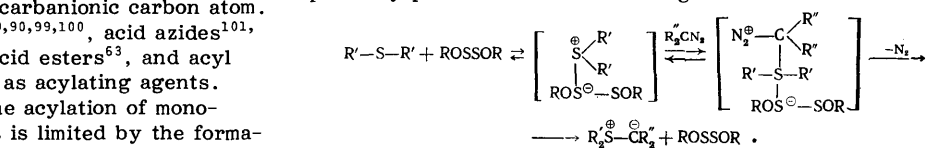
The salt method also includes the condensation of sulphoxides with compounds containing an active methylene group, which proceeds via the intermediate formation of salts[5,18,19,108]:



This reaction takes place under conditions typical for dehydration reactions in the presence of dehydrating agents such as sulphopropionic anhydride[108], acetic anhydride[5,14,18,19] (although in the presence of the latter the yield of the ylide is low owing to the competing Pummerer reaction[109]), phosphorus pentoxide[59], thionyl chloride[59,100], aryl cyanates[111–113], sulphur trioxide[114,115], and dicyclohexylcarbodi-imide[35,52,116,117]. All these reagents form sulphonium salts or complexes with sulphoxides, which readily react with compounds containing an active methylene group. This has been confirmed by the reactions of the stable betaine formed when DMSO reacts with sulphopropionic anhydride[108] and by the reactions of stable sulphonium salts[59,118] with compounds containing an active methylene group or their sodium salts, which led to the formation of the corresponding sulphonium ylides. The yield of the ylide and the rate of its formation when the condensation is carried out in acetic anhydride can be increased by adding to the reaction mixture alkali metal perchlorates, which facilitate the formation of the acyloxysulphonium salt[119]. The reaction of organic selenide dihalides with compounds containing an active methylene group has been used successfully recently to synthesise stabilised selenonium ylides[120]. The attempts to employ this method for the synthesis of sulphonium ylides proved unsuccessful, since the intermediate sulphonium salts readily decomposed with formation of an olefin and an α-halogenocarbonyl compound[121].

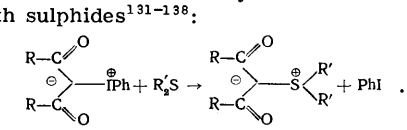
The thermal, photolytic[17,25,66,122–126], or catalytic decomposition[127] of diazo-compounds in the presence of sulphides constitutes a direct method of synthesis of stabilised sulphonium ylides. The reaction evidently proceeds via the nucleophilic attack by the sulphide on the singlet carbene formed on decomposition of the diazo-compound; the high stereoselectivity of this process has been demonstrated[128]. The thermal decomposition of diazo-compounds is usually carried out in the presence of anhydrous copper sulphate or metallic copper powder. This method is applicable to the synthesis of ylides from weakly nucleophilic sulphides such as diaryl sulphides or dibenzothiophen[129]. It is noteworthy that dialkyl sulphides are approximately 4–6 times more reactive in this reaction in relation to the carbene than olefins[126,129].

The catalytic decomposition of diazo-compounds in the presence of sulphides takes place readily at room temperature in the absence of light, provided that dialkoxydisulphides have been added to the reaction mixture[127]; the process probably proceeds via the following mechanism:



The formation of a complex of the sulphide with a dialkoxy disulphide has been observed in the reaction of tetramethylene sulphide with dimethoxy disulphide[127]. In all cases the yield of the ylide decreases with decrease of the nucleophilicity of the sulphide and with increase of the degree of branching of its hydrocarbon groups. Furthermore, the decrease of the yield of the ylide can be caused by the rearrangements and processes involving the cleavage of the ylide under the reaction conditions[17,25,129,130] (see Section IV).

The "iodonium method" of synthesising stabilised sulphonium ylides consists in the transylidation of the iodonium betaines with sulphides[131–138]:



These reactions are catalysed by copper(I) or copper(II) salts[131–135,138] and toluene-*p*-sulphonic acid[136,137]. Although the mechanism of this reaction has not been investigated, when copper salts are used it probably proceeds via the intermediate formation of a carbene or, in the presence of toluene-*p*-sulphonic acid, the intermediate iodonium salt is cleaved by the nucleophilic sulphide at the C–I bond and the resulting sulphonium toluene-*p*-sulphonate is deprotonated further by the counterion, which leads to the corresponding ylide.

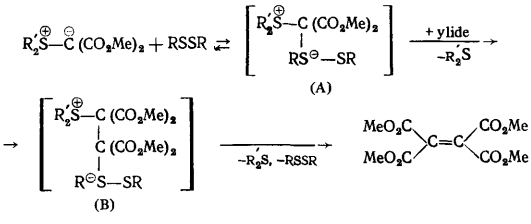
A number of less general methods are also suitable for the synthesis of stabilised sulphonium ylides. Thus ylides can be obtained by the transylidation of other sulphonium ylides in the presence of disulphides activated by electron-accepting groups (dialkoxydisulphides, thiocyanogen, etc.)[139] or electrophilic monosulphides (aryl thiocyanates, *p*-hydroxyphenyl trifluoromethyl sulphide, etc.)[69] as well as by the transylidation of selenonium ylides with sulphides in the presence of carbon disulphide[140]. Stabilised sulphonium ylides can be obtained by adding DMSO to acetylenedicarboxylate[103] or, in the case of the sulphuranylidene derivatives of dicyanomethane, by the interaction of sulphides with tetracyanoepoxyethane[44,110].

IV. CHEMICAL STABILITY. REARRANGEMENTS

It was pointed out above that the stability of sulphonium ylides is determined mainly by the degree of delocalisation of the electron density in their molecules under the influence of electron-accepting substituents.

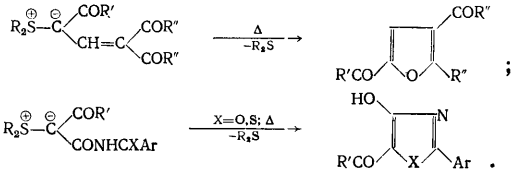
Nothing is so far known about the oxidants on stabilised sulphonium ylides. In a few studies[103,141–143] the reduction reactions have been investigated. When ylides are hydrogenated or are acted upon by sodium hydride, the ylide linkage is cleaved with formation of a sulphide and a hydrocarbon residue. In only one case was the reduction of the carbonyl group without the involvement of the ylide linkage observed[143]. The hydrolytic stability of stabilised sulphonium ylides has been studied in greater detail; it will be examined below in Section VI.

Stabilised sulphonium ylides can be decomposed thermally, photolytically, and catalytically; this very often involves different types of rearrangements. The catalytic decomposition of ylides proceeds readily in the presence of disulphides activated by electron-accepting substituents[144]. Ylides then decompose in the following sequence in terms of the decrease of their reactivity: $R_2\overset{\oplus}{S}-\overset{\ominus}{C}HCOPh > R_2\overset{\oplus}{S}-\overset{\ominus}{C}(\overset{\ominus}{C}O_2Me)_2 \approx R_2\overset{\oplus}{S}-\overset{\ominus}{C}(CN)_2 \gg R_2\overset{\oplus}{S}-\overset{\ominus}{C}(CO_2Me)(COMe)$, which is similar to the series based on the decrease of the nucleophilicity of the carbonionic carbon atom. The decomposition of the ylide, involving its complex with a disulphide, can be represented by the following scheme:



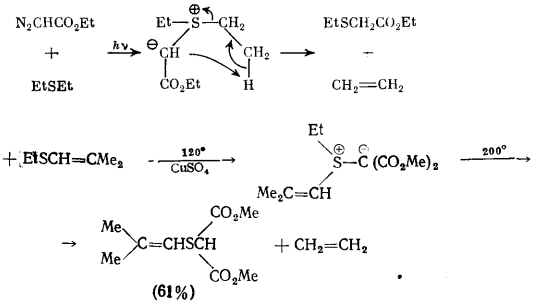
Thus an olefin is formed in the decomposition of the complex (B) obtained as a result of the nucleophilic substitution of the sulphonium group of the complex (A) by another ylide molecule. In the case of highly nucleophilic sulphuranylidene derivatives of acetophenone the olefin formed reacted with the the initial ylide with formation of the corresponding cyclopropane derivatives[144]. The possibility of the formation of cyclopropane derivatives from ylides and olefins has been confirmed by a study of the decomposition of acyldiazo-compounds in the presence of sulphides[144–146].

The thermal and photolytic decomposition of monocarbonyl-stabilised sulphonium ylides leads to the corresponding *trans*-substituted cyclopropane derivatives[18,56–58,98,147–151]. To account for this process, a "carbene" mechanism has been proposed in the case of the photolytic decomposition of the ylide[148,149] and both "carbene" and "ionic" mechanisms have been put forward for the thermal decomposition[56,147–150] and both have been confirmed experimentally: the carbene mechanism by trapping the intermediate carbene with dimethylbenzylamine[56,57], triphenylphosphine[149], cyclohexene[147,148], and other compounds which readily react with carbenes[152] and the ionic mechanism by converting dimethylsulphuranylideneacetophenone (XIb) into *trans*-tribenzoylcyclopropane, the reaction being catalysed by a phenacylsulphonium salt[56,147,150,151]. (For further details of these mechanisms, see Reid[18].) It is noteworthy that sulphonium ylides stabilised by two electron-accepting groups are not converted into cyclopropanes as a result of the low nucleophilicity of the carbanionic carbon atom[144]. However, if one of the stabilising groups is an allyl acetate group or a (thio)carbamoyl group, intramolecular cyclisation of the ylide, leading to furan, oxazole, or thiazole derivatives, becomes possible[100,153]:

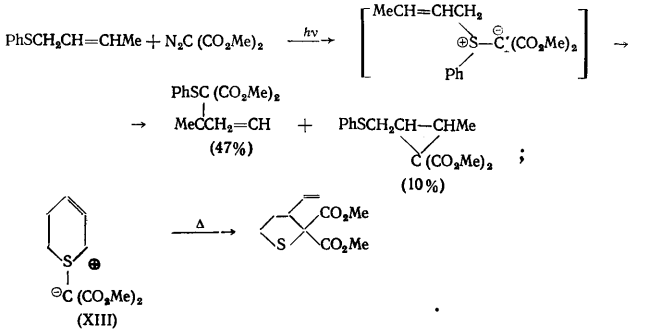


When a substituent with β-hydrogen atoms (ethyl or t-butyl group) is attached to the sulphonium sulphur atom, β-elimination processes are observed instead of conversion into a cyclopropane derivative, which results in the formation of alkyl thioacetates or alkenyl thiomalonates and olefins (Scheme I).[126,154,155] For further details about the β-elimination processes, see Ando[17,25]:

Scheme 1



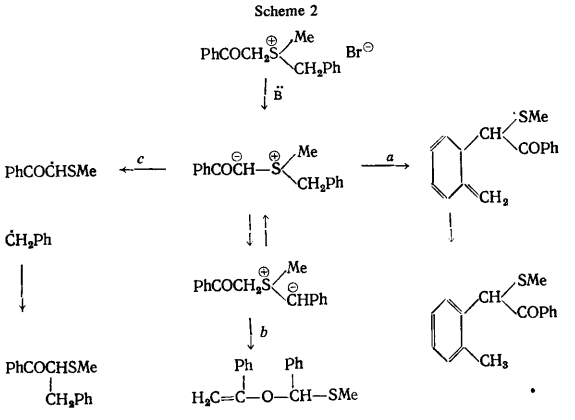
When stabilised sulphonium ylides are decomposed, various rearrangements may occur together with the reactions involving conversion into a cyclopropane derivative, cyclisation, and β-elimination. Thus the thermal or photolytic decomposition of *S*-allyl-substituted sulphonium ylides, including the cyclic ylide (XIII), entails [2,3]-sigmatropic rearrangements leading to the formation of homoallyl sulphides[130,154]:



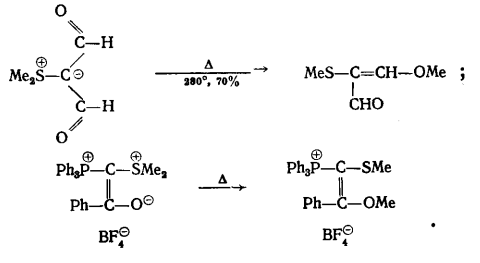
These rearrangements are allowed by the orbital symmetry[156] and occur on heating or photolysis of ylides with complete inversion of the allyl substitutent[130,154]. The method of successive [2,3]-sigmatropic shifts has been used recently in the synthesis of eight- and eleven-membered heterocycles[157]. It is noteworthy that similar [2,3]-sigmatropic rearrangements are observed also for unstable oxonium, ammonium, and halogenonium compounds[130,158].

The Sommelet–Hauser rearrangement, leading to a product substituted in the aromatic ring (pathway *a*),[1,159] and the 1,5-rearrangements of carbonyl- or cyano-stabilised sulphonium ylides, occurring with formation of enolic monothioacetals in the case of carbonyl-stabilised ylides (pathway *b*),[159,160] or keten imines[161], can be included among rearrangements of this type; in the last instance the alkyl group migrates from the sulphur atom to the nitrogen atom of the nitrile group:

Scheme 2

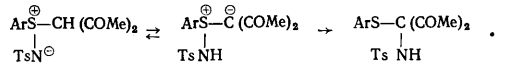


These rearrangements are favoured by a protic solvent, which promotes the proton transfer processes occurring under these conditions. The ratio of the products formed via pathways *a* and *b* depends on the rate of attainment of equilibrium between the two ylide forms and can be controlled by the concentration of a base[159]. The possibility of the 1,5-migration of the alkyl group has been demonstrated not only for monocarbonyl-stabilised sulphonium ylides but also for ylides stabilised by two carbonyl or carbonyl and phosphonium groups[85,162]:

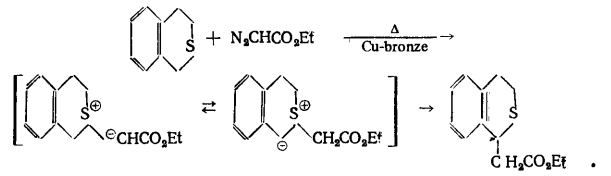


When an aprotic solvent is used, the [1,2]-sigmatropic shift (pathway *c*) of the *S*-alkyl group (the Stevens rearrangement) begins to compete with the above rearrangements (pathways *a* and *b*) and it has been noted that the Stevens rearrangement is favoured by an increase of temperature[159]. Furthermore it has been shown recently for sulphuranylidene derivatives of pyrimido-1,4-benzothiazine[163] that the type of rearrangement depends on the nature of the substituents in the ylide and the reaction conditions (thermolysis or photolysis).

The Stevens rearrangement was discovered in 1932 [164] and consists in the conversion of methylbenzylsulphonium bromide in a methanol solution of sodium methoxide into α-methylthio-β-phenylpropiophenone (evidently via the intermediate formation of an ylide). The concerted mechanism of the thermal Stevens rearrangement is prohibited by orbital symmetry[156], so that the mechanism involving a dissociation–recombination process is more probable. This is confirmed by the finding that the reaction is characterised by a very low value of ρ if the substituents in the benzene ring of the benzyl group are varied[165,166] and by the appearance in the ^{1}H NMR spectrum of benzyl protons of chemically induced dynamic nuclear polarisation[129,165–167]. An interesting example of a 1,2-shift has been observed recently[168] for a new type of sulphonium ylides with an amino-group attached to the sulphonium sulphur atom:

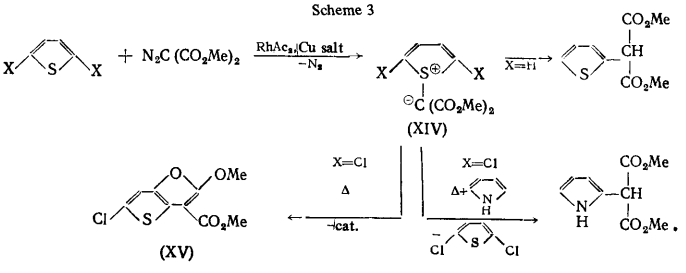


The inclusion of the sulphur atom in a six-membered ring partly makes the 1,2-migration of the *S*-alkyl group energetically unfavourable, since it should occur with formation of a thiepan ring. In this case migration is observed from the methyleneethoxycarbonyl substituent and not the *S*-alkyl substitutent, evidently via an intermediate formation of an unstable ylide[169]:



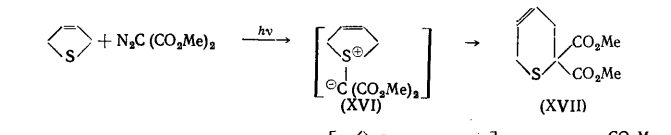
Recently a similar migration of the dimethylmalonate group has been observed in the thermal rearrangement of ylides derived from thiophen occurring on heating them in the presence of rhodium or copper catalysts[170]. Under these conditions, when the α-positions of the thiophen ring are substituted, then in the presence of the above catalysts the ylide dissociates into a sulphide and a carbene; the latter was trapped with activated aromatic compounds (pyrrole, indole, anisole, etc.).[152] It is noteworthy that the ylide (XIV), carefully freed from the catalyst, does not decompose into a sulphide and a carbene but undergoes an intramolecular rearrangement involving the migration of the malonate substituent from the copper atom to the α-position of the thiophen ring with subsequent ring closure, elimination of HCl, and the formation of methyl 5-chloro-2-methoxythieno-[3,2-*b*]furan-3-carboxylate (XV):[171]

Scheme 3

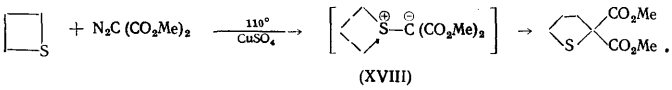


Thus the inclusion of the sulphonium sulphur atom in the ring has a significant effect on the mode of the composition of the ylide. The influence of ring size and the ring substituents on the stability of ylides and the mode of their decomposition can be illustrated by the following examples. Sulphonium ylides obtained from thiophan, tetrahydrothiapyran, thiepan, and dimethyl diazomalonate do not decompose on heating at 235 °C in the course of 10 h.[129] As pointed out above, ylides obtained from derivatives of thiophen

(XIV) or Δ^3-dihydrothiapyran (XIII) and dimethyl diazomalonate behave differently. The former undergoes a 1,2-shift of the malonate group or decomposes into a sulphide and a carbene[152,170,171], while the latter gives rise to products of the [2,3]-sigmatropic rearrangement accompanied by ring contraction[130]. The opposite behaviour has been observed for the ylide (XVI) obtained from 2,5-dihydrothiophen and dimethyl diazomalonate: the Stevens rearrangement, leading to the stable Δ^3-5,5-dimethoxycarbonylthiapyran (XVII) is more favourable than the [2,3]-sigmatropic rearrangement, which leads to the sterically strained thietan[130]:



(XVI) (XVII)



(XVIII)

The sulphonium ylide (XVIII), formed in the reaction of the thietan with dimethyldiazomalonate readily rearranges to 2-dimethylcarbonyltetrahydrothiophen[129]. This process is evidently caused, on the one hand, by the transition of the sulphur from the quadrivalent to the bivalent state and, on the other, by the formation of a less strained five-membered ring. The reactions of ketocarbenes with oxetans proceed similarly[172]. If the sulphur is incorporated in the thi-iran ring, then a stable ylide is also not formed in the reaction of such a sulphide with a carbene. The Stevens rearrangement would lead in this case to a strained thietan, so that α-fragmentation, leading to an olefin and a thiocarbonyl compound, is more favourable under these conditions[173]. Analogous reactions had been observed earlier between carbenes and oxirans[172] and aziridines[174]:



It is noteworthy that the stability of ylides and the mode of their decomposition are influenced also by the nature of the substituents at the carbanionic carbon atom. Thus sulphuranylidene derivatives of dicyanomethane decompose on heating into a sulphide and tetracyanoethylene regardless of the nature of the substituents at the sulphur atom (alkyl, phenyl, tetrahydrothiapyranyl, etc.).[142]

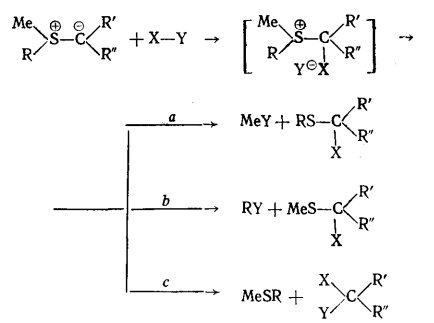
Thus the possibility of the rearrangements must also be taken into account when sulphonium ylides are used in organic synthesis. At the same time the rearrangements of stabilised sulphonium ylides constitute a new method of forming carbon–carbon bonds.

V. REACTIONS WITH ELECTROPHILES

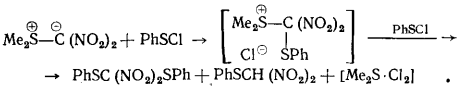
The reactions of stabilised sulphonium ylides with electrophiles are due to the presence of a carbanionic centre in the ylide molecule; with increase of the degree of delocalisation of the negative charge on the carbanion, the reactivity of the ylide with respect to the electrophiles diminishes.

It was started in Section III that one of the main methods of synthesising sulphonium ylides is the "salt method". The reverse reaction involving the regeneration of the sulphonium salt by the addition of hydrogen halides is also possible[13], but the sulphonium salt frequently decomposes under the influence of the nucleophilic counterion in a way which depends both on the substituents in the ylide and on the nature of the nucleophile. A detailed study of these reactions[143,175–179] showed that the sulphonium salts can decompose via three pathways (*a*–*c*). Pathway *a* involves attack by the nucleophilic counterion on the carbon atom of the S–Me group, pathway *b* involves attack on the carbon atom of the S–R group, and pathway *c* involves attack on the carbon atom of the C–X group.

The study of the reactions of dimethylsulphuranylidinedinitromethane with electrophiles (halogens, hydrogen halides, water, sulphuryl chloride, benzenesulphenyl chloride, *N*-halogenoamides, *N*-chloroalkylnitramine, etc.) showed[175–177] that the intermediate sulphonium salt decomposes only via pathway *c*. The formation of products of pathways *a* and *b* is not observed, although this may be caused by their decomposition in the course of the reaction, because it is known that α-polynitroalkyl sulphides are cleaved by both nucleophiles and electrophiles[28,180].



It is noteworthy that the intermediate sulphonium salt can be cleaved not only by the nucleophilic counterion but also by the initial electrophile[176,177]:

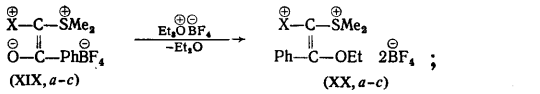


When halogens, sulphuryl chloride, and sulphur monochloride are used in this reaction, competitive halogenation of the *S*-alkyl group takes place[142,176].

In the reactions of sulphuranylidene derivatives of malonic ester with electrophiles (halogens, hydrogen halides, arenesulphenyl thiocyanates, etc.)[178,179] the products of all the above pathways (*a*–*c*) are observed. In the general case the mode of decomposition of the intermediate sulphonium salt depends on the structure of the sulphonium cation (the nature of the groups R and X) and on the nature of the nucleophile. If X is a heteroatomic group, then the substituents at the sulphur atom can be arranged in the following sequence in accordance with the increase of their reactivity with respect to nucleophiles: Me (1.0) ≅ Et (0.6) < iso-Pr (3.0) ≪ CH_2Ph ≅ CH_2SMe (∞). This sequence is different from the sequences based on the reactivity of the substituents in the reactions of alkyl bromides with the bromide anion in acetone at 25 °C: CH_2Ph = Me (1.0) > Et (0.013) > iso-Pr (0.0086), and in reactions of alkylmethylphenylsulphonium perchlorates with the iodide anion in acetone at 50 °C: Me (1.0) > Et (0.20) > n-Pr (0.16) > iso-Pr (0.05),[178] for which the S_N2 mechanism has been established. The higher reactivity of the benzyl and methylthiomethylene groups relative to the methyl group shows that these reactions can proceed via an S_N1 type mechanism[178,179].

In contrast to the reactions of sulphuranylidene derivatives of dinitromethane and malonic ester with electrophiles discussed above, the protonation or alkylation of phenacylide salts (XIX) by acids or triethyloxonium tetrafluoroborate does not take place at the carbanionic carbon atom but

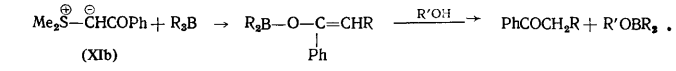
involves the more electronegative end of the carbanionic system—the carbonyl oxygen atom, with formation of the corresponding bis-salts (XX):[162]



(XIX, *a-c*) (XX, *a-c*)

X = (a) Ph_3P—, (b) Me_2S—, or (c) Ph_2Se— .

The reactions of sulphonium ylides with simple electrophiles such as trialkylboranes are of interest[181,182]. The trialkylborane can attack either the carbanionic carbon atom with subsequent C—O rearrangement or directly the oxygen of the enolate form of the ylide, leading to an alkoxydialkylborane after the elimination of the sulphide. It has been established that the alkyl group migrates from the boron atom to the carbon atom in the form of an anion[183]:

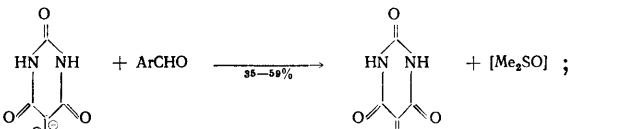


(XIb)

The reactions of sulphonium ylides carrying a proton at the carbanionic carbon atom with acyl halides and alkyl halides have been examined in detail in Section III. Ylides stabilised by two electron-accepting groups also react with them to form sulphonium salts. The structure of the final product is influenced significantly by the nature of the substituents in the sulphonium ion[142,162,184,185]. The reactions of sulphonium ylides with acyl peroxides proceed similarly[186].

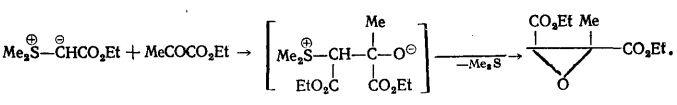
In the study of the chemical properties of stabilised sulphonium ylides much attention was devoted to their reactions with carbonyl compounds and compounds containing multiple bonds[5]. The study of the reactions of ylides with carbonyl compounds was stimulated by the endeavour to extend the Wittig reaction to sulphur ylides. However, instead of the expected olefins, oxirans were obtained in this case. This is probably caused by the lower stability of the S—O bond (E_{diss} = 89 kcal mol^{-1}) compared with the P—O bond (E_{diss} = 128 kcal mol^{-1}) and different tendencies of the sulphide and phosphine groups to be eliminated[1].

The occurrence of the Wittig reaction has been reported in only two instances[187,188]:

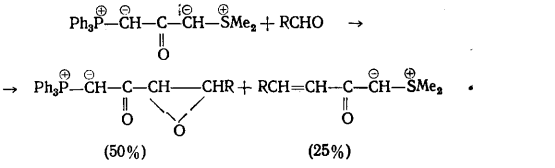


Ar = 4-$Me_2NC_6H_4$, 4-$Et_2NC_6H_4$, or 2-$O_2NC_6H_4$.

The epoxidation of carbonyl compounds by sulphonium ylides involves the reversible attack by the carbanionic carbon atom of the ylide on the electrophilic carbon atom of the carbonyl group. The resulting unstable betaine either decomposes into the initial compounds or gives rise to an oxiran via nucleophilic substitution of the sulphide group by the anionic oxygen atom. The mode of decomposition is determined by the nature of the substituents in both the ylide and in the carbonyl compound. It is noteworthy that stabilised sulphonium ylides give rise to oxirans only by reacting with very reactive carbonyl compounds such as dicarbonyl compounds, α-halogenoaldehydes, etc.[109,189]:

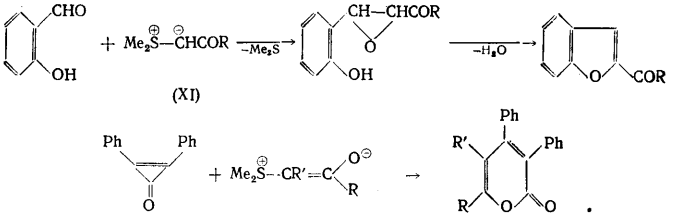


The introduction of a phosphoranylidene substituent in the α-position with respect to the carbonyl group of the sulphonium ylide increases the reactivity of the latter by reducing the involvement of the carbonyl group in the delocalisation of the negative charge over the sulphuranylidene fragment. This ylide reacts readily with carbonyl compounds, epoxidation predominating over "olefination":[190]



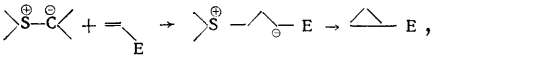
(50%) (25%)

The reactions of sulphonium ylides with aldehydes having a nucleophilic centre located close to the carbonyl group are of interest. Thus oxiran, formed when salicylaldehyde is used, is converted into benzofuran derivatives[191]. The reaction of sulphonium ylides with diphenylcyclopropenone, leading to 2-pyrones, is also unusual[192]:



(XI)

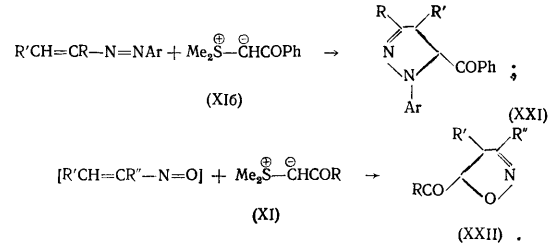
Stabilised sulphonium ylides react readily with olefins activated by electron-accepting substituents and in the case of α,β-unsaturated carbonyl compounds the conversion into a cyclopropane derivative predominates over epoxidation. Here one should note immediately that one is dealing only with the conversion of olefins into cyclopropane derivatives by fairly nucleophilic ylides stabilised by a single electron-accepting group, since in the presence of two such groups the ylide does not react with an extremely reactive chalcone[5]. The role of the electron-accepting substituent in the olefin consists not only in activating the double bond but also in stabilising the intermediate betaine. The specific synthesis of analogues of the latter confirmed the ready conversion of such betaines into cyclopropane derivatives[193]:



where E is an electron-accepting group.

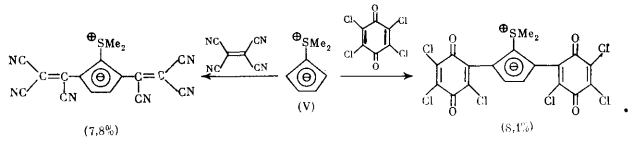
In recent years the reactions of stabilised sulphonium ylides with activated olefins have been used successfully to synthesise cyclopropyl-substituted heterocycles[194-196], sugars[197-200], phosphonium ylides[190], phosphonates[46], and phosphonium salts[201]. It is noteworthy that, when olefins with a conjugated system of multiple bonds are used in reactions of this kind, there is a possibility of the formation of not only the 1,2-addition products but also of 1,4-addition products, which can be due to the stereochemistry of this reaction[5,198-200]. The formation of 1,4-addition products has been recently demonstrated in the reactions of azoalkenes[202], nitrosoalkenes[203,204], and nitroalkenes[197-200] with sulphonium ylides, whereupon derivatives of 4,5-dihydropyrazoline

(XXI), Δ^2-isoxazoline (XXII), and Δ^2-isoxazoline *N*-oxide respectively were obtained:

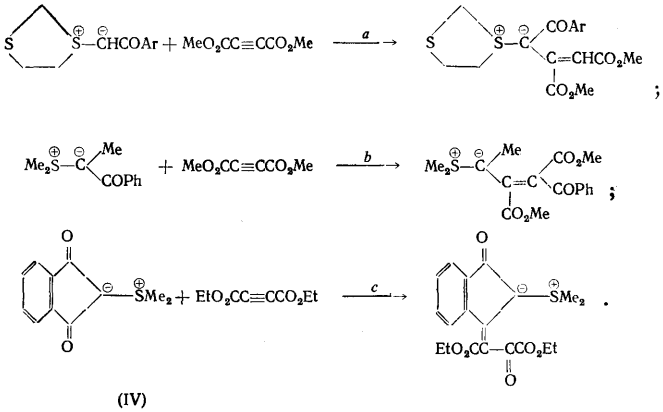


The reactions of sulphuranylidene derivatives of cyclopentadiene (V) with tetracyanoethylene and chloranyl entail the condensation of the latter two compounds at the β-carbon atom of the cyclopentadienyl ring, leading to products of the Michael addition (albeit in a low yield):[185]

Scheme 4



Stabilised sulphonium ylides react readily with alkynes, activated by electron-accepting groups, via pathways *a–c*, which depend on the structure of the ylide and the reaction conditions:



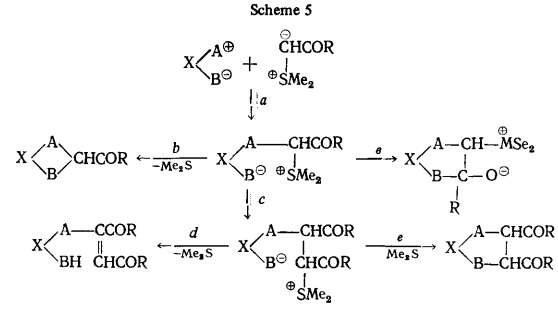
The use of protic solvents and ylides with a proton at the carbanionic carbon atom leads to the formation of new ylides via proton transfer (pathway *a*).[205] In aprotic solvents and for ylides with a disubstituted carbanionic carbon atom, new ylides are formed via the 1,3-migration of the acyl group (pathway *b*).[206] It is noteworthy that allyl-substituted ylides, formed via pathways *a* and *b*, can be cyclised into furan derivatives on heating or using DMSO as the solvent[206].

Pathway *c* obtains in reactions of sulphuranylidene derivatives of cyclic β-dicarbonyl compounds[207]. Here the alkyne adds to the carbonyl group of the enolate form of the ylide with formation and subsequent opening of the oxetan ring, which leads to products resulting from the transfer of the carbonyl oxygen.

One of the most important methods of synthesis of heterocycles is known to involve 1,3-dipolar cycloaddition reactions[208]. The reactions of 1,3-dipolar compounds with sulphonium ylides give rise to new possibilities in this sense.

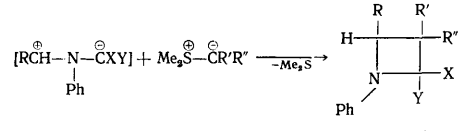
The study of the available literature data makes it possible to formulate six principal reactions of ylides with 1,3-dipolar compounds (*a–f*):

Scheme 5



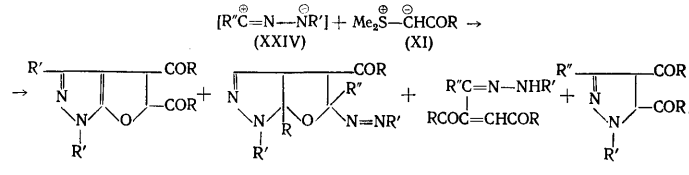
where $\overset{\oplus}{A}-X-\overset{\ominus}{B}$ are 1,3-dipolar compounds (for examples, see below).

In all cases the reaction begins with nucleophilic attack by the carbanionic carbon atom of the ylide on the electrophilic centre of the 1,3-dipole (*a*). The further course of the reaction depends on the nature of the 1,3-dipole and the substituents in the ylide. Thus azetidines (XXIII) are readily formed in the reactions of azomethine and sulphonium ylides (*b*):[209]



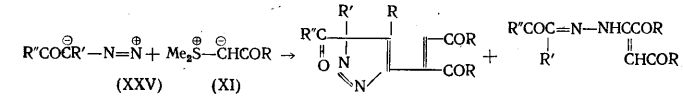
Pathway *b* is unfavourable when the 1,3-dipole contains two or three heteroatoms (nitrile imines, diazocarbonyl compounds, and azides), probably owing to the instability of the corresponding four-membered heterocycles. Depending on the structure of the ylide and the 1,3-dipole as well as the reaction conditions, products of pathways *c–f* are formed in this case.

The following products have been isolated in the reactions of sulphonium ylides with nitrile imines (XXIV):[204,210]



The formation of bicyclic adducts in this reaction shows that the growth of the "ylide chain" takes place not only in the betaines formed in reactions *a* and *d*, but also in the product of reaction *c*, both sulphonium and nitrile imine ylides being involved in its formation.

The reaction of ylides with diazocarbonyl compounds (XXV) is analogous albeit less varied (simple diazo-compounds do not undergo this reaction)[204,211]

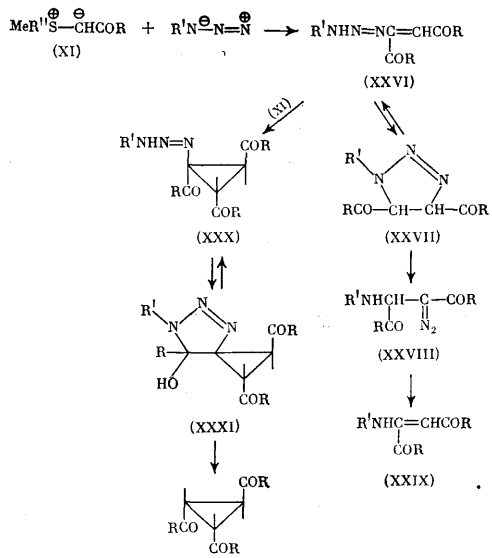


The difference between the structures of the products formed in the reactions of ylides with nitrile imines and diazocarbonyl compounds is evidently due both to the opposite polarisations of the corresponding 1,3-dipoles and to the

different relative reactivities of the 1,3-dipole compound and the intermediate betaines.

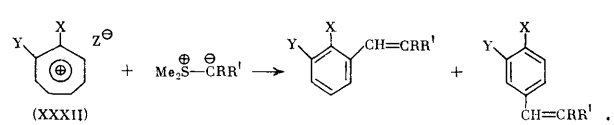
With the exception of alkyl azides[101,204], azides react with sulphonium ylides via pathways *d* and *f*.[101,102,204,212,213] The betaine (XXVI), formed via pathway *d*, can be stabilised by cyclisation to Δ^2-triazoline (XXVII), these forms being readily interconverted. In the presence of bases Δ^2-triazoline (XXVII) is unstable and decomposes to the diazo-compound (XXVIII) and then further (with loss of nitrogen) to the enamine (XXIX). Furthermore, the betaine (XXVI) can combine with a third ylide molecule to form cyclopropane derivatives of triazene (XXX) or Δ^2-triazoline (XXXI). The latter can decompose into the initial azide and a cyclopropane derivative:

Scheme 6



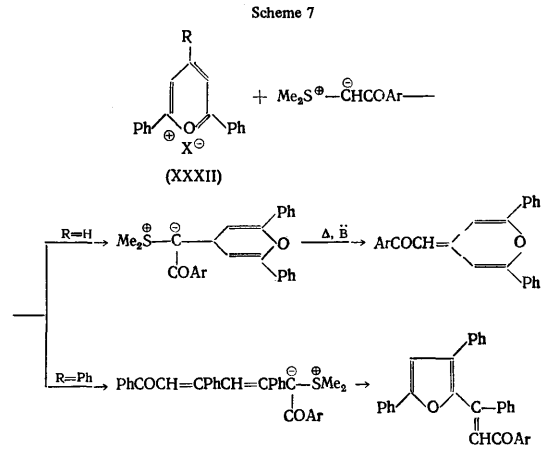
Studies devoted to the reaction of sulphonium ylides with tropylium[214–216], pyrylium[88,217,218], quinazolinium[219], oxathiolium, and dithiolium[220] have been published in recent years.

The reaction of sulphonium ylides with tropylium cations (XXXII) proceeds under mild conditions with formation of substituted styrenes[214–216]. The driving force of this reaction is provided by the formation of a stable benzene ring. By varying the substituents in the reactants, it has been shown that the mode of reaction is influenced by the steric hindrance arising during it and not by the nucleophilic properties of the ylide carbanion[214,215]. The attempts to isolate the intermediate sulphonium salts in these reactions proved unsuccessful, which can be accounted for by the ready elimination of the sulphide[216]:

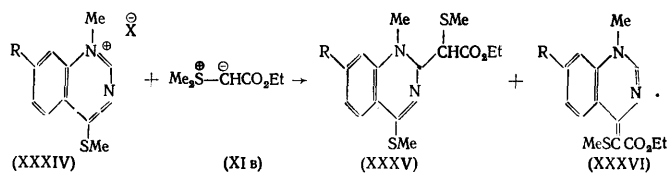


Pyrylium salts (XXXIII) are attacked by the ylide carbanion in the 2-position[88,217,218] or the 4-position[217] of the pyrylium heterocycle. The resulting sulphonium ylides decompose further to furan and 4-phenacylidenepyran derivatives respectively:

Scheme 7



In the reactions of sulphonium ylides with quinazolinium salts (XXXIV) the ylide attacks the 2- or 4-position in the heterocycle with formation of sulphonium salts. The latter are dealkylated by the nucleophilic counterion to give the products of $C_{(2)}$-substitution [compound (XXXV)] and $C_{(4)}$-substitution [compound (XXXVI)] in proportions which are determined by the nucleophilic properties of the anion[219], instead of the expected 1,4-benzodiazepines:

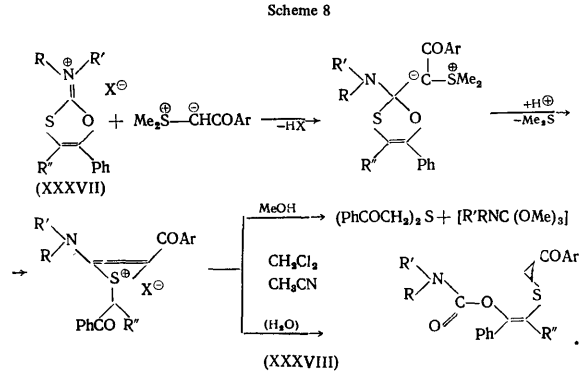


The yields of products (XXXV) and (XXXVI) are given below:

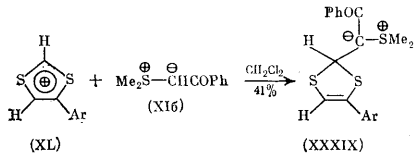
X	Yield of (XXXV), %	Yield of (XXXVI), %
OH	80	—
NO_3	0÷5	90

The oxathiolium cations (XXXVII) are highly reactive electrophiles. The structure of the products formed in their reactions with sulphonium ylides depends on the nature of the solvent employed. Carbamate esters (XXXVIII) are formed in aprotic solvents and diphenacyl sulphide is the product in protic solvents[220]. The overall mechanism of these reactions is presented in Scheme 8.

Scheme 8



The reaction proceeds via the nucleophilic attack by the ylide carbanion on the 2-position in the oxathiole ring. This has been confirmed by the isolation of the intermediate ylide (XXXIX) in the reaction of the dithiolium cation (XL) with the sulphonium ylide (XIb):



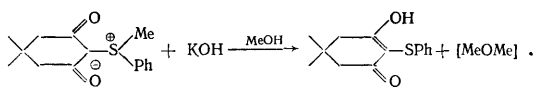
The rearrangement of the ylide, accompanied by the elimination of the sulphide, gives rise to the thi-irenium cation, whose hydrolysis and alcoholysis take place differently and lead to the observed products. The possibility of the existence of the thi-irenium cation has been recently confirmed by the synthesis and investigation of the stable 2,3-di-t-butyl-1-methylthi-irenium tetrafluoroborate[221].

Thus the reactions of stabilised sulphonium ylides with electrophiles constitute a convenient method of synthesising a wide variety of organic compounds, in the first place various carbocycles and heterocycles.

VI. REACTIONS WITH NUCLEOPHILES

The reactions of sulphonium ylides with nucleophiles lead in most instances to results similar to those described for their reactions with electrophiles. This is not surprising, since the reactions of ylides with water, alkoxides, and mercaptans proceed via the initial protonation of the ylide and subsequent attack by the nucleophile on the resulting sulphonium salt. The mode of decomposition of the latter depends both on the nature of the substituents at the sulphonium centre and on the nature of the nucleophile.

Thus the hydrolysis and alcholysis of ylides result mainly in the dealkylation of the sulphonium cation[222–226]:



If the ylide has been stabilised by ester groups, then the dealkylation is accompanied by hydrolysis and the elimination of ester groups[222]. The latter occurs sometimes even without the cleavage of the C–S ylide linkage, leading to the formation of a sulphobetaine[56,57,160,227,228].

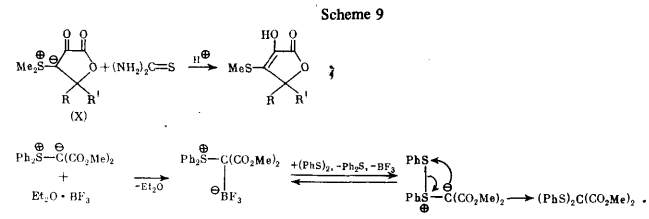
In constrast to what has been stated above, the reactions of sulphonium ylides with mercaptans lead mainly to the cleavage of the C–S ylide linkage[64,141,229,230]:

$$R_2\overset{\oplus}{S}-\overset{\ominus}{C}(COR')R'' + R'''SH \rightarrow R'''SCH(COR')R'' + R_2S\ .$$

The reactions of sulphonium ylides with cyanide[141] and phosphorodithioate[231] anions as well as the anions of compounds containing an active methylene group[232] take place similarly.

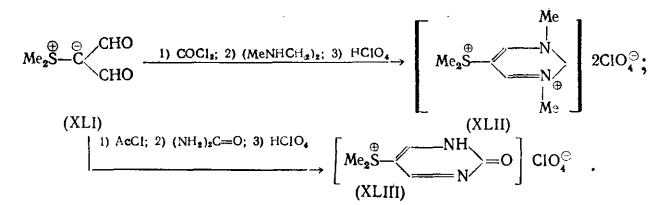
The reactions of thiourea[64] and disulphides[233] with sulphonium ylides take place only in the presence of a proton donor[64] or boron trifluoride etherate[233], i.e. they also involve the intermediate formation of sulphonium compounds:

Scheme 9



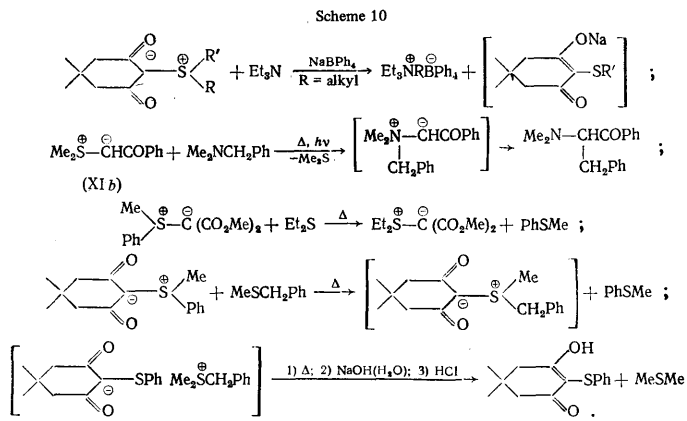
It is noteworthy that more nucleophilic monocarbonyl-stabilised ylides react with disulphides in the absence of a catalyst[233]. In this case the disulphide apparently reacts as an electrophile in a manner similar to that described in Section V.

The reactions of dimethylsulphuranylidenemalonic aldehyde (XLI) with urea and *N,N'*-dimethylethylenediamine are of interest; under these conditions, the condensation reactions lead to the formation of heterocyclic sulphonium salts (XLII) and (XLIII).[85] The authors noted that phosgene and acetyl chloride are used in these reactions to convert the ylide into a more reactive form:



Stabilised sulphonium ylides react in two ways with tertiary amines[57,234] and dialkyl sulphides[139,235], giving rise to transylidation products[57,139] or the product of the dealkylation of the ylides[234,235]:

Scheme 10

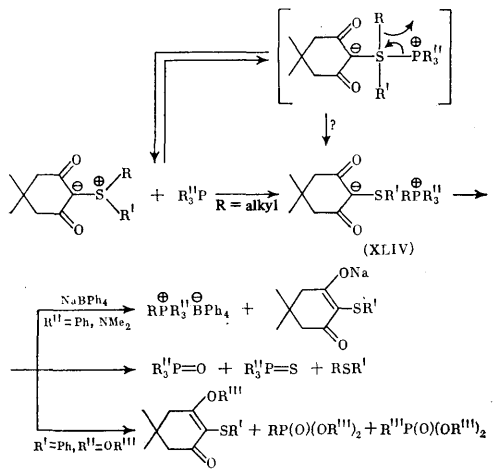


The transylidation reactions of sulphonium ylides with amines and sulphides can be greatly facilitated by carrying them out in the presence of catalytic amounts of dialkoxydisulphides, thiocyanogen, aryl thiocyanates, *p*-hydroxyphenyl trifluoromethyl sulphide, etc.[69,139,144,236]

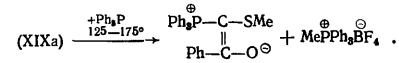
Stabilised sulphonium ylides react with Ph_3P,[162,237–243] $(Me_2N)_3P$,[242–244] and $P(OR)_3$.[243,245] The structures of the products formed in these reactions depend both on the

nature of the substituents in the ylide and on the nature of the substituents in the phosphorus(III) derivative. In the reactions of sulphuranylidene derivatives of dimedone and benzenesulphonylacetophenone with phosphorus(III) derivatives the ylide is dealkylated, which leads to phosphonium salts with an enolate anion[240–245]. Alkyltriphenylphosphonium salts, obtained in the reactions of *S,S*-alkylphenylsulphuranylidine derivatives of dimedone (XLIV) and benzenesulphonylacetophenone were isolated from the reaction products. In the remaining cases they decomposed in the course of the reaction with formation of the products presented in Scheme 11:[214,243,246]:

Scheme 11

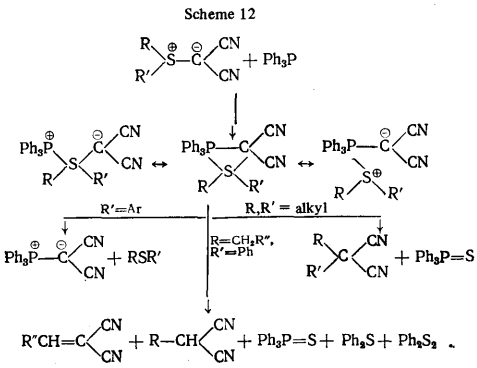


The reaction of the phenacylide salt (XIXa) with Ph_3P proceeds similarly[162]:



The replacement of the carbonyl and sulphonyl groups in the ylide by nitrile groups in the reactions of sulphuranylidene derivatives of dicyanomethane with Ph_3P leads to transylidation or ylide transalkylation–desulphurisation products[237–239]. The mode of reaction is determined by the nature of the substituents at the sulphonium sulphur atom:

Scheme 12



The phosphonium salts formed in the dealkylation of ylides can be obtained either by the intermediate formation and decomposition of σ-sulphuranes or by the direct attack of the phosphorus nucleophile on the electrophilic carbon atom of the *S*-alkyl group. The latter pathway appears to us to be preferable.

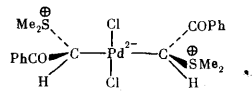
The formation of all the products detected in the reactions of sulphonium ylides with phosphorus(III) derivatives can be accounted for by the intermediated formation and decomposition of phosphonium salts[243,246]. The reactions of diarylsulphuranylidenedicyanomethanes with Ph_3P, where the attack of the latter on the sp^2-hybridised carbon atom of the *S*-aryl group is hindered, constitute an exception[247]. In such cases the mechanism involving the insertion of Ph_3P in the C–S ylide linkage apparently takes place with formation of a resonance-stabilised triad, whose decomposition leads to the observed products[237–239].

It is noteworthy that carbonyl-stabilised sulphonium ylides are dealkylated not only by phosphorus(III) and nitrogen derivatives[234,240–245] but also by tertiary arsines[248], triphenylstibine, and triphenylbismuth[234].

VII. ORGANOMETALLIC DERIVATIVES AND COMPLEXES

It was stated in Section V that stabilised sulphonium ylides react only with olefins activated by electron-accepting substituents. However, it is known that the electrophilic properties of an olefin are enhanced when it forms complexes with transition metal (platinum and palladium) salts[249]. This stimulated attempts to convert olefinic ligands into cyclopropane derivatives in transition metal complexes. However, it was found that, instead of the formation of a cyclopropane derivative, the olefin is readily substituted by the ylide under these conditions[250,251]. Such complexes can be obtained not only by ligand exchange[250–255] but also by their direct synthesis from ylides and metal salts[19,256,257], the structure of the complex formed depending on the nature of the metal, the structure of the ylide, and, in the case of exchange reactions, the structure of the initial complex. Thus sulphuranylidene derivatives of acetophenone form 2 : 1 adducts with $PdCl_2$ or $PdBr_2$,[68,250–252,256,257], 2 : 1 or 1 : 1 adducts with PtCl, depending on the method of synthesis[253,256], and dimers of 1 : 1 adducts with $HgCl_2$, evidently incorporating bridging chlorine atoms[256]. The formation of 1 : 1 adducts is also observed in the formation of complexes of sulphuranylidene derivatives of cyclopentadiene with HgI_2, $ZnCl_2$, and $AgNO_3$,[19] and of the dimethylsulphuranylidene derivative of malonic aldehyde (XLIII) with ZnI_2.[85]

The study of the ^1H and ^{13}C NMR and infrared spectra of the complexes of sulphuranylidene derivatives of acetophenone showed that the metal is coordinated to the carbanionic carbon atom of the ylide[68,250–253,256]. According to the results of X-ray diffraction analysis, the 2 : 1 complexes with $PdCl_2$ have the square planar *d,l-trans*-configuration[250,251]; when they are dissolved, epimerisation takes place readily and the ^1H NMR spectra demonstrate the existence of a mixture of *meso*- and *d,l-trans*-forms:[251]



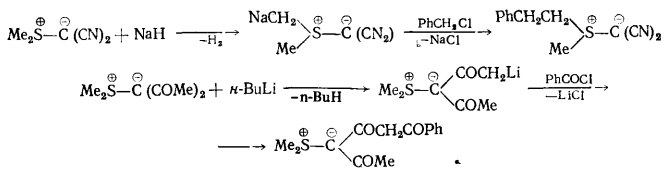
The structure of the complexes of PtX_2 with ylide ligands is influenced by the nature of the halogen[252,253], the amount of the *trans*-isomer increasing under these conditions in the sequence X = Cl < Br < I, which is analogous to that observed for the complexes $PtX_2.(Et_3P)_2$.[258]

The metal atom can be coordinated not only to the carbanionic carbon atom of the ylide but also to a sulphur atom[19,259] or a nitrogen atom, for example in complexes of dimethylsulphuranylidenedicyanomethane (III) with $PdCl_2$.[259] The absence of the coordination of the metal to the carbon atom in the latter case is probably caused by its reduced nucleophilicity due to the delocalisation of the electron density

over the electron-accepting cyano-groups. In the sulphuranylidene derivatives of cyclopentadiene (V) the metal can be coordinated not only to the sulphur atom[19] but, as shown recently in relation to their complexes with chromium, molybdenum, and tungsten carbonyls[260], also to the cyclopentadienyl system.

It was noted in Section VI that the coordination of Lewis acids to the carbanionic carbon atom of the ylide facilitates their reaction with nucleophiles. In this connection attempts were made to investigate the reactions of nucleophiles with ylides functioning as ligands in transition metal complexes. However, it was found that this entails only ligand exchange reactions. Thus it has been found[251] that pyridine substitutes one ylide ligand in the cold and both ylide ligands on heating 2 : 1 complexes of sulphuranylidene derivatives of acetophenone with $PdCl_2$.

Organometallic derivatives of stabilised sulphonium ylides are readily formed on metallation of ylides with BuLi, iso-Pr_2NLi,[261,262] or NaH,[142] a proton being substituted both in the substituent at the carbanionic carbon atom[261,262] and at the *S*-alkyl group[142]. Their further reactions are of the usual type for organometallic compounds:



VIII. PRACTICAL APPLICATIONS

Intensive investigation of the chemistry of sulphonium ylides began approximately 15 years ago and during this relatively short period interesting practical results have been obtained. Sulphonium ylides proved to be effective nucleophiles for the epoxidation of carbonyl compounds and the conversion of olefins into cyclopropane derivatives[5,263]. This constitutes an important addition to the methods for the epoxidation and conversion into cyclopropane derivatives by electrophilic carbenes[264]. The use of ylides for the synthesis of heterocycles is also extremely important[265]. This review presents the results of synthetic applications of stabilised sulphonium ylides. However, this does not exhaust their applications. It has been suggested that sulphonium ylides be used as catalysts of the liquid-phase oxidation of hydrocarbons[266]. There are data showing that 4-dialkylsulphuranylidene-2,6-di-t-butylcyclohexadienones[267] effectively alkylate compounds containing an acidic proton[268]. Diphenylsulphuranylideneacetone and its analogues make it possible to obtain products used to prepare modifying agents for paper, textiles, and leather as well as substances used in the manufacture of polyamides, polyesters, alkyd resins, and plant protecting agents[269].

Sulphuranylidene derivatives of cyclopentadiene accelerate the dyeing of polyester, polyamide, and other fibres by anionic dyes[270]. Dimethylsulphuranylidene-*p*-nitrophenacyloxyethoxycarbonylmethane exhibits a fungicidal activity[271], while 3-dialkylsulphuranylidene-2-oxo-1,4-naphthoquinones exhibit an anti-inflammatory inactivity and can be used in the treatment of arthritis, erythema, oedema, etc.[272]

Thus the range of applications of sulphonium ylides is wide and varied extending from reagents for organic syntheses to effective physiologically active preparations. New studies in this field will undoubtedly lead to a wider practical utilisation of these substances.

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