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Doubly Stabilised Chalcogenonium Ylides

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A systematic and general account is given of the methods of synthesis, structures, and reactivities of sulphur, selenium, and tellurium ylides containing two strongly electron-accepting substituents at the ylide carbon atom. The bibliography includes 166 references.

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I. INTRODUCTION

Recently there has been a considerable growth of interest in ylides—compounds in which the positive charge of the onium group is stabilised by a neighbouring carbanion. This class of compounds is of interest from both theoretical (characteristics of steric and electronic structures and reactivity) and practical points of view. The importance of the Wittig reaction[1] (interaction of phosphonium ylides with carbonyl compounds), whereby one can obtain olefins with a wide variety of structures, is generally known. Sulphonium ylides of different types, which have been examined in a monograph[2], are widely used together with the ylides of other elements for the synthesis of oxirans, cyclopropanes, and five- and six-membered heterocyclic compounds.

However, the sharp increase of the number of publications on sulphonium ylides together with the appearance of communications on the synthesis and properties of their analogues in terms of Mendeleev's Table—the selenonium and telluronium ylides—made necessary a systematic account and a more detailed examination of data obtained for individual classes of chalcogenonium ylides. In the first place, one must distinguish ylides stabilised by two electron-accepting groups capable of delocalising the negative charge of the carbanion; subsequently, such ylides will be called, for brevity, doubly stabilised (distabilised) ylides (DSY). Ylides of this type, which were believed previously to be chemically inert, subsequently began to attract the attention of chemists, because it was found that they react fairly readily with different electrophiles, enter into thermolytic and transylidation reactions, undergo various rearrangements, etc., and in terms of their reactivity they frequently differ significantly from other types of ylides. In many instances the mode of reaction of doubly stabilised chalcogenonium ylides is extremely unusual and is characteristic only of such ylides, which leads to new possibilities for syntheses based on them. The unusual nature of the methods of their synthesis and reactivity requires a separate consideration of ylides of this type.

This review does not deal with carbonyl ylides, i.e. oxygen ylides. This is because, in contrast to chalcogenonium ylides, the oxygen ylides are merely short-lived extremely reactive intermediates and because both these and other related ylides have been examined in a recent review[3].

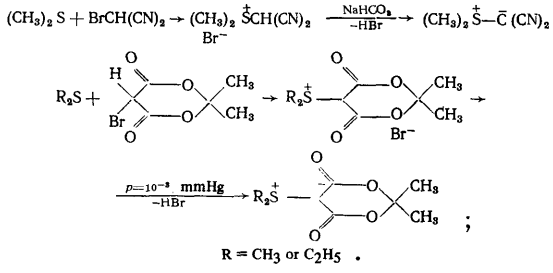
II. METHODS OF SYNTHESIS

The methods of synthesis of the DSY of Group VI elements known at present are in many respects analogous to the procedures found previously for the synthesis of the ylides of Group V elements. At the same time specific methods have been developed recently for the synthesis of DSY which can evidently find applications in the synthesis of selenonium and telluronium ylides. The fundamental problem in the formation of the DSY of Group VI elements is the synthesis of the chalcogenonium component; we therefore based our classification of the methods of synthesis of DSY on the nature of the chalcogenonium component.

1. Ylides from Diorganochalcogenides R^1R^2M (M = S, Se, or Te)

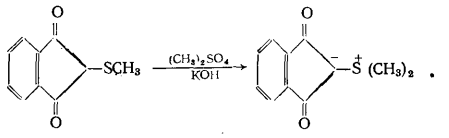
(a) The Salt Method

The salt method is one of the main procedures for the synthesis of non-stabilised and singly stabilised ylides of Group V [1] and VI [2] elements; it is based on the interaction with bases of onium salts containing at least one hydrogen atom at an α-carbon atom. This method has been little used for the synthesis of the DSY of Group VI elements because of the low yields of ylides (owing to the instability of the corresponding chalcogenonium salts) and also because of the frequently poor availability of the initial salt. However, dimethylsulphonium dicyanomethylide[4] and dialkylsulphonium 2,2-dimethyl-4,6-dioxo-1,3-dioxanilides[5,6] have been obtained with the aid of this method:

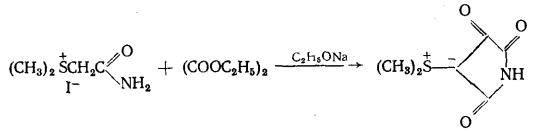


The instability of salts of the type $R_2S^+CHXYHal^-$ is probably associated with the highly electrophilic properties of the 'onium cations, which leads to their ready cleavage by the counterions (Hal^-). One should also note that, in the synthesis of such salts by the alkylation of sulphides by the halogeno-derivatives of active methylene compounds, the reaction apparently does not proceed unambiguously. At the

same time DSY have been synthesised successfully[7] by alkylating a sulphide containing two-electron-accepting groups with dimethyl sulphate in an alkaline medium:



DSY have been synthesised by introducing electron-accepting groups into a pre-existing sulphonium salt during the condensation of sulphonia-acetamides with oxalate esters in the presence of alkoxides[8]:



A specific version of the salt method has been used in the synthesis of sulphonium dinitromethylides[9]: it involves the interaction of dibromodinitromethane with a large excess of dimethyl sulphide or thiourea, which leads to the formation of relatively unstable crystalline compounds, which on treatment with water give rise to the ylides $(CH_3)_2\overset{+}{S}-\overline{C}(NO_2)_2$ and $(H_2N)_2C{=}\overset{+}{S}-\overline{C}(NO_2)_2$.

(b) The Formation of Ylides from Activated Oxirans

One of the most important methods of synthesis of dicyanomethylides involves the interaction of diorganosulphides[4,10–13] and diorganoselenides[14] with activated oxirans—tetracyanoethylene oxide[4,10,11,13] or 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene oxide[4,12] (Table 1):

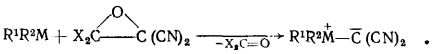
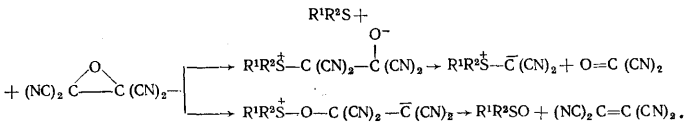


Table 1.

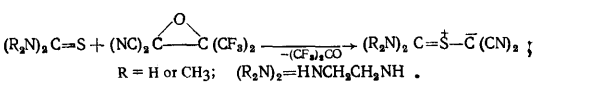
R^1	R^2	Refs.	R^1	R^2	Refs.
	M = S, X = CN			$(CH_2)_4$	[4]
CH_3	CH_3	[4, 10]		$(CH_2)_5$	[11]
C_2H_5	C_2H_5	[4]		$CH_2CH{=}CHCH_2$	[11]
C_3H_7	C_3H_7	[10]		$CH_2CH_2SCH_2CH_2$	[11]
C_4H_9	C_4H_9	[4]		o-$CH_2C_6H_4CH_2$	[11]
$C_6H_5CH_2$	$C_6H_5CH_2$	[11]		o-$CH_2CH_2C_6H_4$	[11]
C_6H_5	C_6H_5	[10]		o-$CH_2CH_2C_6H_4CH_2$	[11]
4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	[11]		$(H_2N)_2C{=}$	[13]
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[11]		M = Se, X = CN	
CH_3	C_2H_5	[11]	$C_6H_5CH_2$	$C_6H_5CH_2$	[14]
CH_3	C_3H_7	[11]	4-$CH_3C_6H_4CH_2$	4-$CH_3C_6H_4CH_2$	[14]
CH_3	$C_6H_5CH_2CH_2$	[11]		M = S, X = CF_3	
CH_3	$C_{12}H_{25}$	[4]	C_6H_5	C_6H_5	[4]
CH_3	C_6H_5	[4, 11]	CH_3	$C_{12}H_{25}$	[4]
CH_3	1-$C_{10}H_7$	[4]	CH_3	C_6H_5	[4]
CH_3	4-$CH_3OC_6H_4$	[4]	CH_3	4-$CH_3SC_6H_4$	[4]
CH_3	4-BrC_6H_4	[4]		$(CH_2)_4$	[4]
CH_3	4-$CH_3SC_6H_4$	[4]		$(H_2N)_2C{=}$	[12]
C_2H_5	C_6H_5	[4, 11]		$[(CH_3)_2N]_2C{=}$	[12]
C_4H_9	C_6H_5	[4]		$HNCH_2CH_2NHC{=}$	[12]
$C_6H_5CH_2$	C_6H_5	[11]			

The reaction can proceed via two different pathways and, depending on the nature of the groups at the sulphur atom, can lead to ylides or sulphoxides[11,13]:



The preferred pathway depends on steric factors—for bulky sulphides, the possibility of the reaction with carbon atoms shielded by the cyano-groups is hindered, so that the interaction involves the oxygen atom. The ease of formation of ylides diminishes in the sequence Alk_2S > AlkSAr > Ar_2S and the yields of sulphoxides as a rule increase.

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene oxide is a more convenient donor of the dicyanomethylene group than tetracyanoethylene oxide, since in its reactions hexafluoroacetone, which is less reactive than the dinitrile of mesoxalic acid, is split off. In the study of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene oxide, side reactions are therefore reduced to a minimum and the yield and purity of the resulting ylides (particularly those obtained from thiourea and its derivatives) are appreciably increased[12]:



(c) The Carbene Method

One of the comparatively new methods of synthesis of DSY is based on the reaction of highly electrophilic carbenes, obtained from the corresponding diazo-compounds by thermal or photochemical methods, with compounds of a bivalent chalcogen. The method, used mainly to synthesise sulphonium ylides, has been recently examined in a review[15] (Table 2):

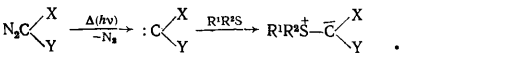


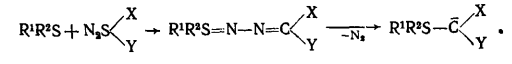
Table 2.

R^1	R^2	Refs.	R^1	R^2	Refs.
X = Y = $SO_2C_6H_5$			CBr=CHCH=CH		[27]
CH_3	CH_3	[16]	o-C_6H_4—CH_2CH_2		[15, 21]
C_4H_9	C_4H_9	[16]	X=Y=$COOC_2H_5$		
CH_3	C_6H_5	[17]	CH_3	CH_3	[18, 20, 21]
X = Y = $COOCH_3$			C_2H_5	C_2H_5	[22]
CH_3	CH_3	[18–25]	CH_3	C_4H_9	[21]
C_2H_5	C_2H_5	[18, 19, 21–23]	CH_3	$C_6H_5CH_2$	[21]
iso-C_3H_7	iso-C_3H_7	[18, 21]	X = Y = $COCH_3$		
C_6H_5	C_6H_5	[18, 21]	CH_3	CH_3	[18, 20, 21, 24, 29]
CH_3	C_6H_5	[18, 19, 21, 22, 24, 25]	CH_3	C_3H_5	[24]
CH_3	iso-C_3H_7	[24, 25]	X=Y=COC_3H_7-iso		
CH_3	n-H_9	[18, 19, 21, 24, 25]	CH_3	CH_3	[29]
CH_3	t-C_4H_9	[18, 19, 21]	X=$COCH_3$, Y=$COOCH_3$		
CH_3	s-C_8H_{17}	[25]	CH_3	C_6H_5	[24]
CH_3	$C_6H_5CH_2$	[18, 19, 21, 23–25]	X=Y=CN		
CH_3	C_6H_5	[18, 19, 21, 24, 25]	C_3H_7	C_3H_7	[11]
CH_3	4-$CH_3C_6H_4$	[17]	$C_6H_5CH_2$	$C_6H_5CH_2$	[11]
CH_3	CH_2COOCH_3	[21]	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	[11]
CH_3	CH_3SCH_2	[25]	$(CH_2)_5$		[11]
CH_3	$CH_2COOC_2H_5$	[23]	$CH_2CH_2SCH_2CH_2$		[11]
C_2H_5	CH_2COOCH_3	[23]	o-$CH_2C_6H_4CH_2$		[11]
C_2H_5	n-C_4H_9	[21]	o-$C_6H_4CH_2CH_2$		[11]
$C_2H_5CH_2$	4-$CH_3C_6H_4$	[17]	XY= $=COCH_2C(CH_3)_2CH_2CO$		
$(CH_2)_4$		[21]	CH_3	CH_3	[30]
$(CH_2)_5$		[21]	XY=C(O)OC$(CH_3)_2$OC(O)		
$(CH_2)_6$		[21]	CH_3	CH_3	[29]
$CH_2CH{=}CHCH_2CH_2$		[15]			
CH=CHCH=CH		[15, 26–28]			
CCl=CHCH=CCl		[27]			
$C(CH_2OH)$=CHCH=CH		[27]			
CBr=$C(CH_3)$CH=CH		[27]			
$C(CH_3)$=CHCH=CH		[27]			

The best yields of ylides are usually attained in the thermal generation of carbenes in the presence of anhydrous copper sulphate of copper powder, which reduce the decomposition temperatures of the diazo-compounds[18,21]. Thus, in

the photochemical decomposition of dimethyl diazomalonate in diphenyl sulphide, the corresponding diphenylsulphonium dimethoxycarbonylmethylide is obtained in 12% yield, while in the thermal decomposition the yield is 85%.[18,21] Furthermore, in the photochemical synthesis of the carbenes the yields of the ylides are greatly reduced when branched sulphides are used in the reaction[18,21]. It is also of interest that, according to the data of Nikolaev et al.[29], cyclic diazoketones completely fail to form sulphonium ylides in the course of their photolysis in alkyl sulphides—the resulting carbene merely undergoes the Wolff rearrangement. The reason for this is probably that the *trans*-disposition of the diazogroups and neighbouring substituents, which is fixed in the molecules of these diazoketones, ensures a higher (compared with acyclic diazoketones) capacity of the alkyl groups for migration (the Wolff rearrangement). In the photolysis of acyclic 2-diazo-1,3-diketones, the formation of the corresponding sulphur DSY is accompanied also by the formation of the products of the Wolff rearrangement, the product ratio depending on the bulk of the alkyl substituents in the ketone: an increase of the bulk of the substituents lowers the yield of the ylides[29].

The addition of a singlet carbene to the sulphur atom is postulated in the thermal and non-sensitised photochemical decomposition reactions of diazo-compounds[21]. At the same time, the ready formation of sulphonium ylides in the benzophenone-sensitised photolysis of dimethyl diazomalonate in alkyl sulphides is evidence, according to the authors[21], of the involvement of a triplet carbene in the reaction. The ylide can be formed either via the attack by the triplet carbene on the sulphur atom with subsequent inversion of spins or via a preliminary conversion of the triplet carbene into a singlet carbene in the presence of dialkyl sulphides with subsequent addition to the sulphur atom[21]. Nor can one rule out the possibility that the ylides are synthesised via the intermediate formation of sulphur azines[11], analogous to the formation of phosphine azines in the reaction of phosphines with diazo-compounds[31]:



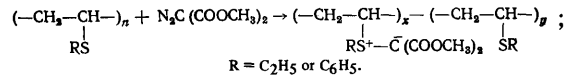
The use of dialkoxydisulphides[22] as catalysts makes it possible to obtain ylides from diazo-compounds at room temperature without irradiation. However, this method has no special advantages over the photochemical and even less so the thermal methods of generating ylides, because many ylides cannot be obtained by this method at all.

Unsaturated sulphides (allyl-, vinyl-, and ethynyl-substituted sulphides) are also capable of forming sulphonium ylides on reaction with carbenes[15,26,32]. However, the DSY derived from allyl sulphides readily undergo the allyl rearrangement[32–35] (see Section III), while in vinyl and ethynyl sulphides the sulphur is less reactive than in alkyl sulphides, owing to conjugation with the double or triple bond and it is therefore not always possible to obtain the sulphonium DSY.[26] Furthermore, the addition of carbenes to the double bond has been observed. Nevertheless, the carbene generated from dimethyl diazomalonate is "captured" by the weakly basic sulphur of thiophen (and its derivatives) or dibenzothiophen to give the corresponding S-ylides[15,21,26,27,28]. The sulphonium ylides formed from carbenes and four- or five-membered non-aromatic cyclic sulphides cannot be isolated, because they readily undergo the Stevens rearrangement with ring expansion; on the other hand, the ylides derived from six-membered sulphides are entirely stable[15,21,32].

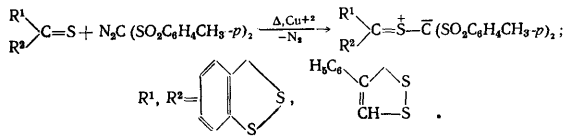
Table 3.

R¹	R²	Refs.
M=S		
X=Y=CONHCONHCO		
CH_3	CH_3	[6, 40–42]
C_2H_5	C_2H_5	[40]
$C_6H_5CH_2$	$C_6H_5CH_2$	[43]
CH_3	C_2H_5	[40]
$(CH_2)_4$		[40]
X=Y=CONHCON(CH₃)CO		
CH_3	CH_3	[40]
C_2H_5	C_2H_5	[40]
CH_3	C_2H_5	[40]
$(CH_2)_4$		[40]
X=Y=CON(CH₃)CON(CH₃)CO		
CH_3	CH_3	[40]
C_2H_5	C_2H_5	[40]
X=Y=*o*-COC_6H_4CO		
CH_3	CH_3	[6, 41, 43, 44]
C_2H_5	C_2H_5	[41]
C_6H_5	C_6H_5	[44]
CH_3	C_6H_5	[44]
CH_3	4-$CH_3OC_6H_4$	[44]
CH_3	4-BrC_6H_4	[44]
CH_3	4-ClC_6H_4	[44]
$(CH_2)_4$		[41]
X=Y=*o*-COC_6H_4COCO		
CH_3	CH_3	[40]
X=Y=1,8-$COC_{10}H_6CO$		
CH_3	CH_3	[6]
X=Y=$COOC(CH_3)_2OCO$		
CH_3	CH_3	[6]
C_2H_5	C_2H_5	[6]
$C_6H_5CH_2$	$C_6H_5CH_2$	[6]
C_6H_5	C_6H_5	[43]
CH_3	$C_6H_5CH_2$	[43]
X=Y=$COCH_2CH_2CH_2CO$		
CH_3	CH_3	[43]
CH_3	C_6H_5	[45, 46]
X=Y=$COOC(CH_3)_2CO$		
CH_3	CH_3	[43]
$C_6H_5CH_2$	$C_6H_5CH_2$	[43]
X=Y=$COCH_2C(CH_3)_2CH_2CO$		
CH_3	CH_3	[30, 41, 42, 45, 46]
$C_6H_5CH_2$	$C_6H_5CH_2$	[30]
CH_3	C_6H_5	[30, 45, 46]
$(CH_2)_4$		[41]
X=Y=COCONHCO		
CH_3	CH_3	[41]
X=Y=$SO_2C_6H_5$		
CH_3	CH_3	[40]
X=$COCH_3$, Y=$COOC_2H_5$		
CH_3	CH_3	[41, 45, 46]
CH_3	C_6H_5	[45, 46]
X=$COCH_3$, Y=$CONHC_6H_5$		
CH_3	CH_3	[41]
M=Se		
XY=$COCH_2C(CH_3)_2CH_2CO$		
CH_3	C_6H_5	[51]
CH_3	2-$CH_3OC_6H_4$	[51]
CH_3	1-$C_{10}H_7$	[51]
CH_3	2,4,6-$(CH_3)_3C_6H_2$	[51]
$C_6H_5CH_2$	C_6H_5	[51, 55]
X=Y=NO_2		
C_6H_5	C_6H_5	[52, 53]
X=Y=CN		
$C_6H_5CH_2$	$C_6H_5CH_2$	[54]
C_6H_5	C_6H_5	[54]
$(CH_2)_4$		[54]
$C_6H_5CH_2$	C_6H_5	[54]
X=Y=COC_6H_5		
C_6H_5	C_6H_5	[55]
X=NO_2, Y=$COOCH_3$		
C_6H_5	C_6H_5	[52, 53]
X=Y=$SO_2OC_6H_5$		
CH_3	CH_3	[47]
X=Y=NO_2		
CH_3	CH_3	[43, 48, 49]
C_2H_5	C_2H_5	[49]
$C_6H_5CH_2$	$C_6H_5CH_2$	[48]
C_6H_5	C_6H_5	[48]
X=Y=CN		
CH_3	CH_3	[6, 41, 42, 44–46]
C_2H_5	C_2H_5	[41]
CH_3	C_6H_5	[44–46]
CH_3	4-$CH_3OC_6H_4$	[44]
CH_3	4-ClC_6H_4	[44]
CH_3	4-BrC_6H_4	[44]
CH_3	4-$CH_3COC_6H_4$	[44]
X=Y=$COCH_3$		
CH_3	CH_3	[41, 45, 46]
C_3H_7	C_3H_7	[41]
CH_3	C_6H_5	[45, 46]
X=Y=$COOC_2H_5$		
CH_3	CH_3	[41]
X=$SO_2C_6H_5$, Y=COC_3H_5		
CH_3	CH_3	[30]
CH_3	C_6H_5	[30]
X=$SO_2CH=CH_2$, Y=$SO_2C_6H_5$		
CH_3	CH_3	[50]
X=NO_2, Y=CN		
CH_3	CH_3	[49]
X=NO_2, Y=$COCH_3$		
CH_3	CH_3	[49]
X=NO_2, Y=COC_6H_5		
CH_3	CH_3	[48]
X=NO_2, Y=$COOCH_3$		
CH_3	CH_3	[48, 49]
X=NO_2, Y=$CONH_2$		
CH_3	CH_3	[49]
X=CN, Y=$COCH_3$		
CH_3	CH_3	[41]
C_3H_7	C_3H_7	[41]
X=CN, Y=$COOC_2H_5$		
CH_3	CH_3	[45, 46]
CH_3	C_6H_5	[45, 46]
X=CN, Y=$PO(OC_2H_5)_2$		
CH_3	CH_3	[41]
X=$COCH_3$, Y=COC_6H_5		
CH_3	CH_3	[45, 46]
CH_3	C_6H_5	[45, 46]
X=NO_2, Y=COC_6H_5		
C_6H_5	C_6H_5	[52, 53]
X=CN, Y=$COOCH_3$		
$C_6H_5CH_2$	$C_6H_5CH_2$	[54]
$(CH_2)_4$		[54]
$C_6H_5CH_2$	C_6H_5	[54]
X=CF_3, Y=COC_6H_5		
C_6H_5	C_6H_5	[56]
$C_6H_5CH_2$	C_6H_5	[56]
X=SCH=CHCH=CCO, Y=$COCF_3$		
C_6H_5	C_6H_5	[56]
X=$COOCH_3$, Y=$COCOOCH_3$		
$C_6H_5CH_2$	$C_6H_5CH_2$	[14]
M=Te		
X=Y=$COCH_2C(CH_3)_2CH_2CO$		
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[57]
X=Y=*o*-COC_6H_4CO		
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[57]
X=Y=$COOC_3H_5$		
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[57]
X=NO_2, Y=$COOC_2H_5$		
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[57]

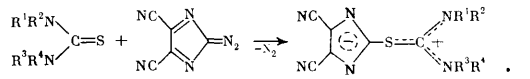
The synthesis of polyvinylsulphonium ylides should be mentioned[36]:



Thiocarbonyl compounds can also "capture" carbenes[37]:

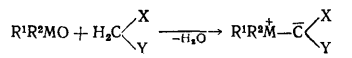


The high stability of thiocarbonyl ylides obtained from 4,5-dicyano-1,3-diazacyclopentadiene is also noteworthy[38,39]:



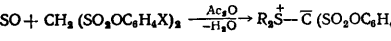
2. Synthesis from Diorganochalcogen Oxides R^1R^2MO (M = S, Se, or Te)

One of the most thoroughly developed methods for the synthesis of the DSY of Group VI elements involves the interaction of diorganochalcogen oxides with compounds containing active methylene groups (Table 3):

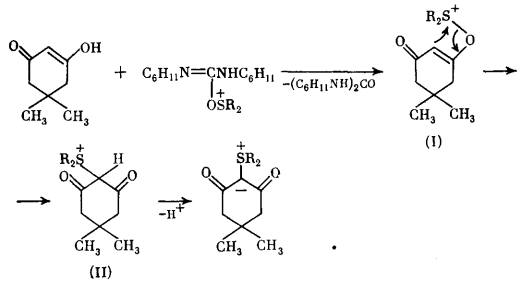


The course of the reaction and the yields of the ylides are influenced significantly by the basicity of the chalocogen oxides. Indeed, whereas in the case of sulphoxides dehydrating agents have to be used, frequently under relatively severe conditions [treatment with hot acetic anhydride[7], P_2O_5 in triethylamine[45,46], aryl cyanates[42], thionyl chloride[4], sulphur trioxide[49], and dicyclohexylcarbodi-imide (DCCD) in the presence of anhydrous phosphoric acid[41]], the more basic diaryl selenoxides[58] readily give rise to the corresponding ylides in the presence of acetic anhydride at room temperature[52,53], DCCD,[55,56] anhydrous sodium sulphate in chloroform[51,54], and (as in the case of diaryl telluroxides[57]) even in the absence of dehydrating agents[54]. The reactions of asymmetric selenoxides with dimedone in the presence of anhydrous sodium sulphate and 10-*d*-camphorsulphonic acid have been used to synthesis optically active selenonium ylides[51].

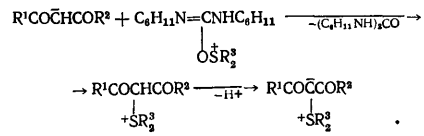
The C–H acidity of the active methylene compounds is also important. Thus, whereas fairly acidic compounds with active methylene groups form ylides, the less acidic compounds (phenylacetonitrile, fluorene, and tetraethyl methylenebisphosphonate) are inert under the usual reaction conditions[41]. However, in the synthesis of ylides from aryl esters of methionic acid, electron-donating substituents X in the aromatic ring, which lower acidity, promote the formation of ylides, while electron-accepting substituents hinder it (with X = *p*-NO_2, the reaction does not occur at all[47]):



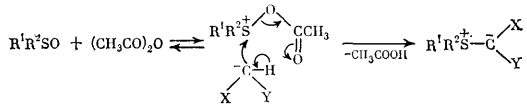
It has been suggested that, when DCCD is used, the reaction of sulphoxides with compounds containing active methylene groups proceeds via the intermediate formation of an adduct of the sulphoxide with DCCD; nucleophilic attack on the adduct by an enol gives rise to an enolsulphonium derivative (I). The latter rearranges to the diketosulphonium derivative (II) and, by losing a proton in a polar medium, is converted into the corresponding ylide[41]:



Another possible reaction mechanism involves the nucleophilic attack on the adduct by a carbanion with subsequent loss of a proton[41]:



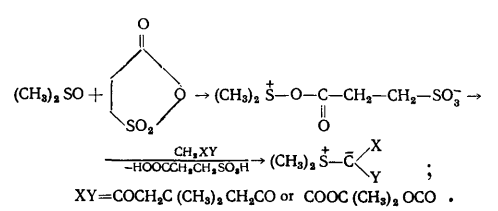
Ylides are formed via a similar mechanism from sulphoxides and active methylene compounds in acetic anhydride[6,46]:



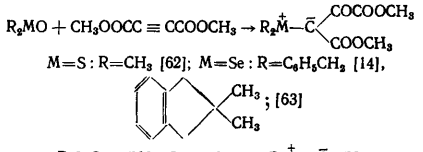
It is of interest to note that, in contrast to diaryl sulphoxides, diaryl telluroxides react with acetic and other anhydrides to form the corresponding diacylates in quantitative yields[59,60].

The use of acetic anhydride as the dehydrating agent lowers the yields of sulphonium ylides somewhat as a consequence of a side reaction—the Pummerer reaction. The best results are therefore obtained, particularly in the case of dimethyl sulphoxide, when DCCD is used. In fact, whereas in the presence of acetic anhydride the malonic ester does not form an ylide with dimethyl sulphoxide and the cyanoacetic ester gives rise to an ylide in a yield of only 2%, in the presence of DCCD the yields of ylides greatly increase and amount to 40 and 62% respectively[41] (other examples have also been quoted[41]).

The inner anhydride of γ-sulphopropionic acid, which is apparently free from the disadvantages characteristic of acetic anhydride, has been recently proposed as the condensing agent for the synthesis of sulphonium ylides[61]. The betaine formed on interaction with the sulphoxide is made to react with active methylene compounds:

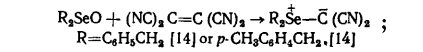


An unusual method of synthesis of the DSY of Group VI elements from diorganochalcogen oxides involves the interaction of the latter with dimethyl acetylenedicarboxylate[14,62,63] or tetracyanoethylene[14]:



M=S: R=CH_3 [62]; M=Se: R=$C_6H_5CH_2$ [14],

; [63]



R=$C_6H_5CH_2$ [14] or p-$CH_3C_6H_4CH_2$, [14]

3. The Formation of Ylides from σ-Chalcogenuranes $R^1R^2MZ_2$ (Z = Hal)

The reaction of σ-selenuranes and σ-telluranes with active methylene compounds in the presence of bases has recently come to be used widely for the synthesis of selonium and telluronium ylides[55,64-69] (Table 4):

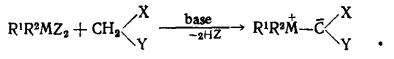


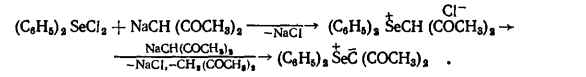
Table 4.

R^1	R^2	Refs.
M = Se, Z = Cl [55, 65—67], Br [64]		
X = Y = $COOC(CH_3)_2OCO$		
CH_3	CH_3	[64]
X = Y = $COCH_2C(CH_3)_2CH_2CO$		
C_6H_5	C_6H_5	[66]
$(CH_2)_4$		[66]
X = Y = $COCH_3$		
C_6H_5	C_6H_5	[66]
CH_3	C_6H_5	[66]
$(CH_2)_4$		[66]
X = Y = COC_6H_5		
CH_3	C_6H_5	[66]
$C_6H_5CH_2$	C_6H_5	[55]
$(CH_2)_4$		[66]
X = Y = CN		
CH_3	CH_3	[67]
C_6H_5	C_6H_5	[66]
CH_3	C_6H_5	[66]
$(CH_2)_4$		[66]
X = $COCH_3$, Y = COC_6H_5		
$C_6H_5CH_2$	C_6H_5	[55]
X = $COCH_3$, Y = $COOC_2H_5$		
$(CH_2)_4$		[66]
X = CN, Y = $COOCH_3$		
$(CH_2)_4$		[66]
X = CN, Y = $COOC_2H_5$		
$(CH_2)_4$		[66]
M = Te, Z = Cl, Br [68, 69]		
X = Y = $COCH_2C(CH_3)_2CH_2CO$		
CH_3	CH_3	[68, 69]
C_6H_5	C_6H_5	[68, 69]
4-$(CH_3)_2NC_6H_4$	4-$(CH_3)_2NC_6H_4$	[69]
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[68, 69]
4-$C_2H_5OC_6H_4$	4-$C_2H_5OC_6H_4$	[69]
4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	[68, 69]
4-FC_6H_4	4-FC_6H_4	[69]
4-BrC_6H_4	4-BrC_6H_4	[69]
CH_3	C_6H_5	[69]
CH_3	4-$CH_3OC_6H_4$	[69]
CH_3	4-$C_2H_5OC_6H_4$	[69]
CH_3	4-$CH_3C_6H_4$	[69]
4-$CH_3OC_6H_4$	4-$(CH_3)_2CHC_6H_4$	[69]
4-$CH_3OC_6H_4$	$C_6H_5CH_2$	[69]

Note. Here and in the other tables the numbers in square brackets denote references (Ed.of Translation).

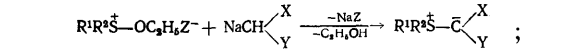
This reaction is apparently inapplicable to the synthesis of sulphonium ylides—possibly because the corresponding σ-sulphuranes do not exist in the form of covalent structures with a bisphenoid bond configuration, like the selenium and tellurium compounds, but in the form of charge-transfer complexes[70,71]. In the synthesis of selenonium and telluronium ylides from σ-chalcogenuranes the bases employed were KOH in methanol[66], pyridine[66,67], triethylamine[64,68,69], and sodium ethoxide[55].

Another version of the use of σ-chalcogenuranes in the synthesis of DSY involves their interaction with two equivalents of the sodium salts of active methylene compounds[72]. This reaction, which so far has been investigated only in relation to a single example, can evidently involve the following mechanism:



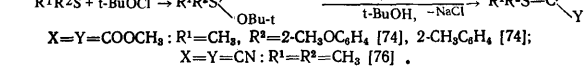
4. Ylides Obtained from Alkoxy- and Aza-sulphonium Salts

A number of DSY of sulphur have been synthesised by the reaction of alkoxydiorganosulphonium fluoroborates[46] or perchlorates[73] with the sodium salts of active methylene compounds:



Z=BF_4^-, X=Y=$COCH_3$: R^1=R^2=CH_3 [46]; X=$COCH_3$, Y=COC_6H_5: R^1=CH_3, R^2=C_6H_5 [46];
X=$COCH_3$, Y=$COOC_2H_5$: R^1=CH_3, R^2=CH_3, R_2=CH_3 or C_6H_5 [46];
X=$COOC_2H_5$, Y=CN: R^1=CH_3 or C_6H_5 [46]
Z=ClO_4^-: X=Y=$COOCH_3$, R^1R^2=2.2′-$C_6H_4OC_6H_4$ [73]

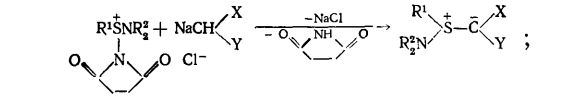
A more convenient modification of this method, not requiring the use of alkoxysulphonium salts prepared beforehand, involves the employment of t-butoxydiorganosulphonium chlorides obtained when sulphides are treated with t-butyl hypochlorite at low temperatures[74-77]:



X=Y=$COOCH_3$: R^1=CH_3, R^2=2-$CH_3OC_6H_4$ [74], 2-$CH_3C_6H_4$ [74];
X=Y=CN: R^1=R^2=CH_3 [76].

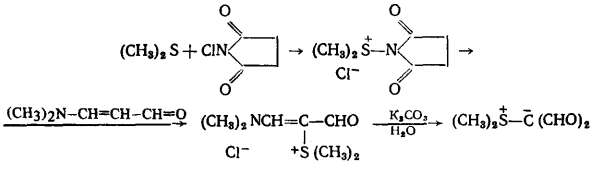
When the reaction is carried out in the presence of menthol, asymmetric induction takes place and optically active sulphonium ylides are obtained[74,75].

Azosulphonium salts behave similarly to alkoxysulphonium salts. Treatment of alkyl- or aryl-(dialkylamino)(succinimido)sulphonium chlorides[77,78] with sodio-derivatives of active methylene compounds leads to the corresponding ylides[77]:

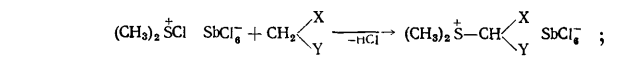


R^1=C_6H_5, R^2=CH_3 or R_2^2=$CH_2CH_2OCH_2CH_2$ or $(CH_2)_5$;
R^1=C_2H_5, R_2^2=$CH_2CH_2OCH_2CH_2$; X=$COOCH_3$, Y=$COOCH_3$, $COOC_2H_5$ [77]; X=Y=$C_6H_5SO_2$ or CH_3SO_2;
XY=$COCH_2C(CH_3)_2CH_2CO$ [77]

Another version of the method, with azasulphonium salts as intermediates in the synthesis of DSY, has been demonstrated[79]:



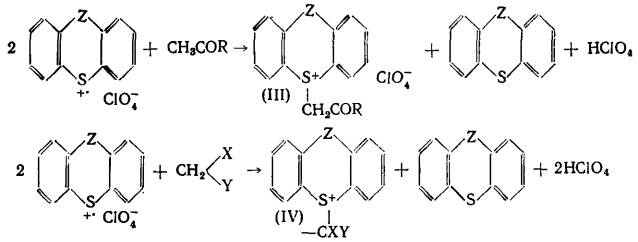
The conversion of diorganochlorosulphonium salts into compounds of the type $R_2\overset{+}{S}CHXYZ^-$, from which one can obtain, for example, sulphur-containing DSY, has been described[80]:



X=Y=CN; X, Y=CON(CH$_3$)CON(CH$_3$)CO .

5. Synthesis Via S-Radical-cations

A specific method of synthesising sulphur-containing DSY involves the interaction of the perchlorates of thianthrene and phenoxathi-in radical-cations with various keto-compounds, which lead either to β-ketosulphonium salts (III) or to sulphur-containing DSY (IV), depending on the nature of the keto-compounds:



Z=O: X=Y=COCH$_3$ [82],
Z=S: X, Y=COCH$_2$C(CH$_3$)$_2$CH$_2$CO [81]; X=COC$_6$H$_5$, Y=COOC$_2$H$_5$ [81] .

It is noteworthy that in the case of dibenzoylmethane the product is the sulphonium salt (II) and not the ylide (IV), whose formation might have been expected by analogy with the reactions of acetylacetone and dimedone. It may be hoped that the reaction under consideration will be useful for the synthesis of chalcogenium ylides whose precursors are capable of forming radical-cations.

6. Preparation of Doubly Stabilised Ylides from Singly Stabilised Compounds

Doubly stabilised ylides of Group VI elements can be obtained by treating various singly stabilised ylides with electrophiles such as carboxylic acid anhydrides and chlorides, sulphonyl halides, isocyanates, and benzoyl isocyanates via the following mechanism:

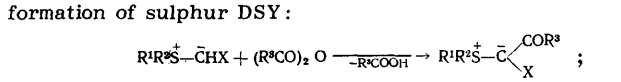


where X and Y are different electron-accepting groups.

The same DSY can be obtained in two ways via these reactions from different singly stabilised ylides and electrophiles. However, hitherto mainly sulphonium ylides have been obtained by this method.

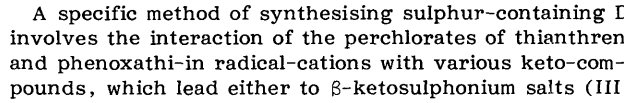
Acylation of Ylides

Singly stabilised sulphonium ylides containing the COOR, COR, and PO(OR)$_2$ substituents at the ylide carbon atom are smoothly acylated by carboxylic acid anhydrides with formation of sulphur DSY:



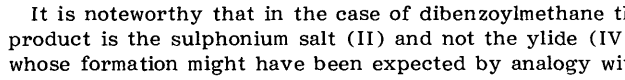
X=COC$_6$H$_5$: R^1=R^2=R^3=CH$_3$ [83]; R^1=C$_6$H$_5$, R^2=R^3=CH$_3$ [84]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [84]; R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [83, 85, 86]or iso-C$_4$H$_9$ [87]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [88]; R^1=R^3=CH$_3$, R^2=C$_2$H$_5$ [83]; R^1=R^2=C$_2$H$_5$, R^3=CH$_3$ [83]; R^1=CH$_3$, R^2=C$_2$H$_5$, R^3=C$_6$H$_5$ [83]; X=COOCH$_3$: R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [85], X=COOC$_2$H$_5$: R^1=R^2=R^3=C$_6$H$_5$ [89]; CH$_3$ [90], R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [89]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [89]; R^1=C$_6$H$_5$, R^2=R^3=CH$_3$ [89]; R^1=R^3=CH$_3$, R^2=C$_6$H$_5$ [90] X=PO(OC$_2$H$_5$)$_2$: R^1=R^2=CH$_3$, R^3=CH$_3$ or C$_6$H$_5$ [91] .

Carboxylic acid chlorides[85,90-92] and esters[92] react similarly to singly stabilised ylides containing the alkoxy carbonyl[85,89,90], diethoxyphosphoryl[91], and cyano-groups[92]:



X=COOCH$_3$: R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [85].
X=COOC$_2$H$_5$: R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [90]; R^1=R^2=R^3=C$_6$H$_5$ [89]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [89]; R^1=R^3=CH$_3$, R^2=C$_6$H$_5$ [89]; R^1=R^3=CH$_3$, R^3=C$_2$H$_5$ [90] or CHCl$_2$ [90].
X=PO(OC$_2$H$_5$)$_2$: R^1=R^2=CH$_3$, R^3=CH$_3$ or C$_6$H$_5$ [91];
X=CN: R^1=CH$_3$, R^2=C$_2$H$_5$, R^3=CH$_3$ or C$_6$H$_5$ [92] .

The behaviour of sulphonium ketoylides in interactions with acyl chlorides is unusual. As a consequence of the considerable contribution of resonance structures of the type $R_2S^+CH{=}C(R)O^-$, they usually yield *O*-acylation and not *C*-acylation products on treatment with acyl chlorides. In the presence of at least one methyl group at the onium sulphur atom, methyl chloride is in most cases eliminated from the resulting sulphonium salt and the products are enol acylates of the corresponding α-mercaptoketones[84-86]:

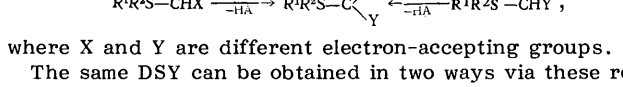


R^1=R^2=R^3=C$_6$H$_5$ [84]; R^1=R^2=C$_6$H$_5$, R^3=CH$_3$ [84];
R^1=CH$_3$, R^2=R^3=C$_6$H$_5$ [85, 86] .

On the other hand, the reaction involving diphenylsulphonium phenacylide stops at the stage involving the formation of the sulphonium salt[88].

The Sulphonation and Cyanation of Singly Stabilised Ylides

On treatment of alkoxycarbonyl- or keto-sulphonium ylides with alkanesulphonyl chlorides in the presence of triethylamine, the initial ylides are *C*-sulphonated with formation of sulphur DSY:[88,93,94]

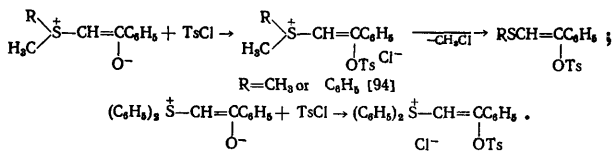


X=C$_6$H$_5$: R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [94], CH$_3$ [94]or C$_6$H$_5$CO [94];
R^1=CH$_3$, R^2=C$_6$H$_5$, R^3=H [94], CH$_3$ [94], C$_6$H$_5$ [94]or C$_6$H$_5$CO [94]; R^1=R^2=C$_6$H$_5$, R^3=H [88].
X=CH$_3$: R^1=R^3=CH$_3$, R^2=C$_6$H$_5$ [94]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [94].
X=OC$_2$H$_5$: R^1=R^3=CH$_3$, R^2=C$_6$H$_5$ [94]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [94]; R^1=R^2=C$_6$H$_5$, R^3=CH$_3$ [94] or C$_6$H$_5$ [94].

The yields of the doubly stabilised ylides are sometimes extremely low owing to the occurrence of many side reactions[94].

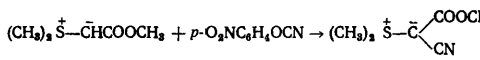
In contrast to aliphatic sulphonyl chlorides, aromatic sulphonyl chlorides (particularly the tosyl chloride) give rise to *O*- and not *C*-derivatives on reaction with sulphonium phenacylides. Dialkyl(arylalkyl) sulphonium ylides give rise to the enol sulphonates derived from α-mercaptoketones as a result of the elimination of methyl chloride from the

intermediate sulphonium salt[94], while diphenylsulphonium phenacylide yields the corresponding sulphonium salts[88]:



R=CH_3 or C_6H_5 [94]

Cyanomethylides can be synthesised by the direct introduction of the cyano-group into singly stabilised ylides[95]:



Reactions of Singly Stabilised Ylides with Isocyanates

The interaction of singly stabilised ylides with isocyanates is widely used for the synthesis of DSY, since singly stabilised ylides containing different electron-accepting substituents at the carbanionic carbon atom readily undergo this reaction (Table 5):

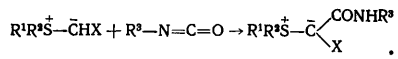
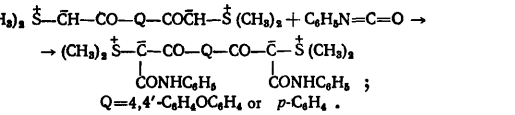


Table 5.

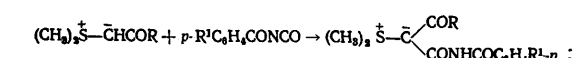
X	R^2	R^1	R^3	Refs.
COC_6H_5	C_6H_5	CH_3	CH_3	[83]
COC_6H_5	C_6H_5	CH_3	C_2H_5	[83]
COC_6H_5	C_6H_5	C_6H_5	$C_6H_5CH_2$	[46]
COC_6H_5	C_6H_5	C_6H_5	C_2H_5	[46]
COC_6H_5	C_6H_5	C_6H_5	CH_3	[84]
COC_6H_5	C_6H_5	$CH_3CH_2SCH_2CH_2$		[96]
COC_6H_5	C_6H_5	$CH_3SCH_2CH_2CH_2$		[96]
4-BrC_6H_4CO	C_6H_5	$CH_3CH_2SCH_2CH_2$		[96]
4-BrC_6H_4CO	C_6H_5	$CH_3SCH_2CH_2CH_2$		[96]
4-$O_2NC_6H_4CO$	C_6H_5	$CH_2CH_2SCH_2CH_2$		[96]
4-$O_2NC_6H_4CO$	C_6H_5	$CH_2SCH_2CH_2CH_2$		[96]
$COCH_3$	C_6H_5	C_6H_5	CH_3	[94]
$COCH_2C_6H_5$	C_6H_5	C_6H_5	CH_2	[94]
$COOC_2H_5$	C_6H_5	CH_3	CH_3	[90]
$COOC_2H_5$	C_6H_5	C_6H_5	C_6H_5	[89]
$PO(OC_2H_5)_2$	C_6H_5	CH_3	CH_3	[91]
$PO(OC_2H_5)_2$	C_6H_5	CH_3	C_6H_5	[91, 97]
$COOC_2H_5$	C_3H_7	CH_3	CH_3	[90]
$COOC_2H_5$	4-$CH_3C_6H_4SO_2$	CH_3	CH_3	[90]
4-$O_2NC_6H_4$	3,4-$Cl_2C_6H_3$	CH_3	CH_3	[98]
4-$O_2NC_6H_4$	C_2H_5OCO	CH_3	CH_3	[98]

The reaction is sometimes used for the identification of comparatively unstable or difficult to purify ylides[94]. Chiral sulphonium DSY have been synthesised by this method from chiral singly stabilised ylides[83]. The reaction with isocyanates is suitable for the preparation of stable bis-DSY:[99]

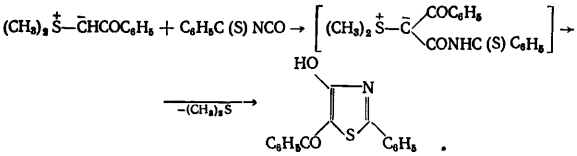


Q=4,4'-$C_6H_4OC_6H_4$ or *p*-C_6H_4 .

Singly stabilised ylides also readily react with benzoyl isocyanates, giving rise to stable benzoylcarbamoylsulphonium ylides[100], whose pyrolysis in decalin leads to substituted oxazoles[100]:

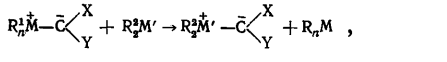


On the other hand, the interaction of dimethylsulphonium phenacylide with thiobenzoyl isocyanate even at room temperature immediately yields a substituted thiazole—via the decomposition of the intermediate ylide[100]:



7. Transylidation

The transylidation reaction involves the exchange of heteroatomic groups between the DSY of any elements and organochalcogenides:

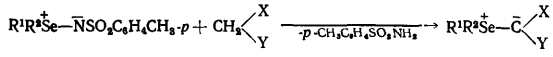


where M is the heteroatom and M' the chalcogen (S, Se, or Te).

These reactions have found fairly limited applications in the synthesis of the DSY of Group VI elements and it is therefore more useful to consider them in the discussion of the chemical properties of the DSY.

8. Synthesis from Imides

A new method of synthesis of DSY by the reaction of active methylene compounds with comparatively readily available selenium imides has been proposed recently[54]:



R^1R^2=$(CH_2)_4$: X=Y=CN, $COCH_3$, $COOCH_3$ or $C_6H_5SO_2$; X=CN, Y=$COOCH_3$.

R^1=R^2=$C_6H_5CH_2$: X=CN, Y=CN or $COOCH_3$,

R^1=R^2=C_6H_5: X=Y=CN .

The authors[54] note the absence of a linear correlation between the pK_a of the active methylene compounds and the rates of their reaction with selenium imides. Evidently, the stability of the resulting selenonium ylides plays a significant role here.

III. STRUCTURE AND PHYSICOCHEMICAL PROPERTIES

1. Molecular and Crystal Structure

The structures of six doubly stabilised chalcogenonium sulphur[27,41,101,102], selenium[72,103,104], and tellurium[105] ylides have now been investigated by X-ray diffraction, the results being presented in Figs. 1–6. They permit a number of conclusions.

A. As was to be expected, the DSY of Group VI elements have the structure of a trigonal pyramid containing the chalcogen atom at the vertex. On passing from sulphur to tellurium ylides, the distance from the central atom to the plane passing through three neighbouring atoms increases,

its values being as follows: 0.73 Å for (V), 0.74 Å for (VI), 0.78 Å for (VIII), 0.91 Å for (IX), and 0.98 Å for (X).

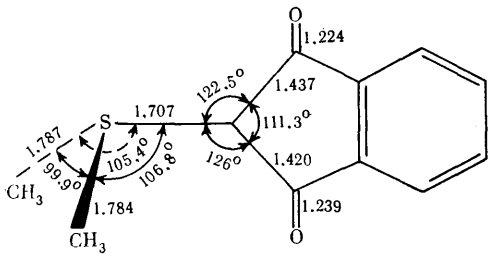


Figure 1. 2-Dimethylsulphuranylideneindan-1,3-dione (V).[102]

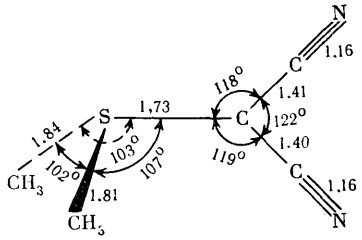


Figure 2. Dimethylsulphonium dicyanomethylide (VI).[41,101]

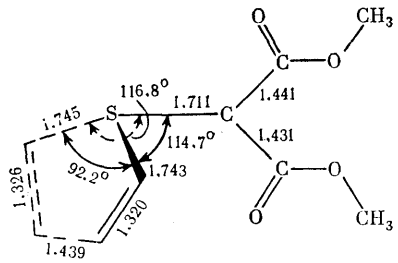


Figure 3. Thiophenium dimethoxycarbonylylide (VII).[27].

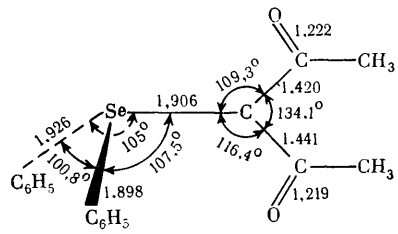
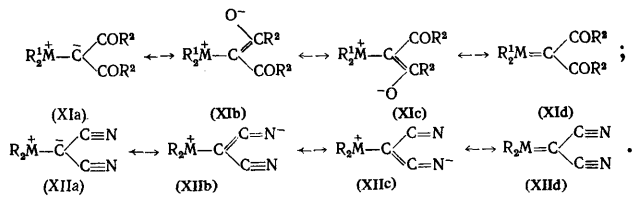


Figure 4. Diphenylselenonium diacetylmethylide (VIII).[72]

B. Analysis of the bond lengths between the chalcogen and the ylide carbon atom and of the bond lengths in the electronegative substituents C=O and C≡N (Figs.1–6) shows that the electronegative groups play an important role in the delocalisation of the negative charge of the carbanion. In other words, the contribution of the resonance structures (XI, b and c) and (XII, b and c) to the ground state of the ylide molecules is important for diketo- and dicyano-methylides:



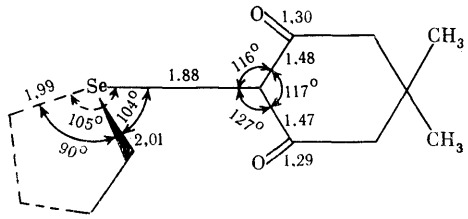


Figure 5. Tetramethyleneselenonium-4,4-dimethyl-2,6-dioxocyclohexanilide (IX).[103,104]

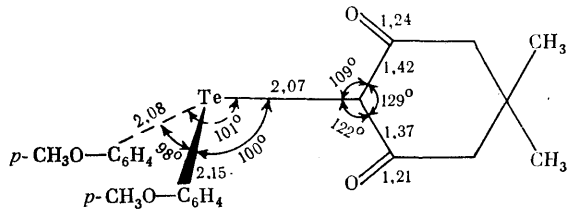


Figure 6. Di(*p*-anisyl)telluronium 4,4-dimethyl-2,6-dioxocyclohexanilide (X).[105]

A number of workers believe that the ylide linkage has a definite double bond character as a consequence of the employment of vacant *d* [101,102,104] or π* orbitals of sulphur and selenium[106].

C. In the case of selenium[104] and tellurium[105] dimedone ylides the oxygen atoms of the dimedone fragment are displaced from the plane of the ring in one direction or another by 0.15 and 0.24 Å (selenium) or 0.11 and 0.16 Å (tellurium) as a result of steric hindrance. Some non-equivalence of the arene rings in the ylide (X) is striking. This is manifested by the fact that one of the methoxy-oxygen atoms is displaced from the plane of the benzene ring by 0.16 Å, while the other lies in the plane of the corresponding ring. This is evidently a consequence of the bending of the dimedone ring, noted also for the corresponding selenonium ylide, and the characteristics of the crystal packing (particularly since in solution both benzene rings and methoxy-groups are completely equivalent judging from the ^{1}H NMR spectra[69]).

2. Ultraviolet Spectra

The ultraviolet spectra of doubly stabilised chalcogenonium ylides have been studied in a number of investigations[6,9,11,12,30,41,46,48,50,52,55,64,66,69,73,79,84,89,94], but these data have usually not been interpreted and the ultraviolet spectra of sulphonium ylides derived from dimedone and benzenesulphonylacetophenones have been examined in greater detail in only one study[30]. The authors[30] believe that the significant displacement of the maximum in the spectra of ylides relative to the spectra of the sodium salts of the initial carbonyl compounds is due to the shift of electron density in the carbanionic part of the ylide under the influence of the sulphuranylidene substituent. An analogous shift has been observed in the ultraviolet spectra of dinitromethylides[48].

Some data on the ultraviolet spectra of doubly stabilised chalcogenonium ylides are presented in Table 6. The replacement of the phenyl group by the methyl group leads to a bathochromic shift of the absorption band of the carbanionic fragment for all the chalcogenonium ylides—evidently as a consequence of the greater compensation of the positive charge on the chalcogen atom by alkyl substituents compared with the phenyl substituent. One should also note that, on passing from sulphur ylides to the selenium and tellurium ylides with similar structures, the long-wavelength absorption band of the ylides undergoes a bathochromic shift, probably as a consequence of the weakening of the electron-accepting properties of the groups R_2M^+ in the sequence $R_2S^+ > R_2Se^+ > R_2Te^+$.

Table 6. The ultraviolet spectra of the ylides $R^1R^2M^+C^-(X)Y$.

R^1	R^2	M	X	Y	λ_{max}, nm (solvent)
CH_3	CH_3	S	$-COCH_2C(CH_3)_2CH_2CO-$		261 [30, 41] (CH_3OH), 258 [46] (C_2H_5OH)
CH_3	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		270 [69] (CH_3OH)
CH_3	CH_3	S	$-COOC(CH_3)_2OCO-$		247 [6, 64] (CH_3OH)
CH_3	CH_3	Se	$-COOC(CH_3)_2OCO-$		241 [64] (CH_3OH)
C_6H_5	CH_3	S	$-COCH_2C(CH_3)_2CH_2CO-$		230, 259 [30] (CH_3OH); 230, 257 [46] (C_2H_5OH)
C_6H_5	CH_3	Se	$-COCH_2C(CH_3)_2CH_2CO-$		261 [66]
C_6H_5	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		268 [69] (CH_3OH)
C_6H_5	C_6H_5	S	$-COCH_2C(CH_3)_2CH_2CO-$		225, 250 [30] (CH_3OH)
C_6H_5	C_6H_5	Se	$-COCH_2C(CH_3)_2CH_2CO-$		257 [68]
C_6H_5	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		262 [69] (CH_3OH)
CH_3	CH_3	S	$COCH_3$	$COCH_3$	233, 270 [46] (CH_3OH); 228, 271 [41](H_2O)
C_6H_5	CH_3	S	$COCH_3$	$COCH_3$	226, 265 [46] (C_2H_5OH)
C_6H_5	CH_3	Se	$COCH_3$	$COCH_3$	268 [66]
C_6H_5	C_6H_5	Se	$COCH_3$	$COCH_3$	265 [66]
C_6H_5	CH_3	S	COC_6H_5	COC_6H_5	288, 317 [84] (C_2H_5OH)
C_6H_5	CH_3	Se	COC_6H_5	COC_6H_5	287, 317 [66]
CH_3	CH_3	S	COC_6H_5	$SO_2C_6H_5$	218, 266 [30] (CH_3OH); 218, 258 [94] (C_2H_5OH)
C_6H_5	CH_3	S	COC_6H_5	$SO_2C_6H_5$	218, 263 [30] (CH_3OH); 254 [94] (C_2H_5OH)
CH_3	CH_3	S	$COCH_3$	$COOC_2H_5$	227, 258 [46] (CH_3OH); 225, 247 [41] (C_2H_5OH)
C_6H_5	CH_3	S	$COCH_3$	$COOC_2H_5$	223, 247 [46] (C_2H_5OH)
CH_3	CH_3	S	$COOC_2H_5$	$COOC_2H_5$	233 [41] (C_2H_5OH)
CH_3	CH_3	S	$COOC_2H_5$	CN	223 [41] (CH_3OH)
C_6H_5	CH_3	Se	CN	CN	277 [66]
C_6H_5	C_6H_5	Se	CN	CN	257, 287 [66]
CH_3	CH_3	S	NO_2	NO_2	329 [9, 48] (CH_3CN)
C_6H_5	C_6H_5	Se	NO_2	NO_2	340 [53] (CH_3CN)

3. Infrared Spectra

The infrared spectra of doubly stabilised chalcogenonium ylides provide one of the most convincing pieces of evidence for the considerable involvement of electronegative substituents in the delocalisation of the negative charge on the ylide carbon atom[4,6,12,21,24,25,27,30,41,43,46,48,49,53,56,65,66,69,72,73,77,79,84,89,91,94].

The absorption frequencies of the electronegative substituents at the carbanionic carbon atom of ylides (COR, COOR, CN, NO_2, or SO_2R) are appreciably lower than in the spectra of the corresponding methylene compounds. If the ylide molecule contains two different electron-accepting substituents, the vibrations of the two groups can be usually readily distingiushed under these conditions. Certain vibrational frequencies of electronegative substituents in ylides are presented in Table 7.

Table 7. The vibrational frequencies of the substituents X and Y in the ylides $R^1R^2M^+-\bar{C}(X)Y$.

R^1	R^2	M	X	Y	ν(X, Y), cm^{-1}
CH_3	CH_3	S	$-COCH_2C(CH_3)_2CH_2CO-$		1560, 1602 [41], 1539 [46]
CH_3	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		1535, 1590 [69]
C_6H_5	CH_3	S	$-COCH_2C(CH_3)_2CH_2CO-$		1570, 1610 [30]; 1572 [46]
C_6H_5	C_6H_5	S	$-COCH_2C(CH_3)_2CH_2CO-$		1567, 1582 [30]
C_6H_5	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		1520, 1530, 1570 [69]
C_6H_5	$N(CH_3)_2$	S	$-COCH_2C(CH_3)_2CH_2CO-$		1580 [77]
C_6H_5	CH_3	Se	$-COCH_2C(CH_3)_2CH_2CO-$		1557, 1612 [66]
C_6H_5	C_6H_5	Se	$-COCH_2C(CH_3)_2CH_2CO-$		1563 [65, 66]
CH_3	CH_3	S	$COCH_3$	$COCH_3$	1560, 1605 [41]; 1570 [46]
C_6H_5	CH_3	S	$COCH_3$	$COCH_3$	1582 [46]
C_6H_5	$N(CH_3)_2$	S	$COCH_3$	$COCH_3$	1650 [77]
C_6H_5	CH_3	Se	$COCH_3$	$COCH_3$	1585, 1610 [66]
C_6H_5	C_6H_5	Se	$COCH_3$	$COCH_3$	1520 [72]; 1577, 1592, 1617 [66]
CH_3	CH_3	S	$COCH_3$	$COOC_2H_5$	1550, 1685 [41]; 1548, 1667 [46]
C_6H_5	CH_3	S	$COCH_3$	$COOC_2H_5$	1595, 1665 [46]
C_6H_5	C_6H_5	S	$COCH_3$	$COOC_2H_5$	1578, 1580 [89]
CH_3	CH_3	S	$COOC_2H_5$	$COOC_2H_5$	1635, 1670 [41]
CH_3	CH_3	S	$COOCH_3$	CN	1660, 2175 [41]
C_6H_5	CH_3	S	$COOC_2H_5$	CN	1660, 2180 [46]
CH_3	CH_3	S	CN	CN	2155, 2190 [41]
C_6H_5	CH_3	Se	CN	CN	2140, 2175 [66]
C_6H_5	C_6H_5	Se	CN	CN	2157, 2190 [66]
CH_3	CH_3	S	COC_6H_5	COC_6H_5	1545, 1577 [30]
C_6H_5	CH_3	S	COC_6H_5	$SO_2C_6H_5$	1560, 1583 [30]
C_6H_5	$N(CH_3)_2$	S	$SO_2C_6H_5$	$SO_2C_6H_5$	1133, 1300 [77]
C_6H_5	$N(CH_3)_2$	S	SO_2CH_3	SO_2CH_3	1116, 1283 [77]
CH_3	CH_3	S	NO_2	NO_2	1260, 1590 [43]; 1052, 1255, 1273, 1502 [48]
C_6H_5	C_6H_5	S	NO_2	NO_2	1062, 1280, 1505 [48]
C_6H_5	C_6H_5	Se	NO_2	NO_2	1270, 1490 [53]

It is noteworthy that the absorption frequencies of the same compounds quoted by different workers are frequently very different. This has been explained[108] by the existence of ketoylides in several stable conformations, which is strongly reflected in the infrared spectra (disappearance of individual absorption bands of CO or the appearance of new bands when the solvent or the state of aggregation of the given substance are altered).

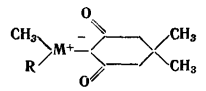
4. ^1H NMR and ^{13}C Spectra

The ^1H [6,30,41,43,46,54–56,69,94] and ^{13}C [24,29,48,111] NMR spectra of doubly stabilised chalcogenonium ylides make it possible to determine the characteristics of their steric and electronic structures. In particular the ^1H and ^{13}C NMR spectra of a number of ylides containing the benzyl, ethyl, and isopropyl groups at the chalcogen atom represent the AB spectrum of the methylene or methyl protons, while the methyl groups of the isopropyl substituent are manifested in the ^{13}C NMR spectrum of isopropylmethylsulphonium methoxycarbonylmethylide as doublets as a consequence of the trigonal-pyramidal structure of the ylide molecule. The magnetic non-equivalence of chemically identical methylene protons and methyl groups of the isopropyl substituent is due to the influence of the solvent[41,69,94]. Indeed, p-anisylbenzyltelluronium 4,4-dimethyl-2,6-dioxocyclohexylide in

methylene chloride gives rise to a signal of the methylene group of the benzyl substituent in the form of a narrow singlet, while in nitrobenzene solution the expected AB spectrum is obtained[69]. The difference between the chemical shifts of the magnetically non-equivalent protons usually diminishes with increase of the number of bonds between the chalcogen atom and the protons active in NMR.[41,69,94,109]

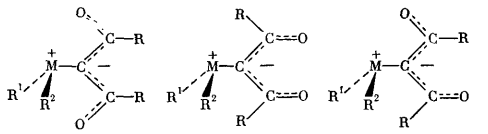
It is of interest to follow the variation of the chemical shifts of the signals due to the methyl groups in dimethyl- and phenylmethyl-chalcogenonium ylides, which have structures of the same type. The available data concerning this problem refer solely to dimedone ylides and are compiled in Table 8. The data presented in Table 8 show that, on passing from sulphur to tellurium, the deshielding effect of the groups RM^+-C^- diminishes, which can be evidently attributed to the weakening of the electron-accepting properties of the groups quoted above on moving from above downwards within the limits of a single Group in Mendeleev's Table.

Table 8. The chemical shifts of the protons of the methyl group in the ^1H NMR spectra of the ylides



R	M	δ_{CH_3}, p.p.m.
C_6H_5	S	3.34 [30]
C_6H_5	Se	3.10 [66]
C_6H_5	Te	2.65 [69]

The question of the conformations of acyclic diketoylides, which can exist in solution as one conformer or a mixture of three possible conformers (XIII, a–c) formed on rotation about the C^-–C bonds, has been raised in a number of studies:



(XIIIa) (XIIIb) (XIIIc)

On the basis of data for the temperature variation of the ^1H NMR spectrum of dimethylsulphonium diacetylmethylide (a singlet due to the acetyl methyls at room temperature and a doublet with an integral intensity ratio of 1 : 1 at -60 °C), the *cis,cis*-conformation (XIIIa) was attributed to this ylide in solution[46]. Despite the repulsion of the two methyl groups, the stabilisation of this conformer is caused, according to the authors, by the strong Coulombic interaction of the unlike charges on the oxygen and sulphur atoms. When one of the acetyl methyl groups is replaced by the bulky mesityl residue, the corresponding ylide exists in solution as a mixture of two conformers—*cis,cis* (XIIIa) and *cis,trans* (XIIIc) in proportions of 1 : 1 at temperatures between -50° and +50 °C.

The broadening of the signals of the acetyl methyl groups in the ^1H NMR spectrum of dimethylsulphonium diacetylmethylide at -25 °C made it possible to estimate the energy barrier to rotation about the S^+-C^- bond as 50 kJ mol^{-1}.[72] In the diphenylselenonium analogue of this ylide, the broadening of the signal due to the methyl groups was not observed even at -60 °C, which shows that the height of the barrier to rotation about the Se^+-C^- bond is less than 41.9 kJ mol^{-1}.[72] The above data (showing that the barrier to rotation in selenonium ylides is lower than in the sulphonium ylides) are consistent with the results of quantum-chemical calculations on different π-chalcogenuranes (oxides, imides, and ylides) and with the fact that in the sulphur–selenium–tellurium series the barriers to rotation about the M^+-C^- or M^+-N^- bonds are lowered, while the barriers to the inversion of the pyramid at the onium atom increase[110].

Table 9. The ^{13}C NMR spectra of the ylides $R^1R^2M^+-C^-(X)Y$.

R^1	R^2	M	X	Y	δ, p.p.m. (w.r.t. TMS) δ_{C^-}	$\delta_{C=O}$	$\delta_{CH_3-M^+}$	Refs.
CH_3	CH_3	S	COC_6H_5	COC_6H_5	88.2[a]	190.9	26.9	[24]
CH_3	CH_3	S	$COCH_3$	$COCH_3$	87.6[a]	190.3	26.7	[24]
CH_3	CH_3	S	$COCH_3$	$COOCH_3$	73.5[a]	166.4; 191.8	26.6	[24]
CH_3	CH_3	S	$COCH_3$	$COOCH_3$	73.4[b]	166.0; 189.9	26.0	[24]
CH_3	CH_3	S	$COOCH_3$	$COOCH_3$	58.6[a]	166.6	27.6	[24]
CH_3	CH_3	S	$COOCH_3$	$COOCH_3$	58.6[b]	165.6	27.1	[24]
CH_3	C_2H_5	S	$COCH_3$	$COOCH_3$	55.7[a]	—	27.7	[24]
CH_3	C_4H_9	S	$COOCH_3$	$COOCH_3$	56.2[a]	167.1	25.9	[24]
CH_3	$(CH_3)_2CH$	S	$COOCH_3$	$COOCH_3$	53.5[a]	167.2	24.4	[24]
CH_3	$C_6H_5CH_2$	S	$COOCH_3$	$COOCH_3$	57.4[a]	167.4	27.7	[24]
CH_3	C_6H_5	S	$COOCH_3$	$COOCH_3$	59.1[a]	167.1	27.1	[24]
$4\text{-}(CH_3)_2NC_6H_4$	$4\text{-}(CH_3)_2NC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.3[c]	190.9	—	[111]
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.4[c]	191.3	—	[111]
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		52.7[d]	191.8	—	[111]
$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.3[c]	190.8	—	[111]
C_6H_5	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.2[c]	190.7	—	[111]
$4\text{-}BrC_6H_4$	$4\text{-}BrC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.3[c]	191.2	—	[111]
CH_3	$4\text{-}CH_3C_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.3[c]	191.6	3.0	[111]
CH_3	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.2[c]	191.4	2.0	[111]
CH_3	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		52.6[c]	192.3	1.2	[111]
CH_3	CH_3	S	$-COCH_2(CH_3)_2CH_2CO-$		86.1[a]	191.9	25.5	[29]
CH_3	CH_3	Se	NO_2	NO_2	124,7[b]	—	26.8	[48]

*Solvents: [a] $CDCl_3$; [b] DMSO-d_6; [c] $CHCl_3$; [d] acetone.

The ^{13}C NMR spectra of doubly stabilised chalcogenonium ylides have been very little investigated[24,29,48,111]. Certain data on these spectra are presented in Table 9, from which follow certain results of interest for the chemistry of ylides.

A. The signal of the ylide carbon atom in dialkoxycarbonylmethylides shifts upfield relative to diketoylides, which indicates a greater contribution of the betaine structures to the ground state of diketoylides compared with dialkoxycarbonylmethylides.

B. Whereas the chemical shift of the ylide carbon atom in sulphonium ylides is independent of the nature of the solvent, in telluronium ylides it varies by approximately 1.5 p.p.m. on passing from chloroform to acetone. This may be an indication of the greater basicity of the telluronium ylides compared with sulphonium ylides.

C. In chalcogenonium ylides containing isotypical electronegative substituents at the ylide carbon atom the chemical shift of the latter is displaced upfield on passing from sulphur to tellurium.

D. The chemical shift of the carbon atom of the methyl group in methylphenyltelluronium ylides (1–3 p.p.m.), which can be accounted for by the influence of the heavy atom, and the pronounced paramagnetic shift of the signal of the ylide carbon atom in *S*-dinitromethylide, located in the region of the signal of the carbon of the dinitrocarbon, are striking[48].

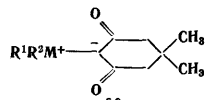
5. The Basicity of Ylides

In contrast to the singly stabilised sulphur ylides[112–114], no systematic studies have been made on the basicity of the series of doubly stabilised sulphonium and selenonium ylides. There exist only scattered data on the pK_a of sulphonium[7,55,115–119] and selenonium[48,120] ylides. It has been shown on the basis of spectroscopic data that sulphonium dimethoxycarbonylmethylides are protonated at the carbon atom[115], while the sulphonium dimedone ylides are protonated at the oxygen atom[118]; sulphonium diphenylacylmethylides[116] and acetylethoxycarbonylmethylides[117] are protonated at both oxygen and carbon atoms. Selenonium diketoylides are protonated at the oxygen atom[120], while sulphonium and selenonium dinitromethylides are protonated at the carbon atom[48].

The basicities of a systematic series of diorganotelluronium ylides have been determined[69] (Table 10) and the correlation between the basicity constants of diaryltelluronium ylides and the polar influence of the substituents has been investigated using different types of σ constants. The data in Table 10 show that the telluronium dimedone ylides are relatively strong bases, whose strength is comparable to that of aromatic amines. Indeed the pK_a for diphenyltelluronium dimedone ylide (10.59) is virtually equal to the pK_a of aniline determined under identical conditions[122]. It is of interest to compare the basicities of the DSY of Group VI elements differing only by the onium atom. Table 10 shows that the basicity of the ylides increases in the sequence S < Se < Te, i.e. with decrease of the electronegativity of the onium atom and with increase of its size. These data are consistent with the determinations of the basicities of the ylides of Group V elements having structures of the same type (the arsenic ylides are more basic than the phosphorus ylides[113]).

The best correlation in the case of symmetrical diaryltelluronium dimedone ylides is obtained using σ^0 constants[69] (the constants of substituents free from polar conjugation), although usually in the interaction of substituents with an electron-deficient centre the best correlation is observed when the electrophilic constants of the substituents are employed[123]. This permits the conclusion that the *p*-substituents in the arene rings interact with the onium tellurium atom mainly via an inductive mechanism[69]. It is noteworthy that many workers arrived at an analogous conclusion on the basis of the pK_a for singly stabilised sulphonium ylides. The data of Goetz et al.[44], who concluded that there is an appreciable mesomeric interaction between the benzene rings and the onium tellurium atom on the basis of a comparison of calculated and measured dipole moments of a series of sulphonium dicyano- and indandione ylides, therefore appear doubtful.

Table 10. The pK_a of the ylides



in acetonitrile at 25 °C.[69]

R^1	R^2	M	pK_a^T
4-$(CH_3)_2NC_6H_4$	4-$(CH_3)_2NC_6H_4$	Te	11.48[a]
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	Te	10.74
4-$C_2H_5OC_6H_4$	4-$C_2H_5CO_6H_4$	Te	10.86
4-$CH_3C_6H_4$	4-$CH_3C_6H_6$	Te	10.69
C_6H_5	C_6H_5	Te	10.59
C_6H_5	C_6H_5	Se	9.59
4-FC_6H_4	4-FC_6H_4	Te	10.22
4-BrC_6H_4	4-BrC_6H_4	Te	10.07
4-$(CH_3)_2CHC_6H_4$	4-$CH_3OC_6H_4$	Te	10.69
C_6H_5	CH_3	Te	11.22
4-$CH_3OC_6H_4$	CH_3	Te	11.40
4-$C_2H_5OC_6H_4$	CH_3	Te	11.25
CH_3	CH_3	Te	12.07
CH_3	CH_3	S	9.67

[a] the second $pK_a^T = 6.61$.

6. Dipole Moments

Comparatively few studies have been made on the dipole moments of the doubly stabilised chalcogenonium ylides[4,44,69,120]. The available literature data on the dipole moments of the DSY of Group VI elements are presented in Table 11. The relatively low dipole moments of diketochalcogenonium ylides[69,120], in the range 2–5 D, are striking. The authors[69] explained this by the fact that the M^+-C^- and C=O bond moments in ylides of this type are pointing in different directions and to a large extent cancel out. Indeed, sulphonium dicyanomethylides, in which the moments of the S^+-C^- and C≡N polar bonds are pointing in the same direction and hence undergo vector addition, have higher dipole moments (7–8 D).[4,44] Quantum chemical calculations on certain dimethylsulphonium and dimethyl selenonium ylides[111] confirmed these hypotheses.

On the basis of the experimental dipole moments of ylides, the ylide bond moments have been calculated in a number of studies[44,120]. However, very drastic assumptions were then made, which greatly diminishes the reliability of the results, In fact, the ylide bond moments were obtained by subtracting from the experimental dipole moment of the ylide $R^1R^2M^+-C^-(X)Y$ the sum of the moments of the corresponding diorganochalcogenide R^1R^2M and the precursor of the carbanionic fragment of the ylide $H_2C(X)Y$, ignoring thereby the significant changes in the M–C and C–X and C–Y bond moments on passing from isolated molecules to ylides where considerable charges appear on the chalcogen and carbon atoms.

7. Mass Spectra

In contrast to the mass spectra of the doubly stabilised sulphonium ylides, those of diketoselenonium[124] and telluronium dimedone ylides[111] have been investigated in fair detail. Without going into the details of the mode of fragmentation of these ylides, which are in many respects similar in all cases, we may note the following features of the mass-spectrometric behaviour of the selenonium and telluronium ylides.

Table 11. The dipole moments of the ylides $R^1R^2M^+-C^-(X)Y$.

R^1	R^2	M	X	Y	μ, D	Refs.
4-$(CH_3)_2NC_6H_4$	4-$(CH_3)_2NC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		5.49	[69]
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		4.16	[69]
4-$C_2H_5OC_6H_4$	4-$C_2H_5OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		4.26	[69]
4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.58	[69]
C_6H_5	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.16	[69]
4-BrC_6H_4	4-BrC_6H_4	Te	$-COCH_2C(CH_3)_2CH_2CO-$		1.74	[69]
4-FC_6H_4	4-FC_6H_4	Te	$-COCH_2C(CH_3)_2CH_2CO-$		2.06	[69]
CH_3	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		2.90	[69]
CH_3	4-$CH_3OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.28	[69]
CH_3	4-$C_2H_5OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.42	[69]
CH_3	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.18	[69]
4-$CH_3OC_6H_4$	4-$(CH_3)_2CHC_6H_5$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		4.05	[69]
CH_3	CH_3	S	CN	CN	7.40	[44]
C_4H_9	C_4H_9	S	CN	CN	7.7	[4]
C_6H_5	C_6H_5	S	CN	CN	7.6	[4]
CH_3	1-$C_{10}H_7$	S	CN	CN	8.1	[4]
CH_3	C_6H_5	S	CN	CN	8.24	[44]
CH_3	4-$CH_3OC_6H_4$	S	CN	CN	8.38	[44]
CH_3	4-ClC_6H_4	S	CN	CN	7.38	[44]
CH_3	4-BrC_6H_6	S	CN	CN	7.30	[44]
CH_3	4-$CH_3COC_6H_4$	S	CN	CN	6.94	[44]
CH_3	CH_3	S	o-COC_6H_4CO-		3.96	[44]
C_6H_5	C_6H_5	S	o-COC_6H_4CO-		4.09	[44]
CH_3	C_6H_5	S	o-COC_6H_4CO-		4.32	[44]
CH_3	4-$CF_3OC_6H_4$	S	o-COC_6H_4CO-		4.79	[44]
CH_3	4-ClC_6H_4	S	o-COC_6H_4CO-		4.18	[44]
CH_3	4-BrC_6H_4	S	o-COC_6H_4CO-		3.45	[44]
CH_3	C_6H_5	Se	COC_6H_5	COC_6H_5	3.38	[120]
	$-(CH_2)_4$	Se	COC_6H_5	COC_6H_5	3.27	[120]

A. The stability of the molecular ions of the ylides depends on the structure of the carbanionic fragment. Among the diketoylides (diacetyl and dibenzoylmethylides, dimedone ylides), the dimedone derivatives are the most resistant to electron impact[124].

B. The intensity of the molecular ion peaks in the total ionic current of the molecules depends in many respects on the nature of the chalcogen atom. Whereas the intensity of the molecular ionic peak is 0.1% in the case of diphenyl- and methylphenyl-telluronium dimedone ylides, the intensities of their selenonium analogues are 25.9 and 14.8% respectively.

C. The mass spectra of the selenonium ylides are characterised by the presence of rearranged ions, formed via the migration of the group linked to the selenium atom to the oxygen atom of the carbanionic fragment. Ions of this type are hardly observed in the mass spectra of tellurium-containing dimedone ylides[69,111]. This difference in the behaviour of selenonium and telluronium ylides is comparable to their behaviour in thermolysis (see below).

IV. CHEMICAL PROPERTIES

The reactivities of the doubly stabilised ylides of Group VI elements differ appreciably from those of the singly stabilised ylides. The significant diminution of the nucleophilic properties of the DSY compared with the singly stabilised ylides results in the failure of the DSY of Group VI elements to enter into reactions characteristic of singly stabilised ylides such as those with aldehydes, ketones, nitrosobenzene, etc.[1,2] On the other hand, they undergo a whole series of other reactions characterising the unusual features of ylides of this class.

Certain DSY, for example diorganosulphonium dicyanomethylides[4], diorganosulphonium dinitromethylides[48], organodialkylaminosulphonium ylides[77], and diorganotelluronium dimedone ylides[69], are highly stable compounds resistant to the action of alcohols[4], water[4,69,77], and aqueous solutions of alkalis[69]. On the other hand, certain other DSY readily react with these nucleophiles[17,53]:

$$C_6H_5(CH_3)\overset{+}{S}-\bar{C}(SO_2C_6H_5)_2 \xrightarrow[CH_3OH]{KOH} C_6H_5SCH(SO_2C_6H_5)_2 + CH_3OCH_3\ ;$$

$$n\text{-}CH_3C_6H_4(R)\overset{+}{S}-\bar{C}(COOCH_3)_2 \xrightarrow[CH_3OH]{KOH} n\text{-}CH_3C_6H_4SCH_2COOH + ROCH_3\ ;$$

R=CH_3 or $C_6H_5CH_2$ [17] ;

$$(C_6H_5)_2\overset{+}{S}e-\bar{C}(NO_2)X \xrightarrow{H_2O} (C_6H_5)_2SeO + XCH_2NO_2\ ;$$

X=NO_2, $COOCH_3$ or COC_6H_5 [53].

Reactions with fairly strong electrophiles and with compounds containing multiple bonds, thermolysis, rearrangements (the Stevens, Pummerer, and allyl rearrangements), transylidation, and certain other reactions are the most characteristic of the doubly stabilised chalcogenonium ylides.

1. Reactions With Electrophiles

(a) Interaction With Acids

Weak inorganic acids in most cases do not have an effect on the DSY, whereas strong inorganic acids readily react with them, the nature of the interaction depending both on the nature of the substituents at the ylide carbon atom and on the reaction conditions. Thus, whereas sulphonium dicyanomethylides[4] are cleaved by sulphuric acid in the cold into sulphides and unidentified products, the treatment of the same ylides in benzene with gaseous HX (X = Cl or Br) results in the formation of salts having the composition $R_2S^+-\bar{C}(CH)_2 \cdot 2HCl$.[119]

Sulphonium[48,125,126], and selenonium[53] dinitromethylides are protonated by strong acids containing weakly nucleophilic anions, giving rise to the corresponding salts:

$$R_2\overset{+}{M}-\bar{C}(NO_2)_2 + HX \rightarrow R_2\overset{+}{M}-CH(NO_2)_2\ X^-\ ;$$

M=S or Se; $X^-=SO_3F^-$, BF_4^- or HSO_4^-.

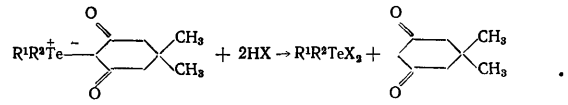
However, when sulphonium and selenonium dinitromethylides are treated with acids having highly nucleophilic anions, the M^+-C^- bond is ruptured. The intermediate onium salt is then capable of being cleaved both by the counterion (pathway *a*) and by yet another electrophile molecule (pathway *b*):[63,107,125,126]

$$R_2\overset{+}{M}-\bar{C}(NO_2)_2 \overset{HX}{\rightarrow} R_2\overset{+}{M}-CH(NO_2)_2\ X^- \begin{cases} \xrightarrow{a} R_2M + XCH(NO_2)_2 \\ \xrightarrow[HX]{b} R_2MX_2 + CH_2(NO_2)_2 \end{cases};$$

M=S or Se; X=Cl or Br.

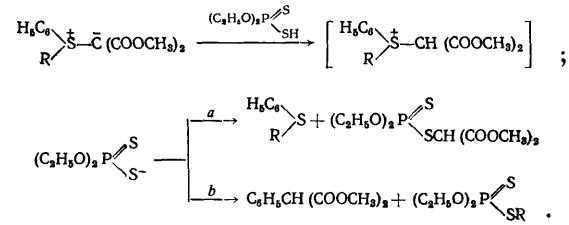
In the case of sulphonium dinitromethylides the reaction proceeds almost wholly via pathway *a*, while in the case of the selenonium compounds both pathways are followed to an approximately equal extent. The enhancement of the nucleophilic properties of the counterion (on passing from HCl to HBr) tends to increase the yield of the nucleophilic cleavage products (pathway *a*). On the other hand, tellurium-containing dimedone ylides always give rise to the corresponding σ-telluranes and dimedone on treatment with HX (X = F, Cl,

Br, or I) regardless of the nature of the substituents at the tellurium atom[127]:



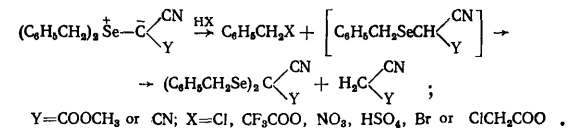
The ability to be cleaved via pathway *b* has hitherto been observed only for DSY. The ease of this process increases in the sequence S < Se < Te, which is probably associated with the greater stability of the tetracoordinate derivatives of tellurium and selenium compared with the analogous sulphur compounds[70,71].

When sulphonium dimethoxycarbonylmethylides are treated with HBr [25] or diethyl hydrogen phosphorodithioate[128], the reaction proceeds with the dissociation of either the S^+-C^- or $R-S^+$ bond depending on the nature of the substituent R at the onium sulphur:



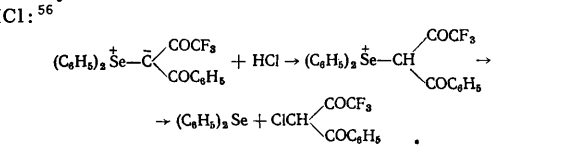
When R = C_6H_5, pathway *a* is followed exclusively, in the presence of R = $C_6H_5CH_2$ pathway *b* is followed exclusively, while in the presence of R = CH_3 both pathways are used to an equal extent.

Dibenzylselenonium dicyanomethylides are cleaved by various acids only at the $C_6H_5CH_2-Se^+$ bond[129]:

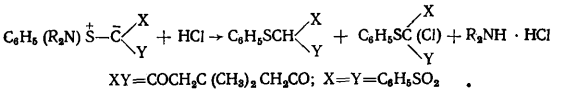


Y=$COOCH_3$ or CN; X=Cl, CF_3COO, NO_3, HSO_4, Br or $ClCH_2COO$.

However, the diphenyl-substituted trifluoroacetylbenzoylselenonium ylide is cleaved at the Se^+-C^- bond on treatment with HCl:[56]



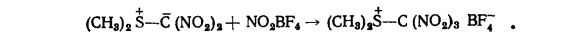
Dialkylarylaminosulphonium ylides react with HCl in an unusual manner, the S^+-N bond being ruptured and not S^+-C^-:[77]



XY=$COCH_2C(CH_3)_2CH_2CO$; X=Y=$C_6H_5SO_2$.

Thus the mode of cleavage of the DSY of Group VI elements by acids (and other strong electrophiles—see below) depends both on the nature of the carbanionic component and on the nature of the substituents at the onium atom. There is no doubt that the nature of the onium centre itself has an effect (cf. the cleavage of the tellurium ylides described above).

A single instance of the nitration of the DSY at the ylide carbon atom is known[130]:

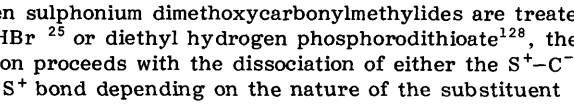


Treatment with N_2O_4 gives rise to tetranitromethane[130]. When the selenonium dinitromethylide is acted upon by nitronium fluoroborate, only tetranitromethane is formed[53].

It has been shown recently[73] that dimethylsulphonium diformylmethylide readily forms 1 : 1 adducts with certain inorganic salts, for example with ZnI_2.

(b) Reactions With Halogens and Other Halogenating Agents

Under mild conditions, the ylide bond in doubly stabilised sulphonium dicyanomethylide[119] and dinitromethylide[126] is ruptured by halogens: Cl_2, Br_2, the mixed halogen BrCl, and their derivatives—S_2Cl_2 and SO_2Cl_2, which leads to diorganosulphides and dihalogenodinitromethanes or dihalogenomalononitriles:



X=Y=NO_2 [126] or CN [119] .

α-Chloromethyl sulphide, formed evidently on chlorination of the methyl group of the sulphide or the ylide, and a certain amount of side products, whose structure depends on the nature of the carbanionic fragment, have also been isolated from the reaction mixture. On the other hand, sulphonium dimethoxycarbonylmethylides are cleaved by halogens not only at the ylide bond but frequently also at the bonds linking other substituents to the onium sulphur[25]. The mode of these reactions depends on the nature of the organic substituents at the sulphur atom.

On treatment with halogens[53,127] or SO_2Cl_2 [53] in inert solvents, the selenonium[53] and telluronium[127] DSY yield the corresponding σ-chalcogenuranes:[53,127]

X=Cl, Br or I [127] .

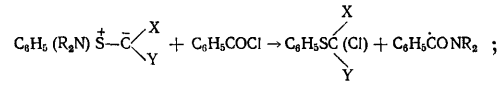
Compounds with a "positive" halogen, namely *N*-chloro and *N*-bromosuccinimides, SO_2ClF, and others, react with sulphonium and selenonium dinitromethylides in an unusual manner[53,107,126]. Here the reaction products are the corresponding dihalogenodinitromethanes, i.e. the cleavage of the above dinitromethylide proceeds in such a way that the two "electrophilic" components of the reactant become linked to the carbanionic fragment, as happens in the interaction of DSY with HX (see above).

(c) Reactions With Acyl Chlorides

The interaction of the DSY of Group VI elements with acyl chlorides has been studied in a number of investigations[77,119,126,131] and it has been found that the sulphonium dinitromethylides do not react with carboxylic acid chlorides[126] while dicyanomethylides give rise to the dicyanovinyl ester of the carboxylic acid together with the salt $(CH_3)_2S^+-\bar{C}(CN)_2.2HCl$ and chloromethyl methyl sulphide[119]:

The interaction diorganosulphonium dimethoxycarbonylmethylides with acetyl chloride proceeds differently depending on the nature of the substituents at the sulphur atom[131]. Whereas the diphenyl derivative yields diphenyl sulphide (the second reaction product was not indicated), in the methylphenyl and benzylphenyl analogues the S^+–Alk bond is cleaved with formation of $C_6H_5SC(COCH_3)(COOCH_3)_2$ and alkyl chlorides.

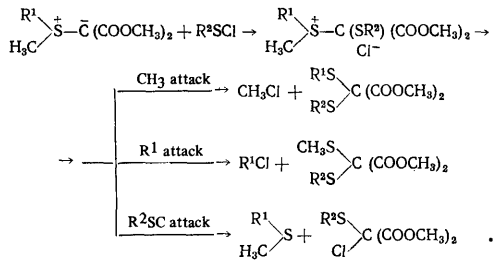
As in the reactions with HX, the S^+–N bond is ruptured in aryl(dialkylamino)sulphonium ylides[77]:



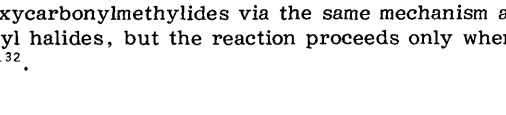
$XY=COCH_2C(CH_3)_2CH_2CO$; $X=Y=C_6H_5SO_2$.

(d) Interaction With Sulphenyl Halides and Sulphenyl Derivatives

The interaction of the ylides of Group VI elements with electrophiles of the type RSX (X = Cl or Br) has been studied in relation to a series of sulphonium[25,125,126] and selenonium[53] ylides. Under the influence of sulphonyl halides, sulphonium dimethoxycarbonylmethylides are initially sulphenated at the carbanionic centre and the resulting salt can be cleaved by the counterion X^- in three ways; the preferential occurrence of a particular reaction depends on the nature of the substituent at the sulphur atom and the nucleophilic properties of X^-:[25]



Electrophiles such as HBr and the halogens react via an analogous mechanism[25]. Sulphonium[125,126] and selenonium[53] dinitromethylides are converted into dinitrodi(phenylthio)-methane and the corresponding chalcogen dichlorides on treatment with benzenesulphenyl chloride. The cause of this effect of C_5H_5SCl is that the chalcogenonium salt formed in the first stage does not have sufficient time to be cleaved by the counterion Cl^- and is in fact cleaved by a second electrophile molecule at the M^+–C^- bond[53,126]:

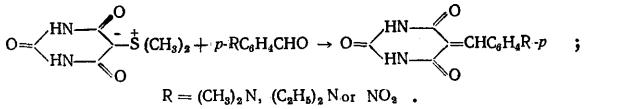


M=S or Se .

Sulphenyl thiocyanates RSSCN react with sulphonium dimethoxycarbonylmethylides via the same mechanism as sulphenyl halides, but the reaction proceeds only when R is an aryl[132].

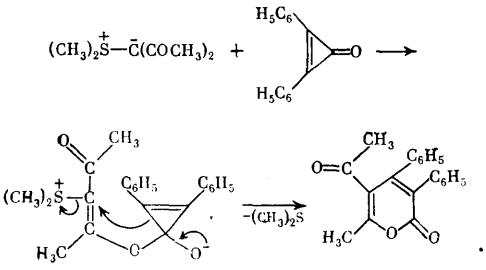
2. Interaction With Compounds Containing Multiple Bonds

Owing to the considerable delocalisation of the negative charge of the carbanion by the two electronegative substituents, the nucleophilic properties of the doubly stabilised chalcogenium ylides are weakened so much that, in contrast to the singly stabilised ylides, they do not usually interact with carbonyl compounds. In essence, there exists only one example of this reaction[133]:

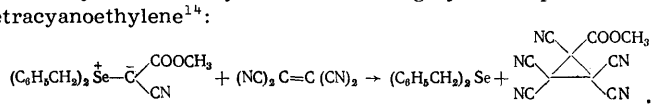


R = $(CH_3)_2N$, $(C_2H_5)_2N$ or NO_2 .

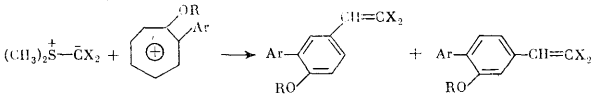
The reaction of the dimethylsulphonium ylide with the highly electrophilic diphenylcyclopropenone proceeds under extremely severe conditions and not via the classical mechanism, because the carbonyl group of the ketone is in fact preserved[134]:



The low nucleophilicity of the doubly stabilised chalcogenonium ylides is manifested by the fact that, in contrast to the singly stabilised ylides, which give rise to cyclopropanes on reaction with activated olefins (dibenzoylethylene, dimethyl fumarate, and acrylonitrile),[1,2] the DSY usually do not react with these compounds. However, substituted cyclopropanes have been obtained in high yields on reaction of dibenzylselenonium ylides with the highly electrophilic tetracyanoethylene[14]:

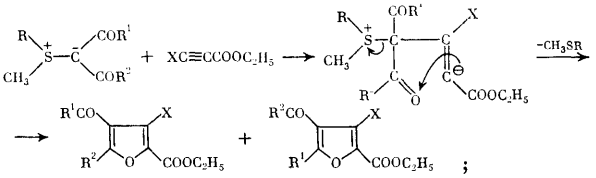


The fairly ready alkylation of dimethylsulphonium dicyano- and diethoxycarbonylmethylides by tropylium cations, which is accompanied by the contraction of the tropylium ring, is also of interest[135]:



The ratio of the reaction products depends on the nature of R and X. For example, the compound with X = CN gives rise exclusively to the isomer in which the dicyanovinyl group is in the *para*-position relative to the RO group.

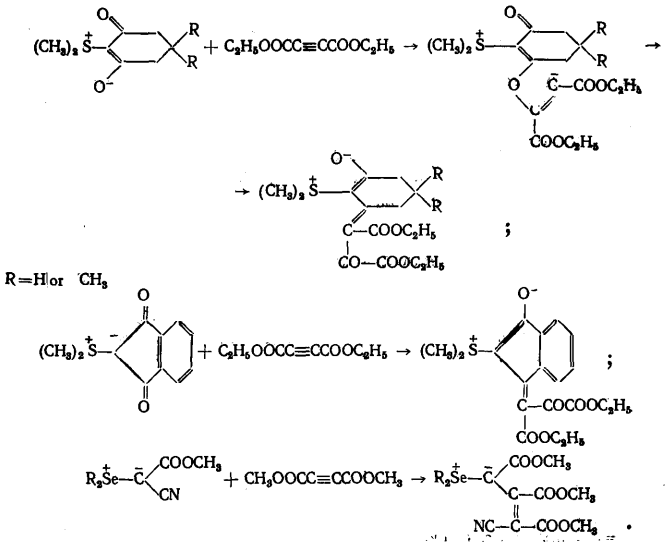
In contrast to compounds with a double bond, ethoxycarbonylacetylenes react with various sulphur[87,136] and selenium[120,121] DSY with at least one keto-group, the products being furans:



M=S [87, 136] or Se [120, 121]; R=CH_3 or C_6H_5;
R^1=Alk, C_6H_5 or OC_2H_5; R^2=Alk or C_6H_5;
X=H or $COOC_2H_5$.

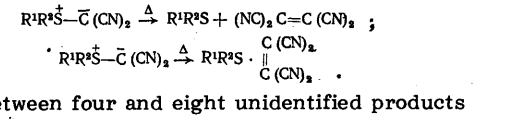
Ylides with two different keto-groups ($R^1 \neq R^2$) give rise to mixtures of two isomeric furans in different proportions, while keto(alkoxycarbonyl)sulphonium ylides ($R^1 = OC_2H_5$,

R^2 = Alk or C_6H_5) yield only one substituted furan—the alkoycarbonyl group is not involved in the cyclisation[87,136]. Cyclic sulphonium diketoylides derived from indandione and dimedone[87,136], as well as selenium ylides with substituents other than carbonyl groups at the carbanionic carbon, react with diethylacetylenedicarboxylate in an extremely unusual manner[14]:



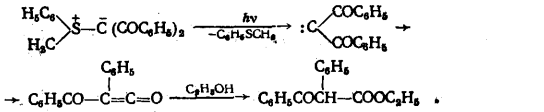
3. Thermolysis and Catalytic Decomposition of Ylides

Although the DSY of Group VI elements are highly stable with rare exceptions (certain selenonium nitroylides[53,107]) under the usual conditions, nevertheless at high temperatures they frequently decompose into diorganochalcogenides and the dimerisation products of the carbanionic fragment (thermolysis). Thus sulphonium dicyanomethylides[4,119] are cleaved, at temperatures exceeding by 30–50 °C their melting points, to give sulphides (if the latter are relatively volatile) and tetracyanoethylene[4,119]; if the sulphides are relatively involatile, charge-transfer complexes are formed between the sulphides and tetracyanoethylene[119]:

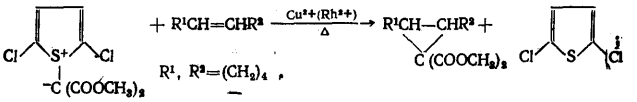


In addition, between four and eight unidentified products are also formed[4].

It has been suggested[119] that the thermolysis of the above ylides proceeds via a carbene formation stage. The possibility of the formation of carbenes on dissociation of the ylide linkage has also been indicated by data for the photolysis of a sulphonium dicarbonyl-stabilised ylide, since the product of the Wolff rearrangement was observed[137] (see also Trost[138]):

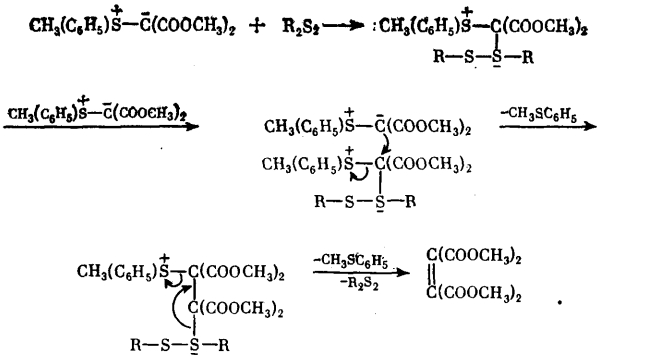


More significant evidence for the formation of carbenes on thermolysis of DSY is provided by the conversion of olefins into cyclopropane derivatives on treatment with 2,5-dichlorothiophenium dimethoxycarbonylmethylide in the presence of copper or rhodium catalysts[139]:

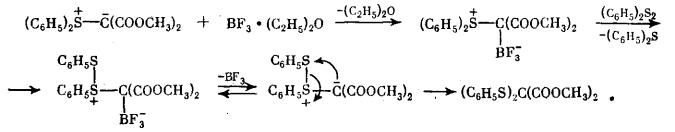


On interaction with activated (with respect to electrophilic substitution) aromatic compounds under analogous conditions, this ylide gives rise to products which are formally a result of the insertion of dimethoxycarbonylcarbene in a C–H bond of the aromatic ring[139,140].

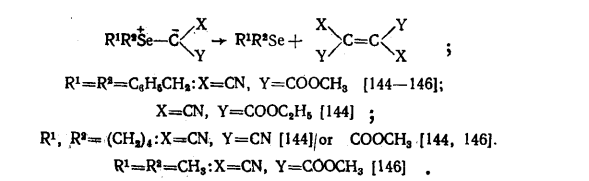
However, there is a possibility also of the catalytic decomposition of the DSY at the ylide linkage under milder conditions. Thus phenylmethylsulphonium dimethoxycarbonylmethylide readily decomposes at 35 °C into a sulphide and tetramethoxycarbonylethylene[141] in the presence of certain disulphides containing electron-accepting substituents: $(AlkO)_2S_2$,[142] $(C_6H_5CO)_2S_2$,[142] and $(CF_3)_2S_2$,[141] while on heating in the absence of a catalyst the ylide undergoes the Stevens rearrangement[20,21] (see below):



One should note that, in the presence of boron trifluoride etherate, the ylide indicated above reacts with disulphides which do not contain electron-accepting substituents at the sulphur atom (for example, with diphenyl disulphide) in a completely different manner[143]:

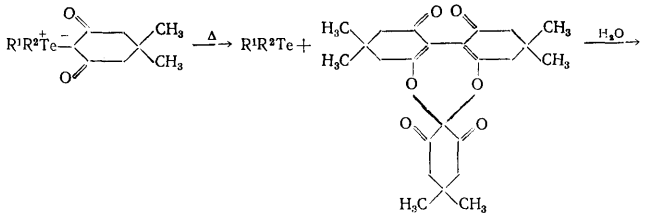


Different DSY readily decompose into the corresponding selenides and dimerisation products of the carbanionic fragment on treatment with catalytic amounts of tetramethylthiourea[144], thioamides[145], and episulphides[146]:

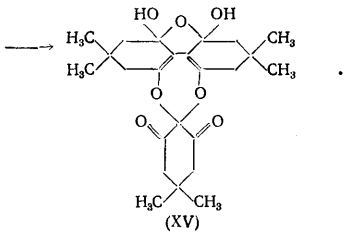


The mechanisms of all the above reactions involve the initial addition of the thio-derivatives to the ylide linkage with their subsequent elimination[144–146].

The anomalous course of the thermolytic reaction from the standpoint of the structure of the conversion product of the carbanionic fragment has been observed for diorganotelluriumdimedone ylides[147]. When these ylides were refluxed in *p*-xylene, the corresponding tellurides and a compound to which the structure of the trimerisation product (XV) of the carbanionic fragment was attributed from spectroscopic data, were isolated in almost quantitative yields. The reaction probably proceeds via a carbene mechanism and compound (XV) is evidently formed as a result of hydration (in the course of the reaction or on subsequent treatment of the reaction mixture) of the compound (XIV) formed initially:



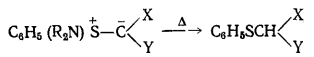
(XIV)



(XV)

Examples of this type of hydration are well known in the carbohydrate chemistry[148].

The unusual behaviour of dialkylaminoarylsulphonium ylides in different reactions has already been noted[77]. Their thermolysis, involving the rupture of the S^+–N bond and not the ylide linkage, also proceeds differently to the cases discussed above[77]:

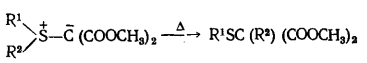


X, Y=$COCH_2C(CH_3)_2CH_2CO$; X=Y=$C_6H_5SO_2$.

4. Rearrangements

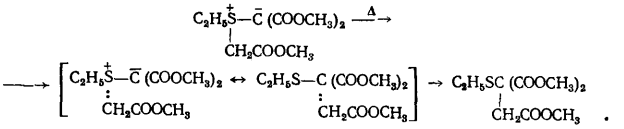
(a) The Stevens Rearrangement

One of the characteristic features of the sulphonium DSY is their ability to form products resulting from the migration of the corresponding groups from the sulphonium centre to the neighbouring carbanionic carbon atom[19,21]. The reaction proceeds under extremely severe conditions requiring heating (for 5–20 h) at 160–200 °C in sealed tubes:



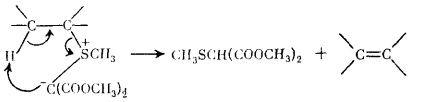
R^1=R^2=CH_3; R^1=C_6H_5, R^2=CH_3; R^1=CH_3, R^2=$C_6H_5CH_2$; R^1=C_2H_5, R^2=CH_3OCOCH_2 .

The observation of a CINP signal (in the region characteristic of methylene protons) on rearrangement of ethylmethoxycarbonylmethylenesulphonium methoxycarbonylmethylide[21] suggested that the reaction proceeds via the homolytic cleavage of the ylide with formation of an intermediate radical pair, which subsequently recombines to the rearrangement product:

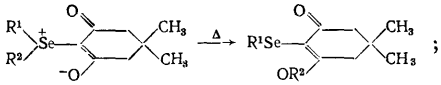


This mechanism has been confirmed by the finding that the groups capable of the resonance delocalisation of the unpaired electron ($C_6H_5\dot{C}H_2$, $\dot{C}H_2COOCH_3$) migrate most readily.

Alkylmethylsulphonium dimethoxycarbonylmethylides in which there is at least one hydrogen atom at the β-carbon atom of the alkyl groups (C_2H_5, n-C_4H_9, t-C_4H_9) undergo the Hofmann elimination on heating, leading to the formation of dimethylmethylthiomalonate and the corresponding olefins, and not the Stevens rearrangement[19,21]. This reaction probably proceeds via a five-membered cyclic transition state:

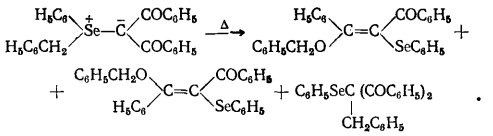


The migration of groups in selenonium diketoylides[149] and dimethylsulphonium formylmethylide[79] takes place differently. Under relatively mild conditions (refluxing in benzene or xylene) (compared with sulphonium ylides), the benzyl and phenyl groups in phenylbenzyl- and phenylmethyl-selenoniumdimedone ylides migrate to the oxygen atom (O-migration) and not the ylide carbon atom (Stevens rearrangement):

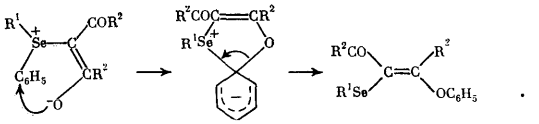


R^1=C_6H_5, R^2=$CH_2C_6H_5$; R^1=CH_3, R^2=C_6H_5; R^1=R^2=C_6H_5 .

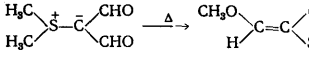
In the rearrangement of methylphenylselenonium dibenzoyl methylide (the phenyl group migrates) and diphenylselenonium benzoylmethylide O-migration also takes place and the C-migration product (Stevens rearrangements) is formed only in the case of phenylbenzylselenonium dibenzoylmethylide together with the products of the O-migration of the benzyl group (a mixture of the benzyl ethers of the *cis*- and *trans*-enols of 1,3-diphenyl-2-phenylselenopropane-1,3-dione):[149]



It is believed[149] that the rearrangement of the phenylbenzylselenonium ylides proceeds via a mechanism similar to that for the sulphur ylides, while the migration of the phenyl group in methylphenyl- and diphenylselenonium ylides proceeds via a mechanism involving intramolecular nucleophilic substitution in the benzene ring:



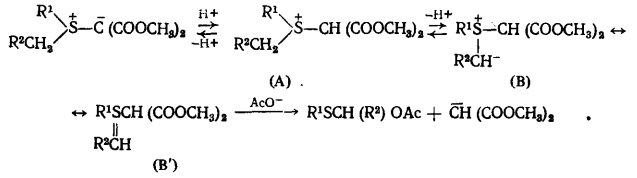
The O-migration in dimethylsulphonium diformylmethylide takes place under very severe conditions[79]:



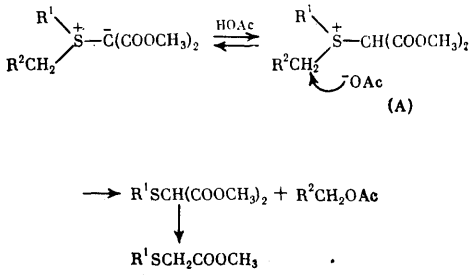
It should be noted yet again that tellurium-containing dimedone ylides undergo only thermolysis on heating regardless of the nature of the substituents at the tellurium atom[147].

(b) The Pummerer Rearrangement

The similarity of the structures of the ylides and sulphoxides containing the semipolar S^+-C^- and S^+-O^- bond suggests the similarity of the chemical properties and in particular the ability of ylides to undergo the Pummerer rearrangement. Indeed sulphonium dimethoxycarbonylmethylides containing sufficiently acidic methylene groups (R^2 = COOR) undergo the Pummerer rearrangement on heating with acetic acid, giving rise to alkoxycarbonyl (alkylthio)methyl acetates and dimethyl malonate[23]. In the presence of acids the ylides are in equilibrium with sulphonium salts A and the less stable but more nucleophilic than the initial compounds ylides (B and B'), nucleophilic attack on which by the acetate ion leads to the final products:

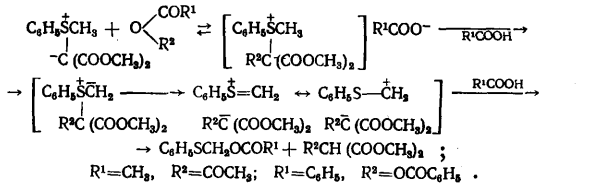


Ylides with less acidic CH_2 groups (R^1, R^2 = Alk or Ph) do not give rise to the products of the Pummerer reaction on heating in acetic acid, forming instead methoxycarbonylmethyl sulphide and alkyl acetates[23]:

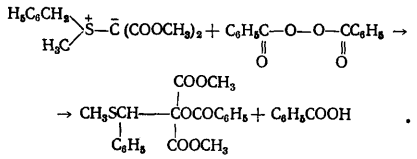


The cause of this mode of reaction is the weaker acidity of the CH_2 groups in the initial ylides, which reduces sharply the concentration of the nucleophilic ylides (B) and drives the reaction via the pathway involving nucleophilic substitution in the sulphonium salt (A), which is present in large amounts. It has been shown[23] that the mode of the Pummerer or substitution reactions depends on the strength of the acids employed: in strong acids (CF_3COOH and $CHCl_2COOH$) ylides of the first type (with alkoxycarbonyl substituents at the onium sulphur atom) undergo the substitution reaction, while in acids weaker than acetic (CH_3CH_2COOH) ylides of the second type can undergo the Pummerer rearrangement together with substitution.

The Pummerer rearrangements have been investigated[150,151] for arylmethylsulphonium dimethoxycarbonylmethylides in the presence of acetic anhydride and benzoyl peroxide. These reactions involve the initial formation of a sulphonium salt as a result of nucleophilic attack on the ylide carbanion, the deprotonation of the salt, the heterolysis of the S^+-C^- bond (rate-determining stage), and the interaction of the intermediate formed with the anion[150,151]:

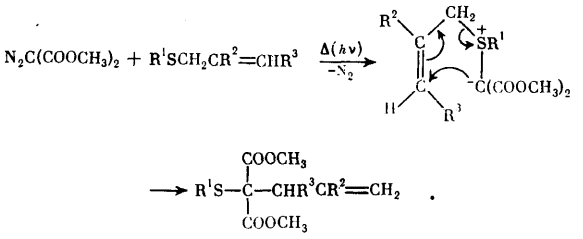


We may note that, in contrast to its methylphenylsulphonium analogue, benzylmethylsulphonium dimethoxycarbonylmethylide undergoes an unusual rearrangement in the presence of benzoyl peroxide via the following mechanism[151]:

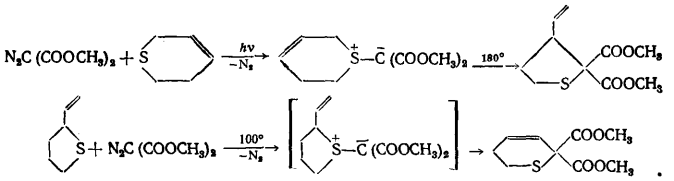


(c) The Allyl Rearrangement

A characteristic feature of doubly stabilised ylides—the intermediates formed in the thermal and photochemical interaction of carbenes and allyl sulphides—is their ability to undergo the allyl rearrangement, from the products of which one in fact infers the intermediate formation of the ylides[32-34]:



This mechanism has been confirmed by the isolation of a stable ylide derived from a cyclic allyl sulphide and its subsequent allyl rearrangement under other conditions[32,35]:

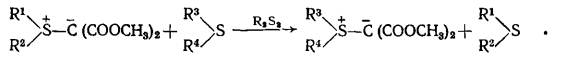


5. Transylidation

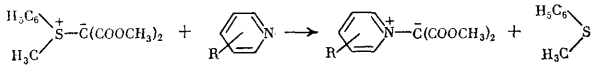
Transylidation is a reaction in which one onium group in ylides is replaced by another. Such reactions are influenced significantly by the nature of the onium group in the ylide and of the element in the reagent, the nature of the substituents at the ylide carbon atom, and the reaction conditions (solvent and catalyst).

The influence of various factors on the transylidation of sulphonium ylides by sulphides and pyridine has been studied in detail[141,142]. In the presence of catalytic amounts of

certain disulphides, methylphenylsulphonium dimethoxycarbonylmethylide undergoes smooth transylidation with various sulphides:



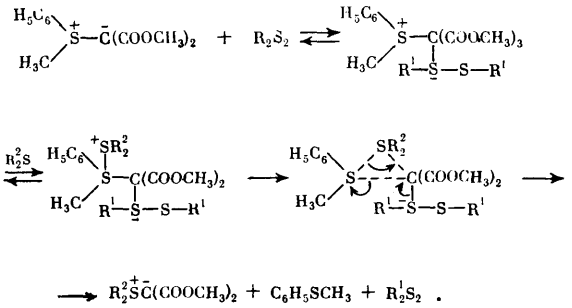
In the absence of a catalyst, the transylidation of the methylphenylsulphonium ylide with dimethyl sulphide (present in a 15-fold excess) proceeds very slowly and does not go to completion. On the other hand, in the presence of a catalyst the transylidation of alkylphenylsulphonium ylides and dialkyl sulphides proceeds readily, that of dialkyl ylides with dialkyl sulphides is much more difficult, and that of dialkylsulphonium ylides with alkyl phenyl sulphides (and probably diphenyl sulphides) hardly occur at all[142]. In other words, as the nucleophilic properties of the sulphides are reduced (Alk_2S < AlkSPh < Ph_2S), their ability to effect transylidation is sharply diminished. The marked influence of the nucleophilic properties of the organoelemental component on transylidation also follows from the results of a study of the reaction of methylphenylsulphonium dimethoxycarbonylmethylide with pyridine and its derivatives[142]:



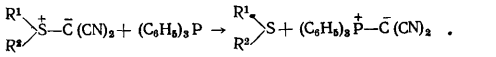
Whereas the yields of the pyridinium ylides in the reaction with 3- and 4-picolines and pyridine are 96–100%, the yield of the reaction with the weakly basic 4-cyanopyridine is only 7%.

The nature of the electronegative substituents at the carbanionic carbon plays a significant role in transylidation. The more nucleophilic the ylide carbon, the greater the ease of the transylidation. Diketoylides, for which the contribution of the betaine structure is relatively important, are transylidated to a much smaller extent than dimethoxycarbonylmethylides with a more nucleophilic carbanionic carbon (owing to the smaller contribution of betaine structures). One should also note that the yields of ylides also depend on their resistance to thermolysis. Indeed, in the reaction of dimethylsulphonium dicyanomethylide with diethyl sulphide, a new ylide was not detected, while the yield of dimethyl sulphide was 95%.

The above transylidation reactions proceed fairly readily only in the presence of catalysts—disulphides with powerful electron-accepting substituents at the sulphur atom (OR, C_6H_5CO, C≡N,[142] and CF_3 [141]). The authors[141,142] therefore proposed the following catalytic mechanism of the transylidation reaction: as a result of the nucleophilic attack on the electron-deficient sulphur atom of the disulphide by the ylide carbon atom, an unstable intermediate complex is formed. Nucleophilic attack on this complex by the sulphide or pyridine leads to a trimolecular complex, which then decomposes to the final ylide and a disulphide[142]:

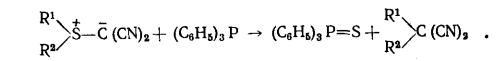


The influence of external conditions (solvent and catalyst) on transylidation can be illustrated by the reaction[152]:

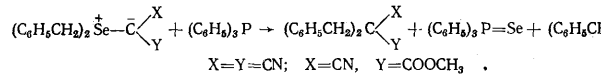


This reaction proceeds neither in benzene, nor in carbon tetrachloride, nor in acetic acid. Only in the presence of a catalyst (BF_3) in acetic acid does transylidation take place fairly readily[152].

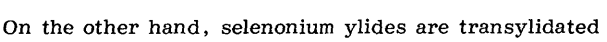
In many instances transylidation is accompanied by side reactions—transalkylation and dechalcogenation. Thus, when sulphonium cyanomethylides interact with triphenylphosphine, the products of the competing desulphuration of the ylide, mainly triphenylphosphine sulphide and dialkylmalononitriles, are formed together with triphenylphosphonium dicyanomethylide and sulphides[153–155]:



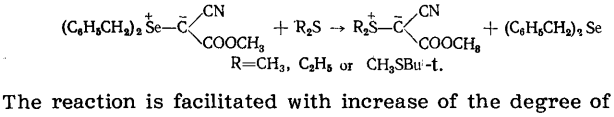
In certain cases dechalcogenation is the main pathway in the reaction between ylides and organoelemental compounds. In the reaction of dibenzylselenonium ylides containing two electron-accepting substituents with triphenylphosphine in CH_2Cl_2 mainly triphenylphosphine selenide is formed together with the products of the alkylation of the carbanionic fragment and a small amount of dibenzyl diselenide[156]:



It is noteworthy that mainly the usual transylidation takes place in the reaction between dibenzylselenonium *N*-tosylimide and triphenylphosphine[156]:

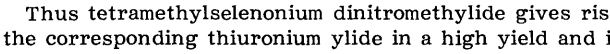


On the other hand, selenonium ylides are transylidated with sulphides, but only in the presence of CS_2, and do not form transalkylation products at all[157]:



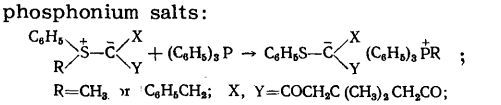
The reaction is facilitated with increase of the degree of branching of the substituent in the sulphide.

The influence of the substituents at the ylide heteroatom can be followed in relation to the interaction of selenonium dinitromethylides with thiourea[107]:



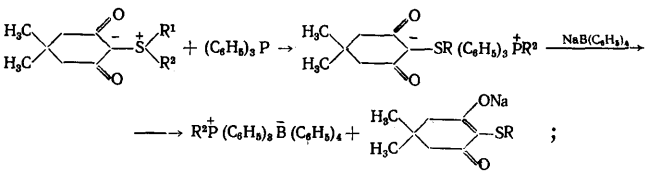
Thus tetramethylselenonium dinitromethylide gives rise to the corresponding thiuronium ylide in a high yield and in the absence of a catalyst. For R = $C_6H_5CH_2$, a 1 : 1 complex with thiourea is formed, while for R = C_6H_5 the reaction does not occur at all.

In the study of the interaction of sulphonium ylides derived from dimedone and phenylsulphonylacetophenone with triphenylphosphine a third possible pathway in the reaction of ylides with organoelemental compounds was discovered[157,158]. This reaction, which can be regarded as partial dealkylation of sulphonium ylides, leads to the formation of the corresponding phosphonium salts:



In the interaction of dialkylsulphonium dimedone ylides with triphenylphosphine the phosphonium salts could not be isolated probably as a consequence of their lability, but their

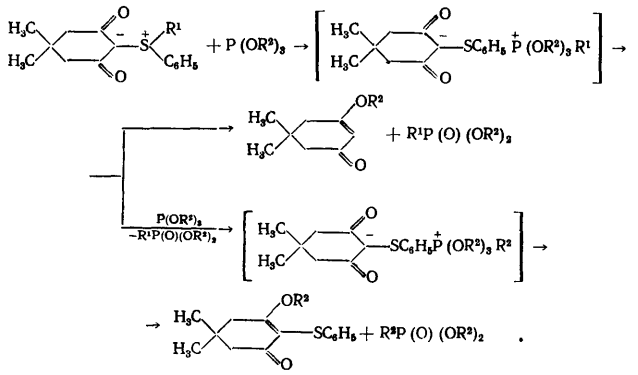
formation was demonstrated by carrying out the reaction in the presence of sodium tetraphenylborate:



R^1, R^2=CH_3, or $C_6H_5CH_2$.

Tris(dimethylamino)phosphine reacts similarly with sulphur-containing DSY.[159,160]

The reactions of sulphonium diketoylides with trialkyl phosphites take place via the intermediate formation of quasi-phosphonium salts and lead ultimately to alkyl phosphinates and 3-alkoxy-2-benzenesulphenyl-5,5-dimethylcyclohex-2-enone:[161]

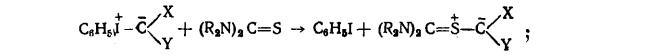


This reaction is a new example of the non-classical Arbuzov rearrangement.

Thus the transylidation reaction can be regarded as a special case of the interaction of the DSY of Group VI elements with organoelemental compounds.

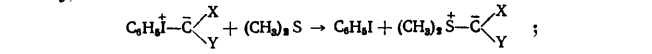
The transylidation reactions examined above are of interest from the standpoint of the chemical properties of ylides, but have not found fairly wide synthetic applications. It is evident, however, that the transylidation of relatively readily available aryliodonium ylides can find applications in the synthesis of certain types of chalcogenium ylides.

For example, thiuronium ylides, which are otherwise difficult to obtain, can be synthesised readily and in the absence of a catalyst[9,162,163]:



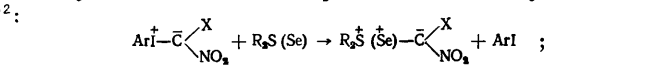
X, Y=$COCH_2C(CH_3)_2CH_2CO$ [163]; X=Y=NO_2 [9] .

Various dimethylsulphonium ylides derived from β-dicarbonyl compounds have been obtained via iodonium ylides in the presence of copper salts[115-118] and toluene-*p*-sulphonic acid[164] as catalysts:



X=Y=$COCH_3$ [115], COC_6H_5 [116]; X=$COCH_3$, Y=$COOC_2H_5$ [117]; XY=$COCH_2C(CH_3)_2CH_2CO$ [118], $COOC(CH_3)_2OCO$ [164] .

Furthermore, iodonium nitromethylides can serve as reagents for the synthesis of various sulphur and selenium ylides[9,107,162]:

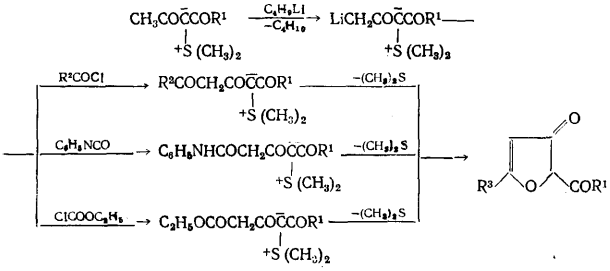


Ar=C_6H_5, or *p*-$O_2NC_6H_4$; X=$COOCH_3$, COC_6H_5, or NO_2; R=CH_3, n-C_4H_9, $C_6H_5CH_2$, or R_2=$(CH_2)_4$.

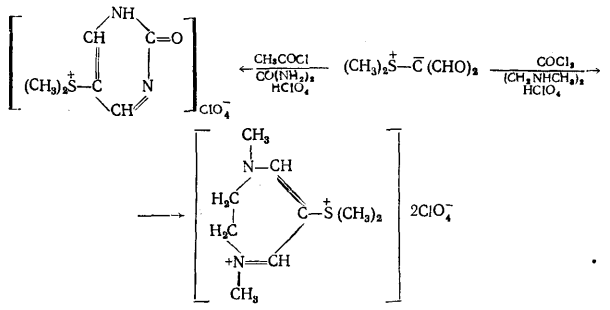
It is noteworthy that diphenyl chalcogenides do not enter into this reaction.

6. Other Reactions of the DSY

The reactions discussed above (with the exception of salt formation and the interaction of certain types of DSY with compounds containing multiple bonds) proceed with dissociation of the M^+–C bond. New reactions of the DSY, in which the groups linked to the onium atom are transformed without the dissociation of the M^+–C bonds, have been discovered recently. Thus at temperatures from −10° to −15 °C various sulphonium diacetylmethylides are readily substituted by lithium in the methyl group of the acetyl residue by reaction with butyl-lithium or lithium isopropylamide in THF, giving rise to monolithio-derivatives[165,166]. Treatment of these compounds with various reagents leads to new sulphur DSY; some of these compounds readily cyclise to furans[165,166]:



Certain heterocyclic compounds can be obtained from dimethylsulphonium diformylmethylide[79]:



After the manuscript had been sent to the editors, a number of studies on doubly stabilised sulphur and selenium ylides were published[167-179]. Condensation of dimethyl sulphoxide with methanedisulphonyl fluoride yielded a new type of sulphur ylides with two sulphonyl fluoride groups at the ylide carbon atom[167]. An unusual method of synthesis of aminosulphonium methylides by the interaction of arenesulphinic acids with active methylene compounds has been developed[168] and it has also been shown that these ylides undergo a Stevens type rearrangement[168]. The reaction of dicarbonyl-stabilised sulphonium ylides with sulphides[169] and the synthesis of thioxanthenium ylides and their base-catalysed rearrangement[170] have been studied and yet another example of the synthesis of a sulphur ylide from an iodonium ylide has been described[171]. The onium structure of doubly stabilised chalcogenonium ylides with complete delocalisation of the negative charge over the carbanionic fragment and with a single bond between the sulphur and the ylide carbon has been confirmed in relation to sulphonium dinitromethylides by X-ray diffraction, by the dipole moment method, and by quantum-chemical calculations[172]. Polarographic oxidation of sulphur-containing nitromethylides proceeds with abstraction of a single electron from the carbanionic fragment

and the formation of the corresponding radical-cations[173]. In the polarographic reduction of dicarbonyl-stabilised selenium ylides the bond between selenium and the ylide carbon atom undergoes two-electron cleavage with formation of a selenide and a dicarbonyl compound[174]. Analogous products are obtained in the chemical reduction of selenium ylides by mercaptans and mercaptoacids[175]. Thermolysis of selenonium ylides based on dimedone and indan-1,3-dione in the presence of copper sulphate proceeds via the corresponding carbenes, judging from the reaction products[176]. The unusual class of doubly stabilised sulphur and selenium ylides with the onium group at the carbanionic carbon atom, namely ylide salts, has begun to be studied systematically in recent times[177-179]. Their synthesis by the reaction of sulphoxides and selenoxides with phosphonium and sulphonium salts containing an active methylene group[177], their protonation, their cleavage by acids[178], and their rearrangements[179] have been described. Ylide salts are cleaved by hydrogen chloride with reformation of the initial active methylene compounds and dichloroselenide[178], i.e. via the same mechanism as sulphur- and selenium-containing dinitromethylides and doubly stabilised tellurium ylides and in this respect they differ from the vast majority of the chalcogenonium ylides.

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