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The Addition of Sulphenyl Chlorides to Unsaturated Compounds

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One of the aspects of the chemistry of sulphenyl chlorides, which is vigorously developing at the present time, is examined. It involves their interaction with unsaturated compounds. The application of modern physical research techniques has made it possible to investigate the addition of sulphenyl chlorides to asymmetric olefins, which results as a rule in the formation of a mixture of isomeric β-halogenoalkyl sulphides. The interconversions of the β-halogenoalkyl sulphides, associated with the vicinal positions of the halogen and sulphur atoms in the molecule, are considered. The high reactivity of the halogen and sulphur atoms in the molecule, are considered. The high reactivity of the halogen permits its ready nucleophilic substitution with formation of a series of new interesting compounds.
The bibliography includes 210 references.

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I. INTRODUCTION

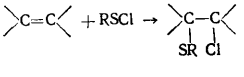
Reactive sulphenyl chlorides add readily and quantitatively to unsaturated compounds. The reaction constitutes a convenient method of synthesising various β-chloroalkyl sulphides, which are used as insecticides, fungicides, and bactericides or serve as the starting materials for the synthesis of aminomercaptans, monomers, etc. Certain β-chloroalkyl sulphides exhibit antitumour or mutagenic activities. The addition of sulphenyl chlorides to unsaturated compounds such as olefins, acetylenes, and steroids is also used for their characterisation and quantitative determination.

Certain reactions involving the addition of sulphenyl chlorides to unsaturated compounds are briefly reviewed in Kharasch's monograph[1], but many new data have been published in recent years, which necessitated significant modifications of the earlier ideas. Gundermann's review[2] deals with the involvement of the sulphur atom in nucleophilic substitution of the halogen in β-halogenoalkyl sulphides. Mueller[3] analysed the influence of steric and electronic factors, confirming the formation of the episulphonium ion as an intermediate in the addition of sulphenyl chlorides to unsaturated compounds and in the cleavage of thiirans by electrophiles. Kuhle[4] described methods for the preparation of sulphenyl chlorides and a wide variety of their reactions.

This review includes new studies on the addition of alkyl, aryl, acetylthio-, dialkoxyphosphoryl, alkoxyalkylphosphinyl, and alkylamino-derivatives of sulphenyl chlorides to olefins, dienes, allenes, acetylenes, and derivatives of αβ-unsaturated acids.

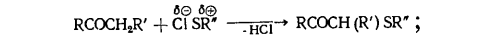
II. ADDITION TO OLEFINS

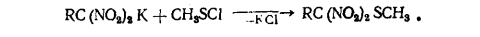
The first data on the addition of sulphenyl chlorides to olefins were published by Lecher et al.[5] in 1925:



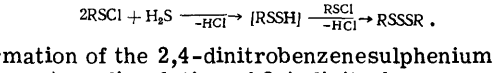
R = C_6H_5; *p*-$CH_3C_6H_4$; or *o*-$NO_2C_6H_4$.

The reaction drew attention, since, owing to their high reactivity, sulphenyl chlorides add easily and quantitatively to double bonds with formation of the corresponding β-chloroalkyl sulphides. According to modern ideas, the sulphenyl chloride molecule is polarised in such a way that the partial positive charge is localised at the sulphur atom. This structure is confirmed also by the interaction of sulphenyl chlorides with compounds containing a mobile hydrogen atom, such as malonic ester, acetoacetic ester, nitromethane, hydrogen cyanide, etc. The reaction leads to the formation of sulphides[6-8]:



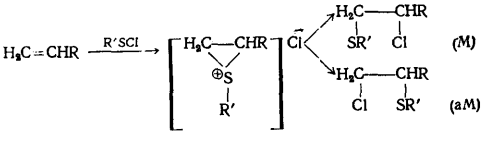


Sulphenyl chlorides react with hydrogen sulphide to form trisulphides[9,10]:



The formation of the 2,4-dinitrobenzenesulphenium cation $(NO_2)_2C_6H_3S^+$ on dissolution of 2,4-dinitrobenzenesulphenyl chloride in concentrated sulphuric acid has also been described[11,12].

Kharasch contributed much to the study of the mechanism of the addition of sulphenyl chlorides to unsaturated compounds. He was the first to suggest the formation in this reaction of the intermediate cyclic episulphonium ion (I). The subsequent opening of the ring by the chloride anion leads to the formation of β-chloroalkyl sulphides. With asymmetric olefins, adducts can be formed both in accordance with (designated subsequently by M) and contrary to (designated subsequently by aM) the Markovnikov rule[13]:



(I)

The study of the kinetics of the addition of sulphenyl chlorides to olefins showed that this is an electrophilic reaction[14,15]. The rate of addition of 2,4-dinitrobenzenesulphenyl chloride (DNBS) to *p*-substituted styrenes is influenced by those *p*-substituents which increase the electron density in the double bond of styrene[16]. The addition to cyclohexene is ten times faster than to styrene and three times faster than to *p*-methylstyrene[17-20]. The rate of addition of DNBS to 4,5-disubstituted cyclohexenes and to norbornene derivatives decreases with enhancement of the electron-accepting properties of the substituents[21]. Methanesulphenyl chloride adds faster to olefins containing methyl groups attached to the double bond. The influence of the nucleophilic properties of the double bond and steric factors on the relative rates on addition of sulphenyl chlorides has been demonstrated for olefin homologues and *cis*- and *trans*-isomers. Comparison of the reactivities of sulphenyl chlorides and chlorine in addition to olefins under analogous conditions showed that the formation of the intermediate sulphonium ion is less sensitive to changes in the nucleophilic properties of the olefins than in the case of chlorine and is extremely sensitive to steric factors. The relative reactivities of olefins with respect to electrophilic attack in non-polar solvents are given below:

Olefin	Cl_2	CH_3SCl	Olefin	Cl_2	CH_3SCl
But-1-ene	1.6	1.0	Isobutene	50	0.75
cis-But-2-ene	63	13.0	Trimethylethylene	11.000	8.26
trans-But-2-ene	58	0.72	Tetramethylethylene	430.000	12.90

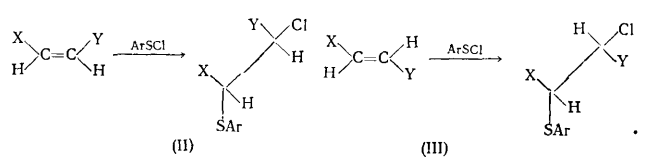
The rate of addition is also influenced by the geometry of the olefins; for example, *cis*-but-2-ene combines with methanesulphenyl chloride faster than its *trans*-isomer[22].

The nature of the substituent in the benzene ring of benzenesulphenyl chloride also affects the rate of addition. *p*-Methyl- and 2,4-dichloro-benzenesulphenyl chlorides add to but-2-ene faster than DNBS.[23] The study of the relative rates of addition of *p*-substituted *o*-nitrobenzenesulphenyl chlorides to cyclohexene led to analogous conclusions[24-26].

It is believed that the formation of the episulphonium ion is the rate-determining stage in the addition of DNBS to styrene[27], *p*-substituted styrenes[16], and cyclohexene[17]. The ionic reaction mechanism is also confirmed by data obtained in the study of the influence of the polarity of the solvent on the rate of addition of DNBS to cyclohexene. The reaction in nitrobenzene is 3000 times faster and in acetic acid 1400 times faster than in carbon tetrachloride[17].

The Hammett and Taft constants calculated for the addition of arenesulphenyl chlorides to olefins also point to the existence of an intermediate episulphonium ion rather than a carbonium ion[25,28].

The addition of sulphenyl chlorides to unsaturated compounds is strictly stereospecific[29]. Different arenesulphenyl chlorides yield respectively the racemic *threo*- and *erythro*-adducts (II) and (III) on interaction with the *cis*- and *trans*-isomers of 2-phenylbut-2-ene,[30] but-2-ene[23,31], stilbene[32-34], and 1-phenylprop-1-ene[35]:



(II) (III)

cis-Stilbene reacts more slowly than its *trans*-isomer. The two adjacent phenyl groups apparently prevent the formation of the intermediate episulphonium ion[32].

Kinetic studies on the addition of 2,4-dinitrobenzenesulphenyl chloride to the vapours of various 1-arylpropenes and the corresponding olefins also showed that all the *trans*-isomers of 1-arylalkenes are more reactive than the *cis*-isomers. On the other hand, the rate of addition of sulphenyl chlorides to *cis*-alkenes is approximately ten times higher than the rate of addition to the *trans*-isomers[36].

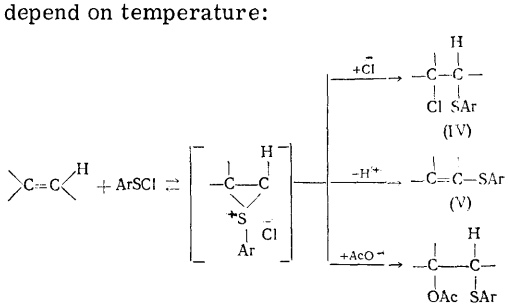
Data indicating the high stereospecificity of the addition of *p*-chlorobenzenesulphenyl chloride to *cis*- and *trans*-but-2-enes over a wide temperature range (from −34° to +180°C) also confirm the formation of an intermediate cyclic episulphonium ion. If an intermediate carbonium ion, which has presumably a planar configuration with free rotation about the central C=C bond, had been formed, the ratio of the *erythro*- and *threo*-adducts would have been identical for both *cis*- and *trans*-but-2-enes[37]. The addition of RSCl to cyclohexenes resulted in the formation of *trans*-adducts[31,38,40]. In some investigations, the configuration of the cyclohexene adducts was not determined[41-48]. *trans*-Adducts were also obtained with other cyclic compounds: norbornene[49,50], norbornadiene[51-54], and sulpholene[55].

Following the addition of benzenesulphenyl chloride to 7-chlorodibenzobicyclo[2,2,2]octatriene[54] and of 2,4-dinitrobenzenesulphenyl chloride to norbornene[56], the Wagner–Meerwein rearrangement was observed.

The *trans*-addition of methanesulphenyl chloride to acenaphthylene, of benzenesulphenyl chloride to 7,7-dimethylnorbornene[57-61], and of various alkanesulphenyl chlorides to dihydropyran[62,63] was confirmed by NMR spectra.

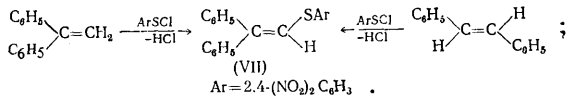
A single non-stereospecific example, involving the addition of 2,4-dinitrobenzenesulphenyl chloride to *cis*- and *trans*-anetholes in tetrachloroethane, has been described. *cis*-Anethole yields 70% of the *threo*-adduct and 30% of the *erythro*-adduct, while the *trans*-isomer gives rise to 5 and 95% of the two adducts respectively. A slow rearrangement was observed until the attainment of equilibrium with approximately equal proportions of the isomers (51.8% of the *erythro*-adduct and 48.2% of the *threo*-adduct)[64].

When arenesulphenyl chlorides react with anethole[13], *p*-methoxystyrene[16], and 3,3-dimethylbutene[65] in glacial acetic acid, several compounds are obtained, whose formation can be explained solely by the transformation of an intermediate episulphonium ion. The addition of the chloride anion to the intermediate episulphonium ion gives rise to a β-chloroalkyl sulphide, while the abstraction of a proton from the latter results in the formation of a vinyl sulphide and solvolysis with glacial acetic acid gives a β-acetoxyalkyl sulphide. The proportions of the compounds depend on temperature:



In the reaction involving *p*-methoxystyrene, the vinyl sulphide (V) and the β-acetoxyalkyl sulphide (VI) are formed from β-chloroethyl sulphide (IV) much more

slowly than in the direct addition of the arenesulphenyl chloride to the olefin[16]. In the addition of ArSCl to 1,1-diphenylethylene, HCl is evolved and the unsaturated sulphide (VII) is formed[13]; it was also obtained from *trans*-stilbene in boiling acetic acid[66]:

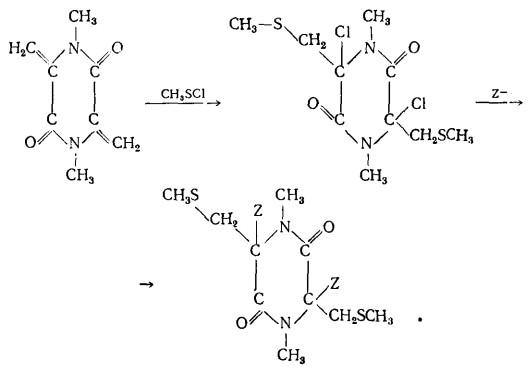


(VII)

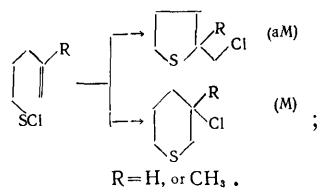
Ar = 2,4-$(NO_2)_2C_6H_3$.

It has been shown that, when 2,3,5,6-tetrachloropyridine-4-sulphenyl chloride adds to asymmetric alkenes, the ratio of the M and the aM adducts is greatly influenced by steric factors and the solvent[67].

The addition of methanesulphenyl chloride to 1,4-dimethyl-3,6-dimethylenepiperazine-2,5-dione results in an adduct which loses HCl on prolonged storage with formation of three isomeric compounds. On treatment with nucleophiles, chlorine is readily substituted[68]:



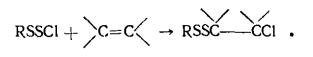
The intramolecular addition of a sulphenyl chloride with formation of a mixture of aM and M compounds has been achieved:



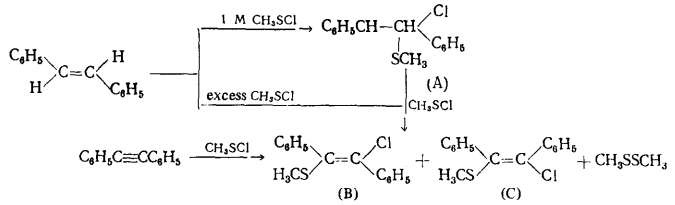
R = H, or CH_3 .

The aM adduct is first formed preferentially and then gradually isomerises to the M adduct. The structures were confirmed by NMR and by oxidation to sulphones[69].

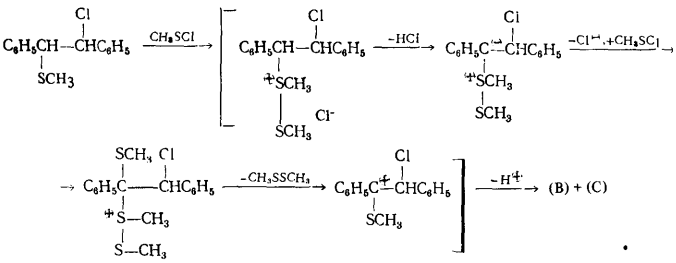
The addition of arenethiosulphinyl chlorides leads to the corresponding mixed β-halogenodisulphides[70]:



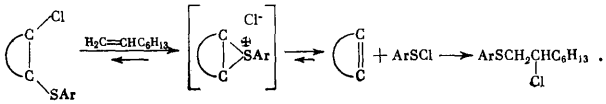
Interesting results were obtained in a study of the addition of methanesulphenyl chloride to *trans*-stilbene[71]. On treatment of *trans*-stilbene with one mole of methanesulphenyl chloride, the adduct (A) is formed, while on treatment with an excess of the reagent the product consists of a mixture of compounds (B) and (C). The same mixture was obtained following the addition of methanesulphenyl chloride to tolane:



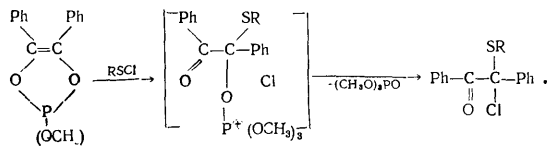
with *cis* : *trans* = 4 : 1. The authors suggested the following mechanism for the formation of compounds (B) and (C):



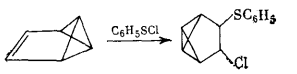
The exchange of sulphenyl chloride between olefins has been achieved[72]. It has been shown that the adducts obtained by the addition of 4-chlorobenzenesulphenyl chloride to cyclic or acyclic olefins exchange it with oct-1-ene on heating in tetrachloroethane:



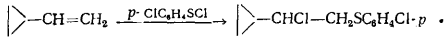
The addition of sulphenyl chlorides to 1,3,2-dioxaphospholen leads to the elimination of phosphate and the formation of α-chloro-α-thioketones[73]:



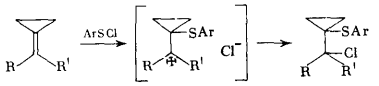
The addition of benzenesulphenyl chloride to benzvalene has been achieved[74]:



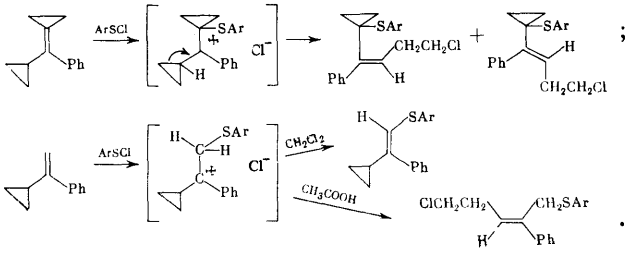
The effect of the cyclopropyl substituents on the rate of electrophilic addition has been investigated[75] and it has been shown that the rate of addition of β-chlorobenzenesulphenyl chloride to cyclopropylethylene is an order of magnitude higher than the rate of addition to n-butylethylene:



The addition of 2,3-dinitrobenzenesulphenyl chloride to phenylmethylenecyclopropanes and α-cyclopropylstyrene[76] has been studied. Phenylmethylenecyclopropanes with R = R′ = Ph and R = Ph, R′ = H normally combine with sulphenyl chlorides via the mechanism



In the reaction of phenylcyclopropylmethylenecyclopropane and α-cyclopropylstyrene, the unsubstituted cyclopropane ring rearranges to homoallyl adducts:

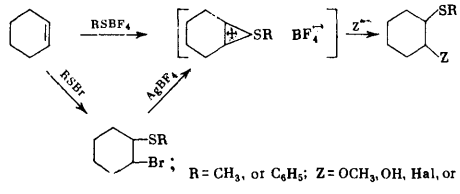


The tendency by the intermediate to lose a proton diminishes with increase of the acidity of the solution in the following sequence:

$$CH_3COOH \gg CH_3NO_2 > CH_2Cl_2 .$$

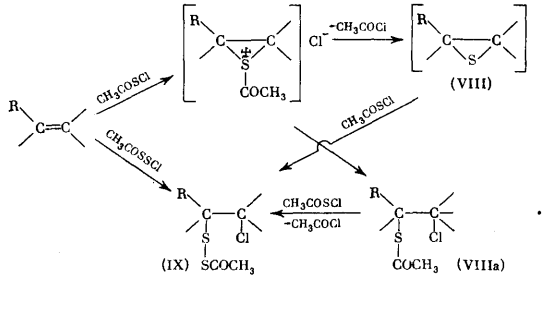
When sulphenyl chloride adds in acetic acid solution, chlorine is partly substituted by the acetoxy-group [76].

The possibility of addition to the multiple bonds of the more highly polarised sulphenyl fluoroborates has also been demonstrated [77,78]:



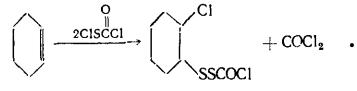
However, the authors were unable to isolate the intermediate in the form of a stable episulphonium salt; only the products of the subsequent nucleophilic substitution were isolated. Under these conditions, there was *trans*-addition to tetradeuterocyclohexene [79].

The addition of acetylsulphenyl chloride to olefins takes place in an unusual manner. It is suggested that here too an episulphonium ion is formed as an intermediate and is stabilised by ejecting acetyl chloride with formation of the thiiran (VIII). The latter is immediately cleaved by a second molecule of acetylsulphenyl chloride with formation of the β-chloroalkyl acetyl disulphide (IX), which is also obtained by the addition of acetylthiosulphenyl chloride to an olefin [80-82]. However it has been shown recently [83] that the *S*-acetyl-β-chloromercaptan (VIIIa) likewise readily reacts with acetylsulphenyl chloride to form compound (IX). Thus another mechanism is also possible in this instance:

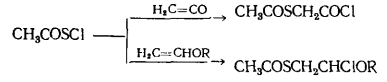


If the rate of addition of acetylsulphenyl chloride to olefins with the reactants taken in equimolar amounts is much higher than the rate of cleavage, only the normal adducts are formed—*S*-acetyl-β-chloromercaptans (VIIIa); on the other hand, if the rate of addition of acetylsulphenyl chloride is lower than the rate of cleavage of compound (VIIIa) by the sulphenyl chloride, only the disulphides (IX) are formed.

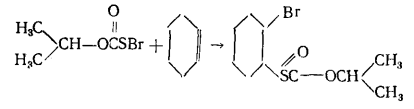
Chlorocarbonylsulphenyl chloride adds similarly to a cyclic olefin [84]:



Like other sulphenyl chlorides [85], acetylsulphenyl chloride reacts normally with ketones [81,86] and vinyl ethers [81] to form monoadducts:

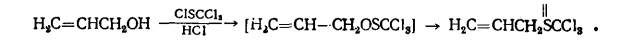


Isopropoxycarbonylsulphenyl bromide likewise reacts with cyclohexene to form a monoadduct [87]:

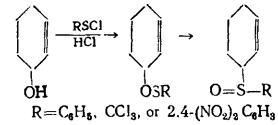


The addition of sulphenyl chlorides to enolic esters [88], allyl chloride [89,90], vinyl chloride [91] and the phthalimide derivative of allylamine [92] has been achieved.

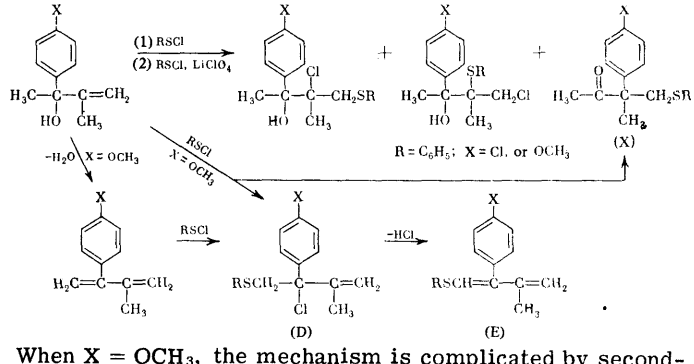
Allyl alcohol reacts with sulphenyl chlorides preferentially via the hydroxy-group, forming unstable allyl sulphenates. The latter readily rearrange to the isomeric sulphoxide [93-95]:



Analogous reactions have been carried out with cyclohexen-2-ol [96]:



However, sulphenyl chlorides normally add to the double bond of 3-methyl-2-(4-X-phenyl)but-3-en-2-ols. The subsequent rearrangement of the adduct gives the ketone (X), whose amount is much larger in the presence of $LiClO_4$ (51%):



When X = OCH_3, the mechanism is complicated by secondary processes; compounds (D) and (E) were isolated in addition to the ketone [97,98].

Kharasch was the first to note that the asymmetric olefins propene and pent-2-ene react with DNBS to form simultaneously two adducts, M and aM, the M adduct predominating (65%). The authors demonstrated the

structure of these isomeric β-chloroalkyl sulphides by converting them into alkyl aryl sulphones (XI):[13]

$$2,4\text{-}(NO_2)_2C_6H_3SCH_2CHClCH_3 \xrightarrow[(3)\ H_2/Ni]{\substack{(1)\ KMnO_4/CH_3COOH \\ (2)\ (C_2H_5)_3N \\ (4)\ C_6H_5COCl}} \rightarrow 2,4\text{-}(C_6H_5CONH)_2C_6H_3SO_2CH_2CH_2CH_3 .$$

(XI)

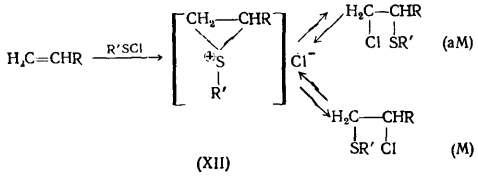
In a number of studies on the addition of sulphenyl chlorides to unsaturated compounds, the structures of the adducts were also determined solely by chemical methods: by converting them into sulphones[23,43,99], lactones, and thiolactones[100,101], by dehydrohalogenation[47,102], and by specific synthesis[48,49]. Some workers adopted the M structure solely on the basis of the Markovnikov rule[93-99].

Table 1. Dependence of the initial isomer ratio on the structure of the initial reactants.

Initial olefin	Substituent R in RSCl	Adducts, % $CH_2(Cl)-CH(SR)$ (aM)	Adducts, % $CH_2(SR)-CH(Cl)$ (M)	References
$H_2C=CHCH_3$	CH_3	82	18	59
$H_2C=C(CH_3)_2$	CH_3	80	20	
$H_2C=CHCH(CH_3)_2$	CH_3	94	6	
$H_2C=CHC(CH_3)_3$	CH_3	95	5	
$H_2C=CHCH_3$	$(CH_3)_2N$	78	22	110
$H_2C=C(CH_3)_2$	$(CH_3)_2N$	71	29	
$H_2C=CHCH(CH_3)_2$	$(CH_3)_2N$	90	10	
$H_2C=CHC(CH_3)_3$	$(CH_3)_2N$	95	5	
$H_2C=CHCH_3$	C_6H_5	68	32	59
$H_2C=CHCH(CH_3)_2$	C_6H_5	87	13	
$H_2C=CHCH_3$	$CH_3C(O)S$	60	40	82
$H_2C=C(CH_3)_2$	$CH_3C(O)S$	32	68	
$H_2C=CHC(CH_3)_3$	$CH_3C(O)S$	82	18	
$H_2C=CHCH_3$	$(CH_3O)_2P(O)$	50	50	59
$H_2C=C(CH_3)_2$	$(CH_3O)_2PO$	19	57*	
$H_2C=C(C_6H_5)_2$	CH_3	10	90	59,82
$H_2C=CHC_6H_5$	CH_3	2	98	
$H_2C=CHC_6H_5$	$CH_3C(O)S$	—	100	
$H_2C=CHCH_2CH(CH_3)_2$	$2\text{-}NO_2\text{-}4\text{-}CH_3O\text{-}C_6H_3$	52	47	112
$H_2C=CHCH_2CH(CH_3)_2$	$2,4\text{-}(NO_2)_2\text{-}C_6H_3$	47	51	
$H_2C=CHCH_2CH(CH_3)_2$	$2\text{-}NO_2\text{-}C_6H_4$	44	54	
$H_2C=CHCH_2CH(CH_3)_2$	$2,4\text{-}(NO_2)_2\text{-}C_6H_3$	38	61	

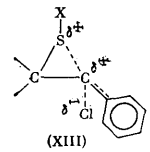
*21% of $RSCH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH_2$ was also obtained.

The application of NMR for the determination of the structures of the adducts enabled Mueller and coworkers[58,59] not only to establish a number of characteristics of the addition of sulphenyl chlorides to unsaturated compounds but also to explain some of them. Thus, in order to prevent isomerisation, alkane- and arene-sulphenyl chlorides were added in the presence of calcium carbonate to asymmetric olefins in methylene chloride at a low temperature. It was established that aM adducts are formed preferentially in the first instance (Table 1). The selectivity of the formation of the aM adducts increases with increase of the size of the substituent at the double bond from methyl to t-butyl. This shows that the mode of addition of sulphenyl chloride depends not only on electronic factors but also on the steric influence of the substituents. In the intermediate episulphonium ions (XII), they direct the attack by the chloride anion to the less substituted carbon atom with formation of the aM adduct[57,59].



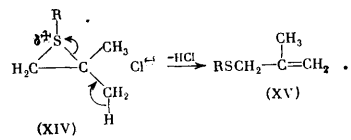
(XII)

Only the M adduct is formed in the reaction with styrene, while in the reaction with 1,1-diphenylethylene the proportion of M is up to 90% (Table 1) owing to the stabilisation of the positive charge of the α-carbon atom in the transition state (XIII):[59]



(XIII)

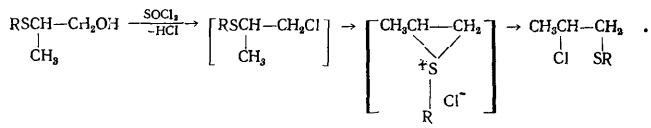
In the reaction with isobutene, the two methyl groups attached to the same carbon atom create conditions for the formation of an intermediate ion having some of the properties of a carbonium ion. On interaction with *OO*-dimethylphosphorylsulphenyl chloride, this olefin gives rise to the unsaturated sulphide (XV) apparently via the intermediate state (XIV) (Table 1). The electron-accepting phosphoryl group makes the sulphur less nucleophilic and facilitates the elimination of a proton from the methyl group[59,111]:



(XIV) (XV)

The ratio of the adducts in the reaction mixture is also influenced by the nature of the sulphenyl chloride (Table 1);[59,82,110-112] as the electron-accepting properties of the substituent R in the sulphenyl chloride become more marked, the amount of the M adduct increases. The explanation is that the electron-withdrawing group R in the intermediate episulphonium ion favours the formation of a positive charge on the substituted carbon atom, directing thereby the chloride ion to this atom.

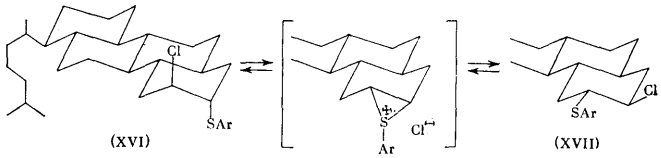
Fuson et al. described for the first time the isomerisation of β-chloroalkyl sulphides in which the chloro- and alkylthio- or arylthio-groups change places[99]. The authors postulated that the isomerisation proceeds via an episulphonium ion:



A similar isomerisation was later observed by other workers, who synthesised β-chloroalkyl sulphides by various methods[114,118].

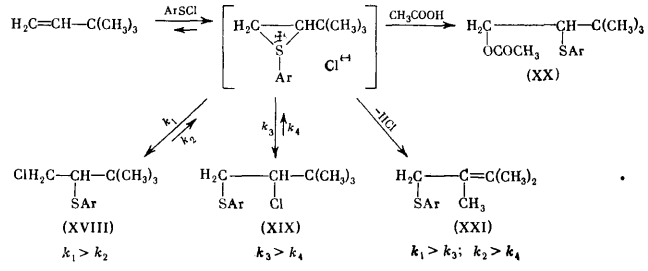
The rate of isomerisation of β-chloroalkyl sulphides in various solvents has been studied in relation to the adduct formed by arenesulphenyl chloride with 5-α-cholest-2-ene[119,120]. The addition reaction involves the initial formation of the diaxial adduct (XVI), which isomerises on heating to the diequatorial adduct (XVII). The isomerisation is accelerated by solvents promoting ionisation; for example, the isomerisation is 1600 times faster in butanol than in decalin. The introduction of the *p*-nitro-group into benzenesulphenyl chloride retards isomerisation in butanol to a greater extent than in decalin. This observation confirms the ionic mechanism of the

isomerisation process, which may proceed via an episulphonium ion:



(XVI) (XVII)

The variation of the rate of isomerisation of β-chloroalkyl sulphides with temperature and the duration of heat treatment has been studied in relation to the addition of 2,4-dinitrobenzenesulphenyl chloride to 3,3-dimethylbut-1-ene in glacial acetic acid[65]:



(XVIII) (XIX) (XXI) (XX)

$k_1 > k_2$ $k_3 > k_4$ $k_1 > k_3$; $k_2 > k_4$

It is suggested that the activation energy for the stage involving the formation of the initial adduct (XVIII) is smaller than the activation energy for the formation of compound (XIX). At lower temperatures and for shorter reaction times, the kinetically controlled aM adduct (XVIII) is therefore formed, while at higher temperatures and for longer reaction times the product is the thermodynamically stable M adduct (XIX). This is accompanied by the simultaneous acetolysis and elimination of HCl with formation of compounds (XX) and (XXI).

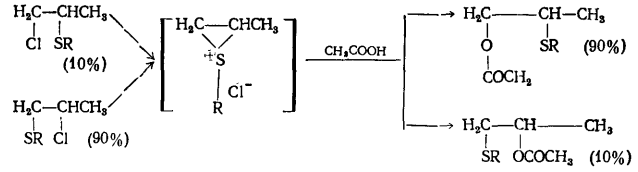
The ready isomerisation of the kinetically controlled aM adducts to thermodynamically stable isomers when the former are stored was observed by NMR.[57,59] At a temperature below 0°C in the presence of $CaCO_3$, the ratio of the aM and M isomers remain unchanged. In the absence of $CaCO_3$, slow isomerisation took place (to give 90% of the M adduct) until equilibration. At room temperature the equilibrium was attained after 200 h, the isomerisation being accelerated by traces of acids. The isomerisation of the aM adduct of 2,4-disubstituted benzenesulphenyl chlorides with 4-methylpent-1-ene to the M adducts took place to the extent of 92–95% on heating in glacial acetic acid[102].

The substituents at the sulphur atom have a significant influence on the isomerisation of β-chloroalkyl sulphides. The adducts of methanesulphenyl chloride isomerise comparatively rapidly, while those of benzenesulphenyl chloride isomerise much more slowly[57,59]. The rate of isomerisation of the adducts of substituted arenesulphenyl chlorides is reduced to a particularly marked extent by the *o*-nitro-group, which can be explained either by steric hindrance or by the reaction of the nitro-group with the sulphur atom[112]. The isomerisation of adducts of olefins with acetylthio- and *OO*-dimethylphosphorylsulphenyl chlorides takes place to a very slight extent or does not occur at all[59,111]. Only a slight isomerisation of the adducts of olefins with dimethylaminosulphenyl chloride has been noted[110]. Increasing electronegativity of the substituent at the sulphur atom makes the latter less nucleophilic and weakens or eliminates the ability of sulphur to attack a β-carbon atom with formation of an episulphonium ion.

The rate of isomerisation depends also to some extent on the structure of the initial olefin. The M adduct formed in the reaction of methanesulphenyl or acetylthiosulphenyl chloride with styrene at room temperature does not isomerise. Slight isomerisation was achieved only on heating in the presence of acid catalysts[59,82].

β-Chloroalkyl sulphides isomerise with retention of configuration. Thus it has been shown by NMR that the aM *trans*-adducts of methanesulphenyl chloride with norbornene or acenaphthylene isomerise to the M adduct without change of the *trans*-configuration[57]. The *threo*- and *erythro*-configurations are retained in the isomerisation of the adducts of 4-chlorobenzenesulphenyl chloride with *cis*- and *trans*-1-phenylpropenes[35], which also confirms the hypothesis that the isomerisation proceeds via a three-membered episulphonium ion.

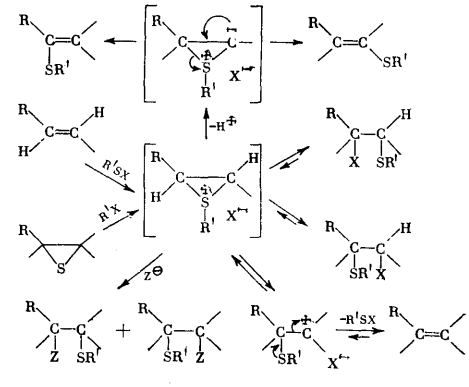
Acetolysis of diastereoisomeric pairs of adducts of arenesulphenyl chlorides with *trans*- or *cis*-but-2-ene gives rise to the diastereoisomeric pairs of the corresponding acetates[31]. The acetolysis of a mixture of the isomeric adducts of 2,4-dinitrobenzenesulphenyl chloride[31] and methanesulphenyl chloride[59] with propene led to identical mixtures of acetates, which is significant evidence for the existence of an intermediate episulphonium ion in the isomerisation of β-chloroalkyl sulphides:



III. STABLE EPISULPHONIUM SALTS

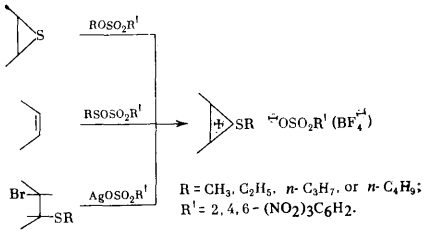
Thus experimental factors and kinetic evidence confirm indirectly that the addition of sulphenyl chlorides to olefins proceeds via the formation of an intermediate episulphonium ion. Subsequent nucleophilic attack by an anion on a ring carbon atom leads to the final reaction products with formation of the individual chloroalkyl sulphides or their mixture, consisting of the kinetically controlled aM adducts and the thermodynamically stable M isomers[23].

The initial ratio of the isomers is influenced both by steric and electronic factors in the initial olefin and by the nature of the substituents at the sulphur atom in the sulphenyl chloride, the solvent polarity, and the reaction temperature. At lower temperatures, the kinetically controlled aM adduct is formed preferentially, while at higher temperatures the M product is favoured:



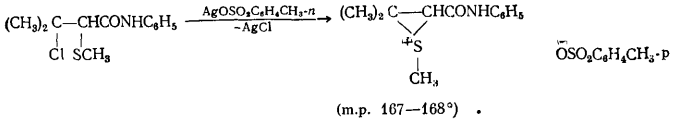
The concept of the formation of an intermediate episulphonium ion also proved important for the interpretation of a number of reactions of β-halogenalkyl sulphides. Thus it becomes clear from this point of view that the isomerisation of β-halogenalkyl sulphides (the conversion of the aM adducts into the M isomers) until equilibration proceeds via an intermediate episulphonium ion. The formation of a mixture of isomers in the nucleophilic substitution of the halogen atom in β-halogenalkyl sulphides occurs as a result of attack by the anion on one of the carbon atoms in the intermediate ion [120]. The elimination of the hydrogen halide from β-halogenalkyl sulphides with formation of isomeric vinyl sulphides evidently also proceeds with elimination of a proton from the episulphonium ion [2,59]. Finally the elimination of the sulphenyl halide from β-halogenalkyl sulphides with formation of an olefin on heating or on treatment with a nucleophile involves the same process [121] and the opening of the thiiran ring by electrophiles with formation of a mixture of isomeric compounds probably likewise proceeds via an episulphonium ion [122].

The episulphonium ion has not so far been isolated. The difficulty of its isolation is associated with its high reactivity and in most cases an equilibrium almost wholly displaced to the right is established under the usual conditions (see the scheme below). The stability of the episulphonium ion depends primarily on the nature of the nucleophile (on whether it is strong or weak), the electrophilic properties of the sulphur atom, and probably on steric factors.



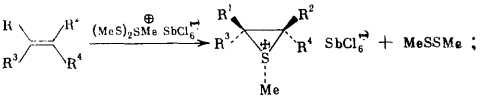
The formation of stable episulphonium salts was first confirmed in relation to two examples—the formation of *cis*-cyclo-octenyl-*S*-methylepisulphonium 2,4,6-trinitrobenzenesulphonate and a steroid *S*-phenylepisulphonium hexafluoroantimonate, where the thiiran ring was part of a complex condensed system [123–126]. The high stability of the episulphonium salt in the first instance enabled the authors to obtain it in three different ways, which confirms that the same episulphonium ion is a common intermediate in these reactions.

A stable episulphonium salt was obtained in this system (R = CH_3) also with the aid of silver tetrafluoroborate [125]. Stable episulphonium salts have been obtained recently for the acyclic series too. The anilide of β-chloro-α-methylthiovaleric acid reacts with silver toluene-*p*-sulphonate to form a stable salt, which is readily soluble in water and insoluble in ether [126]:



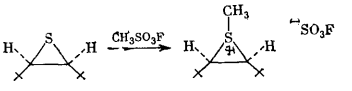
(m.p. 167–168°).

Stable episulphonium salts have been recently obtained also from alkenes [127]:



(a) R' = R² = R³ = R⁴ = Me;
(b) R' = R⁴ = Et; R² = R³ = H;
(c) R'R² = —(CH₂)₆—; R³ = R⁴ = H;
(d) R' = R³ = Me; R² = R⁴ = H;
(e) R' = R² = Me; R³ = R⁴ = H;
(f) R' = R⁴ = Me; R² = R³ = H;
(g) R' = R² = R³ = Me; R⁴ = H.

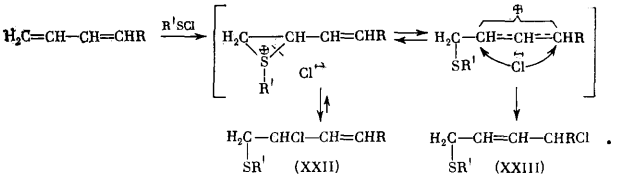
The first three salts were isolated in the form of analytically pure crystalline compounds, which are stable for a long time in the absence of moisture at temperatures below −10°C. The structure of the salts was also confirmed by NMR. It is noteworthy that analogous salts were obtained for selenium derivatives [128]. It was observed that, on methylation by methyl fluorosulphonate at 0°C in methylene chloride, *cis*-2,3-di-t-butylthiiran yields *cis*-2,3-di-t-butyl-*S*-methylepisulphonium fluorosulphonate in the form of crystals, which decompose at approximately 20°C:[129]



The geometrical parameters of the intermediate episulphonium ions have been calculated by the molecular orbital method for ethylene, propene, isobutene, and butadiene [130].

IV. INTERACTION WITH CONJUGATED DIENES

It has been established by NMR that methane-, benzene-, and *p*-chlorobenzenesulphenyl chlorides add to 1,3-dienes with the initial formation of 1,2-adducts (XXII), mainly with the M structure, which isomerise to the 1,4-adducts (XXIII) (Table 2): [131–133]



The ratios of the aM and M isomers of the 1,2-adducts is influenced by the position of the alkyl substituents in the diene. Thus in the case of piperylene and 4-methylpenta-1,3-diene, where the methyl group is in the 4-position, steric factors promote the addition of the sulphenyl chloride to the unsubstituted double bond. In the isoprene molecule, having a methyl group in the 2-position, steric factors do not have a significant influence and virtually equal amounts of the aM and M isomers are formed. In the reaction involving chloroprene, the influence of electronic factors becomes significant, the more nucleophilic unsubstituted double bond being preferentially attacked with formation of the M adduct.

1,2-Adducts readily isomerise at room temperature to 1,4-adducts. The ease of isomerisation increases in the following sequence of dienes: buta-1,3-diene < isoprene < piperylene < 4-methylpenta-1,3-diene [132]. This isomerisation is also influenced by the nature of the substituent

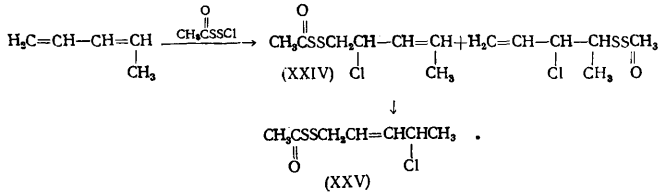
at the sulphur atom. The 1,2-adducts of benzenesulphenyl chloride with dienes do not isomerise, which has already been noted for the adducts with olefins. This also confirms that the intermediate episulphonium ion is involved in the isomerisation.

Table 2. The influence of the structure of the diene on the initial isomer ratio.

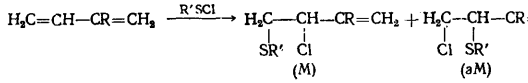
Diene	Adducts	Ratio of adducts, %	
		R=CH_3	R=C_6H_5
$H_2C{=}CHCH{=}CH_2$	$RSCH_2CHClCH{=}CH_2$	95	98
	$ClCH_2CHSRCH{=}CH_2$	5	—
$H_2C{=}CHCH{=}CHCH_3$	$RSCH_2CHClCH{=}CHCH_3$	86	82
	$CH_3{=}CHCHClCHSRCH_3$	14	18
$H_2C{=}CHCH{=}C(CH_3)_2$	$RSCH_2CHClCH{=}C(CH_3)_2$	33	—
	$RSCH_2CH{=}CHCl(CH_3)_2$	12*	—
$H_2C{=}C(CH_3)CH{=}CH_2$	$RSCH_2CClCH_2CH{=}CH_2$	57	60
	$CH_3{=}CCH_2CHClCH_2SR$	43	40
$H_2C{=}CHCCl{=}CH_2$	$RSCH_2CHClCCl{=}CH_2$	85	—
	$ClCH_2CHSRCCl{=}CH_2$	15	—
		85	—

*This result most probably represents postisomerisation.

The 1,2-adduct (XXIV) with the M structure, obtained from piperylene and acetylthiosulphenyl chloride, isomerises appreciably to the 1,4-adduct (XXV): [82]

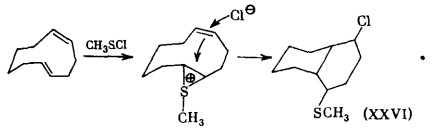


The M adduct predominates in mixtures of the M and aM isomers of the 1,2-adducts of *OO*-dimethylphosphorylsulphenyl chloride with butadiene and isoprene[99]. In an earlier study, where the structure of the adduct had been determined by a chemical method, only the presence of the M adduct was indicated[134];

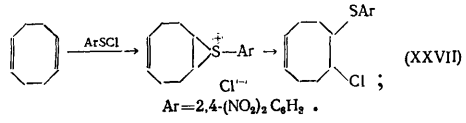


R=H (73% M and 27% aM); R=CH_3 (65% M and 35% aM); R'=$PO(OCH_3)_2$.

Methanesulphenyl chloride reacts with *cis,trans*-cyclodeca-1,5-diene to form the adduct (XXVI), whose structure has been demonstrated by NMR: [135]

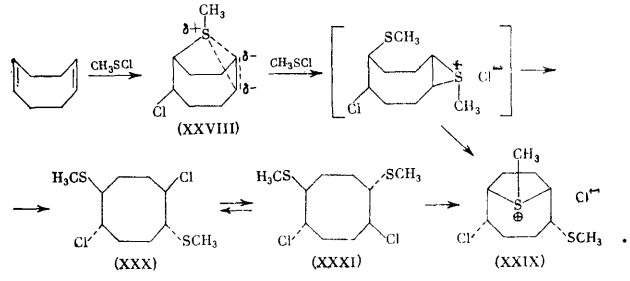


It has been shown that *cis,cis*-cyclo-octa-1,5-diene combines with 2,4-dinitrobenzenesulphenyl chloride to form the adduct (XXVII): [136,137]

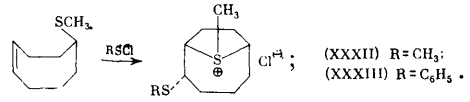


Ar=2,4-$(NO_2)_2C_6H_3$.

On the other hand, when methanesulphenyl chloride adds to *cis,trans*-cyclo-octa-1,5-diene, 80–90% of the diadducts (XXIX), (XXX), and (XXXI) and 8–13% of the monoadduct (XXVIII) are formed [127,138], although dienes usually combine with one equivalent of the sulphenyl chloride. This unusual behaviour can be explained by the transannular effect of the sulphur atom, which makes the double bond in the monoadduct more nucleophilic.



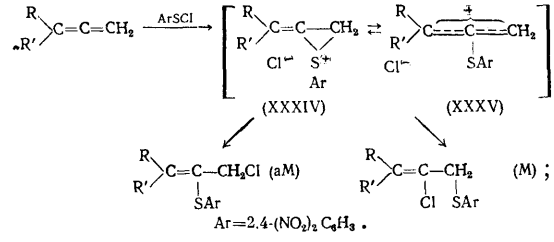
This mechanism is proved by the formation of the adducts (XXXII) and (XXXIII) together with adducts corresponding to (XXX) and (XXXI) when 5-methylthiocyclooctene reacts with methane- and benzene-sulphenyl chlorides:



V. REACTIONS WITH ALLENES

2,4-Dinitrobenzenesulphenyl chloride adds to allene with formation of two adducts: aM (87%) and M (13%). [139] The authors explained the observed proportions of the two adducts by the fact that the intermediate episulphonium ion (XXXIV) is attacked by the chloride anion at the terminal methylene carbon atom faster than at the vinyl carbon atom.

When the ring of the episulphonium ion is opened, the energetically more favoured carbonium ion (XXXV) is formed as an intermediate from the terminal carbon atom. The addition of $(CH_3O)_2POSCl$ to allene leads only to the aM adduct [58]:

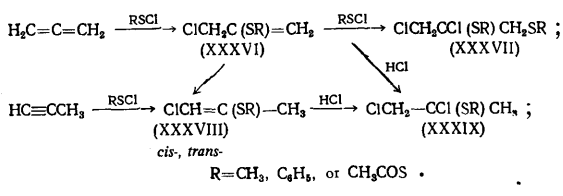


Ar=2,4-$(NO_2)_2C_6H_3$.

In the reactions with substituted allenes [140,141], steric factors direct the addition of sulphenyl chlorides to the unsubstituted double bond with formation of the aM adduct only. However, it was later shown that substituted allenes also form a mixture of adducts of types aM and M. [142]

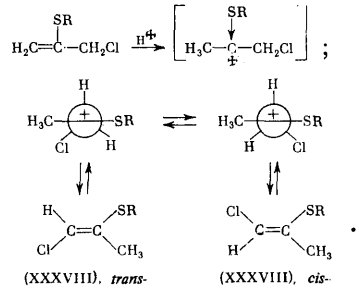
Methanesulphenyl, benzenesulphenyl, and acetylthiosulphenyl chlorides add to allenes with formation of a number of compounds, as shown by NMR and infrared spectroscopy [143]. Apart from the 1 : 1 adduct (XXXVI),

the 1 : 2 adduct (XXXVII) as well as the products of their subsequent reactions (XXXVIII) and (XXXIX) are formed:

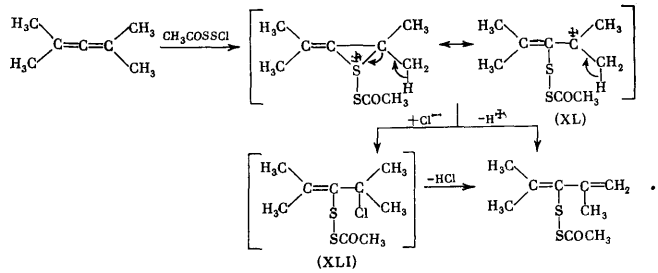


The stability of the adducts (XXXVI) and (XXXVII) depends on the nature of the substituent at the sulphur atom and decreases in the sequence R = $CH_3COS \gg C_6H_5 > CH_3$. Compound (XXXVII) decomposes with liberation of HCl and the amount of compound (XXXIX) in the reaction mixture increases.

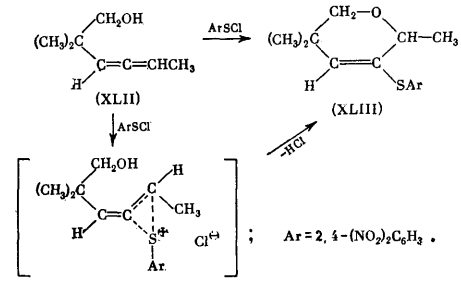
In the presence of acids, the monoadduct (XXXVI) isomerises to (XXXVIII). The authors postulate the possibility of the involvement in this isomerisation reaction of an intermediate carbonium ion, which is converted into the *cis*- or *trans*-isomer of compound (XXXVIII). The *cis*-isomer is kinetically controlled, being partly converted into the *trans*-isomer during the reaction. When the *trans*-isomer is acted upon by an acid, it may revert to the *cis*-isomer:



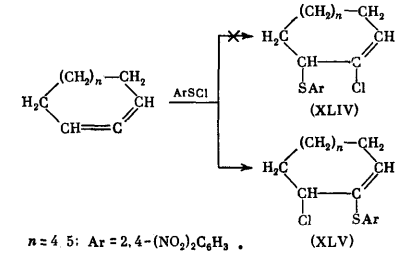
The addition of acetylthiosulphenyl chloride to tetramethylallene is accompanied by the subsequent elimination of HCl. The authors postulate the possibility of the formation of the allylcarbonium ion (XI), since additional signals due to the methylene groups in the postulated adduct (XLI) were detected in the NMR spectrum of the reaction mixture:



Sulphenyl chlorides add to allenes with rigorous stereospecificity. The optically active allene alcohol 2,2-dimethylhexa-3,4-dien-1-ol (XLII) combines with 2,4-dinitrobenzenesulphenyl chloride, forming the optically active adduct (XLIII). This indicates the absence of an intermediate carbonium ion in the addition reaction[144,145]:



The structure (XLIV) was initially adopted for the adduct of 2,4-dinitrobenzenesulphenyl chloride with the cyclic allenes cyclonona-1,2-diene and cyclododeca-1,2-diene[146]. However, it was later established by NMR that the adducts have the structure (XLV):[140]



VI. ADDITION TO ACETYLENES

The addition of sulphenyl chlorides to acetylenes proceeds similarly to their addition to ethylene. However, the greater stability of the acetylenic π-bonds, in view of the reduced bond length compared with ethylene, and the greater degree of overlapping of *p*-orbitals require an elevated temperature in many instances of this reaction and sometimes also a catalyst. This is consistent with the addition of one mole of sulphenyl chloride exclusively to the double bond of vinylacetylene[147,148]. The rate of addition of 2,4-dinitrobenzenesulphenyl chloride to phenylacetylene is 0.01 of the rate of addition to styrene and the rate of addition to hex-3-yne is 0.1 of the rate of addition to cyclohexene[149].

The rate of addition of benzenesulphenyl chloride to the following olefin/acetylene pairs has been investigated: styrene/phenylacetylene, 1-phenylpropene/1-phenylpropyne, hex-1-ene/hex-1-yne, and hex-3-ene/hex-3-yne. The ratio of the rates in $Cl_2CHCHCl_2$ was 1 : 100, but it depends strongly on the solvent[150].

The rate of addition of various *p*-substituted arenesulphenyl chlorides to acetylene in ethyl acetate decreases in the following sequence of *p*-substituents: $OCH_3 > CH_3 > H > Cl > NO_2$.[151] The *o*-methyl and *o*-chloro-substituents have little influence on the rate of addition and only *o*-nitro- and 2,4-dinitro-benzenesulphenyl chlorides add to acetylenes 2000–3000 times more slowly than other benzenesulphenyl chlorides. This can be accounted by the strong interaction of the sulphur atom with the *o*-nitro-group[152].

The rate of addition of alkanesulphenyl chlorides to hex-1-yne increases with decrease of the degree of branching of the alkane from which the sulphenyl chloride

was derived and with increase of solvent polarity and temperature [153].

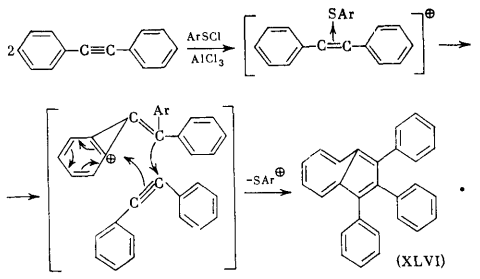
The addition of 2,4-dinitrobenzenesulphenyl chloride to acetylene in chloroethylene requires the presence of $AlCl_3$. Kharasch proposed the following mechanism for this reaction [154]:

$$ArSCl + AlCl_3 \rightleftarrows \overset{\oplus}{Ar}S\overset{\ominus}{A}lCl_4$$

$$\overset{\oplus}{Ar}S\overset{\ominus}{A}lCl_4 + CH{\equiv}CH \rightleftarrows \left[\begin{matrix} CH{=}CH \\ | \\ ArS \end{matrix}\right]^{\oplus} AlCl_4^{\ominus} \rightarrow ClCH{=}CH{-}SAr + AlCl_3 ;$$

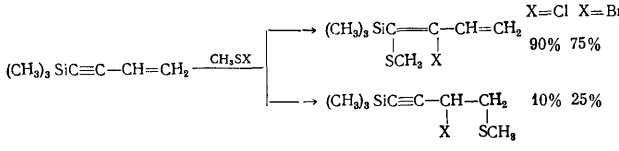
$Ar = 2.4\text{-}(NO_2)_2C_6H_3$.

For the higher acetylenes but-2-yne, hex-3-yne, and diphenylacetylene, the presence of aluminium chloride is not obligatory. It has been shown that $AlCl_3$ complicates the addition of the arenesulphenyl chloride to phenylacetylene, since triphenylazulene (XLVI) is formed instead of the normal adduct [155]:



(XLVI)

Since electron-accepting groups deactivate the acetylenic bond towards attack by electrophiles, acetylenedicarboxylic acid and its diethyl ester do not react with 2,4-dinitrobenzenesulphenyl chloride [154]. However, methyl acetylenemonocarboxylate combines on heating with methane-, benzene-, and *p*-substituted arenesulphenyl chlorides [156]. Electron-donating substituents activate the triple bond in acetylenes. Thus methanesulphenyl halides add preferentially to the triple bond of 1-trimethylsilylbut-3-en-1-yne [157]:



Methanesulphenyl chloride adds to alkylthiovinylacetylenes at the acetylenic bond only [158]:

$$H_2C{=}CH{-}C{\equiv}C{-}SR \xrightarrow[CCl_4,\ -20^\circ]{CH_3SCl} H_2C{=}CHC(SCH_3){=}C(SR)Cl ;$$

$R = CH_3$, C_2H_5, C_3H_7, or C_4H_9.

Various alkanesulphenyl chlorides add to acetylene with formation of both the monoadducts (XLVII) [43,47] and the diadducts (XLVIII). [105,159] The latter readily lose HCl on heating, undergoing conversion into the vinyl sulphides (XLIX), which tend to polymerise:

$$HC{\equiv}CH \xrightarrow{RSCl} \underset{(XLVII)}{RSCH{=}CHCl} \xrightarrow{RSCl} \underset{(XLVIII)}{RSCHClCH_2SR} \xrightarrow{-HCl} \underset{(XLIX)}{RSC(Cl){=}CH_2} ;$$

$R = ClCH_2$, $ClCH_2CH_2$, or CH_3CHCl .

The reaction of asymmetric acetylenes with sulphenyl chlorides can yield two isomeric adducts, M and aM, and their ratio is influenced both by the solvent and the temperature in the addition reaction [160]. But the addition of benzenesulphenyl chloride to phenylacetylene in benzene gave the adduct (L) with the aM structure, established by conversion into benzyl phenyl sulphone (LI): [161]

$$C_6H_5C{\equiv}CH \xrightarrow{C_6H_5SCl} \underset{(L)}{C_6H_5C(SC_6H_5){=}CHCl} \xrightarrow{H_2O_2} C_6H_5C(SO_2C_6H_5){=}CHCl \xrightarrow{KOH/H_2O} \rightarrow [C_6H_5CH(SO_2C_6H_5)CHO] \rightarrow \underset{(LI)}{C_6H_5CH_2SO_2C_6H_5} .$$

The adduct of phenylacetylene and 2,4-dinitrobenzenesulphenyl chloride, obtained in glacial acetic acid, has the M structure (LII), which was confirmed by specific synthesis from acetophenone [139]:

$$C_6H_5C{\equiv}CH \xrightarrow{\cdot ArSCl} \underset{(LII)}{C_6H_5C(Cl){=}CHSAr} \xleftarrow{-HCl} C_6H_5CCl_2CH_2SAr \quad (\uparrow PCl_5)$$

$$C_6H_5COCH_3 \xrightarrow[HCl]{ArSCl} C_6H_5COCH_2SAr ;$$

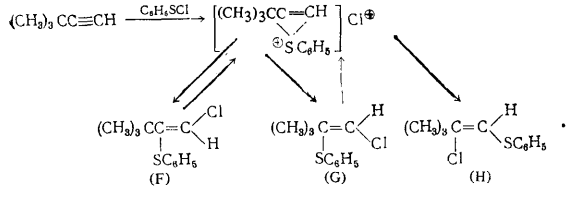
$Ar = 2,4\text{-}(NO_2)_2C_6H_3$.

Studies by a group of Italian chemists helped to resolve the contradictions in the determination of the mode of addition of sulphenyl chlorides to acetylenes [142,143,162-169]. The reactions of *p*-methylbenzene-, *p*-nitrobenzene, and *o*-nitrobenzene-sulphenyl chlorides with but-1-yne, phenylacetylene, and other substituted acetylenes were investigated in various solvents: acetic acid, acetonitrile, and ethyl acetate in the presence of different amounts of trifluoroacetic or hydrochloric acid. The adducts were characterised either by the infrared spectra of the corresponding sulphones or chromatographically. It was shown that the nature of the *p*-substituents in the benzenesulphenyl chloride hardly influences the mode of addition and that aM adducts are formed preferentially. *o*-Nitrobenzenesulphenyl chloride gives rise to an approximately 1 : 1 mixture of the M and aM adducts under these conditions.

The influences of the solvent and the substituent at the acetylenic bond are mutually related. Thus the addition to but-1-yne or its homologues in any solvent gives rise to the aM adduct only, which has also been demonstrated by other investigations [170,171]. On the other hand, the mode of addition to phenylacetylene depends on the solvent: for example, more of the aM adduct is formed in ethylacetate and more of the M adduct is formed in acetic acid. Chloroform and acetonitrile occupy an intermediate position in this respect. As in the addition of sulphenyl chloride to olefins, this is associated with acid catalysis.

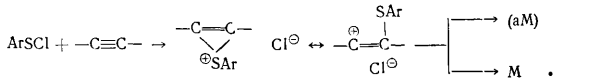
In the addition of sulphenyl chlorides to acetylenes in any solvent, the amount of the M adduct increases with increase of the concentration of acid. However, this effect was not noted for but-1-yne [169].

The addition of benzenesulphenyl chloride to isobutylacetylene gave three adducts (F, G, and H) in the proportions 75 : 17 : 8 respectively. Compounds F and G isomerised to H on ultraviolet irradiation in benzene or on heating [172]:



Kinetic studies on the addition of sulphenyl chlorides to acetylenes showed that this reaction is ionic and that its rate depends on the nucleophilic properties of the triple bond [149,153,164,166]. On the basis of these data, Calo et al. [152] proposed a reaction mechanism according to which the addition proceeds via a stage involving the formation

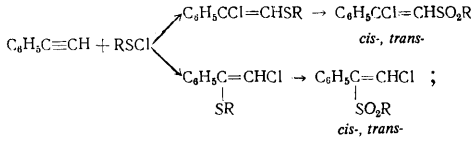
of an intermediate complex, consisting of the chloride ion and the organic cation. The degree of separation of this ion pair depends on the solvent and the structure of the cation determines the ratio of the aM and M adducts:



Later studies confirmed that the intermediate compound has the structure of an unsaturated episulphonium ion [127,128].

The addition of sulphenyl chlorides to acetylenes usually leads to the formation of *trans*-adducts, as shown by infrared [173] and NMR spectra [174] and by comparing the corresponding known *trans*- and *cis*-sulphones [152,153,170,175] as well as by studying the dipole moments [176-178].

p-Methylbenzene- and methane-sulphenyl chlorides interact with phenylacetylene in ethyl acetate in the presence of HCl to give a mixture of the *cis*- and *trans*-isomers, whose structure was determined by the NMR analysis of their sulphones and by specific synthesis [168,169]:

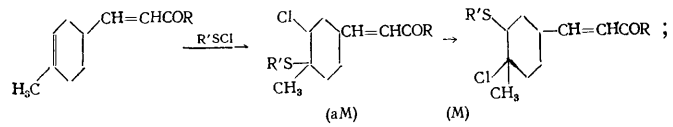


The formation of the *cis*-isomers in this reaction seemingly contradicts the results of other investigations showing the stereospecificity of the addition of sulphenyl chlorides, but the authors showed that the *cis*-isomers are formed owing to the isomerisation of the primary *trans*-adducts. The *trans*-adduct, obtained by the addition of *p*-methylbenzenesulphenyl chloride to phenylacetylene in acetic acid, is partly converted into the *cis*-isomer on storage in ethyl acetate containing 5% HCl.

VII. REACTIONS WITH $\alpha\beta$-UNSATURATED ACIDS AND THEIR DERIVATIVES

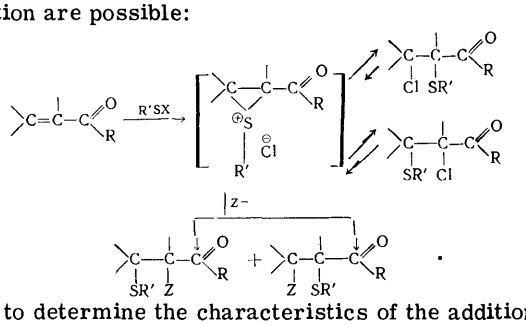
The double bond in $\alpha\beta$-unsaturated acids is little involved in electrophilic addition reactions owing to the electron-accepting properties of the carboxy- and related groups. The reactions of the $\alpha\beta$-unsaturated nitriles with sulphenyl chlorides are particularly difficult. Thus acrylonitrile and similar compounds do not react with 4-chloro-2-nitrobenzene- and 4-nitrobenzene-sulphenyl chlorides in chloroform [48]. 4-Substituted arene- and dichloromethane-sulphenyl chlorides add to acrylonitrile only on heating in glacial acetic acid [179-181]. In glacial acetic acid, the rate of addition of 2,4-dinitrobenzenesulphenyl chloride to vinylacetone, which also contains a powerful electron-accepting group, was 300 times lower than the rate of addition to styrene and 3000 times lower than the rate of addition to cyclohexene [182].

Alkanesulphenyl chlorides initially added in equimolar amounts to the ring double bonds of 3-(4′-methylcyclohex-3′-enyl)acrylic acid and its derivatives with formation of the aM adducts, which then readily isomerised to the M adducts [183]:



R=OH, OEt, NH_2, NHC_6H_5, or Cl; R′=CH_3, or CH_2CH_2Cl.

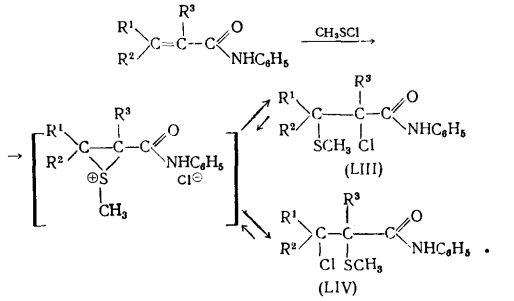
The interaction of sulphenyl halides with $\alpha\beta$-unsaturated acids may lead to a series of valuable polyfunctional compounds when specific addition and subsequent nucleophilic substitution are possible:



In order to determine the characteristics of the addition of sulphenyl halides to acrylic acids and their derivatives, a study was made of the influence of the position of the methyl groups and of the nature of the changes in the carboxy-group in homologues of $\alpha\beta$-unsaturated acids on the rate of addition of sulphenyl chlorides and also on the structures and stabilities of the adducts formed under these conditions.

The addition of various sulphenyl chlorides (CH_3SCl, $ClCH_2CH_2SCl$, C_2H_5SCl, CH_3COSCl, $CH_3COSSCl$, and SCl_2) to acrylic, methacrylic, crotonic, and dimethylacrylic acids and their derivatives (acid chlorides, esters, amides, substituted amides, and nitriles) was investigated. The studies elucidated the influence of the number and positions of the methyl groups in $\alpha\beta$-unsaturated acids, of the nature of the derivatives of $\alpha\beta$-unsaturated acids, and finally of the structure of the sulphenyl chloride on the rate of addition, the initial ratio of isomers, and the stability of the adducts formed. For this purpose, the reactions involving the addition of the same sulphenyl chloride to the same derivative of different $\alpha\beta$-unsaturated acids were compared. This was followed by a comparison of the additions of the same sulphenyl chloride to different derivatives of the same $\alpha\beta$-unsaturated acid and finally of the addition of different sulphenyl chlorides to the same derivative of the same $\alpha\beta$-unsaturated acid.

The studies on the influence of the position of methyl groups showed that, when methanesulphenyl chloride adds to the anilides of acrylic [184,185], crotonic [186], and dimethylacrylic acids [187], the kinetically controlled adducts of type (LIII) are formed preferentially in the initial stage:



Addition to methacrylic acid anilide [188] results in the initial preferential formation of the adduct (LIV), which is likewise unstable.

The addition of sulphenyl chlorides to $\alpha\beta$-unsaturated acids is also a process consisting of two consecutive steps: the initial formation of the intermediate episulphonium ion and further nucleophilic attack by the chloride ion on one of the carbon atoms in the ring with formation of a mixture of adducts (LIII) and (LIV). Evidently the preferred site of attack in acrylic, crotonic, and dimethyl-

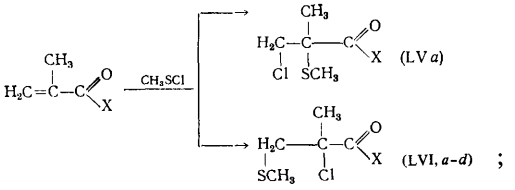
acrylic acids is the carbon atom in the α-position relative to the carboxy-group, since the electron density at the α-carbon atom in the intermediate episulphonium ion is relatively lower owing to the inductive effect of the carboxy-group. Steric factors, the presence of one and two methyl groups in the β-positions in crotonic and dimethylacrylic acids, also promote the attack by the chloride ion on the α-carbon atom. The presence of the methyl group in the α-position of methacrylic acid partly compensates the influence of the carboxy-group and creates an additional steric hindrance to attack on the α-carbon atom. For this reason, the kinetically controlled adduct (LIV) is formed preferentially in this case.

It was established that in this instance the rate of addition of methanesulphenyl chloride decreases in the series of anilides of acids ranging from acrylic and methacrylic to crotonic and dimethylacrylic. The addition to both *cis*- and *trans*-derivatives of crotonic acid was studied[189,190]. The results obtained are inconsistent with the successive enhancement of the nucleophilic properties of the double bond. The decrease of the reactivity of the double bond is probably due to steric factors. Adducts with cinnamic acid could be obtained only in glacial acetic acid[191]. The rate of isomerisation of the kinetically controlled adducts formed initially to thermodynamically stable adducts increases in the inverse sequence: α-chloro-β-methylthiopropionic acid anilide < butyric acid anilide < isovaleric acid anilide. The anilide of α-alkylthio-β-chlorobutyric acid is an exception.

Changes in the carboxy-group of the $\alpha\beta$-unsaturated acid have a significant influence on the rate of addition of sulphenyl chlorides. In all cases, sulphenyl chlorides react most easily with amides, than with acids and esters, the reaction with acid chlorides and nitriles being more difficult. This is consistent with the decrease of electron density in the double bond of $\alpha\beta$-unsaturated acids as a function of the derivative employed. The nature of the changes in the carboxy-group has a significant influence on the initial ratio of the kinetically controlled and thermodynamically stable isomers. The amount of the kinetically controlled adduct decreases in the same sequence, from the amide to the nitrile, and the amount of the thermodynamically stable isomer naturally increases. Thus ^{1}H NMR made it possible to observe the preferential formation in the mixture of products of the reactions of $\alpha\beta$-unsaturated acids and their amides and methyl esters of kinetically controlled unstable adducts, which can sometimes be isolated in a pure form[192].

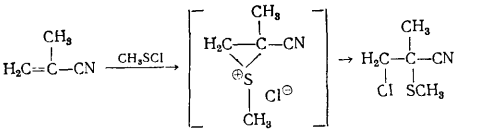
The addition of sulphenyl chloride to the chlorides and nitriles of $\alpha\beta$-unsaturated acids leads as a rule to the formation of a stable equilibrium mixture or of thermodynamically stable adducts.

The influence of the changes in the carboxy-group on the initial ratio of the isomers and on their stability has been demonstrated for the reaction of methanesulphenyl chloride with various derivatives of methacrylic acid. When methanesulphenyl chloride was allowed to add to methacrylic acid anilide, a single kinetically controlled isomer (LV*a*) was obtained:

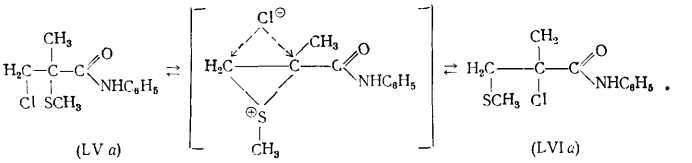


X=NHC$_6$H$_5$ (*a*); OH (*b*); OCH$_3$ (*c*) or Cl (*d*).

The reaction of methanesulphenyl chloride with methacrylic acid, its methyl ester, and chloride gives the following ratios of the isomers (LV, *b*–*d*) to the isomers (LVI, *b*–*d*): 89/11, 72/28, and 52/48 respectively. The addition of methanesulphenyl chloride to methacrylonitrile again leads to a single thermodynamically stable isomer: β-chloro-α-methylthioisobutyronitrile (LV*e*):

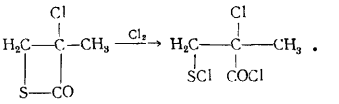


The unstable adducts usually isomerise to the stable adducts on storage or heating. The isomerisation is accelerated in the presence of catalytic amounts of acid. The stability of the adducts formed, which depends mainly on the nucleophilic properties of the sulphur atom, is clearly confirmed by the data obtained for the isomerisation reaction. Thus the unstable anilide (LV*a*) isomerises almost completely to the stable anilide of α-chloro-β-methylthioisobutyric (LVI*a*):



In the addition to methyl methacrylate, the simultaneous formation of a mixture of the isomers (LV*c*) and (LVI*c*) is observed, with the kinetically controlled adduct (LV*c*) predominating. The ratio of isomers obtained is displaced towards the accumulation of the isomers (LVI*c*), equilibrium being attained when (LV*c*) : (LVI*c*) = 60 : 40.

β-Chloro-α-methylthioisobutyronitrile (LV) is a stable isomer and remains unaltered under comparable conditions. The structure of methacrylic acid derivatives was confirmed, apart from ^{1}H NMR data, by the cleavage of α-chloro-α-methyl-β-thiolactone by electrophilic agents, in which the position of the sulphur atom is rigorously specified[193]:

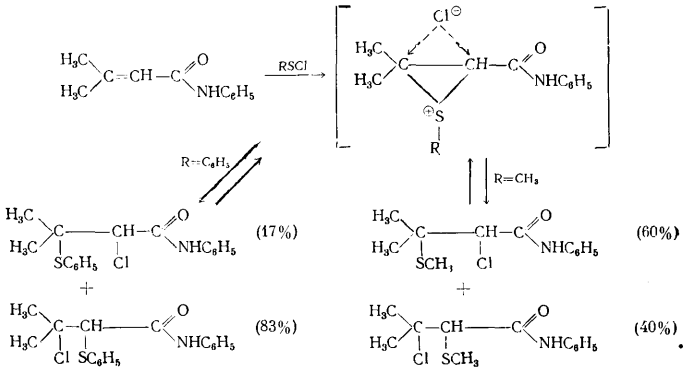


Thus the interconversions of the isomers, sometimes with formation of a single thermodynamically stable compound or an equilibrium mixture of isomers, can be explained by postulating an important role of the episulphonium ion in these processes. It follows from the above data that the outcome of the process is influenced significantly by changes in the carboxy-group and in the positions of the methyl groups, which affects in its turn the nucleophilic properties of the sulphur atom. The isomerisation of the adducts, based on the intermediate formation of the episulphonium ion, proceeds more readily as the sulphur atom of the adduct becomes more nucleophilic and the carbon atom subjected to nucleophilic attack by the sulphur atom becomes less effectively shielded in space.

Naturally, the nucleophilic properties of the sulphur atom decrease in the sequence $CON\langle > COOH > COOCH_3 > COCl > CN$ as a function of the substituent at the carboxy-group, which is consistent with the $-I$ and $-\epsilon$ effects of the substituents. This results in the complete absence of isomerisation of the nitriles.

The influence of the nature of the sulphenyl chloride on the rate of addition of methane-, β-chloroethane-, benzene-, acetyl-, and acetylthio-sulphenyl chlorides and of sulphur dichloride to αβ-unsaturated acids and their derivatives and on the ratio of the adducts showed that the ease of addition of sulphenyl chloride to the same derivative of the αβ-unsaturated acid decreases in the following sequence: $AlkSCl > ClCH_2CH_2SCl$ [194] $> C_6H_5SCl$ [195] $> ClSCl$ [196] $> CH_3COSCl$.[197] $CH_3COSSCL$ could not be added at all to αβ-unsaturated acids.

The ratio of the isomers in reactions involving addition to αβ-unsaturated acids changes significantly as a function of the nature of the substituent in the sulphenyl chloride. Thus, whereas in the addition of methanesulphenyl chloride to dimethylacrylic acid anilide the kinetically controlled α-chloro-β-methylthioisovaleric acid anilide is initially formed preferentially (60 : 40), in the addition of benzenesulphenyl chloride, the preferred product is the stable anilide of β-chloro-α-phenylthioisovaleric acid (83 : 17):[192]



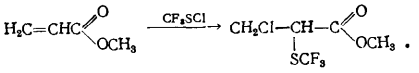
The results obtained were confirmed by kinetic data. The addition of benzenesulphenyl chloride to αβ- and βγ-unsaturated acids and their derivatives was investigated and it was shown that the rate of addition decreases in the sequence anilide > ester > acid > acid chloride as a function of the changes in the carboxy-group and in the sequence $H_2C{=}CH{-}CH_2COOCH_3 > H_2C{=}CHCOOCH_3 > H_2C{=}C(CH_3)COOCH_3 > CH_3CH{=}CHCOOCH_3 > (CH_3)_2C{=}CHCOOCH_3 > C_6H_5CH{=}CHCOOCH_3$ as a function of the changes in the molecular structure.

It was established that the addition of benzenesulphenyl chloride to unsaturated acids is a first-order reaction with respect to each reactant. The high negative activation entropy (~ -30 cal mole^{-1} K^{-1}) and energy are consistent with a polar mechanism of the addition reaction [198].

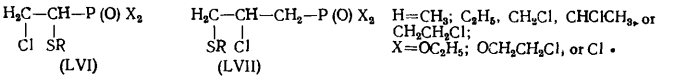
The above results, both for the addition of sulphenyl chlorides to αβ-unsaturated acids and their derivatives and for the isomerisation of the adducts, are consistent with the results of other workers [199-201].

When sulphenyl chlorides react with the nitriles of αβ-unsaturated acids, there is a possibility of addition not only to the C=C double bond but also to the nitrile group [200, 202].

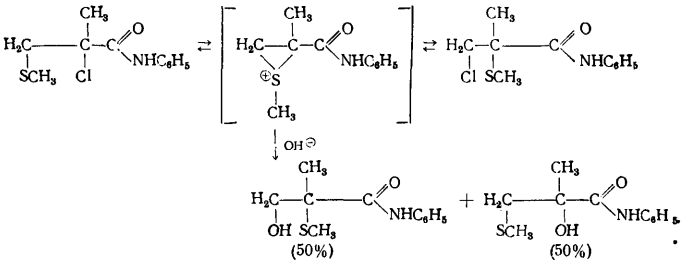
The free-radical addition of trifluoromethanesulphenyl chloride to methyl acrylate leads to the preferential formation (90%) of methyl β-chloro-α-trifluoromethylthiopropionate [202]:



Sulphenyl chloride add also to other αβ-unsaturated compounds containing electron-accepting groups: keten [202], α-chloroacrolein [204], trichloromethylethylene [205], alkenyl phosphites and phosphinates [204,205], and methyl vinyl sulphone [199]. The mode of addition being similar to that observed in the addition to carboxylic acid derivatives. The aM structure (LVI) and the M structure (LVII) were attributed to the adducts obtained in the reaction with vinyl- and allyl-phosphinates respectively:



Nucleophilic substitution of the chlorine atom in the isomeric derivatives of β-alkylthio-α-chloro- and α-alkylthio-β-chloro-carboxylic acids has so far been little studied. The kinetic investigations which have been carried out have shown that the rate of nucleophilic substitution depends significantly on the structure of the initial adduct [208]. The kinetically controlled adduct is always hydrolysed faster, approximately by an order of magnitude, than the thermodynamically stable isomer [209]. It has been observed that α-chloro-β-methylthio-isomers always react faster than the corresponding derivatives of the α-chloro-β-phenylthio-carboxylic acid. The rate of nucleophilic substitution is also influenced significantly by the changes in the carboxy-group: amides react more readily than the corresponding esters. The proportions of the isomers formed are independent of the position of the halogen in the molecule (the α- or β-position) and depend primarily on the substituents in the molecule and on the nature of the nucleophile. According to preliminary data, the solvent also affects the ratio of the isomers. For example, the hydrolysis of the anilides of both α-chloro-β-methylthio- and β-chloro-α-methylthio-isobutyric acids gives rise to a 1 : 1 mixture of the isomeric anilides of α-hydroxy-β-methylthio- and β-hydroxy-α-methylthio-isobutyric acids [209]:



The relative amount of the β-hydroxy-isomer in the hydrolysis of the anilides of β(α)-chloro-α(β)-methylthioalkanoic acids increases in the following sequence as a function of their structure: β(α)-chloro-α(β)-methylthiopropionic acid (1 : 1 : 5); corresponding derivatives of butyric acid (1 : 3); corresponding derivatives of isovaleric and hydrocinnamic acid—β-hydroxy-isomer only [210].

Thus the study of the addition of sulphenyl chlorides to αβ-unsaturated acids and their derivatives showed that kinetically controlled (unstable) adducts can be obtained in some instances, but stable isomers are produced as a rule. When nucleophiles act both on individual β-halogenosulphides and on their mixtures, the intermediate is the same episulphonium ion, the opening of the ring of which by the nucleophile may be made specific with the preferential formation of the α- or β-isomer by altering the structure and conditions.

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