70. G. Natta, G. Mazzanti, and F. Pregaglia, Gazzetta, quoted in Ref. 67.
71. F. Herman and K. Nelson, J. Amer. Chem. Soc., 75, 3877 (1953).
72. G. Natta, L. Porri, and G. Zanini, Chimica e Industria, quoted in Ref. 67.
73. A. A. Korotkov, S. P. Mitsengendler, V. N. Krasulina, and L. A. Volkova, Vysokomol. Soed., 1, 1319 (1959).
74. T. Fox, B. Garrett, and W. Goode, J. Amer. Chem. Soc., 80, 1768 (1958).
75. V. A. Kabanov, "Initsirovanie Polimerizatsii Vinilovykh Monomerov, Nakhodyashchikhsya Nizhe i na Grani Plavleniya" (Initiation of Polymerisation of Vinyl Monomers, below and at the Fusion Front), Thesis, Moscow State University, 1959.
76. V. A. Kabanov, G. E. Sergeev, V. P. Zubov, and V. A. Kargin, Vysokomol. Soed., 1, 1859 (1959).
77. V. A. Kabanov, V. P. Zubov, and V. A. Kargin, Vysokomol. Soed., 1, 1422 (1959).
78. V. A. Kargin, V. A. Kabanov, and G. P. Andrianova, Vysokomol. Soed., 1, 301 (1959).
79. N. A. Plate, V. A. Prokopenko, and V. A. Kargin, Vysokomol. Soed., 1, 1713 (1959).
80. G. Natta, J. Polymer Sci., 34, 21 (1959).

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METHODS OF PREPARATION AND PROPERTIES OF SUBSTITUTED VINYL ETHERS AND SULPHIDES

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INTRODUCTION

From the 'thirties onwards a large number of papers were published on the methods of preparation and the reactions of vinyl ethers[1-3], which, by virtue of their high chemical reactivity, have been used extensively in organic syntheses. Vinyl ethers[1-3] and vinyl sulphides[4,5] became easily accessible, especially after the industrial application of the Favorskii–Shostakovskii method of preparation:

$$CH{\equiv}CH+RXH \xrightarrow{\Delta,\ KOH} CH_2{=}CHXR,$$

where X = O, S, N, Si; R = alkyl, aryl.

With the growth in the industrial production of acetylene homologues, there is now a possibility of the latter being applied in the synthesis of substituted vinyl compounds.

Unlike unsubstituted vinyl ethers and vinyl sulphides, substituted ethers and sulphides of the general formula

$$R^1{-}\underset{\displaystyle R^2}{\underset{|}{C}}{=}\underset{\displaystyle R^3}{\underset{|}{C}}{-}X,$$

where R, R^1, R^2, R^3 = alkyl, aryl, halogen, and X = O, S, cannot easily be obtained and as a result are little known. Substituted vinyl ethers and sulphides are of considerable interest in preparative organic chemistry. Like their unsubstituted analogues[2,3], they can, in the presence of acid catalysts, add on a compound containing a mobile hydrogen atom; in this reaction the nature of the substituent has a considerable effect on the rate, yield, and stability of the product. Besides additions to the double bond, they are capable of a number of reactions which are brought about by the presence in the molecule of another reactive centre, such as an alkoxy or mercapto group, or a halogen atom.

The present review deals with the methods of preparation and the basic reactions of substituted vinyl ethers and sulphides and compares them with the like reactions of their unsubstituted analogues. For convenience, the reactions of ethers and sulphides are treated in separate sections.

The review does not cover diene ethers, which can be considered as substituted vinyl ethers containing unsaturated radicals R^1 or R^3, whose double bond is conjugated with that of the vinyl group. Methods of preparation of diene ethers were reviewed by Petrov[6] and Nazarov *et al.*[7]

I. PREPARATION OF SUBSTITUTED VINYL ETHERS

1. Preparation from α-Haloalkenes

Substituted vinyl ethers were first obtained by Butlerov[8] and El'tekov[9] by the reaction of alkenyl bromides with sodium alcoholates. In 1870 Butlerov synthesised β,β'-dimethylvinyl ethyl ether by the following reaction:

$$(CH_3)_2C{=}CHBr+C_2H_5ONa \rightarrow (CH_3)_2C{=}CHOC_2H_5.$$

This method[1-3] has found wide application in the synthesis of unsubstituted vinyl ethers from vinyl chloride. It is of limited value in the synthesis of alkyl-substituted ethers, owing to difficulties involved in the preparation of the starting α-haloalkenes. So far only a few papers have been published on the preparation of alkyl(aryl)-substituted ethers by this method[8-16]. Of note is the work of Niederl

and Storch[12], who obtained isopropenyl aryl ethers by heating 2-bromopropene with potassium phenolate at about 48°:

$$CH_2=CBr-CH_3+ArOK \rightarrow CH_2=C(CH_3)-OAr+KBr.$$

The authors of this review have been unable to reproduce these results. The experimental conditions are far too mild for the reaction to take place. The similar reaction of 2-chloropropene with sodium ethylate requires heating at 180° for several hours in an autoclave[13,14].

The Butlerov method is applied extensively in the preparation of the halogen derivatives of vinyl ethers from the easily obtainable polyhaloethylenes[17-26]. For instance, heating dibromoethyelene with potassium phenolate in an autoclave gives β-bromovinyl phenyl ether[17-19]:

$$CHBr=CHBr+C_6H_5OK \xrightarrow[-KBr]{} CHBr=CHOC_6H_5,$$

while trichloroethylene yields a series of β,β′-dichlorovinyl ethers[20-25].

2. Vinylation

Favorskii[27] discovered vinylation in 1887, in his attempt to prepare isopropenyl ethyl ether from methylacetylene and ethanol:

$$CH_3C\equiv CH+C_2H_5OH \xrightarrow{\Delta,KOH} CH_2=C(CH_3)OC_2H_5.$$

This reaction was later used for the preparation of unsubstituted vinyl ethers from acetylene. Its application in the preparation of substituted ethers from acetylene homologues is limited by the tendency of acetylenic hydrocarbons to isomerise under the action of the alcoholic alkali into disubstituted acetylenes and allenes[28,29], which are unable to react with alcohols. Those acetylenes which do not isomerise under the conditions of vinylation are used successfully for the preparation of substituted vinyl ethers. Thus, phenylacetylene reacts easily in alkaline solution with alcohols to form β-alkoxystyrenes[16,30-35]:

$$C_6H_5C\equiv CH+ROH \xrightarrow{KOH} C_6H_5CH=CHOR,$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9.

Trifluoromethylacetylene reacts with ethanol on merely mixing in an alkaline solution[36]:

$$CF_3C\equiv CH+C_2H_5OH \xrightarrow{KOH} CF_3CH=CHOC_2H_5.$$

Chloroacetylenes also react with alcohols[37,38], for example,

$$C_6H_5C\equiv CCl+C_2H_5OH \rightarrow C_6H_5CH=CClOC_2H_5.$$

Vinylation also includes the reaction of alcohols with diacetylene[39] and vinylacetylene[40]. They all yield β-substituted vinyl ethers as a result of the electron-withdrawing power of the acetylene substituents[34]. On the other hand, reaction of alcohols[41-43] and phenols[44] with methylacetylene yields α-substituted vinyl ethers. It should be noted that under the conditions of vinylation, namely in alkaline solution and at high temperatures, methylacetylene is in equilibrium with the isomeric allene:

$$CH_3C\equiv CH \rightleftarrows CH_2=C=CH_2.$$

Physicochemical calculations[45] show that at high temperatures the equilibrium is shifted towards methylacetylene. This is consistent with the data on the isomerisation of allene at high temperatures to methylacetylene[46,47]. Consequently[44], allene, methylacetylene, or a mixture of the two, can be used in the synthesis of isopropenyl aryl ethers.

Preparation of alkyl(aryl)-substituted vinyl ethers by this method is limited by the impossibility of using alkylacetylenes in the reaction. For the preparation of vinyl ethers containing functional groups (COOH,[48] OR,[49] etc.), however, vinylation has great possibilities.

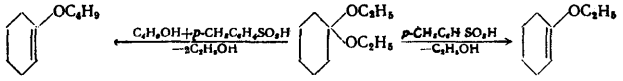
3. Decomposition of Ketals and Acetals

In 1896 Claisen[50,51], in a study of the properties of the ketals he had synthesised, discovered a method for preparing substituted vinyl ethers by the decomposition of ketals. Ketals were shown to eliminate readily a molecule of alcohol, sometimes merely on distillation. By distilling acetophenone ketal Claisen obtained α-ethoxystyrene[50]:

$$C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}(OC_2H_5)_2 \rightarrow CH_2=C(C_6H_5)OC_2H_5+C_2H_5OH.$$

Later he used catalysts to decompose ketals, for example, phosphorus pentoxide and quinoline (as in the preparation of isopropenyl ethyl ether)[51].

In further studies of the preparation of α-substituted vinyl ethers by this method, various other catalysts were used, in particular, *p*-toluenesulphonic acid[52,53], volatile mineral acids (in the vapour phase)[54], and catalysts containing noble metals of Groups I–VIII of the Periodic Table[55,56]. Of special interest is the work of Johanissian[52] and Nieuwland[53] who used the reversiblity of the decomposition of ketals in the presence of acid catalysts for the synthesis of substituted vinyl ethers. Johanissian, the first to use *p*-toluenesulphonic acid as a catalyst, carried out the synthesis according to the following scheme:



Similarly, Nieuwland synthesised a series of α-alkylvinyl ethers[53], from 2,2-dimethoxyalkanes, which, after his discovery of the reaction of alkylacetylenes with methanol in the presence of mercury and boron fluoride etheradduct[58], had become readily available:

$$RC\equiv CH+2CH_3OH \rightarrow R-\underset{\displaystyle CH_3}{\underset{|}{C}}(OCH_3)_2$$

$$RC(CH_3)(OCH_3)_2+R'OH \xrightarrow{p\text{-}CH_3C_6H_4SO_3H} CH_2=C(R)OR'+2CH_3OH,$$

where R = CH_3, C_4H_9, C_5H_{11}, C_6H_5; R′ = CH_3, C_2H_5, C_3H_7, C_4H_9.

Under similar conditions acetals of type $RCH(OCH_3)_2$ do not yield unsaturated ethers derived from the alcohol used in the reaction. This is due to the harsher reaction conditions required for the decomposition of acetals[69-80]. Such decomposition is best carried out in the vapour phase, *e.g.* Sigmund and Uchann[62] passes acetal vapours over hot alumina. Noble metals deposited on asbestos, kieselguhr, etc., also act as catalysts in this reaction[55,56,69,70]. Nazarov and his collaborators[58] described a new catalyst ($MgHPO_4$, NaH_2PO_4), which yields 60–75% of ethers when acetal vapour is passed over it at 325°. This method is of considerable importance for the preparation of α- and β-substituted vinyl ethers.

4. Decomposition of Substituted α,β-Unsaturated Acids

Certain, mainly α-substituted, vinyl ethers have been prepared by thermal decomposition of unsaturated alkoxy--acids, according to the equation[31,81-87]

$$R{-}\underset{\displaystyle OR'}{\underset{|}{C}}{=}CHCOOH \xrightarrow[-CO_2]{\Delta} CH_2{=}\underset{\displaystyle R}{\underset{|}{C}}{-}OR',$$

where R = CH_3, C_5H_{11}, C_6H_{13}, C_6H_5; R′ = CH_3, C_2H_5, C_3H_7, C_6H_5, $C_6H_4CH_3$, $C_{10}H_7$.

This method has no preparative significance, as the alkyl-substituted vinyl alkyl ethers can be obtained more simply by the decomposition of acetals and ketals. But it is the only one for the preparation of ethers of the general formula $CH_2{=}C(Ar){-}OAr$.

5. Preparation from Halogen Derivatives of Ethers

(a) Elimination of the hydrogen halide from β-halo-ethers. Lauer and Spielman[88-89] were the first to prepare α,β-substituted vinyl ethers from β-halo-ethers[85-105], according to the scheme

$$RCH_2CHO + R'OH + HCl \rightarrow RCH_2CHClOR' + H_2O$$

$$RCH_2CHClOR' + Br_2 \rightarrow RCHBrCHBrOR' + HCl$$

$$RCHBrCHBrOR' + R''MgBr \rightarrow RCHBrC\underset{\displaystyle R''}{\underset{|}{H}}OR' + MgBr_2$$

$$RCHBr{-}\underset{\displaystyle R''}{\underset{|}{C}}HOR' \xrightarrow{KOH} RCH{=}\underset{\displaystyle R''}{\underset{|}{C}}{-}OR' + KBr\ .$$

The first three steps had been worked out earlier[90]. The particular value of this method lies in the fact that it yields ethers substituted in both the α- and β-positions, while nearly all the other methods mentioned above yield ethers substituted in either one or the other. α,β-Dibromo-ethers required for the preparation of α-substituted vinyl ethers can be obtained from vinyl alkyl ethers[92-94].

$$CH_2{=}CHOR + Br_2 \rightarrow CH_2BrCHBrOR.$$

The hydrogen halide can be eliminated not only from β-bromo-ethers, but also from β-iodo-ethers[95] and β-chloro-ethers[96,97]; however, these cannot be so readily obtained.

A modification of this method is the elimination of hydrogen chloride from β-chloro-ethers by means of finely granulated metals (Cu, Al, Mg)[98]. The yield of α-propyl-vinyl methyl ether obtained by this method from 1-chloro--2-methoxypentane can reach 60%. Hydrogen chloride and the metal chlorides formed in the reaction can cause polymerisation and hydrolysis of vinyl ether, thereby lowering the yield. The use of excess alkali as in the Lauer method stops such processes and gives better yields.

(b) β-Alkylvinyl ethers from α-chloroalkyl ethers. A number of papers have recently appeared on the synthesis of vinyl ethers from α-chloro-ethers[106-108], which are readily obtainable from aldehydes and alcohols in the presence of hydrogen chloride. It has been shown[109] that the reaction of dimethylaniline with α-chloroethyl alkyl ethers hydrogen chloride splits off and vinyl ethers are formed. A number of β-alkylvinyl ethers was obtained by using organic bases to remove hydrogen chloride from α-chloroalkyl alkyl ethers[106-108]:

$$RCH_2CHClOR' \xrightarrow[HCl]{} RCH{=}CHOR',$$

where R = CH_3, C_2H_5, C_5H_{11}; R′ CH_3, C_3H_7, C_4H_9, C_7H_{15}. The bases used were dimethylaniline[106] or triethylamine[107]. Unfortunately, in many cases the yields of ethers were not larger than 20–30%.

Erickson[108] prepared β-alkylvinyl ethers by the conversion of α-chloro-ethers into 1-alkoxyalkyl acetates, followed by pyrolysis:

$$RCH_2CHClOR' + CH_3COONa \xrightarrow[-NaCl]{} RCH_2CH(OCOCH_3)OR'$$

$$RCH_2CH(OCOCH_3)OR' \rightarrow RCH{=}CHOR' + CH_3COOH,$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}; R′ = C_2H_5, iso--C_4H_9, $CH_2CH(C_2H_5)_2$, $CH(C_2H_5)C_4H_9$. The vinyl ethers formed can easily combine with acetic acid, which clearly makes the separation of the final products somewhat difficult.

(c) Some methods for the preparation of halogen derivatives of vinyl ethers. The difference in the chemical behaviour of halogen atoms in the α- and β-positions is used, in the same way as in the two preceding methods, for the preparation of β-halovinyl ethers from α,β-dihalo-ethers. It was shown in a number of papers[110-117] that under the action of organic bases (dimethylaniline, diethylaniline, pyridine) α,β-dihalo-ethers split off a molecule of hydrogen halide forming β-halovinyl ethers in good yields:

$$RCHX{-}CHXOR' \xrightarrow[-HX]{} RCHX{=}CHOR',$$

where R, R′ = alkyl, X = Cl, Br.

The reaction of α,β-dihalo-ethers with inorganic bases does not yield vinyl ethers[110,118]; nonetheless, ethers of type $CCl_3CHClOC_2H_5$,[119] $CHClBrCClBrOC_2H_5$,[120] or C_6H_5. .$CHBrCHBrOR$[121] split off hydrogen halide in the presence of alkali yielding the halogen derivatives of vinyl ethers, for example:

$$C_6H_5CHBrCHBrOR \xrightarrow{KOH} C_6H_5CBr{=}CHOR,$$

where R = CH_3, C_2H_5.

The mobility of the α-halogen atom is also utilised in the preparation of dihalovinyl ethers from tetrahaloalkyl ethers[79,122,123]:

$$CCl_3CHClOR \xrightarrow{Zn,\ alcohol} CCl_2{=}CHOR,$$

where R = CH_3, C_2H_5.

A variation of this reaction is the synthesis of β-halovinyl ethers from dibromo-acetals[124,125]:

$$CHX_2CH(OR)_2 \xrightarrow{Zn} CHX{=}CHOR,$$

where R = alkyl, X = Cl, Br.

Mention may be made of the interesting synthesis of α-methyl-β,β-dichlorovinyl alkyl ethers by the reaction of α,β,β,β-tetrachloroethyl alkyl ethers with Grignard reagents[126]:

$$CCl_3CHClOR + CH_3MgCl \longrightarrow CCl_2{=}C(CH_3)OR,$$

where R = CH_3, C_2H_5, C_3H_7. Unfortunately, no data on the yield of this reaction are available.

6. Miscellaneous Methods of Preparation

In addition to those described above, there are a number of special reactions which also lead to the formation of substituted vinyl ethers.

Favorskii and Shchukina [110,127] synthesised a number of alkoxyacetylenes from unsubstituted vinyl ethers, which reacted with hydrogen chloride to give α-chlorovinyl ethers:

$$HC\equiv COR \xrightarrow{HCl} CH_2=CClOR,$$

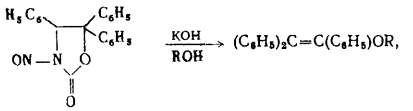
where R = C_2H_5, C_3H_7, C_4H_9.

It should be noted that, in contrast to the chlorine atom in α-chloroalkyl ethers, the α-chlorine in α-chlorovinyl ethers is inert in substitution reactions, *i.e.* it behaves in a way characteristic of a halogen atom attached to a double bond.

Arens [116] established the experimental conditions for the preparation of alkoxyacetylenes, and from them, β-chloro- and β-bromovinyl ethers. Of special note is the method whereby substituted vinyl ethers are obtained after the migration of the double bond in certain hydrocarbons under the action of potassamide in liquid ammonia. For instance, after the migration of the double bond, 3-butoxy-2-methylpropene yields β,β-dimethylvinyl butyl ether [129]:

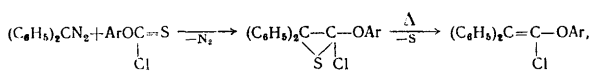
$$CH_2=C(CH_3)CH_2OC_4H_9 \xrightarrow{KNH_2} (CH_3)_2C=CHOC_4H_9.$$

Newman [130] described the preparation of some vinyl ethers, otherwise difficult to obtain, by the decomposition of substituted oxazolidones in alcoholic alkali:



where R = CH_3, C_2H_5.

Schönberg [131] obtained α-chloro-β,β-diphenylvinyl ethers by the following scheme:



where Ar = C_6H_5, 2,4,6-$Cl_3C_6H_2$.

There are a number of other papers [132-140] dealing with the formation of substituted vinyl ethers, but they are of little preparative significance.

II. PREPARATION OF SUBSTITUTED VINYL ALKYL-(ARYL) SULPHIDES

1. Preparation from Alkenyl Halides

The reaction of vinyl halides with mercaptides yields vinyl sulphides [3,141]; in the same way, substituted vinyl halides give substituted vinyl sulphides [142,143]:

$$RCH=CHBr+C_2H_5SNa \rightarrow RCH=CHSC_2H_5,$$

where R = CH_3, C_5H_{11}.

Trichloroethylene reacts with thiophenoxide to give α,β-dichlorovinyl aryl sulphides [144,145]:

$$CCl_2=CHCl+ArSNa \rightarrow CHCl=CClSAr.$$

However, in reactions of trichloroethylene with sodium ethylmercaptide [114] and of tetrachloroethylene with *p*-methylphenylmercaptide [146], instead of the expected chlorovinyl sulphides, products are obtained in which chlorine atoms are substituted further by ethylthio and *p*-tolylthio groups, respectively. Under similar conditions trichloroethylene and t-butylmercaptide react to form α,β-dichlorovinyl t-butyl sulphide [147], according to the equation

$$ClCH=CCl_2+NaSC(CH_3)_3 \xrightarrow[-NaCl]{} ClCH=CClSC(CH_3)_3.$$

2. Vinylation of Thiols

A number of papers by Truce and his collaborators [148-152] deal with the reactions of thiols with substituted acetylenes in alkaline solutions. They established this to be a stereospecific reaction involving nucleophilic addition, and yielding, as a rule, the *cis*-isomers, *e.g. cis*-β-*p*-tolylthiostyrene:

$$C_6H_5C\equiv CH+p\text{-}CH_3C_6H_4SNa \rightarrow p\text{-}CH_3C_6H_4SCH=CHC_6H_5.$$

In the main, the authors used acetylenes containing electron-withdrawing substituents such as C_6H_5, COOR, COC_6H_5, which facilitate the addition of thiols yielding in alkaline solution β-substituted vinyl sulphides [148-153]. These products are inconsistent with the Markownikoff rule. If acetylenes which do not contain an electron-withdrawing group are used, the addition results in "normal" reaction products. Thus, the authors showed that methylacetylene reacts with thiols giving α-methylvinyl sulphides:

$$CH_3C\equiv CH+RSH \xrightarrow{KOH} CH_2=C(CH_3)SR,$$

where R = C_2H_5, C_3H_7, C_4H_9, C_6H_5. These products are consistent with the Markownikoff rule.

A series of α,β-dichlorovinyl aryl sulphides was prepared by the reaction of dichloroacetylene with thiophenols [154]:

$$CCl\equiv CCl+ArSH \xrightarrow{C_2H_5ONa} ArSCCl=CHCl.$$

3. Decomposition of Mercaptoles

This method can be used in principle for the preparation of different vinyl sulphides containing substituents in the vinyl radical [155-157]. However, as regards alkyl sulphides only isopropenyl ethyl and isopropenyl butyl sulphides could be obtained in this way [158-160], namely by thermal decomposition of acetone mercaptoles:

$$(CH_3)_2C(SR)_2 \xrightarrow{80-120^\circ} CH_2=C(CH_3)SR+RSH,$$

where R = C_2H_5, C_4H_9.

Difficulties involved in the decomposition of mercaptals and mercaptoles may be accounted for not only by their greater stability as compared with that of acetals and ketals [157], but also by the different course of the thermal decomposition of sulphur compounds from that taken by the corresponding oxygen compounds. For instance, compounds of type $Ar_2C(SCH_2C_6H_5)_2$ decompose to yield $Ar_2C=S$, $(C_6H_5CH_2)_2S$, $C_6H_5CH_2SH$, and resinous products [161].

4. Decomposition of Substituted α,β-Unsaturated Acids

Thermal decomposition of unsaturated acids according to the equation

$$RC(SR')=CHCOOH \xrightarrow[-CO_2]{\Delta} RC(SR')=CH_2,$$

where R = CH_3, C_6H_5, R' = C_2H_5, yields α-substituted vinyl

alkyl(aryl) sulphides[155,162,163]. This method is of greater preparative significance in the sulphur than in the oxygen series, despite the complicated preparation of the starting unsaturated acids.

5. Preparation from the Halogen Derivatives of Sulphides

As in the oxygen series, this method is based on the ability of the halogen atoms in α-position to split off under the action of bases. By varying the starting components in the first stage,

$$RCH_2CHO+R'SH+HCl \rightarrow RCH_2CHClSR',$$

various β-substituted vinyl sulphides can be obtained[164]:

$$RCH_2CHClSR' \xrightarrow{C_5H_5N(C_5H_5)_2} RCH=CHSR'.$$

α,β-Dibromo sulphides, obtained by the bromination of α-chloro-sulphides, can split off hydrogen bromide to form β-bromovinyl sulphides[165]:

$$RCH_2CHClSR' \xrightarrow{Br_2} RCHBrCHBrSR' \xrightarrow{C_5H_5N(C_5H_5)_2} RCBr=CHSR'.$$

In the presence of inorganic bases polyhalogeno-sulphides[166] or α,β-dibromoethyl vinyl sulphide[167] split off hydrogen halide, for example:

$$CCl_3CHClSR \xrightarrow{KOH,NaOCH_3} CCl_2=CClSR,$$

where R = CH_3, C_2H_5, C_6H_5, $CH_2C_6H_5$.

Mention may be made of the interesting fact that the same differences in the action of various bases are observed here as in the oxygen series (see p. 209).

6. Preparation of β-Halovinyl Sulphides

The addition of sulphenyl chlorides to acetylenes can be used for the synthesis of β-chlorovinyl aryl sulphides[150,154,168,169]:

$$RC\equiv CR+ArSCl \rightarrow RCCl=C(R)SAr,$$

where R = H, alkyl, aryl.

By this method α-chloroethyl and β-chloroethyl-β-chlorovinyl sulphides were prepared[170,171] from α-chloroethyl- and β-chloroethyl-sulphenyl chlorides, respectively.

The simplest β-chlorovinyl alkyl sulphides can probably be obtained by the method described in the preceding section, but the β-chlorovinyl sulphides described in the literature were obtained in more complicated ways. Thus, β-chlorovinyl methyl sulphide was obtained in small yield as a final product in the following reactions[172]:

$$CH_3SSCH_3 \xrightarrow{Cl_2} 2CH_3SCl$$
$$CH_3SCl+CH_2=CH_2 \rightarrow CH_3SCH=CHCl.$$

Other members of the β-chlorovinyl sulphide series were isolated from the products of the chlorination of saturated sulphides[173,174].

A number of β-chloro- and β-bromo-vinyl aryl sulphides were obtained by the following reaction scheme[175,177]:

$$ArSCH=CHCOOH \xrightarrow{Br_2} ArSCHBrCHBrCOOH \rightarrow ArSCH=CHBr.$$

The acid obtained decomposes on mixing with water to yield β-halovinyl sulphide.

The same authors described the preparation of α,β-dibromovinyl sulphides[177]:

$$C_6H_5SC\equiv CH \xrightarrow{Br_2} C_6H_5SCBr=CHBr.$$

7. Miscellaneous Methods of Preparation

The following method of preparation of propenyl alkyl-(aryl) sulphides, which is specific for sulphur compounds, is of interest. The Claisen rearrangement, which is typical of allyl ethers[182], does not proceed with allyl aryl sulphides[178-181]. Boiling allyl phenyl sulphide, with or without alcoholic alkali, yields propenyl phenyl sulphide, not allyl thiophenol:

$$C_6H_5SCH_2CH=CH_2 \xrightarrow{\Delta} C_6H_5SCH=CHCH_3.$$

Allyl alkyl sulphides isomerise in the same manner. Since allyl alkyl(aryl) sulphides can easily be prepared from allyl bromide and a mercaptide, and the isomerisation proceeds with satisfactory yields, this method can be used for the preparation of various propenyl alkyl(aryl) sulphides.

α-Chloro-β,β-diphenylvinyl sulphide, which is difficult to obtain by other methods[131], was prepared by the same method as the similar oxygen compounds (see p. 210).

III. REACTIONS AND PROPERTIES OF SUBSTITUTED VINYL ETHERS

1. Physical Properties

Substituted vinyl ethers are colourless, transparent liquids, sometimes with a pleasant ethereal smell; the polyhalo-ethers are lachrymatory. The higher ethers, oily liquids or solids, are easily soluble in the usual organic solvents. The lower ones have anaesthetic properties[183,184].

Substituted vinyl ethers, like the unsubstituted derivatives[185,186], form azeotropic mixtures with alcohols. The azeotropic mixture of an ether and an alcohol has a lower boiling point and a lower refractive index than the pure ether. For example, impure isopropenyl ethyl ether has a boiling point of 52.5°–53.5° and the refractive index n_D^{20} 1.3805, whereas the pure ether has b.p. 61° and n_D^{20} 1.3918. To purify ether from alcohol, which is usually present as a result of the method of preparation, it should be washed several times with aqueous alkali and then water, dried over potassium hydroxide, and distilled. For further purification, the ether should be treated in the cold (a diethyl ether solution may be used) with sodium. (This method of purification is not suitable for α- and α,β-halo-ethers, which are unstable).

2. Chemical Properties

Hydrolysis. Vinyl ethers have a pronounced unsaturated character and rapidly decolorise bromine water and permanganate solution. Their ability to hydrolyse readily and quantitatively in aqueous acid is used in the laboratory to determine their structure. On hydrolysis, α- and

α,β-substituted vinyl ethers yield ketones [41,42,83,89,176], and β- and β,β-substituted ethers give aldehydes [9,10,88,89,95]:

$$RCH{=}C(OR)R' \xrightarrow[-ROH]{H^+,H_2O} RCH_2COR'$$

$$RR'C{=}CHOR'' \xrightarrow[-R''OH]{H^+,H_2O} RR'CHCHO.$$

The structure of the ether can be established by determining the physical constants of ketones or aldehydes obtained by hydrolysis, or those of their derivatives (hydrazones, semicarbazones, etc.). The hydrolysis of alkyl-substituted vinyl ethers proceeds quantitatively in dilute acid solutions or on passing the ether–water vapour mixture over acid catalysts (WO_3 on Al_2O_3,[188] W_2O_5 on Al_2O_3,[189] aluminosilicates, silver oxide,[190] $Ca_3(PO_4)_2$ [191]). The resulting aldehyde or ketone can be determined quantitatively, and from it the quantity of hydrolysed ether can be calculated; in this way the purity of the starting vinyl ether can be determined.

The rate of hydrolysis depends on the structure of the unsaturated radical which is bound directly to oxygen, and on the number and nature of the substituents in the vinyl group. Since the acid-catalysed hydrolysis proceeds through the addition of a proton to the double bond of the molecule [112], the effect of the substituents on the hydrolysis rate depends on the way in which they polarise the molecule, *viz.* on whether they facilitate or hinder the addition of a proton. The structure of the final product of the hydrolysis of unsaturated ethers depends on the course of the decomposition of the intermediate hemiacetals, which in its turn depends on the nature and position of the substituents. This can be verified on the example of the hydrolysis of β-methyl vinyl ethers. The introduction of an electron-withdrawing substituent in α-position causes a certain amount of polarisation, which facilitates the addition of a proton and consequently accelerates the hydrolysis compared with that of unsubstituted ether. In fact, as is apparent from the data on the hydrolysis of vinyl phenyl and isopropenyl phenyl ethers, other conditions being equal, it is the latter compound which is the more completely hydrolysed [191]. Substituted vinyl aryl ethers [44] are more difficult to hydrolyse than the substituted vinyl alkyl ethers. A similar difference is observed in the case of unsubstituted ethers.

In view of the foregoing, the difference in the hydrolysis of α- and β-halo-ethers is noteworthy. α-Chlorovinyl ethyl ether reacts vigourously with water, giving ethyl acetate [127]:

$$CH_2{=}CClOC_2H_5 + H_2O \rightarrow \left[CH_3{-}\overset{\displaystyle OH}{\overset{|}{C}}{-}OC_2H_5\right] \rightarrow CH_3COOC_2H_5 + HCl.$$
$$\qquad\qquad\qquad\qquad\qquad\quad \underset{\displaystyle Cl}{|}$$

A β-halovinyl ethyl ether does not hydrolyse in water even on boiling [110], and in acid solution it decomposes upon long heating into the haloacetaldehyde and alcohol [110,113,126]; thus, β-halo-ethers are more difficult to hydrolyse than the substituted vinyl ethers, let alone α-chloro-ethers:

$$XCH{=}CHOC_2H_5 + H_2O \rightarrow [XCH_2CH(OH)OC_2H_5] \rightarrow CH_2XCHO + C_2H_5OH,$$

where X = Cl, Br.

Like α-chlorovinyl ethyl ether, α,β-dichloro- and α,β,β-trichlorovinyl alkyl ethers hydrolyse forming chloro- and dichloroacetates [192-195]. α-Chloro-β,β-diphenylvinyl phenyl ether, however, yields diphenylacetic acid on hydrolysis [131]. β,β-Dichlorovinyl ethyl ether hydrolyses in the same way as β-chlorovinyl ethyl ether, giving dichloroacetaldehyde [138].

Addition of alcohols. In a number of papers dealing with unsubstituted vinyl ethers it was shown that the ethers react vigorously and exothermically with alcohols, and that the reaction proceeds both in the presence of catalysts (metal chlorides, acids) and without them on heating. Acetals of a wide variety of structures are thereby formed: symmetrical dialkyl- [1,196] and diaryl acetals [197], unsymmetrical dialkylacetals [1,196] and alkylarylacetals [197-201]. Since unsubstituted vinyl ethers can easily be prepared by vinylation, and the reaction of alcohols with the ethers is almost quantitative, this is a good preparative method for acetals.

Although the reaction of alcohols with substituted ethers proceeds as readily as with the unsubstituted ones [42], with the former it has less importance as they themselves are often obtained from acetals and ketals. Moreover, as will be shown later, the reaction of alcohols with α-substituted ethers has a number of features which limit its preparative value.

Acetals, as we know, have a tendency to disproportionation [1,196], whereby a mixed acetal yields, on simple distillation, the two symmetrical acetals:

$$2CH_3CH(OR)(OR') \rightarrow CH_3CH(OR)_2 + CH_3CH(OR')_2.$$

Disproportionation is easier, the greater the difference in the molecular weight of R and R'. [201-203] This tendency is much stronger in ketals [205-206]. For instance, by virtue of the greater mobility of alkoxy groups in ketals, alkyl-substituted ethers can be prepared from dimethyl ketals and alcohols [53]:

$$CH_3{-}\underset{\displaystyle R}{\overset{|}{C}}(OCH_3)_2 + R'OH \xrightarrow[-2CH_3OH]{p\text{-}CH_3C_6H_4SO_3H} CH_2{=}\underset{\displaystyle R}{\overset{|}{C}}{-}OR'.$$

Under similar conditions dimethyl acetals, $RCH(OCH_3)_2$, do not yield the vinyl ethers derived from the reacting alcohol. The tendency to disproportionation is obviously the reason why mixed dialkyl ketals are almost unknown [205].

In view of what has been said above, the results of studies [206] on the addition of alcohols and phenols to α-methylvinyl ethers as a method of preparation of acetone dialkyl and diaryl ketals are of interest:

$$CH_2{=}\underset{\displaystyle CH_3}{\overset{|}{C}}{-}OAr \xrightarrow{H^+} \begin{cases} \xrightarrow{+ROH} (CH_3)_2C\begin{matrix}OR\\OAr\end{matrix} \\ \xrightarrow{+ArOH} (CH_3)_2C(OAr)_2 \end{cases}.$$

Acetone diaryl ketals were obtained in good yields, but alkyl aryl ketals could not be obtained owing to their decomposition into phenols and isopropenyl alkyl ethers:

$$(CH_3)_2C\begin{matrix}OR\\OAr\end{matrix} \rightarrow ArOH + CH_2{=}\underset{\displaystyle CH_3}{\overset{|}{C}}{-}OR.$$

Mixed alkyl aryl ketals have not been described except for methyl phenyl ketals derived from aliphatic-aromatic α-keto-alcohols [207-209]; they were first prepared by Temnikova and Myukhyurdari [207] by the following scheme:

$$C_6H_5COCHBrCH_3 \xrightarrow[2)\ CH_3OH]{1)\ C_6H_5ONa} C_6H_5\overset{\displaystyle OCH_3}{\overset{|}{C}}{-}CH(OH)CH_3.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{\displaystyle OC_6H_5}{|}$$

These mixed ketals are stable by virtue of the presence in

them of the electron-withdrawing phenyl and hydroxyl groups.

Finally, some features of the addition of alcohols to halogen-substituted vinyl ethers are considered. α-Chlorovinyl ethyl ether reacts vigorously with alcohol, forming an acetate[127]:

$$CH_2=CClOC_2H_5 + C_2H_5OH \rightarrow [CH_3-\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}-(OC_2H_5)_2] \rightarrow CH_3COOC_2H_5 + C_2H_5Cl.$$

β-Chlorovinyl ethyl ether adds on one molecule of alcohol in the presence of acids (sulphuric and hydrochloric)[113,125]:

$$CHCl=CHOC_2H_5 + C_2H_5OH \xrightarrow{H^+} CH_2ClCH(OC_2H_5)_2.$$

Dichloro-acetal was obtained by heating β,β-dichlorovinyl methyl ether with alcohol at 100° for 3 h in the presence of hydrochloric acid[79]. As in the case of α-chlorovinyl ethyl ether, the alcoholysis of α,β-dichlorovinyl ethyl ether yields acetates[22,23]; their structure depends on the course of the decomposition of the intermediate acetal[23]:

$$CHCl=CClOC_2H_5 + ROH \rightarrow \left[CH_2Cl-\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}\begin{matrix}OC_2H_5\\OR\end{matrix}\right] \rightarrow \begin{matrix}\nearrow CH_2ClCOOR + C_2H_5Cl & (I)\\ \searrow CH_2ClCOOC_2H_5 + RCl. & (II)\end{matrix}$$

The reaction with methanol proceeds predominantly by the second pathway, but that with other alcohols and phenols by the first. The reaction of alcohols with α,β-dichloro-β-bromovinyl ethyl ether is more difficult than with α,β-dichlorovinyl ethyl ether[120]:

$$CClBr=CClOC_2H_5 + ROH \rightarrow CClBrCOOR + C_2H_5Cl,$$

where R = alkyl, aryl.

Addition of acids. The reaction of organic acids with alkyl-substituted vinyl ethers has not been described. It can be assumed, however, that it should differ in the same way from the corresponding reaction with unsubstituted vinyl ethers as in the case of alcohols. Halogen-substituted ethers react in the same manner with acids as with alcohols. For instance, acetic, chloroacetic and benzoic acids combine with α,β-dichlorovinyl ethyl ether in the following way[23]:

$$CHCl=CClOC_2H_5 + RCOOH \rightarrow \left[CH_2Cl-\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}\begin{matrix}OCOR\\OC_2H_5\end{matrix}\right] \rightarrow RCOCl + CH_2ClCOOC_2H_5.$$

Reactions with naphthoic and anisic acids are accompanied by the evolution of ethyl chloride. The general reaction of halogen-substituted ethers with organic acids can be represented by the following scheme:

$$X-\underset{\displaystyle Y}{\overset{\displaystyle |}{C}}=\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}-OC_2H_5 + RCOOH \rightarrow \left[X-\underset{\displaystyle Y}{\overset{\displaystyle |}{C}}-\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}\begin{matrix}H\\OCOR\end{matrix}\begin{matrix}\\OC_2H_5\end{matrix}\right] \rightarrow X-\underset{\displaystyle Y}{\overset{\displaystyle |}{C}}H-COOC_2H_5 + RCOCl.$$

where (1) X = H, Y = Cl;[23] (2) X = H, Y = H;[210] (3) X = Br, Y = Cl.[120] This reaction may be used as a preparative method for acid chlorides. For instance, Heslinga and Arens[211] prepared peptides in that way:

$$CH_2=CClOC_2H_5 + YNHCHRCOOH \rightarrow [CH_2CCl(OC_2H_5)OCOCHRNHY] \rightarrow$$
$$\rightarrow CH_3COOC_2H_5 + YNHCHRCOCl;$$

$$YNHCHRCOCl + HCl\cdot NH_2CHR'COOC_2H_5 \rightarrow YNHCHRCONHCHR'COOC_2H_5 + 2HCl,$$

where Y = benzyloxycarbonyl or YH = phthaloyl radical.

Addition of hydrogen halides. The addition of hydrogen halides to unsubstituted vinyl alkyl or vinyl aryl ethers has been thoroughly studied and can be used as a preparative method for α-chloro-ethers[1]. Only a few cases of additions to substituted ethers have been described. To obtain α-chloroisopropyl alkyl ethers the authors of this review reacted hydrogen halides with α-methylvinyl alkyl ethers:

$$CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-OR + HCl \rightarrow (CH_3)_2CClOR.$$

However, only the decomposition products of the α-chloro-ether were isolated:

$$(CH_3)_2CClOR \rightarrow CH_3COCH_3 + RCl.$$

Similar decomposition was observed earlier by a number of workers[204,212].

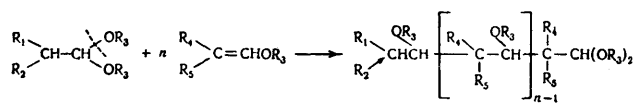
Hydrochlorination of isopropenyl aryl ethers gave α-chloroisopropyl aryl ethers[213]; they are more stable than α-chloroisopropyl alkyl ethers, but not so stable as the α-chloro-ethers obtained by the hydrochlorination of vinyl phenyl ether[214].

The tendency to decomposition of α-chloro-ethers containing the α-chloroisopropyl group was also observed by Hall and Sirel[215]. These authors failed to isolate even traces of the α-chloro-ethers in their attempt to chlorinate di-isopropyl ether by the same method as that which had been used earlier for the preparation of bis(α-chloroethyl) ether by the chlorination of diethyl ether.

The reaction of hydrogen halide with α-halovinyl alkyl ether yields the very stable α,α-dihaloethyl alkyl ether[128,211], which can be distilled and kept without decomposition. The addition of hydrogen chloride to β-chlorovinyl ethyl ether has also been described[216].

Addition of halogens. The addition of halogens to the double bond in substituted ethers has not received much attention. The cases described are the addition of bromine to α-ethylvinyl methyl ether[101], of chlorine to α,β-dichlorovinyl phenyl ether[24,25], and of bromine and chlorine to α,β,β-trichlorovinyl ethyl ether[217]. This reaction is exothermic, and is carried out with cooling under conditions analogous to those described for the halogenation of unsubstituted ethers[1].

Reactions with acetals and ketals. Hoaglin and Hirch[218] studied the addition of vinyl ethers to acetals in the presence of boron fluoride etheradduct, and found it to proceed as follows:



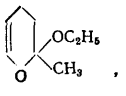
This reaction was subsequently used in a great many syntheses involving the lengthening of the chain in polyenic aldehydes and ketones[219]. Acetals can be condensed with β-substituted vinyl ethers (for instance propenyl methyl and propenyl ethyl ethers[218,220], β-ethylvinyl and β-ethyl-β-butylvinyl ethyl ethers[218], and β-bromovinyl ethyl ether[221]) as well as with α-substituted ones, the latter

being less reactive[59,220,223]. Unlike unsubstituted and β-alkyl-substituted vinyl ethers, which form acetals, α-alkyl-substituted ethers yield ketals on condensation with acetals, which on hydrolysis give ketones; for instance, crotonaldehyde acetal[223] reacts with isopropenyl ethyl ether to give 4-ethoxyhept-5-en-2-one ketal, which hydrolyses into hepta-3,5-dien-2-one:

$$CH_3CH{=}CHCH(OC_2H_5)_2 + CH_2{=}C(CH_3)OC_2H_5 \xrightarrow{ZnCl_2}$$
$$\rightarrow CH_3CH{=}CHCH(OC_2H_5)CH_2C(OC_2H_5)_2CH_3 \xrightarrow{H^+,H_2O} CH_3(CH{=}CH)_2COCH_3.$$

Diene synthesis. Vinyl ethers have been used as dienophiles in reactions with cyclopentadiene[224,225], cyclones[226,227], hexachlorocyclopentadiene[225], acrolein and crotonaldehyde[228,229]; they were found, however, to be less reactive than α,β-unsaturated carbonyl compounds. As regards substituted vinyl ethers, β-substituted ethers are inactive in diene synthesis[187], while α-substituted ethers give much smaller yields than the unsubstituted ones[187,229]. Diene synthesis with acrolein and α-alkyl--substituted ethers (isopropenyl ethyl and n-butyl cyclohexenyl ethers)[229]:

$$CH_2{=}CHCHO + CH_2{=}C(CH_3)OC_2H_5 \rightarrow$$



and the reactions of α-methyl- and α-phenylvinyl ethers with cyclones[187] have been described.

Polymerisation of vinyl ethers, like their addition reactions, proceeds as a result of the formation of carbonium ions in the presence of acid catalysts ($SnCl_2$, $SnCl_4$, $FeCl_3$, $AlCl_3$, BF_3) with or without solvents. In the presence of these catalysts α-alkyl-substituted ethers form many polymers[230-232]. α-Methylvinyl ethers were shown[206,233] to be more reactive in polymerisation than unsubstituted vinyl ethers; this is reflected in the fact that, under the most favourable conditions, they polymerise at lower temperatures than the corresponding vinyl alkyl ethers[1]. The reason for this difference in behaviour, the authors ascribed to the different stability of oxonium complexes formed by the reaction of the oxygen atom in the ethers with ionic catalysts.

β-Halovinyl ethers also polymerise in the presence of ionic catalysts[110,112,125], although not so easily as the unsubstituted vinyl ethers. α-Chloro(bromo)vinyl ethyl ether polymerises spontaneously on standing[113,125].

Miscellaneous reactions of substituted vinyl ethers. In addition to the above-mentioned reagents, various other compounds can be added on to the double bond in substituted vinyl ethers, for example, hydrogen[57,74,84], ozone[57,102,107], amines[112], organic acid chlorides[101,104], and mercury salts[92].

By virtue of the ease with which alcohols react with the double bond and form ketals, α-substituted ethers can be used instead of ketals and ketones. For instance, the condensation of isopropenyl ethyl ether with the ester of oxalic acid[234] has been described:

$$CH_2{=}C(CH_3)OC_2H_5 + (COOC_2H_5)_2 \xrightarrow{C_2H_5ONa}$$
$$\rightarrow C_2H_5OOCCOCH_2COCH_2COCOOC_2H_5.$$

Acetone can be used in this reaction under the same conditions, instead of isopropenyl ethyl ether. In this connection the preparation of isoprene from ethylene and isopropenyl ethyl ether or acetone diethyl ketal may be noted[235].

Reactions of substituted vinyl ethers with Grignard reagent have recently been studied[102,105,107]. Arylmagnesium bromides react with α-phenyl-substituted ethers forming substituted ethylenes[105]:

$$RCH{=}C(C_6H_5)OC_2H_5 + ArMgBr \rightarrow RCH{=}C(C_6H_5)Ar + C_2H_5OMgBr,$$

where R = alkyl, aryl. Olefinic hydrocarbons have been prepared by the same method from β-alkyl-substituted vinyl ethers and alkylmagnesium bromides[107]:

$$RCH{=}CHOR' + R''MgBr \rightarrow RCH{=}CHR'' + R'OMgBr.$$

α,β-Dialkylvinyl ethers[102] react differently. The Grignard reagent cleaves them at the C–O bond, yielding ketones:

$$RCH{=}\underset{\displaystyle R'}{\underset{|}{C}}{-}OR'' \xrightarrow[2)\ +NH_4Cl]{1)\ +R''MgBr} RCH_2COR' + R''H. \dagger$$

α-Phenyl-substituted ethers are characterised by their tendency to thermal rearrangement[50,89,236]:

$$CH_2{=}C(C_6H_5)OR \rightarrow RCH_2COC_6H_5$$

and β-bromovinyl ethers by their ability to split off hydrogen halide upon heating with potassium hydroxide[33,112,115,116,124-126,127].

$$RCBr{=}CHOR' \xrightarrow[-HBr]{KOH} RC{\equiv}COR'.$$

IV. REACTIONS AND PROPERTIES OF SUBSTITUTED VINYL SULPHIDES

1. Physical Properties

Vinyl sulphides are unpleasant-smelling liquids insoluble in water but miscible with the usual organic solvents. They turn yellow on standing in air, especially in the light, and should be kept in the dark, in sealed tubes.

2. Chemical Properties

Vinyl sulphides are stable in alkaline media, but decompose in acid media. They decolorise bromine water. Their reactions are similar to those of vinyl ethers, but they do not enter into addition reactions quite so readily; it is therefore supposed that their double bond is less nucleophilic than that of vinyl ethers[237]. On the other hand, they take part more readily in reactions involving a radical mechanism[3,4,5,238], such as those involving the addition of mercaptans, contrary to Markownikoff's rule, and in radical polymerisations[237]. These conclusions were reached following systematic study of unsubstituted vinyl sulphides. Owing to difficulties involved in obtaining substituted vinyl sulphides, there is little information in the literature concerning their reactions, but what is available is consistent with the principles stated above.

† The stoichiometry of this reaction is not clear (Ed. of Translation).

In the present chapter sections on polymerisation and diene synthesis [237,239,240] are omitted, as these reactions have not been described for substituted vinyl sulphides.

Halovinyl sulphides have a number of specific properties which do not exist in their oxygen analogues. Some characteristic properties of sulphides concern the sulphur atom (oxidation to sulphoxides and sulphones, desulphurisation, decomposition by an alcoholic solution of mercuric chloride) and naturally have no equivalents among oxygen compounds.

Hydrolysis. Vinyl sulphides react less vigorously with water in acid solution than vinyl ethers. For instance, in the hydrolysis of $CH_2=CHSCH_2CH_2OCH=CH_2$ [241] and $C_2H_5SCH=CHOC_2H_5$ [242] by dilute hydrochloric acid, the ether group hydrolyses first, and $CH_2=CHSCH_2CHO$ and $C_2H_5SCH_2CHO$ are formed respectively. Only by using harsher conditions is the hydrolysis of the alkylmercapto group achieved. In contrast to the oxygen analogues, the hydrolysis is complicated by the formation, in acid media, of mercaptals and mercaptoles from α-substituted sulphides, which, unlike acetals and ketals, are stable in aqueous solution. Thus, in the hydrolysis of isopropenyl ethyl sulphide, acetone diethyl mercaptole was isolated in addition to acetone:

$$2\,CH_3=C(CH_3)SC_2H_5+H_2O \xrightarrow{H^+} CH_3COCH_3+(CH_3)_2C(SC_2H_5)_2.$$

The formation of by-products naturally precludes the use of hydrolysis for the quantitative determination of vinyl sulphides. It can, however, be used both for their qualitative determination and in structure determination [179]. If there is no formation of mercaptals and mercaptoles, hydrolysis yields thiols and carbonyl compounds. Thus, by hydrolysis of isopropenyl and propenyl phenyl sulphides we obtained acetone and propionaldehyde respectively, and identified them as the 2,4-dinitrophenylhydrazones. Böhme and Gran [173] obtained 80–90% of chloroacetone and thiols by hydrolysing β-chloro-α-methylvinyl sulphides:

$$CHCl=C(CH_3)SR+H_2O \xrightarrow{H^+} CH_3COCH_2Cl+RSH,$$

where R = CH_3, C_6H_5.

Addition of alcohols and thiols. Vinyl sulphides react with alcohols in the presence of acid catalysts [238] to yield monothioacetals, *e.g.* $CH_3CH(OC_2H_5)SC_2H_5$, which are unstable and have a greater tendency to disproportionation and transetherification than the mixed acetals [1,196]. There is no information in the literature on the addition of alcohols to substituted vinyl sulphides, but, in the case of α-substituted vinyl sulphides, the products (mixed monothioketals) should presumably be less stable than monothioacetals.

Vinyl sulphides react with mercaptans in the presence of acid catalysts according to the Markownikoff rule [4,237]. Addition to α-methylvinyl sulphides [4,237] occurs similarly:

$$CH_2=C(CH_3)SR+RSH \xrightarrow{HCl} (CH_3)_2C(SR)_2,$$

where R = C_2H_5, C_3H_7, C_4H_9.

Isopropenyl phenyl sulphide combines with ethanethiol also in accordance with the Markownikoff rule, but the resulting ethyl phenyl mercaptole decomposes in the same way as acetone alkyl aryl ketals [206], to give isopropenyl ethyl sulphide and thiophenol:

$$CH_2=C(CH_3)SC_6H_5+C_2H_5SH \xrightarrow{SO_2} \left[(CH_3)_2C(SC_6H_5)(SC_2H_5)\right] \rightarrow$$
$$\rightarrow CH_2=C(CH_3)SC_2H_5+C_6H_5SH.$$

Unlike their oxygen analogues, vinyl sulphides undergo free-radical reactions, such as the addition of mercaptans. Shostakovskii and Prilezhaeva [4,5,238] showed this reaction to proceed by a free-radical mechanism, the presence of the merest traces of peroxides being sufficient for the reaction to be completed quantitatively simply on mixing the reagents. They studied the addition of mercaptans to isopropenyl alkyl sulphides and observed that the reaction is more difficult owing to the presence of an α-methyl group:

$$CH_2=C(CH_3)SR+RSH \longrightarrow RSCH_2CH(CH_3)SR,$$

where R = C_2H_5, C_3H_7, C_4H_9.

Thus, to prepare 1,2-dibutylmercaptopropane, a radical catalyst should be added (azoisobutyric dinitrile) and the mixture heated, while 1,2-dibutylmercaptoethane can be prepared merely by mixing the components [5]. The authors allowed thiols to react with isopropenyl and propenyl phenyl sulphides in the presence of azoisobutyric dinitrile and obtained the isomeric sulphides:

$$CH_2=C(CH_3)SC_6H_5+C_2H_5SH \longrightarrow C_2H_5SCH_2CH(CH_3)SC_6H_5$$
$$CH_3CH=CHSC_6H_5+C_2H_5SH \longrightarrow C_2H_5SCH(CH_3)CH_2SC_6H_5.$$

Addition of hydrogen halides. The reaction of vinyl alkyl sulphides with hydrogen halides proceeds under the conditions already described for the hydrohalogenation of vinyl ethers, namely on stirring at low temperatures, and the resulting products are consistent with the Markownikoff rule [238]. The hydrochlorination of α-methylvinyl sulphides was studied:

$$CH_2=C(CH_3)SR+HCl \longrightarrow (CH_3)_2CClSR,$$

where R = alkyl, aryl. It was shown that α-chloroisopropyl alkyl sulphides are less stable than α-chloro-sulphides of the general formula RCHClSR [167,173,238,243] and that at temperatures below zero they decompose into a complex mixture of products, from which a thiol can be isolated.

α-Chloroisopropyl aryl sulphides are more stable than the corresponding alkyl sulphides, but they also partly decompose on distillation.

Hydrogenation of sulphides. Hydrogenation of organic sulphides over oxides or sulphides of heavy metals at high temperatures is usually accompanied by hydrogenolysis (rupture of the C–S bond). Hydrogenation of unsaturated sulphides without the rupture of the C–S bond can be carried out rapidly and quantitatively in the cold over a palladium–charcoal catalyst [178,179,244]. For instance, β-alkylvinyl sulphides are hydrogenated quantitatively in 2–4 h by vigorous shaking in an atmosphere of hydrogen [244]:

$$CH_3(CH_2)_5CH=CHSR \xrightarrow{H_2Pd/C} CH_3(CH_2)_7SR,$$

where R = CH_3, C_2H_5.

Oxidation to sulphones. The oxidation of sulphides to sulphones is widely used in the chemistry of substituted vinyl sulphides for their identification (sulphones

are crystalline compounds) as well as for the activation of the vinyl double bond by the electron-withdrawing SO_2 group; the resulting unsaturated sulphones can be used in further reactions (*e.g.* in diene synthesis or in polymerisation). Sulphones are usually prepared by oxidation with 30% hydrogen peroxide in glacial acetic acid in the cold (as in the oxidation of alkyl sulphides [147,150]), or by heating (as for aryl sulphides [145,149,154,180,245,246]. Good results were obtained in oxidations by monoperoxyphthalic acid in ether solution in the cold [164,173,178]. For instance α-methyl-β--chlorovinyl sulphides were oxidised to sulphones in 70–80% yields by monoperoxyphthalic acid [163,173]:

$$CHCl{=}C(CH_3)SR \xrightarrow{2(O)} CHCl{=}C(CH_3)SO_2R,$$

where R = CH_3, C_6H_5.

If the oxidation is carried out under milder conditions, sulphoxides are obtained. Thus, at 28°–30° hydrogen peroxide oxidises α,β-dichlorovinyl t-butyl sulphide into sulphone, whereas at 0° it yields sulphoxides [147].

Miscellaneous reactions of β-halovinyl sulphides. Like β-halovinyl ethers, β-halovinyl sulphides split off a molecule of hydrogen halide in the presence of alkalis and form alkyl(aryl)mercaptoacetylenes [165,175]:

$$RSCH{=}CHX \longrightarrow RSC{\equiv}CH,$$

where R = alkyl, aryl; X = Cl, Br.

It is interesting that when R is an aryl group, the elimination of hydrogen halide proceeds extremely easily at comparatively low temperatures [175]. By virtue of the mobility of substituents in the β-position with respect to the sulphur atom, the β-chlorine atom in β-chlorovinyl sulphides is very reactive to nucleophilic exchange reactions. In alkaline media the β-chlorine atom can be substituted by alkylmercapto [165], arylmercapto [143 146 247], naphthoxy [174], and amino groups [248]. The ease of the substitution of β-chlorine is especially pronounced in the reaction of polychloroethylenes with thiophenols in alkaline media. Thus, the main product in the reaction of tetrachloroethylene with *p*-toluenethiol is not α,β,β-trichlorovinyl tolyl sulphide, but α,β-dichloro-α,β-bis(*p*-tolylmercapto)ethylene [146]:

$$CCl_2{=}CCl_2 + ArSNa \xrightarrow[-NaCl]{} ArSCCl{=}CCl_2$$

$$ArSCCl{=}CCl_2 + ArSNa \xrightarrow[-NaCl]{} ArSCCl{=}CClSAr.$$

The nucleophilic reactivity of the β-chlorine atom in β-chlorovinyl sulphones is even higher than in β-chlorovinyl sulphides [248].

Reactions of sulphides involving the rupture of the C–S bond. Substituted vinyl sulphides undergo desulphurisation on boiling over Raney nickel [180,245]. The hydrocarbons formed in the process can be used as an indication of the structure of the sulphide.

The reaction of vinyl sulphides with alcoholic mercuric chloride solution leads to the rupture of the C–S bond; in contrast, mercury salts combine with the double bond in vinyl alkyl ethers to yield a mercuri-derivative of an aldehyde or ketone [92]. In vinyl sulphides the action of mercury is directed towards a different reactive centre — the sulphur atom — and the reaction proceeds by the elimination of the thiol group. Shostakovskii and Prilezhaeva showed [4,5,237,238,249] that the decomposition of vinyl sulphides by alcoholic mercuric chloride solution proceeds at room temperature:

$$CH_2{=}CHSR + 2\,HgCl_2 + C_2H_5OH \longrightarrow RSHgCl + CH_3CH(OC_2H_5)_2 + HCl.$$

This reaction is quantitative and can be used for the analysis of vinyl sulphides.

α-Methylvinyl sulphides are decomposed by alcoholic mercuric chloride solution. For the quantitative decomposition of isopropenyl alkyl and aryl sulphides the reaction mixture has to be heated, *i.e.* harsher reaction conditions are required than in the case of unsubstituted vinyl sulphides. Decomposition of the isomeric propenyl and isopropenyl phenyl sulphides proceeds at different rates. Thus, after mixing the mercuric chloride solution with isopropenyl phenyl sulphide the phenylmercury chloride precipitate separates in 30 sec, while in the case of propenyl phenyl sulphide it separates in 10–15 sec. Karaulova and collaborators [181] also observed the slow and incomplete decomposition of propenyl phenyl sulphide. According to the available date [173], the decomposition of various sulphides gets progressively more difficult in the order vinyl alkyl > isopropenyl alkyl > vinyl phenyl > isopropenyl phenyl > propenyl phenyl.

We conclude that the substituted vinyl compounds containing oxygen, sulphur, and nitrogen are capable of reacting with various compounds containing a mobile hydrogen atom in the molecule; they can be used in high-polymer chemistry and in polymerisations and copolymerisations, and their significance is bound to grow with the further development of these fields.

1. M. F. Shostakovskii, "Prostye Vinilovye Efiry" (Vinyl Ethers), Izd. Akad. Nauk SSSR, 1952.
2. J. W. Copenhaver and M. H. Bigelow, "Acetylene and Monoxide Chemistry", New York, 1949, p. 32.
3. W. Reppe, Annalen, 601, 81 (1956).
4. M. F. Shostakovskii, E. N. Prilezhaeva, and N. I. Uvarova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 526 (1954).
5. M. F. Shostakovskii, E. N. Prilezhaeva, and N. I. Uvarova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 906 (1955).
6. A. A. Petrov, Uspekhi Khim., 21, 452 (1952).
7. I. N. Nazarov, S. M. Makin, V. K. Kruptsov, and V. A. Mironov, Zhur. Obshch. Khim., 29, 111 (1959).
8. A. M. Butlerov, Zhur. Russ. Fiz.-Khim. Obshch., 2, 192 (1870).
9. A. P. El'tekov, Zhur. Russ. Fiz.-Khim. Obshch., 9, 163 (1877).
10. M. Sheshukov, Zhur. Russ. Fiz.-Khim. Obshch., 16, 495 (1884).
11. G. V. Isagulyants, Dokl. Akad. Nauk Armyansk. SSR, 1, 13 (1944).
12. J. Niederl and E. Storch, J. Amer. Chem. Soc., 55, 284 (1933).
13. B. P. 332 605; Chem. Zentr., II, 2572 (1930).
14. F. P. 684 722; Chem. Abs., 24, 5306 (1930).
15. E. Erlenmeyer, Ber., 14, 1868 (1891).
16. J. V. Nef, Annalen, 308, 264 (1899).
17. A. Sabanejeff, Annalen, 216, 277 (1882).
18. M. Slimmer, Ber., 36, 289 (1903).
19. T. Jacobs, R. Cramer, and F. T. Weiss, J. Amer. Chem. Soc., 62, 1849 (1940).
20. B. P. 617 820; Chem. Abs., 43, 7045 (1949).

21. Swedish P. 249 117; Chem. Abs., 43, 7966 (1949).
22. A. Geuther and F. Brockhoff, J. prakt. Chem., (2), 7, 101 (1873).
23. H. Crompton and P. Z. Vanderstichele, J. Chem. Soc., 117, 691 (1920).
24. E. Ziegler and W. Klementschitz, Monatsh., 81, 1113 (1950).
25. E. Ziegler, *et al.*, Monatsh., 83, 1 (1952).
26. A. Sabanejeff and P. Dworkowitsch, Annalen, 216, 279 (1882).
27. A. E. Favorskii, Zhur. Russ. Fiz.-Khim. Obshch., 19, 414 (1887).
28. A. E. Favorskii, Zhur. Russ. Fiz.-Khim. Obshch., 20, 518 (1888).
29. "Sbornik Izbrannykh Trudov Akademika A. E. Favorskogo k 55-letiyu Nauchnoi Deyatel'nosti" (Collected Works of Academician A. E. Favorskii on the Occasion of the 55th Year of His Scientific Career), Izd. Akad. Nauk SSSR, 1940, p. 32
30. C. Moureu, Bull. Soc. chim. France, (3), 31, 526 (1904).
31. K. Auwers, Ber., 44, 3514 (1911).
32. D. Dufraisse and R. Chaux, Bull. Soc. chim. France, (4), 39, 905 (1926).
33. T. A. Jacobs and W. R. Scott, J. Amer. Chem. Soc., 75, 5500 (1953).
34. S. I. Miller and G. Shkapenko, J. Amer. Chem. Soc., 77, 5038 (1955).
35. S. I. Miller, J. Amer. Chem. Soc., 78, 6091 (1956).
36. A. Z. Henne and M. Nager, Annalen, 74, 650 (1952).
37. J. V. Nef, Annalen, 308, 318 (1899).
38. E. Ott and C. Dittus, Ber., 76, 80 (1943).
39. M. F. Shostakovskii, A. V. Bogdanova, and G. K. Krasil'nikova, Uspekhi Khim., 28, 1066 (1959).
40. A. Treibs, Angew. Chem., (A), 60, 289 (1948).
41. M. F. Shostakovskii and E. P. Gracheva, Zhur. Obshch. Khim., 23, 1153 (1953).
42. M. F. Shostakovskii and E. P. Gracheva, Zhur. Obshch. Khim., 23, 1320 (1953).
43. M. F. Shostakovskii and E. P. Gracheva, Zhur. Obshch. Khim., 27, 355 (1957).
44. M. F. Shostakovskii, E. P. Gracheva, and N. K. Kul'bovskaya, Zhur. Obshch. Khim., 28, 1253 (1958).
45. D. A. Frank-Kamenetskii and V. G. Markovich, Zhur. Obshch. Khim., 12, 619 (1942).
46. Ya. M. Slobodin, Zhur. Obshch. Khim., 6, 1892 (1936).
47. U. S. P. 2 594 706; Chem. Abs., 47, 1180 (1953).
48. L. N. Owen, J. Chem. Soc., 385 (1945).
49. L. Claisen, Ber., 36, 3664 (1903).
50. L. Claisen, Ber., 29, 2931 (1896).
51. L. Claisen, Ber., 31, 1019 (1898).
52. A. Johanissian and E. Akinian, Chem. Zentr., II, 552 (1930).
53. D. B. Killian, G. F. Hennion, and J. A. Nieuwland, J. Amer. Chem. Soc., 57, 544 (1935).
54. B. P. 603 471; Chem. Abs., 43, 1050 (1949).
55. G. P. 525 836; Chem. Zentr., II, 1191 (1931).
56. F. P. 703 509; Chem. Zentr., II, 1191 (1931).
57. H. P. Crocker and R. H. Hall, J. Chem. Soc., 2052 (1953).
58. I. N. Nazarov, S. M. Makin, V. K. Kruptsov, and V. A. Mironov, Zhur. Obshch. Khim., 29, 111 (1959).
59. B. M. Mikhailov and L. S. Povarov, Zhur. Obshch. Khim., 29, 2079 (1959).
60. C. D. Hurd and M. A. Pollack, J. Amer. Chem. Soc., 60, 1905 (1938).
61. C. Moureu, Bull. Soc. chim. France, (3), 31, 499 (1904).
62. F. Sigmund and R. Uchann, Monatsh., 51, 234 (1929).
63. A. E. Arbuzov and B. M. Mikhailov, Zhur. Obshch. Khim., 6, 390 (1936).
64. C. A. Mackenzie and J. H. Stocker, J. Org. Chem., 20, 1695 (1955).
65. Z. M. Utintseva, Uch. Zap. Kaz. Gos. Univ., 101, No. 3; Sborn. Stud. Rabot, No. 2, 64 (1941).
66. A. Kirrman, Bull. Soc. chim. France, (5), 6, 848 (1939).
67. G. P. 614 462; Chem. Zentr., II, 2246 (1935).
68. D. B. Killian, C. F. Hennion, and J. A. Nieuwland, J. Amer. Chem. Soc., 56, 1384 (1934).
69. F. P. 710 602; Chem. Zentr., I, 1438 (1932).
70. G. P. 560 354; Chem. Zentr., II, 3960 (1932).
71. M. G. Voronkov, Zhur. Obshch. Khim., 20, 2060 (1956).
72. J. Dechamps, M. Paty, and P. Pineau, Compt. rend., 238, 2006 (1954).
73. M. G. Voronkov, Zhur. Fiz. Khim., 22, 975 (1948).
74. R. H. Hall, A. R. Philpotts, E. S. Stern, and W. Thain, J. Chem. Soc., 3341 (1951).
75. P. Mastagli and A. Floc'h, Bull. Soc. chim. France, 21, 51 (1954).
76. E. Fiecher, Monatsh., 51, 240 (1929).
77. U. S. P. 2 578 724; Chem. Abs., 46, 6666 (1952).
78. J. F. Arens, J. Vegter, and T. de Boer, Rec. Trav. chim., 77, 753 (1958).
79. S. M. McElvan and M. J. Curry, J. Amer. Chem. Soc., 70, 3784 (1948).
80. Jap. P. 158 (1958); Chem. Abs., 52, 19 953 (1958).
81. L. Claisen, Ber., 29, 1005 (1886).
82. S. Ruheman and E. Wragg, J. Chem. Soc., 79, 1190 (1901).
83. C. Moureu, Compt. rend., 138, 286 (1904).
84. M. A. Dolliver *et al.*, J. Amer. Chem. Soc., 60, 440 (1938).
85. S. Ruhemann and F. Beddow, J. Chem. Soc., 77, 984 (1900).
86. S. Ruhemann and F. Beddow, J. Chem. Soc., 77, 1119 (1900).
87. A. E. Tschitshibabin, J. prakt. Chem., (2), 74, 423 (1906).
88. W. M. Lauer and M. A. Spielman, J. Amer. Chem. Soc., 53, 1533 (1931).
89. W. M. Lauer and M. A. Spielman, J. Amer. Chem. Soc., 55, 4923 (1933).
90. L. C. Swallen and C. E. Boord, J. Amer. Chem. Soc., 52, 651 (1930).
91. H. B. Dynstra, J. F. Lewis, and C. E. Boord, J. Amer. Chem. Soc., 52, 3396 (1930).
92. A. N. Nesmeyanov, I. F. Lutsenko, and N. I. Vereshchagina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 67 (1947).
93. M. F. Shostakovskii and M. Mamedov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1636 (1959).
94. M. F. Shostakovskii and M. Mamedov, Zhur. Obshch. Khim., 29, 3922 (1959).
95. A. A. Petrov, Zhur. Obshch. Khim., 4, 1217 (1934).
96. V. I. Isagulyants and I. S. Maksimova, Dokl. Akad. Nauk Armyansk. SSR, 22, 203 (1956); Zhur. Prikl. Khim., 30, 775 (1957).
97. M. V. Likhosherstov and S. V. Alekseev, Zhur. Obshch. Khim., 4, 1281 (1934).
98. V. I. Isagulyants and I. S. Maksimova, Dokl. Akad. Nauk, 114, 102 (1957); Zhur. Prikl. Khim., 31, 1578 (1958).
99. M. L. Scherill and G. F. Walter, J. Amer. Chem. Soc., 58, 742 (1936).
100. C. G. Schmitt and C. E. Boord, J. Amer. Chem. Soc., 54, 758 (1932).
101. R. Pineau, J. rech. Centre nat. rech. scient., No. 14, 302, (1951).
102. C. M. Hill, R. M. Prigmore, and G. J. Moore, J. Amer. Chem. Soc., 77, 352 (1955).
103. S. Winstein and L. L. Ingraham, J. Amer. Chem. Soc., 77, 1738 (1955).
104. M. Tiffeneau, Compt. rend., 145, 813 (1907).
105. C. M. Hill, R. A. Walker, and M. E. Hill, J. Amer. Chem. Soc., 73, 1663 (1951).
106. H. Böhme and H. Bentler, Ber., 89, 1468 (1956).
107. C. M. Hill, R. Woodberry, D. S. Simmons, M. E. Hill, and L. Haynes, J. Amer. Chem. Soc., 80, 4602 (1958).
108. J. L. E. Erickson and M. Z. Woskow, Org. Chem., 23, 670 (1958).
109. M. F. Shostakovskii and A. V. Bogdanova, Zhur. Obshch.

Khim., 17, 565 (1947).
110. A. E. Favorskii and M. N. Shchukina, Zhur. Obshch. Khim., 15, 385 (1945).
111. M. F. Shostakovskii, Yu. B. Kagan, and F. P. Sidel'kovskaya, Zhur. Obshch. Khim., 17, 963 (1947).
112. M. N. Shchukina, Zhur. Obshch. Khim., 18, 1350 (1948).
113. M. F. Shostakovskii and F. P. Sidel'kovskaya, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 394 (1950).
114. M. F. Shostakovskii and F. P. Sidel'kovskaya, "Sintezy Organicheskikh Soedinenii" (Organic Syntheses), Izd. Akad. Nauk SSSR, Vol. 2, 1952, p. 144.
115. J. Ficini, Bull. Soc. chim. France, 21, 1367 (1954).
116. J. F. Arens, Rec. Trav. chim., 74, 271 (1955).
117. I. N. Nazarov, Zh. A. Krasnaya, and V. P. Vinogradov, Zhur. Obshch. Khim., 28, 460 (1958).
118. M. F. Shostakovskii and F. P. Sidel'kovskaya, Zhur. Obshch. Khim., 20, 620 (1950).
119. L. Godefroy, Compt. rend., 102, 869 (1886).
120. I. A. Smith, J. Chem. Soc., 1099 (1927).
121. T. L. Jacobs and W. R. Scott, J. Amer. Chem. Soc., 75, 5500 (1953).
122. F. Neher and W. Foster, J. Amer. Chem. Soc., 31, 413 (1909).
123. F. Neher and C. L. Fleece, J. Amer. Chem. Soc., 48, 2416 (1926).
124. T. L. Jacobs, R. Gramer, and J. E. Hanson, J. Amer. Chem. Soc., 64, 223 (1942).
125. D. A. Van Dorp, J. F. Arens, and O. Stephenson, Rec. Trav. chim., 70, 289 (1951).
126. E. Victoria, Rec. Trav. chim., 24, 291 (1905).
127. A. E. Favorskii and M. N. Schukina, Zhur. Obshch. Khim., 15, 394 (1945).
128. R. Broekema, S. Van Der Werf, and J. F. Arens, Rec. Trav. chim., 77, 258 (1958).
129. A. J. Birch, J. Chem. Soc., 1647 (1947),
130. M. S. Newman and A. Kuther, J. Amer. Chem. Soc., 73, 4204 (1951).
131. A. Schönberg and L. Vargha, Annalen, 483, 176 (1930).
132. W. Wislecenus and E. A. Bilhuber, Ber., 51, 1366 (1918).
133. E. Späth, Monatsh., 36, 1 (1915).
134. J. Ficini and A. Normant, Compt. rend., 237, 731 (1953).
135. A. Geuther and E. Fischer, Jahr. bericht. Fortschritte der Chemie, 316 (1864).
136. A. Geuther, Z. phys. Chem., 128 (1871).
137. L. Henry, Ber., 1839 (1879).
138. G. Oddo and E. Mamell, Gazzetta, 33, 11, 383 (1903).
139. A. Sabaneeva, Zhur. Russ. Fiz.-Khim. Obshch., 17, 173 (1885).
140. J. V. Nef, Annalen, 298, 334 (1897).
141. D. Strömholm, Ber., 33, 840 (1900).
142. J. Loevenich, J. Losen, and A. Dietrichs, Ber., 60, 950 (1927).
143. W. E. Truce and M. M. Boudakian, J. Amer. Chem. Soc., 78, 2748 (1956).
144. N. W. Cusa and H. McCombie, J. Chem. Soc., 767 (1937).
145. F. Montanari and G. Modene, Gazzetta, 86, 432 (1956).
146. W. E. Truce and R. Kassinger, J. Amer. Chem. Soc., 80, 6450 (1958).
147. H. J. Backer, J. Strating, and J. F. A. Hazenberg, Rec. Trav. chim., 72, 813 (1953).
148. W. E. Truce, J. A. Simms, and M. M. Boudakian, J. Amer. Chem. Soc., 78, 695 (1956).
149. W. E. Truce and J. A. Simms, J. Amer. Chem. Soc., 78, 2756 (1956).
150. W. E. Truce, H. E. Hill, and M. M. Boudakian, J. Amer. Chem. Soc., 78, 2760 (1956).
151. W. E. Truce and R. F. Heine, J. Amer. Chem. Soc., 79, 1770 (1957).
152. W. E. Truce and R. F. Heine, J. Amer. Chem. Soc., 79, 5311 (1957).
153. E. P. Kohler and H. Potter, J. Amer. Chem. Soc., 57, 1316 (1935).
154. F. Montanari and A. Negrini, Gazzetta, 87, 1061 (1957).
155. R. Escales and E. Baumann, Ber., 19, 1787 (1886).
156. T. Posner, Ber., 32, 2801 (1900).
157. D. S. Tarbell and D. P. Harnisch, Chem. Rev., 49, 67 (1951).
158. P. J. Wiezewich, L. B. Turner, and P. K. Florich, Ind. Eng. Chem., 25, 295 (1933).
159. U. S. P. 2 066 191; Chem. Abs., 31, 1038 (1937).
160. A. Sporzynski, Chem. Zentr., II, 1704 (1936).
161. A. Schönberg and O. Schütz, Ber., 62, 2322 (1929).
162. W. Autenrith, Annalen, 254, 222 (1889).
163. S. Ruheman and H. E. Stapleton, J. Chem. Soc., 77, 1179 (1900).
164. H. Böhme and H. Bentler, Ber., 86, 1464 (1956).
165. J. F. Arens and T. Doornbos, Rec. Trav. chim., 75, 481 (1956).
166. H. Böhme, H. D. Lohmeyer, and I. Wickop, Annalen, 587, 51 (1954).
167. E. Angelleti, F. Montanari, and A. Negrini, Gazzetta, 87, 1086 (1957).
168. N. Kharasch and S. J. Assony, J. Amer. Chem. Soc., 75, 1081 (1953).
169. F. Montanari, Gazzetta, 86, 406 (1956).
170. R. C. Fuson, C. C. Price, *et al.*, J. Org. Chem., 469 (1946).
171. A. Brintzinger and H. Ellwanger, Ber., 87, 300 (1954).
172. K. R. Brower and I. B. Douglass, J. Amer. Chem. Soc., 73, 5787 (1951).
173. H. Böhme and H. J. Gran, Annalen, 577, 68 (1952).
174. W. E. Lawson and T. P. Dawson, J. Amer. Chem. Soc., 49, 3119 (1927).
175. E. Angeletti, F. Montanari, and A. Negrini, Gazzetta, 87, 1115 (1957).
176. V. I. Isagulyants, Dokl. Akad. Nauk Armyansk. SSR, 1, 13 (1944).
177. F. Montanari and A. Negrini, Boll. sci. Fac. Chim. Ind. Bologna, 14, 68 (1956).
178. D. S. Tarbell and M. A. McCall, J. Amer. Chem. Soc., 74, 48 (1952).
179. D. S. Tarbell and W. E. Lovett, J. Amer. Chem. Soc., 78, 2259 (1956).
180. E. N. Karaulova, D. Sh. Meilanova, and G. D. Gal'pern, Dokl. Akad. Nauk SSSR, 113, 1280 (1957).
181. E. N. Karaulova, D. Sh. Meilanova, and G. D. Gal'pern, "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds in Petroleum and Its Products), Izd. Akad. Nauk SSSR, 1959, p. 164.
182. D. S. Tarbell, "Organic Reactions" (Translated into Russian), Izd. Akad. Nauk SSSR, Vol. 2, 1957, p. 7.
183. J. C. Krantz, *et al.*, Chem. Abs., 37, 4799 (1943).
184. C. D. Leake and Mei Iü Chen, Chem. Zentr., I, 2081 (1931).
185. M. F. Shostakovskii and E. N. Prilezhaeva, Zhur. Obshch. Khim., 17, 1129 (1947).
186. M. F. Shostakovskii, E. N. Prilezhaeva, and N. I. Uvarova, Zhur. Prikl. Khim., 26, 1074 (1953).
187. V. S. Abramov and A. P. Pakhomov, Zhur. Obshch. Khim., 24, 1198 (1954).
188. B. P. 630 926; Chem. Abs., 44, 4021 (1950).
189. U. S. P. 2 533 172; Chem. Abs., 45, 367 (1951).
190. U. S. P. 2 662 919; Chem. Abs., 49, 367 (1955).
191. L. Kh. Freidlin and V. Z. Sharf, Dokl. Akad. Nauk SSSR, 124, 849 (1959).
192. G. P. 209 268; Chem. Zentr., I, 1785 (1909).
193. F. P. 375 167; Chem. Abs., 2, 2600 (1908).
194. G. P. 210 502; Chem. Zentr., II, 78 (1909).
195. H. Crompton and P. M. Triffitt, J. Chem. Soc., 119, 1874 (1921).

196. I. A. Shikhiev, N. V. Komarov, and I. Aslanov, Uspekhi Khim., 27, 1504 (1954).
197. M. F. Shostakovskii and M. G. Zelenskaya, Zhur. Prikl. Khim., 25, 1221 (1952).
198. E. Levas and M. Levas, Compt. rend., 228, 100 (1949).
199. M. F. Shostakovskii, Zhur. Obshch. Khim., 20, 608 (1950).
200. M. F. Shostakovskii, A. B. Kalabina, and A. D. Dariev, Zhur. Obshch. Khim., Suppl. 2, 1297 (1953).
201. M. F. Shostakovskii, B.M.Mikhant'ev, and N.N.Ovchinnikova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1099 (1952).
202. M. F. Shostakovskii, M. I. Batuev, V. I. Belyaev, and A. D. Matveeva, Dokl. Akad. Nauk SSSR, 94, 261 (1954).
203. M. F. Shostakovskii and M. R. Kulibekov, Zhur. Obshch. Khim., 28, 578 (1958).
204. A. A. Baum and G. F. Hennion, J. Amer. Chem. Soc., 60, 569 (1938).
205. H. W. Post, J. Amer. Chem. Soc., 55, 4176 (1933).
206. M. F. Shostakovskii, E. P. Gracheva, and N. K. Kul'bovskaya, Zhur. Obshch. Khim., 28, 2344 (1958).
207. T. Temnikova and S. Myukhyurdari, Zhur. Obshch. Khim., 24, 1819 (1954).
208. G. A. Ugol'nikova, Zhur. Obshch. Khim., 27, 343 (1957).
209. G. A. Ugol'nikova, Vestnik Leningrad Gos. Univ., No. 10, 106 (1957).
210. C. R. Rix and J. F. Arens, Proc. k. ned. Akad. Wetenschap., 56, 372 (1953).
211. L. Heslinga and J. F. Arens, Rec. Trav. chim., 76, 982 (1957).
212. F. Straus and H. G. Weber, Annalen, 498, 101 (1932).
213. M. F. Shostakovskii, E. P. Gracheva, and N. K. Kul'bovskaya, Zhur. Obshch. Khim., 28, 2341 (1958).
214. M. F. Shostakovskii and A. V. Bogdanova, Zhur. Obshch. Khim., 20, 1326 (1950).
215. G. E. Hall and I. Sirel, J. Amer. Chem. Soc., 74, 836 (1952).
216. L. Godefroy, Compt. rend., 102, 869 (1886).
217. J. Busch, Ber., 11, 445 (1878).
218. R. J. Hoaglin and D. H. Hirsch, J. Amer. Chem. Soc., 71, 3468 (1949).
219. L. A. Yanovskaya, Uspekhi Khim., 28, 948 (1959).
220. O. Isler, H. Lindlar, M. Moutavon, R. Rüegg, and P. Zeller, Helv. Chim. Acta, 39, 249 (1956).
221. Jap. P. 4678; Ref. Zhur. Khim., 12753 P (1959).
222. O. Isler, M. Moutavon, R. Rüegg, and P. Zeller, Annalen, 603, 129 (1957).
223. I.N.Nazarov, I. I. Nazarova, and I. V. Torgov, Dokl. Akad. Nauk SSSR, 122, 82 (1958).
224. A. F. Plate and T. A. Meerovich, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 219 (1947).
225. A. F. Shostakovskii, A. V. Bogdanova, and T. M. Ushakova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1245 (1957).
226. V. S. Abramov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 330 (1945); 60 (1944).
227. V. S. Abramov and L. A. Shapshinskaya, Zhur. Obshch. Khim., 22, 1450 (1952).
228. C. W. Smith, D. G. Norton, and S. A. Ballard, J. Amer. Chem. Soc., 73, 5267 (1951).
229. R. L. Lougley and W. S. Emerson, J. Amer. Chem. Soc., 72, 3079 (1950).
230. B. P. 378644; Chem. Zentr., II, 3183 (1932).
231. C.E.Schildknecht, "Vinyl and Related Polymers", London, 1952, p. 617.
232. C. E. Schildknecht, Ind. Eng. Chem., 50, 107 (1958).
233. M. F. Shostakovskii and E. P. Gracheva, Zhur. Obshch. Khim., 26, 1679 (1956).
234. W. Wislicenus and K. Schöllkopf, J. prakt. Chem., 95, 297 (1917).
235. U. S. P. 2415878; Chem. Abs., 41, 3810 (1947).
236. L. Claisen and E. Haase, Ber., 33, 3778 (1900).
237. M. F. Shostakovskii and E. N. Prilezhaeva, "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds in Petroleum and Its Products), Izd. Akad. Nauk SSSR, 1959, p. 337.
238. M. F. Shostakovskii, E. N. Prilezhaeva, and N. I. Uvarova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 154 (1955).
239. K. Alder, H. F. Rieckert, and E. Windemuth, Ber., 71, 2451 (1938).
240. M. F. Shostakovskii, A. V. Bogdanova, and T. M. Ushakova, Dokl. Akad. Nauk SSSR, 118, 520 (1958).
241. M. F. Shostakovskii, E. N. Prilezhaeva, and N. T. Uvarova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1245 (1955).
242. J. F. Arens, A. C. Herman, and A. S. Weiland, Prok. k. ned. Akad. Wetenschap., 58, 78 (1955).
243. H. Böhme, H. Fischer, and R. Frank, Annalen, 563, 54 (1949).
244. L. Bateman and F. W. Shipley, J. Chem. Soc., 2888 (1958).
245. N. Kharasch and S. J. Assony, J. Amer. Chem. Soc., 77, 3390 (1955).
246. F. Montanari, Gazzetta, 86, 406 (1956).
247. F. Montanari, Gazzetta, 86, 420 (1956).
248. F. Montanari, Gazzetta, 86, 415 (1956).
249. M. F. Shostakovskii and E. N. Prilezhaeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 517 (1954).

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MODERN VIEWS ON GELATION IN POLYMER SOLUTIONS AND ON THE STRUCTURE OF GELS

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1. INTRODUCTION

The problem of gelation in polymer solutions is of great theoretical and practical interest. The practical importance of the study of gelation is due to the fact that it is necessary to obtain gels having definite physicochemical properties in several branches of industry (*e.g.* in the food, soap, paint, and other industries); but in several other