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Sulfur-Containing Vinyl Ethers

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SULFUR-CONTAINING VINYL ETHERS

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Synthesis and properties of sulfur-containing vinyl ethers with sulfide, thiol, sulfoxide, tosylate, isothiocyanate, thiocarbamate, and thiirane functions are discussed.

Key words: Vinylation, acetylene, 2-hydroxyethyl sulfides, ethanolamines, vinyl ether, 2-(vinyloxy)ethyl isothiocyanate, 2-(vinyloxy)ethoxymethylthiirane, thioureas, isothiocyanates, thiocarbamates, amino thiols, thiiranes, acetals, acylals.

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1. INTRODUCTION

The reactions of acetylene give much promise for the synthesis of diverse unsaturated sulfur-containing polyfunctional compounds from sulfur and nitrogen analogs of diols (thioglycols and ethanolamines).[1] These reactions as extended to sulfur- and nitrogen-containing compounds with functional groups which make it possible not only to prepare new interesting classes of substances, but to reveal novel "daughter" reactions, unexpected effects and earlier known properties of the products.

One of the most extensively developing trends in this field is the reaction of thio alkanols and their ethers with acetylene.[1] Anomalous processes found in the vinylation of some diols in cases of their sulfur analogs turned out to be more clearly expressed.

At the same time, for the past decades, much concern has been given to a systematic search for simple routes to new unsaturated (linear and cyclic) sulfur-nitrogen-containing monomers, reagents and intermediates from available ethanolamines and acetylene.

The summarized and critically considered material of the present review indicates that the synthesis of sulfur-containing vinyl ethers based on the selective transformation of functional structural elements of some parent compounds with retention of the active double bond,[1] is ever developing. This approach was further applied successively to large groups of functionally substituted sulfur- and nitrogen-containing vinyl ethers and vinyl sulfides. In most cases the results attained support the synthetic versatility of this approach.

2. PREPARATION OF SULFUR-CONTAINING VINYL ETHERS

2.1. *Vinylation of Sulfur-Containing Alcohols with Acetylene*

2.1.1. β-*Sulfur-containing alcohols* According to Shostakovsky *et al.*,[2] in the vinylation of 2-(ethylthio)ethanol with acetylene (135–145 °C, 20% KOH) the expected vinyl ether **1** is obtained in 40–60% yield. Later it has been shown that

in this reaction together with vinyl ether **1** ethyl vinyl sulfide is also formed in a yield up to 36%.[3]

$$C_2H_5S(CH_2)_2OH + HC{\equiv}CH \xrightarrow[140\text{–}245^\circ C]{KOH} \underset{\mathbf{1}}{C_2H_5S(CH_2)_2OCH{=}CH_2} + C_2H_5SCH{=}CH_2 + [-CH_2CH_2O-]_n$$

Scheme 1

The second fraction of the cleaved molecule of 2-(ethylthio)ethanol, ethylene oxide, is mainly subject to polymerization. High-boiling products turned out to be ethylene oxide oligomers with terminal ethylthio, hydroxy and vinyloxy groups of the type

$$C_2H_5S(CH_2CH_2O)_{1\text{–}4}(CH_2)_2OH$$

The corresponding monomer oxide (propylene oxide) was identified (GLC) in the vinylation of 2-(ethylthio)propanol-1 for which the above cleavage is even more clearly defined.[3]

2-(Ethylthio)ethanol vinyl ether is prone to analogous cleavage under vinylation conditions. In the reaction with acetylene in the presence of 5% KOH at 215 °C under pressure, it affords ethyl vinyl sulfide in 15% yield.[3] A few possible routes to ethyl vinyl sulfide from 2-(ethylthio)ethanol during its vinylation have been considered:[4]

(*a*) dehydration[5–8]

$$C_2H_5S(CH_2)_2OH \xrightarrow[-H_2O]{KOH} C_2H_5SCH{=}CH_2$$

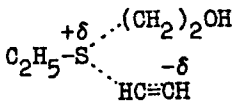
Scheme 2

(*b*) elimination of ethanethiolate, followed by vinylation (stepwise elimination-addition)

$$C_2H_5S(CH_2)_2OH \xrightarrow{KOH} C_2H_5S^- \xrightarrow{HC{\equiv}CH} C_2H_5SCH{=}CH_2$$

Scheme 3

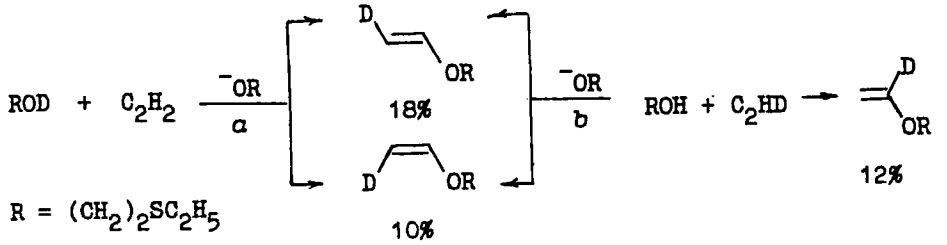
(*c*) direct participation of acetylene in the cleavage of the C-S bond (synchronous elimination-addition)



Scheme 4

The possibility of dehydration of 2-(ethylthio)ethanol during vinylation was experimentally checked[3] by its heating in an atmosphere of nitrogen under analogous reaction conditions, but without acetylene. The reaction mixture contained 1.6% of ethyl vinyl sulfide (GLC), thus showing the dehydration to be negligible. The assumption that ethyl vinyl sulfide is formed exclusively due to the dehydration of 2-(ethylthio)ethanol does not agree with the fact of its presence among the reaction products of vinyl ether **1** and acetylene. More reliable data concerning the nature of this reaction have been obtained with deuterium-labelled acetylene.[3] The ^{1}H NMR spectrum of 2-(ethylthio)ethanol recovered from the reaction shows that the acetylene deuterium is nearly completely exchanged for the hydroxy group hydrogen.

Vinylation is considered[9–11] to be a stereospecific reaction exclusively leading to *Z*-isomers. However, the work done in this field mainly deals with the addition of thiols to monosubstituted acetylenes. The conclusions thus drawn can hardly be extended to the classical example of vinylation involving alcohol and unsubstituted acetylene. In this respect, analysis of the ratio of deuterated isomers of 2-(ethylthio)ethanol vinyl ether obtained with deuteroacetylene, was of some value. In fact, it provided supplementary information on the stereochemistry of vinylation. Of a number of possible combinations of deuterated reagents the greatest contribution (with exception of the reaction leading to an undeuterated product) is established[3] to be made by the following isomers:



Scheme 5

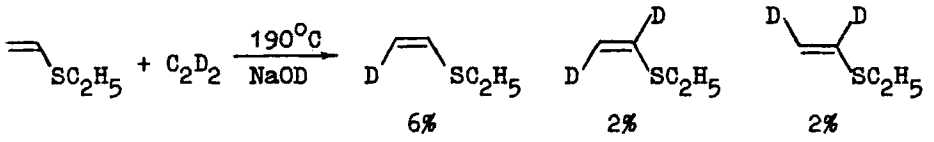
If the vinylation reaction is not stereoselective the ratio of β-deuterated *Z*- and *E*-forms should equal 1. In fact the ratio is approaching 2 (18% *E* and 10% *Z*).[3]

In the case of *Z*-addition the vinyl ether generated should contain about 20% *Z*-form according to reaction *a* and the known ROD content (20%) in the reaction mixture.[3] Under the same conditions reaction *b* should give a mixture of α-deuterated product and β-deuterated *E*-form in equal proportions, which was

not observed. On the contrary, the assumption of a concerted *trans*-addition is fully consistent with the experimental data. Indeed, the reaction mixture contained about 18% of *E*-isomer which corresponds to the quantity expected according to reaction *a*. On the other hand, reaction *b* leads to the *Z*-form which should be present in nearly equal quantities with the α-deuterated product, which was also consistent with the experiment. Consequently, we have to do with a concerted *trans*-addition:

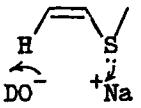
Scheme 6

A study of isotopic exchange between ethyl vinyl sulfide and deuteroacetylene has shown that under the reaction conditions (190 °C, 1 h, 5% NaOD) about 10% of deuterium is introduced into vinyl sulfide.[3] The isotope is located in the vinyl group, the major portion (6%) belonging to the *Z*-form, while the *E*-form has not been found at all (NMR, mass spectrometry).



Scheme 7

Thus, the hydrogen atom in the *cis*-position with respect to the sulfur atom turned out to be most mobile which does not agree with the normal mechanism of *trans*-elimination. This seems to be due to the fact that NaOD is insoluble in ethyl vinyl sulfide and therefore the reaction proceeds as a heterogeneous process on the interface, the substrate being probably held by coordination to the sulfur atom.



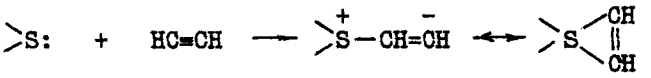
Scheme 8

The presence of a mixture of dideuterated vinyl isotopomers in the absence of monodeuterated *Z*- and α-forms as well as the dideuterated geminal isotopomer indicate that reversible vinylation of thiols takes place under the given conditions.

From the ^1H NMR spectrum of ethyl vinyl sulfide obtained by vinylation of 2-(ethylthio)ethanol-*D* (85% of $C_2H_5SCH_2CH_2OD$) the yields of $CD_2{=}CDSC_2H_5$ and $CH_2{=}CHSC_2H_5$ are 65 and 35%, respectively.[3] The absence of partially deuterated products (no more than 5% of $CHD{=}CDSC_2H_5$) deserves attention.

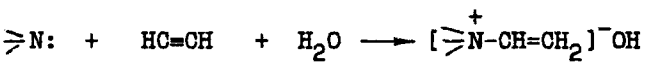
A considerable predominance of vinyl sulfide totally deuterated in the vinyl group shows that the dehydration of 2-(ethylthio)ethanol is not the main reason for the formation of vinyl sulfide, although it seemingly also occurs which is indicated by the presence of undeuterated ethyl vinyl sulfide in the reaction mixture.[3] Vinyl sulfide was considered to be formed chiefly by cleavage of the C—S bond.

The preparation of α,β-unsaturated sulfides by cleavage of $RSCH_2CH(SR)_2$ and $RSCH(C_6H_5)CH_2SR$ (R is mainly alkyl) with bases in the presence of acetylene is known.[12-15] Schneider and Bagnell[13] explain this reaction by elimination and subsequent vinylation of the thiol, neglecting any role of acetylene in the cleavage of the C—S bond. The facts[3] suggest possible intermolecular interaction between the sulfide sulfur atom and acetylene leading to the formation of a bipolar ion (quasi-sulfonium center).[16-19]



Scheme 9

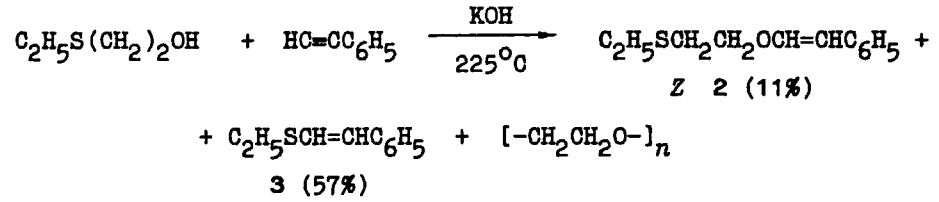
This interaction was supposed to be to some extent similar to the reaction of tertiary amines with acetylene:[20,21]



Scheme 10

The above suggestion concerning the formation of the bipolar ion is based on the onium properties of the sulfur atom, the high polarizability of the acetylene molecule, the possibility of π-electron transfer to vacant orbitals of the sulfur atom, and the decrease in the energy of the complex due to *p*-π-overlap during the closure of the three-membered ring. The conclusion has been drawn[4] that the cleavage of the C—S bond observed in the reaction with acetylene under base-catalyzed conditions should be a general property of compounds prone to effectively stabilize the fragments formed and, first of all, those having in the β-position with respect to the sulfur atom another heteroatom with lone electron pairs. The ready decomposition of β-hydroxyalkyl substituted ammonium bases is an analogy.[22,23]

The reaction of 2-(ethylthio)ethanol with phenylacetylene in the presence of potassium hydroxide follows the scheme:[19]



Scheme 11

In this case cleavage of the C-S bond becomes the main reaction, the yield of 1-phenyl-2-(ethylthio)ethene **3** reaching 57%. At the same time, the classic vinylation is reduced to a level of intermediate process, the yield of the β-phenylvinyl ether **2** being as low as 11%.

The isolation of the sulfide **3** presents additional evidence for the fact that dehydration is not the main reason for the formation of anomalous products. In the reaction mixture neither ethyl vinyl sulfide nor ethanethiol were detected (GLC). Under comparable conditions, but without phenylacetylene, no more than 2% of ethyl vinyl sulfide is formed, ethanethiol being found in traces (0.1%, GLC). This, in principle negative, analysis for the presence of ethanethiol testifies against the two-stage scheme, "elimination-addition".

The sulfide **3** formed by cleavage of 2-(ethylthio)ethanol with phenylacetylene consists mainly of the *E*-isomer (70%).[19] Truce *et al.*[24–27] believe that the nucleophilic addition of thiols to phenylacetylene leads exclusively to (*Z*)-1-phenyl-2-[alkyl(aryl)thio]ethenes. From this it was concluded that cleavage of 2-(ethylthio)ethanol is not a stepwise process like the "elimination-vinylation", since only the *Z*-isomer should be formed in this case. However, the absence of *cis-trans*-isomerization under the cleavage conditions (200–225 °C) was doubted[28] (in particular, relying on[29]). A study of the stereochemistry of the addition of ethanethiol to phenylacetylene in the 100–225 °C temperature range in the presence of KOH was carried out. It shows that even if this reaction is stereospecific, the final result is distorted by parallel *cis-trans*-isomerization.[28] Under comparatively mild conditions (100–120 °C) the *Z*-isomer is mainly formed indeed. With increasing reaction temperature and time the ratio is changed in favor of the *E*-isomer. Under the conditions corresponding completely to those of the cleavage of 2-(ethylthio)ethanol with phenylacetylene, seemingly the same mixture of isomers close to equilibrium (65–71% *E*-isomer) is formed. Thus, due to fast isomerization the isomeric content of the 1-phenyl-2-(ethylthio)ethene formed cannot be of use in analyzing the stereochemistry of elimination.

The configuration of the "normal" reaction product, the β-phenylvinyl ether of 2-(ethylthio)ethanol, was established by ^{1}H NMR.[19] The coupling constant of the olefinic protons (7.1 Hz) shows a *cis*-array of hydrogen atoms at the double bond. Thus, unlike vinyl sulfides, β-substituted vinyl ethers are not subject to any noticeable *cis-trans*-isomerization under vinylation conditions.

Discussing the general features of the cleavage of β-sulfur-containing alcohols in vinylation one cannot but notice that the base-catalyzed interaction of 2,2-

bis(alkylthio)propanols with acetylene (130–140 °C, 10% KOH, dioxan) occurs evidently without complications and leads to the corresponding vinyl ethers in 60–70% yield.[30,31]

$$(RS)_2C(CH_3)CH_2OH + HC{\equiv}CH \xrightarrow[130\text{–}140^{\circ}C]{KOH} (RS)_2C(CH_3)CH_2OCH{=}CH_2$$

$R = n\text{-}C_3H_7,\ i\text{-}C_3H_7,\ n\text{-}C_4H_9,\ i\text{-}C_4H_9$

Scheme 12

In this work, however, the authors did not intend to identify abnormal reaction products.

2.1.2. *Bis(2-hydroxyethyl) sulfide and other sulfur analogs of diols* A study of the vinylation of some sulfur analogs of ethylene glycol such as bis(2-hydroxyethyl) sulfide (thiodiglycol),[32] 1,2-ethanedithiol, and 2-mercaptoethylthioethanethiol[33] was carried out. These sulfides and dithiols behave in a peculiar manner in the vinylation reaction. The direct synthesis of thioglycol vinyl ethers was examined previously with 2-mercaptoethanol.[34]

Similarly to 2-(ethylthio)ethanol and 2-(ethylthio)propanol-1, under the vinylation conditions (120–140 °C, 5% KOH) thiodiglycol undergoes considerable cleavage (up to 50%) at the sulfide bonds, which gives, together with the expected vinyl ethers **4** and **5**, anomalous products, the vinyl ethers of 2-mercaptoethanol **6** and **7**.

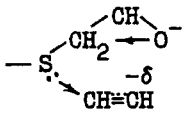
$$(HOCH_2CH_2)_2S \xrightarrow[KOH]{HC{\equiv}CH} \begin{cases} CH_2{=}CHO(CH_2)_2S(CH_2)_2OH \ (\mathbf{4}) + (CH_2{=}CHOCH_2CH_2)_2S \ (\mathbf{5}) \\ CH_2{=}CHS(CH_2)_2OH \ (\mathbf{6}) + CH_2{=}CHS(CH_2)_2OCH{=}CH_2 \ (\mathbf{7}) \end{cases}$$

Scheme 13

Control tests in the absence of acetylene again failed to support the scheme of dehydration.

Thus, cleavage of the C—S bond under vinylation conditions should be regarded as a reaction common to β-hydroxyethyl sulfides. The cleavage is likely to start with interaction of the sulfide bridge and acetylene of a nucleophilic attack type,[32] which results in cleavage of the sulfur-hydroxyalkyl bond and the formation of a stronger sulfur-vinyl bond.

The following transition state appears quite probable:

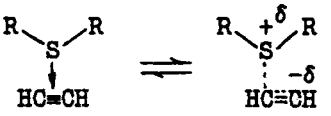


Scheme 14

Analyzing the above mechanism it is necessary to take into account that the C—S bond in β-hydroxyethyl sulfides may differ much in its reactivity from an analogous bond in dialkyl sulfides. As known, in some systems with β-alternation of heteroatoms the carbon-heteroatom bonds are noticeably weakened. Thus, 1,2-dimethoxyethane, unlike monoatomic alcohol ethers, is able to react with organomagnesium reagents (the Iocič complex) at the C—O bond.[35] A reversible interconversion of ethylene glycol and diethylene glycol monoethyl ethers under comparatively mild conditions, followed by cleavage of the C—O bond, has been described.[36] The weakness of polyethylene glycol ether bonds is also apparent in the vinylation reaction, which conditions the appearance of marked quantities of vinyl ethers of low-molecular diols.

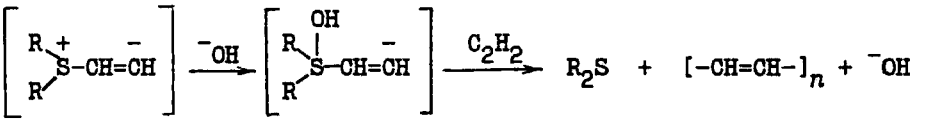
The anomalous reaction of β-hydroxy sulfides with acetylene may formally be regarded as a kind of substitution of the β-hydroxyalkyl group by a vinyl group. In this case it should be borne in mind that this exchange must be accompanied by a certain energy gain due to the appearance of p-π-conjugation in the $CH_2=CHS$ system. Nevertheless, the determining prerequisite for anomalous vinylation is hidden, beyond any doubt, in the structure of the starting sulfides. This conclusion follows from the different behavior of β-hydroxyethyl sulfides and sulfides without hydroxyl substituents.

Under the vinylation conditions dibutyl sulfide rapidly absorbs a stoichiometric amount (and more) of acetylene, however, eventually, the starting sulfide is recovered nearly totally.[33] The only reaction product is polyacetylene $[-CH=CH-]_n$. In the case of dibutyl ether, although a similar polymerization of acetylene indeed takes place,[4] the reaction rate is much lower and the yield of polyacetylene is not high (43%), the latter being quite different from the polymer obtained in the presence of dibutyl sulfide (a greater amount of a resin-like soluble fraction is formed).[33] These results indicating the activation of acetylene under the effect of the diorganyl sulfide-alkali system may be considered as another argument in favor of specific intermolecular interaction between an alkali metal hydroxide, the sulfide bridge and the carbon-carbon triple bond. Taking into account the fact that sulfides are prone to form sulfonium cations, the above interaction may be modelled in the first approximation as a nucleophilic attack on the polarized triple bond, which results in the formation of a bipolar transition structure.



Scheme 15

The formation of the sulfonium-like intermediate should be facilitated by its stabilization due to the closure of the three-membered ring or *via* "through space" interaction of charges in the same direction owing to the ability of the sulfur atom to expand its outer electron shell. Further the complex can either decompose with cleavage of the S—C bond, if the structure of the starting sulfide favors stabilization of the $RSCH=\overline{C}H$ carbanion and the R fragment (as is the case with β-hydroxyethyl sulfides) or initiates the polymerization of acetylene by an anionic mechanism (if decomposition is energetically disadvantageous).

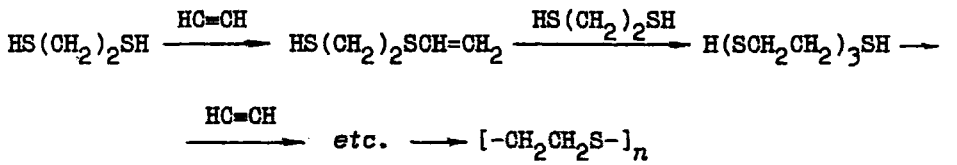


Scheme 16

A certain contribution to the formation of the vinyl sulfides **6** and **7** can also be due to the elimination of vinyl alcohol from the vinyl ethers **4** and **5** like the one occurring with 1,2-bis(vinyloxy)ethane.[37]

Dithiols (1,2-ethanedithiol and bis(2-mercaptoethyl) sulfide) undergo vinylation with similar complications.[33] Under normal conditions vigorous absorption of acetylene starts already at 80–100 °C; however, instead of the expected vinyl sulfides, polyethylene sulfide $[-CH_2CH_2S-]_n$ is formed in nearly quantitative yield. According to its properties and IR spectra, the product obtained from 1,2-ethanedithiol proved to be identical with the product from bis(2-mercaptoethyl) sulfide.[38]

The synthesis of polyethylene sulfide is the result of the superposition of two reactions, *i.e.*, normal vinylation and addition of dithiols or monovinyl derivatives thereof to the vinylthio group (thiylation):



Scheme 17

Interestingly, under these conditions polythiylation cannot be suppressed even

with antioxidants (pyrogallol, hydroquinone, up to 5% of dithiol weight). The polyethylene sulfide had a molecular mass of 1000–1500 as determined by total titration of terminal SH and $CH_2=CHS$ groups in the presence of mercury chloride. For a separate determination of the two groups in the polymer use was made of a combination of the mercury chloride method with hydrolytic oximation. The polyethylene sulfide binds the mercury chloride molecules to form a polymeric complex:

$$[-CH_2CH_2S-]_n$$
$$\downarrow$$
$$HgCl_2$$

Scheme 18

For the synthesis of corresponding divinyl sulfides from dithiols some special conditions have been suggested,[33] which enabled suppression of competing addition to the vinylthio group and led to the formation of 1,2-bis(vinylthio)ethane **8** and bis(2-vinylthioethyl) sulfide **9** in *ca.* 40 and 70% yield, respectively.

$$CH_2=CHS(CH_2)_2SCH=CH_2 \qquad (CH_2=CHSCH_2CH_2)_2S$$
$$\mathbf{8} \qquad\qquad\qquad \mathbf{9}$$

Scheme 19

Vinylation is effected under the following conditions: temperature 80–100 °C; dilution 1:4 (by volume) and more in *t*-butanol or dioxan; two-fold (and more) molar excess of acetylene; in the presence of 0.3–1% (of the weight of the reaction mixture) of pyrogallol or hydroquinone; catalysts, alkali metal hydroxides or alkoxides in an amount of 1.5–7% (of the weight of the reaction mixture); initial acetylene pressure 10–15 atm (autoclave).

It is of interest that the sulfide **9** is formed not only by vinylation of bis(2-mercaptoethyl) sulfide, but by vinylation of 1,2-ethanedithiol. In the latter case the yield of **9** amounts to 30%, the reaction mixture contains hydrogen sulfide. Consequently, the following condensation takes place:

$$2\ RSH \longrightarrow RSR + H_2S$$
$$R = HSCH_2CH_2,\ CH_2=CHSCH_2CH_2$$

Scheme 20

In the vinylation of bis(2-mercaptoethyl) sulfide one should expect, by analogy with diethylene glycol and bis(2-hydroxyethyl) sulfide, decomposition of the molecule. Indeed, in spite of a lower reaction temperature (80 instead of 120 °C) 1,2-bis(vinylthio)ethane **8** was isolated in about 10% yield from the products

of vinylation of bis(2-mercaptoethyl) sulfide. This shows cleavage of the C—S bond. Some representative products of the vinylation of thioglycols are listed in Table 1.

TABLE 1 The products of the vinylation of thioglycols

Cpd. No.	Formula	Yield, %	B.p., °C (*mm* Hg)	n_D^{20}	d_4^{20}	*Ref.*
4	$CH_2=CHO(CH_2)_2S(CH_2)_2OH$	24	86.5(3)	1.5049	1.0836	32, 33
5	$(CH_2=CHOCH_2CH_2)_2S$	9	79.5–80(3)	1.4909	1.0177	32, 33
		43	91–92(3)	1.4910	1.0170	39
		14	112–113(7)	1.4897	1.0126	40
6	$CH_2=CHS(CH_2)_2OH$	30	74–75(9)	1.5220	1.0612	32, 33
		70–75	70–71(6)	1.5221	1.0612	34
7	$CH_2=CHS(CH_2)_2OCH=CH_2$	21	66–67(20)	1.5005	0.9912	32, 33
		70–75	48–48.5(7)	1.5000	0.9903	34
8	$CH_2=CHS(CH_2)_2SCH=CH_2$	36	77.5–78(7)	1.5627	1.0506	33
		68[a]	74.5–75(5)	1.5670	—	41
9	$(CH_2=CHSCH_2CH_2)_2S$	—	57–60(1.6)	—	—	42
		69	143(3)	1.5870	1.1069	33

[a]Hydrolytic vinylation of 1,2-bis(acetylthio)ethane.

Alkaline cleavage of the C—S bond in the presence of acetylene was also used in another route to divinyl derivatives of dithiols, elaborated by Prilezhaeva *et al.*:[41,43]

$$CH_3COS(CH_2)_nSCOCH_3 \xrightarrow[CH_3OH,\ ^-OH]{HC\equiv CH} CH_2=CHS(CH_2)_nSCH=CH_2$$

Scheme 21

In dipolar aprotic solvents (hexamethyl phosphorus triamide, dimethyl sulfoxide) the destructive vinylation of the dithioacetates works already at 10–15 °C, the yield of α,ω-bis(vinylthio)alkanes being 60–76%.[41] This technique is especially attractive because it does not require dithiols which are difficultly accessible and unpleasant to handle since the starting dithioacetates can be obtained from the corresponding dihaloalkanes and sodium thioacetate or by addition of thioacetic acid to dienes.

2.2. *Sulfur-Containing Vinyl Ethers via Vinyloxy Alkanols and Their Sulfur Analogs*

2.2.1. *2-Vinyloxyethyl tosylate* 2-Vinyloxyethyl tosylate has been obtained from 2-(vinyloxy)ethanol and *p*-toluenesulfonyl chloride:[44,45]

$$CH_2{=}CHO(CH_2)_2OH + ClSO_2C_6H_4CH_3 \xrightarrow{C_5H_5N} CH_2{=}CHO(CH_2)_2OSO_2C_6H_4CH_3 + C_5H_5N.HCl$$

Scheme 22

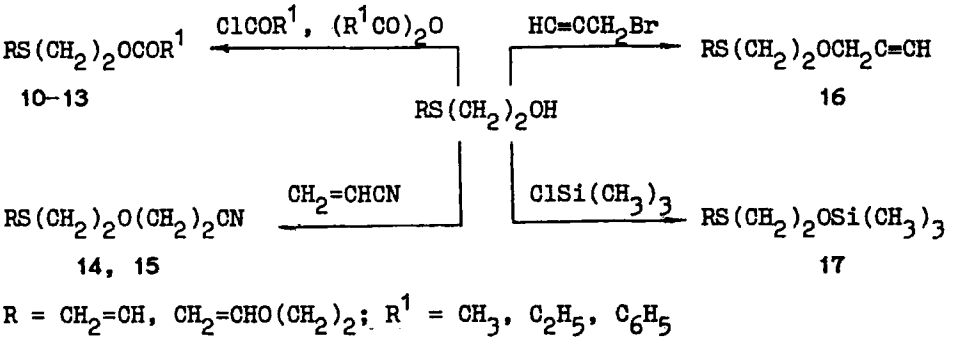
The vinyloxyethyl ester of *p*-toluenesulfonic acid has been used in the synthesis of 2-fluoroethyl vinyl ether:[44]

$$CH_2{=}CHO(CH_2)_2OSO_2C_6H_4CH_3 + KF \longrightarrow CH_2{=}CHOCH_2CH_2F + CH_3C_6H_4SO_3K$$

Scheme 23

The reaction was carried out by heating of the reagents in diethylene glycol with simultaneous distillation of the 2-fluoroethyl vinyl ether formed (the yield is about 30%).

2.2.2. *From vinylated thioglycols* Various acyloxy (**10–13**), cyanoethoxy (**14, 15**), propargyloxy (**16**), and trimethylsiloxy substituted (**17**) vinyl ethers and sulfides have been synthesized[46] from monovinyl derivatives of sulfur analogs of diols (Table 2):



$R = CH_2{=}CH,\ CH_2{=}CHO(CH_2)_2;\ R^1 = CH_3,\ C_2H_5,\ C_6H_5$

Scheme 24

TABLE 2 Thioglycol-based vinyl ethers and sulfides[1,46]

Cpd. No.	Formula	Yield, %	B.p., °C (*mm* Hg)	n_D^{20}	d_4^{20}
10	$CH_2{=}CHS(CH_2)_2OCOCH_3$	71	58–59(3)	1.4911	1.0708
11	$CH_2{=}CHS(CH_2)_2OCOC_2H_5$	70	67(3)	1.4810	1.0428
12	$CH_2{=}CHS(CH_2)_2OCOC_6H_5$	73	139–140(4)	1.5578	1.1328
13	$CH_2{=}CHO(CH_2)_2S(CH_2)_2OCOCH_3$	81	74.5–76(1)	1.4850	1.0802
14	$CH_2{=}CHS(CH_2)_2O(CH_2)_2CN$	59	147–147.5(7)	1.4995	1.0574
15	$CH_2{=}CHO(CH_2)_2S(CH_2)_2O(CH_2)_2CN$	71	168(3)	1.4931	1.0721
16	$CH_2{=}CHS(CH_2)_2OCH_2C{\equiv}CH$	22	82–85(9)	1.5080	1.0197
17	$CH_2{=}CHS(CH_2)_2OSi(CH_3)_3$	45	71(20)	1.4693	0.9482

With radical initiators (2,2′-azobisisobutyric acid dinitrile, di-*t*-butyl peroxide) acyloxyvinyl sulfides are polymerized to colorless solids or viscous resins soluble in organic solvents.[47] Ester groups in the polymer chain undergo ready hydrolysis with dilute alkali which leads to sticky highly water swelling elastomers $[-CH_2CH(SCH_2CH_2OH)-]_n$.[46]

Sulfur-phosphorus-containing vinyl ethers have been synthesized by the following scheme:[48,49]

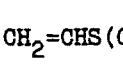
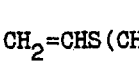
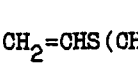
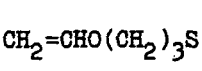
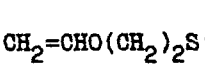
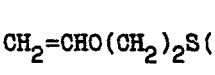
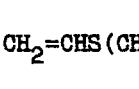
$$RS(CH_2)_2OH + ClP(OR^1)_2 \xrightarrow{C_5H_5N} \underset{\textbf{18–27}}{RS(CH_2)_2OP(OR^1)_2} + C_5H_5N.HCl$$

$R = CH_2{=}CH,\ CH_2{=}CHO(CH_2)_2$

Scheme 25

The substituents R^1, yields and physical data of representative phosphites **18–27** are presented in Table 3.

TABLE 3 Thioglycol-based phosphorus-containing vinyl ethers and sulfides[1,48,49]

Cpd. No.	Formula	Yield, %	B.p., °C (*mm* Hg)	n_D^{20}	d_4^{20}
18	$CH_2{=}CHS(CH_2)_2OP(OC_2H_5)_2$	27	97–97.5(4)	1.4778	1.0627
19	$CH_2{=}CHS(CH_2)_2OP(OC_3H_7)_2$	38	120–121(4)	1.4768	1.0313
20	$CH_2{=}CHS(CH_2)_2OP(OC_4H_9)_2$	50	106–106.5(1)	1.4733	1.0068
21	$CH_2{=}CHS(CH_2)_2OP$ 	70	107–111(5)	1.5249	1.2454
22	$CH_2{=}CHS(CH_2)_2OP$ 	90	95(2)	1.5080	1.1777
23	$CH_2{=}CHS(CH_2)_2OP$ 	60	100–102(2)	1.4990	1.1402
24	$CH_2{=}CHO(CH_2)_2S(CH_2)_2OP(OC_4H_9)_2$	48	172–174(4)	1.4735	1.0175
25	$CH_2{=}CHO(CH_2)_3S(CH_2)_2OP$ 	66	140–141(2)	1.5100	1.2095
26	$CH_2{=}CHO(CH_2)_2S(CH_2)_2OP$ 	58	136.5(3)	1.5001	1.1671
27	$CH_2{=}CHO(CH_2)_2S(CH_2)_2OP$ 	59	130–133(2)	1.4922	1.1346
28	$CH_2{=}CHS(CH_2)_2OP$ 	83	126(0.4)	1.5230	1.2148

Upon distillation of phosphites without cyclic substituents a partial disproportionation, especially noticeable for dibutyl (2-vinyloxyethyl) phosphite **20** (up to 30%) took place. As a result of the reaction of 2-(hydroxyethyl) vinyl sulfide with dibutylphosphorous acid chloride[48] together with the expected phosphite **20** tributyl phosphite was isolated in 27% yield.

The phosphite moiety of the vinyl ethers and sulfides **18–27** adds heavy-metal halides, reacts with sulfur to form the corresponding thiophosphates (see, for example, **28**, Table 3), and is subject to the Arbuzov rearrangement. In the presence of 2,2′-azobisisobutyric acid dinitrile diethyl (2-vinylthioethyl) phosphite **18** is readily transformed to a colorless transparent glassy polymer whereas the vinyl sulfide **23** gives a viscous product.

An attempt to trace the effect of the structure and mass of substituents on spectral characteristics of the vinylthio group has been made.[48] A tendency towards higher double bond stretching vibrations (from 1582 to 1590 cm^{-1}) with increased electron withdrawal by the substituents has been found. However, the highest sensitivity to structural effects is observed with the $=CH_2$ non-planar deformational vibrations. The frequencies of these vibrations vary as much as 26 cm^{-1}. The displacement with respect to ethyl vinyl sulfide (856 cm^{-1}) depends linearly on the Taft σ^*-constants.

2.3. *Synthesis from Ethanolamine Vinyl Ethers*

2.3.1. *Aminomethylation* Aminomethylation with diethanolamine divinyl ether was employed for synthesis of sulfur-containing divinyl ethers[50] and a simple route to the di(vinyloxyethyl) aminomethylorganyl sulfides **29–31** has been elaborated.

$$R_2NH \xrightarrow{CH_2O} [R_2NCH_2OH] \xrightarrow{R^1SH} \underset{\textbf{29–31}}{R_2NCH_2SR^1}$$

$R = CH_2{=}CHO(CH_2)_2$; $R^1 = n\text{-}C_4H_9$ (**29**), $CH_2CH{=}CH_2$ (**30**), C_6H_5 (**31**)

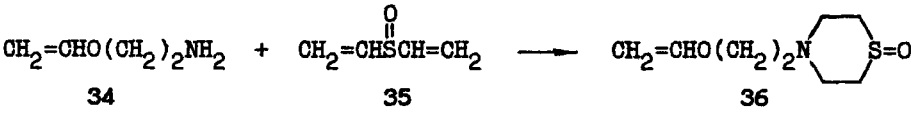
Scheme 26

Apart from the Mannich bases **29–31**, the thiols form adducts to the vinyloxy group. In the case of allyl mercaptan, thiylation is the prevailing reaction. The adducts **32** and **33** have been isolated and characterized (Table 4).

2.3.2. *4-(2-Vinyloxyethyl)-1,4-perhydrothiazine 1-oxide* Ethanolamine vinyl ether **34** reacts with divinyl sulfoxide **35** in ethanol upon heating (60 °C, 6 h) to give 4-(2-vinyloxyethyl)-1,4-perhydrothiazine 1-oxide **36** in 82% yield.[51]

TABLE 4 Di(vinyloxyethyl) aminomethylorganyl sulfides and derivatives[90]

Cpd. No.	Formula	B.p., °C (*mm* Hg)	n_D^{20}	d_4^{20}
29	$[CH_2{=}CHO(CH_2)_2]_2NCH_2SC_4H_9$	104–105(0.4)	1.4790	1.0464
30	$[CH_2{=}CHO(CH_2)_2]_2NCH_2SCH_2CH{=}CH_2$	88–89(0.3)	1.4880	0.9819
31	$[CH_2{=}CHO(CH_2)_2]_2NCH_2SC_6H_5$	147.5(0.5)	1.5681	1.2429
32	$CH_2{=}CHO(CH_2)_2N(CH_2)_2O(CH_2)_2SCH_2CH{=}CH_2$ $CH_2SCH_2CH{=}CH_2$	156–157(0.4)	1.4912	1.0209
33	$C_4H_9S(CH_2)_2O(CH_2)_2N(CH_2)_2OCH{=}CH_2$ $CH_2SC_4H_9$	158(0.5)	1.4820	0.9982



Scheme 27

2.3.3. *Syntheses of 2-(Vinyloxy)ethyl Isothiocyanate*

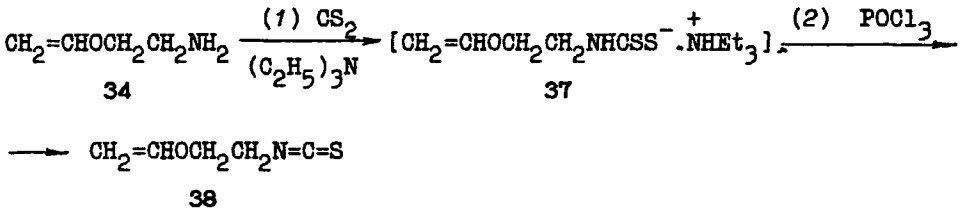
2.3.3.1. *Via phosphorus oxochloride* Vinyl ethers of isothiocyanato alkanols were scarcely studied for a long time: only one short note[52] was published before the systematic studies.[53–92] Meanwhile, these compounds which contain such so different and highly reactive functions as the isothiocyanato and the vinyloxy group could open the route to diverse vinyloxyalkylthio- and -dithiocarbamates, -thioureas, mono- and diisothiocyanates, new families of organic intermediates, monomers and biologically active compounds.

One of the simplest synthetic routes to isothiocyanates is the decomposition of *N*-monosubstituted dithiocarbamates by acidic reagents.[93] However, in the case of vinyloxyalkyl dithiocarbamates the synthesis may be complicated by intramolecular cyclization,[94] hydrolysis and cationic polymerization across the vinyloxy moiety.[1]

Perhaps that is why vinyl ethers of isothiocyanato alkanols remained unknown until recently and no attempts of their synthesis have been undertaken before the cited work.[52]

In,[52,55] the reaction of phosphorus oxochloride and triethylammonium 2-(vinyloxy)ethyl dithiocarbamate **37**, generated *in situ* from 2-(vinyloxy)ethylamine **34**

and carbon disulfide in the presence of triethylamine, has been studied, in an attempt to synthesize 2-(vinyloxy)ethyl isothiocyanate **38**.



Scheme 28

One may see from Table 5 that the reaction conditions (the reactant ratio and duration of the first and the second reaction steps) during the observation period do not influence the yield of **38** as substantially as could be anticipated (it varies just from 9 to 39%). Obviously, the above-mentioned side processes take place here, seriously limiting the yield.

TABLE 5 Effect of the reaction conditions on the yield of 2-(vinyloxy)ethyl isothiocyanate **38** (molar ratio **34**:$(C_2H_5)_3N$:CS_2:$POCl_3$ = 1:3:1:1)

Duration, h		
step 1	step 2	Yield, %
2.5[a]	20	9
0.1–0.2	19–20	17.4
3.0	19	25.0
5.0	17	36.4
0.5	1.5	39.0
20	0.1–0.2	32.0[b]

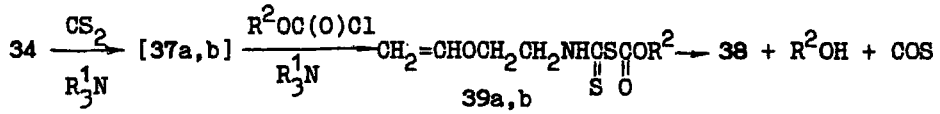
[a]At −(5–10) °C.
[b]Molar ratio **34**:$(C_2H_5)_3N$:CS_2:$POCl_3$ = 4:0:1:1.

In the IR spectrum of **38** there remains a set of principal absorption bands also present in the spectrum of **34** which belong to the vinyloxy group:[1] 3110, 3065, 1635, 1620, 1320, 1200, 1090, 1040, 950, 820 cm^{-1}. A broad, intensively split, absorption in the region 2000–2200 cm^{-1} is evidence of the presence of an isothiocyanate moiety.

The ^1H NMR spectrum of **38** (δ, ppm): 6.37 q (OCH=), 4.13 dd (CH_2=, *trans*), 4.00 dd (CH_2=, *cis*), 3.77 m (OCH_2CH_2N).

2.3.3.2. *Via alkyl chloroformates* In Ref. 56 there has been studied the reaction of trialkylammonium 2-(vinyloxy)ethyl dithiocarbamate **37**, generated *in situ* from 2-(vinyloxy)ethylamine **34** and carbon disulfide in a tertiary amine medium, with

alkyl chloroformates to produce 2-(vinyloxy)ethyl isothiocyanate **38** in almost quantitative yield. The synthesis is carried out as a one-pot procedure.



$R^1 = C_2H_5$, n-C_4H_9; $R^2 = CH_3$ (a), C_2H_5 (b)

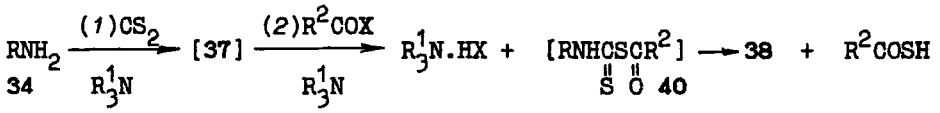
Scheme 29

The intermediates **37** and **39** have been isolated and characterized (IR, NMR).

2.3.3.3. *Via acyl halides* Of numerous methods of isothiocyanate synthesis,[93,95,96] the most widespread is a method[97] based on the decomposition of salts of *N*-monosubstituted dithiocarbamic acids, readily generated from primary amines and carbon disulfide in the presence of a base. These salts decompose to isothiocyanates when treated with ethyl chloroformate, the process being usually carried out in two preparative steps with isolation of the intermediate salt of a dithiocarbamic acid. It appears strange that the more accessible, stable, and, what may be even more important, less toxic acyl halides have seemingly not been employed in the synthesis of isothiocyanates until the present work.

In the course of a systematic study with the target to develop convenient synthetic procedures for 2-(vinyloxy)ethyl isothiocyanate **38**,[52,55,56] the present authors[57,59,61] have found that acyl halides can be successfully used as acylating agents instead of ethyl chloroformate in the synthesis of isothiocyanates.

A trialkylammonium organyl dithiocarbamate **37** is condensed with an acyl halide at ambient temperature in a chloroorganic solvent, *e.g.*, trichloromethane, carbon tetrachloride, *etc.* The molar ratio amine **34**:CS_2:R^1_3N:acyl halide is 1:1:2:1:1.



$R = CH_2{=}CHOCH_2CH_2$; $R^1 = C_2H_5$, n-C_4H_9; $R^2 = CH_3$, C_6H_5; X = Cl, Br

Scheme 30

The process is carried out as a one-pot procedure without isolation of the intermediate trialkylammonium organyl dithiocarbamate **37** and the mixed acid anhydride **40**. The yield of the isothiocyanate is nearly quantitative.

The conditions and results of the reaction are illustrated in Table 6.

TABLE 6 Effect of the reaction conditions on the yield of 2-(vinyloxy)ethyl isothiocyanate **38** (molar ratio **34**:CS_2:$(C_2H_5)_3N$:R^2COX = 1:1:2:1; CS_2 and R^2COX are introduced at −10-0 °C)[59]

R^2COX	Duration of the second stage[a], h	Yield, %
CH_3COCl	1	79
CH_3COCl	1	88
CH_3COCl[b]	3	79
CH_3COCl	1	95
CH_3COCl	2	100
CH_3COBr	1	53
CH_3COBr[c]	0.7	76
C_6H_5COCl[d]	1	51[e]

[a]Ambient temperature.
[b]The first step was carried out at −30 °C.
[c]Both steps were carried out at 20–45 °C.
[d]CS_2 and PhCOCl were introduced at −5-0 °C.
[e]Preparative yield.

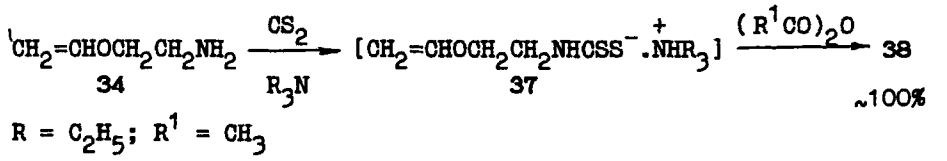
When the reaction is carried out at low temperature (down to −30 °C), the yield of 2-(vinyloxy)ethyl isothiocyanate remains practically unchanged (Table 6). However, this is not necessary since no advantages are obtained in this case.[59]

Generally, the acyl halide of any carboxylic acid can be used for the preparation of **38**. However, from the preparative point, acetyl chloride is most convenient and available. Moreover, when this reagent is employed, the highest yields of isothiocyanates are achieved. With acetyl bromide and benzoyl chloride, for example, the yield of 2-(vinyloxy)ethyl isothiocyanate is 76 and 51%, respectively.[59]

The thiolcarboxylic acids formed along with the isothiocyanate are of independent interest. If necessary, they can be isolated from the reaction mixture by conventional procedures.

The physico-chemical and spectral (IR, NMR) characteristics of isothiocyanate **38** synthesized *via* acyl halides are in agreement with those from the literature.[52,55]

2.3.3.4. *Via carboxylic acid anhydrides* Until the work described in Ref. 60 no example of the use of carboxylic anhydrides as acylating agents in the synthesis of isothiocyanates was known. Recently, 2-(vinyloxy)ethyl isothiocyanate was obtained in practically quantitative yield by a one-pot reaction of triethylammonium 2-(vinyloxy)ethyl dithiocarbamate generated *in situ* from 2-(vinyloxy)ethylamine **34**, carbon disulfide and triethylamine with acetic anhydride in a chloroorganic solvent (CCl_4, $CHCl_3$, *etc.*).[60]

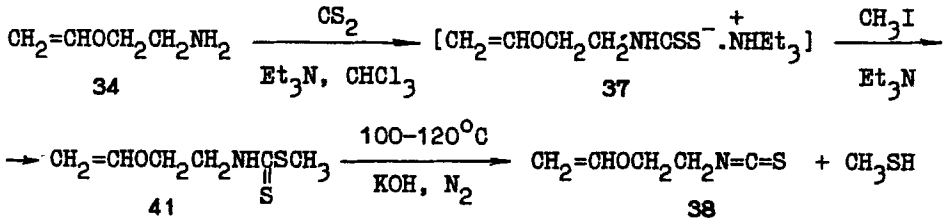


Scheme 31

The reaction is carried out at 0–30 °C with stoichiometric amounts of reagents.

2.3.3.5. *Via alkyl halides* Thermolysis of *S*-alkyl dithiocarbamates (alkyl = C_2H_5, *n*-C_4H_9, *t*-C_4H_9, *n*-$C_{12}H_{25}$), obtained from the salts of *N*-monosubstituted dithiocarbamic acids and alkyl halides (chlorides,[98] bromides and iodides[99]), provides a convenient method for simultaneous preparation of isothiocyanates and thiols in 81–97% yield.

In Ref. 76 some data concerning the synthesis of 2-(vinyloxy)ethyl isothiocyanate by catalytic cleavage of *S*-methyl *N*-(2-vinyloxyethyl)dithiocarbamate **41** are reported.



Scheme 32

The dithiocarbamate **41** was prepared in high yield by condensation of triethylammonium *N*-(2-vinyloxyethyl)dithiocarbamate **37** with methyl iodide in chloroform. The composition of **41** was proven by elemental analysis and IR spectroscopy, no absorption in the 2100–2200 cm^{-1} region (N=C=S) being observed.

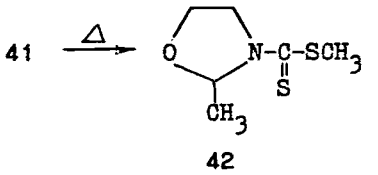
Upon GLC the dithiocarbamate **41** undergoes cleavage to form 2-(vinyloxy)ethyl isothiocyanate and methanethiol.

Reflux of **37** with potassium hydroxide (0.5%) in a high-boiling organic solvent such as diglyme, toluene, xylene, or decane (4 h, N_2) leads to the isothiocyanate **38** in 70% yield. In the IR spectrum of the reaction mixture there was an intense band in the isothiocyanate group absorption region. The yield of the isothiocyanate **38** isolated by vacuum distillation was 62%.[76]

Unlike *S*,*N*-alkyl dithiocarbamates, the thermolysis of *S*-methyl *N*-(2-vinyloxyethyl)dithiocarbamate is complicated by intramolecular cyclization at the vinyloxy group to form *N*-(methyldithiocarbonyl)-2-methyl-1,3-oxazolidine **42**, unknown before this work.[76]

In the IR spectrum of **42** there are no bands corresponding to vibrations of NH (3250 cm^{-1}) and vinyloxy groups (820, 1200, 1320, 1610, 1630, 3100 cm^{-1}). At the same time, a strong absorption band N—C(=S) appears in the 1420 cm^{-1} region and the intensity of the band at 2960 cm^{-1} (CH_3) increases noticeably.

^{1}H NMR spectrum [$(CD_3)_2CO$, δ, ppm]: 5.82 q (CH), 4.25 m (CH_2O), 3.84 m (CH_2N), 2.59 s (SCH_3), 1.51 d (CH_3-CH).



42

Scheme 33

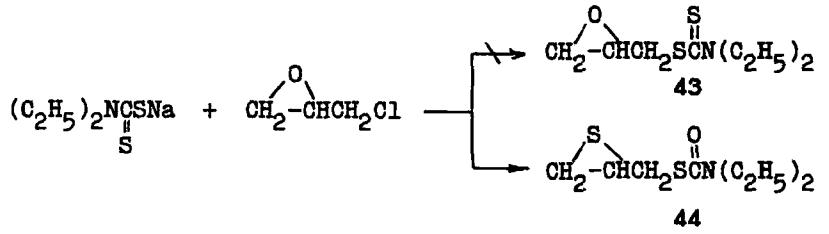
Upon thermolysis (reflux in toluene, 1% KOH, 4 h) of the dithiocarbamate **41**, contaminated with $Et_3N \cdot HI$, the preparative yield of the isothiocyanate **38** decreases to 26% with a simultaneous increase of the distillation residue represented by oxazolidine **42** (according to IR and ^{1}H NMR spectra and elemental analysis).

Upon vacuum distillation of the dithiocarbamate **41**, still containing triethylammonium iodide, in the presence of KOH (0.5%) the product is quantitatively cyclized to the oxazolidine **42**. In the IR spectrum of the first fraction only traces of the isothiocyanate group are present, the second fraction being the oxazolidine **42**.[76]

2.3.4. *Reaction of 2-(Vinyloxy)ethylamine with CS_2 and Epichlorohydrin* The reaction of epichlorohydrin with dithiocarbamic acids and their salts has not been studied much. There are evidently only a few contributions dealing with it, among them patents[100–102] and short communications,[103,104] the results being inadequate. The reaction of alkali and ammonium salts of dithiocarbamic acids with epichlorohydrin has been shown to give 2,3-epithiopropyl esters of thiocarbamic *S*-acids[100–102,104] instead of the expected 2,3-epoxypropyl esters of dithiocarbamic acids.[103] However, no data or working hypotheses concerning the mechanism of this rearrangement, uncommon to dithiocarbamates, have been reported. The reaction product has been assigned[103] structure **43** without any evidence.

Continuing systematic studies of functional epoxides and thiiranes and in the search for supplementary information on this reaction, authors[105] have examined the interaction of *N,N*-diethyl- and *N*-(2-vinyloxyethyl)dithiocarbamic acids and their alkali salts with epichlorohydrin.

At first the reaction of epichlorohydrin with dithiocarbamates was studied in the earlier described model with sodium *N,N*-diethyldithiocarbamate. Indeed, when the reaction was carried out under the conditions reported in,[104] instead of the expected 2,3-epoxypropyl *N,N*-diethyldithiocarbamate **43**[103] *S*-(2,3-epithiopropyl) *N,N*-diethylthiocarbamate **44**[100–102,104] was formed in 44% yield.

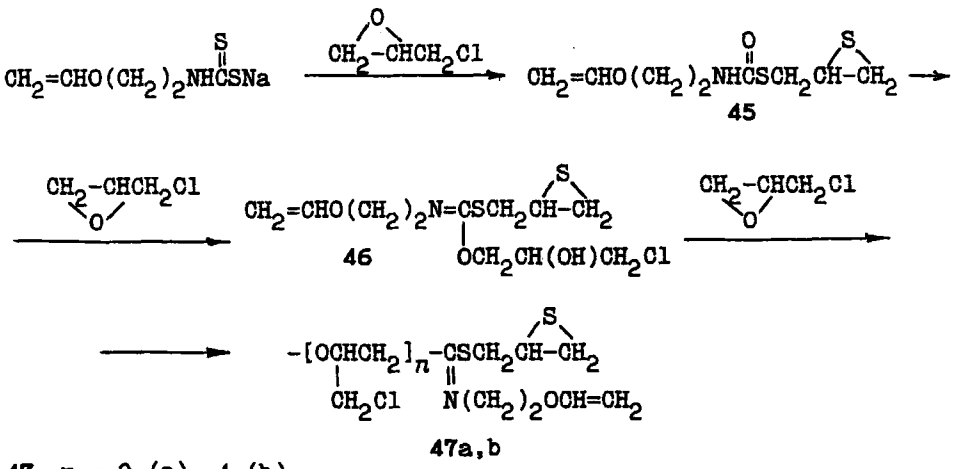


Scheme 34

Its structure was proven by IR and ^{1}H NMR spectra, other physico-chemical constants of **44** being also in agreement with the literature data.[104]

Prior to the studies of Ref. 105 *N*-(2-vinyloxyethyl)dithiocarbamic acid and its salts had not been investigated in this reaction and any reference to the reaction of epichlorohydrin with *N*-monosubstituted dithiocarbamic acids and their derivatives seemed to be absent.

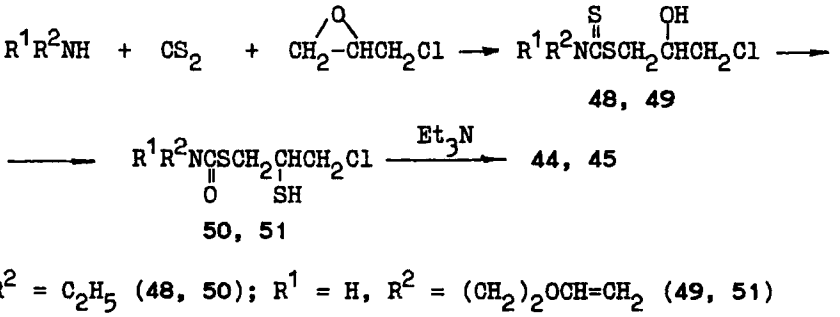
Recent experiments demonstrated that in this case, analogously to *N,N*-disubstituted dithiocarbamates,[100-102,104] the reaction leads to thiocarbamic *S*-acid derivatives (as shown by IR and ^{1}H NMR spectroscopy). However, unlike the case of *N,N*-disubstituted dithiocarbamates, the reaction results depend greatly on the reaction conditions, first of all the ratio of reagents. When the reaction is carried out in epichlorohydrin the expected product **45** is formed in ~80% yield. However, the process does not cease at this stage; it seems to develop as a double alkylation (*N*-monosubstituted dithiocarbamates are subject to dialkylation with excess organyl halides[95]) to afford at first **46** and then oligomers **47**. The low boiling portion of the reaction mixture contained (GLC) about 3% of epithiochlorohydrin. The intermediate formation of the latter is part of the reaction mechanism given below (Scheme 37).



Scheme 35

When the reagents are used in equimolar quantities the IR spectrum of the reaction mixture does not exhibit absorption bands of N=C, C—Cl and O—H bonds (1740–1750, 760 and 3400 cm^{-1}, respectively), *i.e.* dialkylation and oligomerization do not occur in this case. The intense absorption at 1650 and 3250 cm^{-1} indicated the presence of the NHC=O moiety[106] and the 610 and 670 cm^{-1} absorption bands were assigned to the thiirane ring vibrations. The purity of the reaction product was proven by GLC. According to elemental analysis, IR and ^1H NMR spectra, the product was *S*-(2,3-epithiopropyl) *N*-(2-vinyloxyethyl)thiocarbamate **45**.

In order to elucidate at which stage of the reaction between dithiocarbamates and epichlorohydrin the rearrangement leading to thiiranes takes place, the authors of Ref. 105 investigated the interaction of epichlorohydrin with *N,N*-diethyl- and *N*-(2-vinyloxyethyl)dithiocarbamic acid formed *in situ* from carbon disulfide and the corresponding amine:



Scheme 36

In the IR spectrum of a freshly prepared sample of **48**, together with a set of absorption bands arising from bond vibrations in the dithiocarbamate fragment, there was a moderately intense absorption band of the C=O group (1640 cm^{-1}), and two spots were observed by TLC. In the IR spectrum recorded two days later the intensity of the 1640 cm^{-1} band was considerably higher than those of the 1540 and 1490 cm^{-1} bands [NC(S)S], whereas the broad well-shaped absorption band with a maximum at 3300 cm^{-1} was displaced towards the 3250 cm^{-1} region, its shape being noticeably distorted. In the IR spectrum run five days later this region showed only a narrow intense band at 3200 cm^{-1}. After heating of **48** (60 °C, 2 h) its IR spectrum contained very intense absorption bands at 1650 (C=O) and 670, 610 cm^{-1} (C—S) as well as absorption bands of intermediate intensity at 2490 and 2540 cm^{-1} (SH). There was no absorption in the region 3500–3000, 1540 and 1490 cm^{-1}. This indicated that the alcohol **48** was fully rearranged to the thiol **50**.

The IR spectra of **48** and **50** treated with triethylamine were identical to that of **44** obtained by reaction of sodium *N,N*-diethyldithiocarbamate with epichlorohydrin.

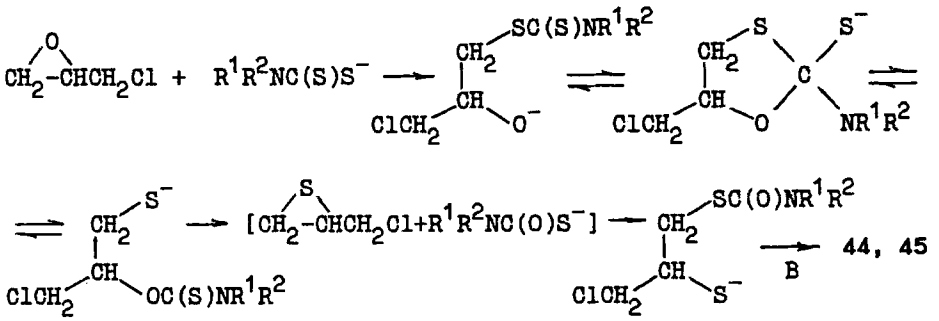
As with *N,N*-diethyldithiocarbamic acid, the reaction of *N*-(2-vinyloxyethyl)dithiocarbamic acid with epichlorohydrin[105] at first gave the product of epoxide ring opening, the alcohol **49**, which underwent gradual rearrangement to the thiol **51**. However, unlike the alcohol **48**, the **49** → **51** rearrangement rate was much slower. Fast isomerization of the alcohol **49** to the thiol **51** is possibly hindered by thiylation and acetalization involving the vinyloxy group. Already a few hours after the start of the synthesis compound **49** is getting glassy and its IR and ^{1}H NMR spectra show no absorption bands and signals corresponding to the vinyloxy group; instead, signals of the acetal fragment appear.[1,105]

Relying upon the data obtained it may be stated that the nucleophilic opening of the epichlorohydrin epoxide ring by dithiocarbamate anions leads to unstable alcohols **48** and **49** which undergo a fast alkoxide-thiolate rearrangement. In this case, in contrast to the known rearrangements of this type,[107] with the alcohols **48** and **49**, the rearrangement of an *S*-substituted oxyanion to an *O*-substituted thiolate anion proceeds at a noticeably lower rate already at room temperature and is completed upon slight heating. Evidently, a latent catalytic effect is produced by the starting amines [diethyl- and 2-(vinyloxy)ethylamine], which may be present in small amounts in the reaction mixture and the reaction products due to equilibration of the corresponding dithiocarbamic acid with amine and carbon disulfide.[93]

Triethylamine treatment of **49** and **51** yields the thiocarbamate **45**.[105]

In the presence of bases such as Et_3N, KOH, and upon heating the rate of the alkoxide-thiolate rearrangement of **48** and **49** increases greatly[105] which implies that the formation of the thiirane ring proceeds in analogy with the known reactions of olefin oxides with thionic systems (thiourea, xanthogenates, dithiophosphoric acids, *etc.*).[107]

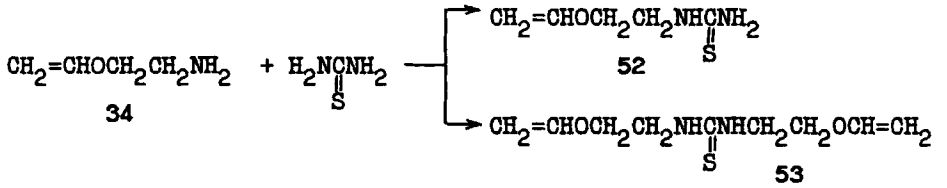
The mechanism of the anionotropic substitution of the oxirane ring oxygen by a sulfur atom may include a series of successive ionic reactions involving the intermediate formation and cleavage of an oxathiolane ring and epithiochlorohydrin:



B – base; $R^1 = R^2 = C_2H_5$; $R^1 = H$, $R^2 = (CH_2)_2OCH{=}CH_2$

Scheme 37

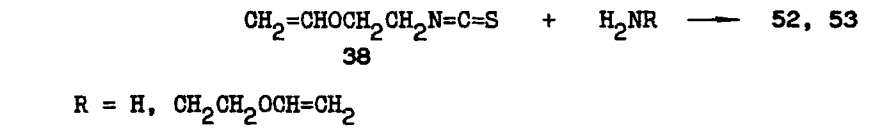
2.3.5. *Reactions of 2-(Vinyloxy)ethylamine with Thiourea* A promising way to *N*-mono- and *N,N*^{1}-bis(vinyloxyalkyl) substituted thioureas is provided by the reaction of thiourea with 2-(vinyloxy)ethylamine. This synthesis has been mentioned in patents,[108,109] however, no experimental details, yields, or characteristics of the products have been reported. The authors of Ref. 70 have examined the reaction of 2-(vinyloxy)ethylamine **34** with thiourea and found that with an equimolar ratio of reagents at 120 °C for 5 h the monosubstituted product **52** is formed whereas refluxing in the vinyl ether gives the disubstituted product **53**:



Scheme 38

It was not possible to find satisfactory methods for the purification of **53** although the IR and ^{1}H NMR spectra and elemental analysis of the crude sample indicated that the desired product had formed. This was most likely due to the resinification of the product during the reaction. An attempt to carry out the reaction in toluene did not meet with success: the reaction did not proceed even upon reflux for over 20 h (the reagents were recovered unchanged).

N-(2-Vinyloxethyl)- and *N,N*^{1}-bis(2-vinyloxyethyl)thiourea **52** and **53** were obtained much more readily by reaction of 2-(vinyloxy)ethyl isothiocyanate[57] with aqueous ammonia and 2-(vinyloxy)ethylamine, respectively:[58,66,70]



Scheme 39

2.4. *Nucleophilic Substitution of Vinyloxyorganyl Halides*

The chlorine atom of 2-(chloroethyl) vinyl ether is readily substituted by an alkyl(aryl)thio group upon reflux with the corresponding thiol in an alkaline alcohol solution.[39,110,111] The yield of 2-alkyl(aryl)thioethylvinyl ethers, $CH_2{=}CHO(CH_2)_2SR$ (**54–58**, Table 7) amounts to 97%.

TABLE 7 Sulfur-containing vinyl ethers, the products of nucleophilic substitution of halogen in haloalkoxyethenes[49,113,115,116]

Cpd. No.	Formula	Yield, %	B.p., °C (*mm* Hg)	n_D^{20}	d_4^{20}
54	$CH_2=CHO(CH_2)_2SC_2H_5$	81.2	65–66(10)	1.4760	0.9477
55	$CH_2=CHO(CH_2)_2SC_4H_9$	96.8	82–85(5)	1.4725	0.9251
56	$CH_2=CHO(CH_2)_2SC_6H_5$	90.0	110–112(4.5)	1.5630	1.0745
57	$CH_2=CHO(CH_2)_2SCH_2CH=CH_2$	45.2	70(7)	1.4900	0.9604
58	$CH_2=CHO(CH_2)_2SCH_2C_6H_5$	79.9	102–104(1)	1.5513	1.0521
59	$(CH_2=CHOCH_2CH_2)_2S$	42.5	91–92(3)	1.4910	1.0170
60	$(CH_2=CHOCH_2CH_2S)_2$	65.1	90–91(1)	1.5253	1.0995
61	$CH_2=CHO(CH_2)_2SCN$	65.4	73–74(3)	1.4920	1.0982
62	$CH_2=CHO(CH_2)_3SCN$	56.0	79–80(2)	1.4868	1.0630
63	$CH_2=CHO(CH_2)_4SCN$	47.2	80–81(1)	1.4860	1.0476
64	$CH_2=CHO(CH_2)_2S(S)CN(C_2H_5)_2$	70.4	126(1)	1.5650	1.0374
65	$CH_2=CHO(CH_2)_4S(S)CN(C_2H_5)_2$	69.1	134(0.6)	1.5525	1.0533

In the presence of cationic catalysts (BF_3) the vinyl ethers **54–58** are readily polymerized to colorless transparent gels. The reaction of 2-(chloroethyl)vinyl ether with sodium sulfide gives the divinyl ether $(CH_2=CHOCH_2CH_2)_2S$ **59** which can also be obtained by direct vinylation of the corresponding diol with acetylene.[32] Reflux of 2-chloro(bromo)ethylvinyl ether with sodium disulfide in methanol leads to 2,2′-bis(vinyloxyethyl) disulfide **60** which so far seems to be the only known vinyl ether containing a disulfide group.[112,113]

$$CH_2=CHO(CH_2)_2X \xrightarrow{Na_2S_2} (CH_2=CHOCH_2CH_2S)_2; \quad X = Cl, Br$$

60

Scheme 40

The vinyl ether **60** is readily polymerized in the presence of cationic catalysts and can be used for the preparation of polymers which exhibit electron-exchange (redox) properties due to transition.

Upon short heating (130–135 °C) of haloalkylvinyl ethers with potassium thiocyanate in DMFA substitution of the halogen by a thiocyanate group takes place. In this way the first members of thiocyanatoalcohol vinyl ethers (**61–63**, Table 7) were prepared.[113,114]

$$CH_2=CHORX + KSCN \longrightarrow CH_2=CHORSCN$$

61–63

$$R = (CH_2)_2 \ (61), \ (CH_2)_3 \ (62), \ (CH_2)_4 \ (63)$$

Scheme 41

Haloalkoxyethenes react with the potassium salt of diethyldithiocarbamic acid to form[113] the vinyl ethers of *S*-(oxyalkyl)diethyldithiocarbamates (**64, 65**, Table 7).

$$CH_2{=}CHO(CH_2)_nX + KS(S)CN(C_2H_5)_2 \longrightarrow CH_2{=}CHO(CH_2)_nS(S)CN(C_2H_5)_2$$

X = Cl, Br — **64** (*n*=2), **65** (*n*=4)

Scheme 42

2.5. *Cleavage of C—O and C—S Bonds*

2.5.1. *Transformations of some sulfur-containing vinyl ethers* The disulfide **60** is cleaved with dialkyl phosphites in the presence of sodium to form vinyl ethers of *O,O*-dialkyl *S*-(vinyloxyethyl) thiophosphates **66–68** and 2-(vinyloxy)ethanethiol (**69**, Table 8), representatives of vinyl ethers with a free thiol function.[117,118]

Due to the known high reactivity of the vinyloxy group towards the thiol function, one would expect that a vinyloxy group and a free thiol function are hardly compatible in one molecule under normal conditions. This was reported to be true,[117–119] in spite of the fact that the thiol **69** can be isolated upon continuous vacuum removal from the reaction mixture and condensation at −50 °C.

$$(CH_2{=}CHOCH_2CH_2S)_2 + (RO)_2P(O)H \longrightarrow CH_2{=}CHO(CH_2)_2SP(O)(OR)_2 + CH_2{=}CHO(CH_2)_2SH$$

60 — **66–68** — **69**

R = C_2H_5 (**66**), *n*-C_3H_7 (**67**), *n*-C_4H_9 (**68**)

Scheme 43

TABLE 8 Some derivatives of 2,2'-bis(vinyloxyethyl) disulfide **60**[118,119]

Cpd. No.	Formula	Yield, %	B.p., °C (*mm* Hg)	n_D^{20}	d_4^{20}
66	$CH_2{=}CHO(CH_2)_2SP(O)(OC_2H_5)_2$	91	104–105(1)	1.4783	1.1310
67	$CH_2{=}CHO(CH_2)_2SP(O)(OC_3H_7)_2$	90	111–113(1)	1.4775	1.0944
68	$CH_2{=}CHO(CH_2)_2SP(O)(OC_4H_9)_2$	95	126(1)	1.4700	1.0545
69	$CH_2{=}CHOCH_2CH_2SH$	55	50(50)	1.4713	0.9914
70	$CH_2{=}CHO(CH_2)_2S(CH_2)_2OC_4H_9$	21	101(3)	1.4680	0.9643

The structure of 2-(vinyloxy)ethanethiol was confirmed by its addition to butyl vinyl ether affording the sulfide **70**.

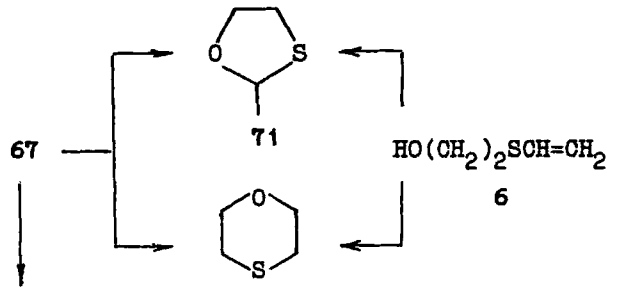
$CH_2{=}CHO(CH_2)_2S(CH_2)_2OC_4H_9$

70

Comparison of the IR spectra of 2-(vinyloxy)ethanethiol and 2-methyl-1,3-oxathiolane **71** indicates the latter to be an impurity of the thiol. Together with the characteristic absorptions of the vinyloxy group (826, 966, 1200, 1320, 1620, 1638, 3050, 3115 cm^{-1}) the spectrum of 2-(vinyloxy)ethanethiol contains bands corresponding to a methyl group (1376, 1440, 2975 cm^{-1}) and to a 1,3-oxathiolane ring (1045, 1090, 1120, 1214, 1255 cm^{-1}).

At room temperature 2-(vinyloxy)ethanethiol is converted fairly fast to the polymer **72** and partially isomerized to 2-methyl-1,3-oxathiolane.

Analogous conversions occur to a greater or lesser degree upon distillation of 2-(vinyloxy)ethanethiol.



$CH_2{=}CHO(CH_2)_2S{-}[{-}(CH_2)_2O(CH_2)_2S{-}]_{10\text{-}15}{-}H$

72

Scheme 44

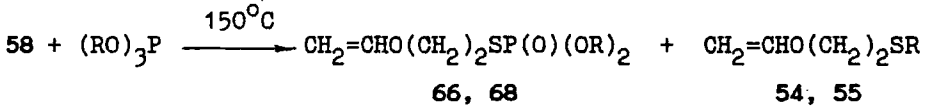
Comparison of the physico-chemical constants, GLC and IR data prove[119] the identity of 2-methyl-1,3-oxathiolane and the authentic sample synthesized from 2-mercaptoethanol[120] and provide evidence for the absence of its 1,4-oxathiane isomer (the IR spectra of 2-methyl-1,3-oxathiolane and of 1,4-oxathiane differ considerably[120]). The spontaneous transformation of 2-(vinyloxy)ethanethiol to 2-methyl-1,3-oxathiolane does not cease even in the presence of bases (K_2CO_3) which implies a homolytic character of this process. Thus, the cyclization observed may be regarded as a rare example of radical Markovnikov addition of thiols to vinyl ethers. Seemingly, in certain cases the course of the homolytic addition to alkoxyethenes may be governed by steric factors (*e.g.* ring strain) rather than by the stability of the intermediate radical.

2-(Vinylthio)ethanol **6**, the "inverted" analog of **69**, also undergoes a ready transformation to 2-methyl-1,3-oxathiolane both spontaneously and under the effect of acids. In the two versions the polymer **72** is formed supplementary,

however, the 1,4-oxathiane being absent among the cyclization products.[119] Therefore, the formation of 2-methyl-1,3-oxathiolane from bis(2-hydroxyethyl) sulfide by alkaline dehydration[120] is connected with intermediate 2-(vinylthio)ethanol cyclization.

An analysis for mercaptal group content carried out with mercury chloride[121] and hydroxylamine,[44,122,123] shows the polymer **72** to consist of alternating $(CH_2)_2O$ and $(CH_2)_2S$ units. However, in the IR spectrum of this polymer there are weak absorption bands caused by methyl groups which indicates that $SCH(CH_3)O$ mercaptal groups are also present in the polymer.

The reaction products of disulfide **60** with trialkyl phosphites[118] are *O,O*-dialkyl *S*-(vinyloxyethyl) thiophosphates (**66, 68**, Table 8) and vinyl ethers of alkylthioethanols (**54, 55**, Table 7).



Scheme 45

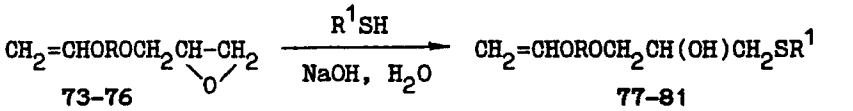
2.5.2. *Reactions of Vinyloxy Epoxides with Sulfur Compounds*

2.5.2.1. *With thiols* The present Section deals with the application of ω-vinyloxyalkoxymethyl oxiranes as starting materials for the synthesis of sulfur-containing vinyl ethers.[1]

In aqueous alkaline solution thiols open smoothly and quantitatively the oxirane ring of **73–76** to form vinyloxyalkyl ethers of 3-alkylthio-2-hydroxypropanol-1 (**77–81**, Table 9).

With excess alkali thiols react as thiolates which prevents possible thiylation of the double bond[4,124,125] which otherwise occurs readily with vinyl ethers.

Analysis of the regiodirection of the reaction[1] shows that opening of the oxirane ring takes place exclusively at the less substituted carbon atom, the hydroxy sulfides **77–81** being secondary alcohols.



R = $(CH_2)_2$ (**73**), R^1 = *n*-C_3H_7 (**77**), *n*-C_4H_9 (**78**); R = $(CH_2)_4$ (**74**), R^1 = *n*-C_4H_9 (**79**); R = $(CH_2)_2O(CH_2)_2$ (**75**), R^1 = *n*-C_4H_9 (**80**); R = $(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**76**), R^1 = *t*-C_4H_9 (**81**)

Scheme 46

Under the effect of acid catalysts the hydroxy sulfides **77–81** readily take part in polyaddition to form viscous oligomers with the polyacetal structure **82**.[1]

$$CH_2{=}CHOROCH_2\underset{\displaystyle CH_2SR^1}{\underset{|}{CH}}{-}[-OCH(CH_3)OROCH_2\underset{\displaystyle CH_2SR^1}{\underset{|}{CH}}-]_n-OCH(CH_3)OROCH_2CH(OH)CH_2SR^1$$

82

Scheme 47

With weak aqueous solutions of mineral acids **77–81** are subject to hydrolytic decomposition at the vinyloxy group, exemplified by the preparation of the sulfide **83**.[125]

$$\mathbf{81} \xrightarrow[H_2O]{1\%\ HCl} HO(CH_2CH_2O)_3CH_2CH(OH)CH_2SC_{12}H_{25}\text{-}t$$

83

Scheme 48

Attempted dehydration of the hydroxy sulfides **77–81** failed:[125] a technique based on the use of phosphorus oxochloride in pyridine, which allowed (with retention of the vinyloxy group) the elimination of water from tertiary vinyloxyalkoxyalkynols[1] proved inapplicable to **77–81**. Neither could the expected products of dehydration be prepared by alkali treatment of **77–81**, a procedure which is normally efficient in the conversion of 2-hydroxyethyl sulfides to the corresponding vinyl suflides.[5,6]

2.5.2.2. *With thiourea and KSCN* Compounds containing amino and mercapto groups show good anti-radiation effects.[126,127] The high potential of vinyl ethers the alkoxy group of which contains a thiirane moiety, as starting material for the preparation of anti-radiation drugs (β-mercapto amines and derivatives thereof) attracted attention to the reaction of ω-vinyloxyalkoxymethyl oxiranes with thiourea.[4]

The exchange reaction between the vinyl epoxy ethers **73–76, 84** [R = $(CH_2)_3$], and **85** [$(CH_2)_2CH(CH_3)$] and thiourea proceeds without serious complications to give the expected thiirane **86** (see Table 9) only in the case of 2-(vinyloxy)ethoxymethyloxirane **73**.[128]

$$\mathbf{73} \xrightarrow[-5\text{–}0^{\circ}C]{(H_2N)_2C=S} CH_2{=}CHOCH_2CH_2OCH_2\underset{\displaystyle S}{\underset{\diagdown\ \diagup}{CH}}{-}CH_2$$

86

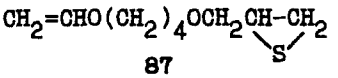
Scheme 49

TABLE 9 Sulfur-containing vinyl ethers from ω-vinyloxyalkoxymethyl oxiranes[1,125,129]

Cpd. No.	Formula	Yield, %	B.p., °C (*mm* Hg)	n_D^{20}	d_4^{20}
77	$CH_2{=}CHO(CH_2)_2OCH_2CH(OH)CH_2SC_3H_7$	82	121(1)	1.4840	1.0363
78	$CH_2{=}CHO(CH_2)_2OCH_2CH(OH)CH_2SC_4H_9$	93	132(1)	1.4823	1.0234
79	$CH_2{=}CHO(CH_2)_4OCH_2CH(OH)CH_2SC_4H_9$	90	156(1)	1.4807	1.0430
80	$CH_2{=}CHO(CH_2)_2O(CH_2)_2OCH_2\underset{CH_2SC_4H_9}{\underset{\vert}{CHOH}}$	96	162(3)	1.4810	0.9982
86	$CH_2{=}CHO(CH_2)_2OCH_2\underset{\diagdown S \diagup}{CH{-}CH_2}$	61	71–72(2)	1.4923	1.0652

Under the action of thiourea the vinyl epoxy ethers **75** and **76** with β-alternation of oxygen atoms between the vinyloxy group and the epoxide ring are subject to polymerization which could not be averted in spite of variation of the experimental conditions over a wide range.[125] This fact is another demonstration of the special properties of systems with β-alternation of heteroatoms which was already mentioned in preceding sections.[1]

The epoxide **74**, the functions of which are separated by a chain of four methylene groups, does not undergo polymerization under the reaction conditions, but reacts with thiourea considerably more slowly than the epoxide **73**. As a result, a mixture of the thiirane **87** and the initial epoxide is formed.[1,125]



87

Scheme 50

The polymerization of thiiranes often occurs already during their synthesis, the same parameters (temperature, solvent) influencing in a similar way the rate of both major and side reactions.[107,130-135]

A study of the effect of the nature of the solvent and the reagent, as well as that of the reaction time on the conversion of oxirane **73** and the yield of thiirane **86** has been carried out.[129] The reaction course was checked by ^{1}H NMR spectra and GLC. Water, methanol, dimethyl sulfoxide (DMSO), 10% aqueous DMSO, hexane, and 1,3-dimethylcyclohexane were used as solvents. Thiourea and potassium thiocyanate served as reagents. The results are summarized in Table 10.

In all the cases during the first three hours the yield of thiirane **86** is increased; the highest reaction rate is observed in the system thiourea-methanol and the lowest rate in the system KSCN-H_2O, the yield of thiirane **86** being 67 and 24%, respectively. Further increase in the reaction time affects the results in different ways. In the system thiourea-water the yield of thiirane **86** increases smoothly approaching the maximum value (90–92%) after 6 h. In DMSO and aqueous DMSO the maximum yield of thiirane **86** (67 and 45%, respectively) was detected after 4 h, then the yield of **86** decreased due to polymerization. When the reaction of oxirane **73** with thiourea is carried out in DMSO at room temperature the product is fully polymerized in 5 h. In methanol the polymerization of thiirane **86** becomes prevalent over its formation already within 3 h; during the next 2 h the yield of **86** decreases from 67 to 48%. In this case the rate of polymerization can be diminished to a considerable extent by continuous cooling of the reaction mixture. Discontinuation of cooling (even 5 h after the reaction start) leads to an abrupt spontaneous rise of temperature to 90 °C and the formation of a gel-like polymer with a strong odor of thiol.

In 1,3-dimethylcyclohexane and hexane, on the contrary (Table 10), the major reaction proceeds so slowly that 1 h after the start of the reaction (even when carried out at 25–32 °C) the reaction mixture contains no traces of the thiirane **86** in the first case and as little as 13% (2 h later) in the second case.

TABLE 10 The dependence of the yield of 2-(vinyloxy)ethoxymethylthiirane **86** on the reaction conditions [-5-0 °C, oxirane **73**:thiourea (KSCN) = 1:1, 1.2%, K_2CO_3][129]

Time, h	Thiirane **86** content of the reaction mixture, %[a]						
	H_2O[b]	H_2O	CH_3OH	DMSO	DMSO-H_2O (1:9)	*cyclo*-C_6H_{10}-1,3-$(CH_3)_2$[c]	C_6H_{12}[d]
1	17	25	30	16	15	*traces*	
2	20	42	47	23	20	16	13
3	24	52	67	60	25	28	
4	31	62	56	67	45	36	
5	49	85	48	61	39	50	
6	42	90–92	*traces*				
7	—	90					

[a]GLC.
[b]KSCN.
[c]Reaction temperature 25 °C.
[d]KSCN, reaction temperature 32 °C.

Thus, it is concluded that the system thiourea-water is most favorable for 2-(vinyloxy)ethoxymethyloxirane to exchange its oxirane oxygen for sulfur. In this case the synthesis of 2-(vinyloxy)ethoxymethylthiirane is not compromised by polymerization under the reaction conditions. According to the well-consistent data of GLC and ^{1}H NMR spectroscopy, after 6 h the reaction mixture contains 90–92% of the thiirane **86** and 8–10% of the starting oxirane **73**. In the ^{1}H NMR spectrum of the reaction mixture the multiplet in the 3.06 ppm region corresponds to 1H in $\overset{\diagdown\diagup}{CH}—CH_2S$, the doublet of doublets having at 2.20 and 2.50 ppm arises from the $\overset{\diagdown\diagup}{CH}—CH_2S$ *cis* and *trans* protons, respectively. The oxirane ring signals are displaced downfield: the multiplet at 3.14 ppm, the quartet at 2.56 and the triplet at 2.73 ppm correspond to the CH, *cis* and *trans* CH_2 protons in $\overset{\diagdown\diagup}{CH}—CH_2O$. The considerable displacement of the signals of the thiirane and oxirane ring protons makes it possible to carry out both qualitative (recognition in the spectrum) and quantitative analyses. The position of the vinyloxy group signals in the spectra of 2-(vinyloxy)ethoxymethyloxirane and the corresponding thiirane remains unchanged (q 4.6 ppm, OCH=, two dd 4.18 and 4.00 ppm, CH_2=, *trans* and *cis*).

Polymerization which could be avoided at the stage of the synthesis of 2-(vinyloxy)ethoxymethylthiirane (under optimal conditions) leads to a ~30% loss of the product during distillation. However, it is possible to use the undistilled product for numerous preparative and commercial purposes. Moreover, the "raw" product contaminated with small quantities (a few percents) of the starting oxirane **73** turned out to be more stable (on prolonged storage) than the distilled thiirane **86**.[129]

2.5.2.3. *With Na_2S_x* The reactions of ω-vinyloxyalkoxymethyl oxiranes (**73, 75, 88**) with sodium sulfide and polysulfides have been studied.[136]

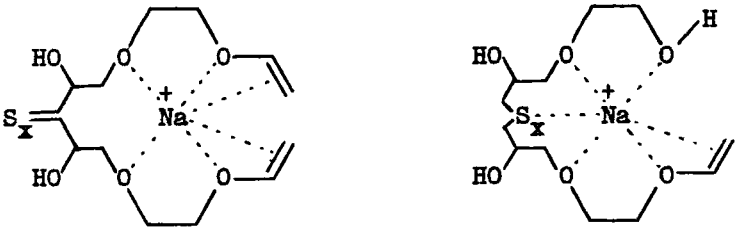
The interaction starts already at room temperature, however, at a low rate (16 days, ~33% yield). Intensive stirring markedly accelerates the reaction (3 days, 61% yield). Optimal conditions: presence of water, 40–50 °C, 1.5–2 h, quantitative yield. With increasing reaction temperature (to 95 °C), the yield slightly increases (~90%).

$$\underset{\textbf{73, 75, 88}}{CH_2{=}CHOROCH_2CH{-}CH_2\ (O)} + Na_2S_x \xrightarrow[-NaOH]{n\ H_2O} \underset{\textbf{89-93}}{[CH_2{=}CHOROCH_2CH(OH)CH]_2S_x}$$

R = $(CH_2)_2$ (**73**), x = 1 (**89**), 2 (**90**), 3 (**91**); R = $(CH_2)_2O(CH_2)_2$ (**75**), x = 1 (**92**); R = $(CH_2)_2O(CH_2)_2OCHCH_3$ (**88**), x = 1 (**93**)

Scheme 51

Water (0.7–2.2 g per 1 g of $Na_2S_x \cdot 9\ H_2O$) was used for the creation of a more active two-phase system in which the reaction products **89–93** of polyethyleneglycol structure, capable to form crown ether type complexes with alkali metal cations, act as phase-transfer catalysts.[136]



Scheme 52

The hydroxyl groups and double bonds facilitate the cation binding. Besides, the hydrolysis of sodium sulfide and the formation of small amounts of H_2S make possible the closure of the macrocycle by its addition to the double bonds.

Sodium disulfide was obtained from sodium sulfide and the calculated quantity of elemental sulfur in the same reaction vessel. When use is made of analytical grade (no less than 95%) sodium sulfide and polysulfide, the individual compounds **89–93**, are formed in quantitative yield.

It should be mentioned that the x value in sodium sulfide and polysulfide and in their adducts with 2-(vinyloxy)ethoxymethyloxirane **73** only coincide for reactions with sodium sulfide and disulfide. For the preparation of compound **91** ($x = 3$) the amount of sulfur corresponding to sodium tetrasulfide must be taken. With the amount of sulfur necessary for the preparation of sodium trisulfide the disulfide **90** is obtained.[136]

In spite of the fact that the reaction conditions were varied over a wide range (at the stage of the synthesis of sodium polysulfide: 50–120 °C, 2–40 h, 3–5 mol sulfur per mol sodium sulfide), organic polysulfides with $x > 3$ were not obtained.[136] In all runs no more than 3 equivalents of sulfur were involved in the reaction. The unbound sulfur could be filtered off.

Apparently, this obstacle could not be overcome either in a patent;[137] one notes in particular the formation of an unseparable mixture with a fractional x value instead of the expected individual organic polysulfides with $x > 2$.

Unlike the reaction of vinyl epoxy ethers with sodium sulfide which normally occurs smoothly without any marked change in temperature, with sodium polysulfides ($x = 3, 4$) a sudden temperature rise to ~100 °C is observed during the addition to the ether **73**. Apparently, at this temperature the reversible reaction is

$$NaS_2 + (x-1)\ S \rightleftharpoons Na_2S_x$$

displaced to the left, with partial decomposition of the polysulfide chain. How-

ever, the principal obstacle to the formation of polysulfides with $x > 3$ is the alkali released in the reaction course, which facilitates the cleavage of the S—S bonds.[138]

With sodium tri- and tetrasulfide derived from commercial sodium sulfide and elemental sulfur (without isolation and special purification) a mixture of products with a fractional x value between 2 and 3 is formed which seems to be due to the complex composition of the sodium polysulfide generated.

The use of sodium sulfide (or polysulfide) as a reagent instead of hydrogen sulfide[137] excludes parallel side-reactions at the vinyloxy group (as known,[139] bases do not inhibit the radical addition of hydrogen sulfide to vinyl ethers), thus ensuring 100% selectivity.

Upon heating the products **89–93** undergo polymerization to form cross-linked polymers.

In the IR spectra of the products **89–93** an intense hydroxyl absorption is observed (3450 cm^{-1}) and the vinyloxy group bands are: 820–840, 960, 1200, 1320, 1620, 1640, 3070, and 3120 cm^{-1}. The bands at 915, 1250, and 3000 cm^{-1} corresponding to the epoxy ring of the starting epoxides **73, 75, 88** are absent.

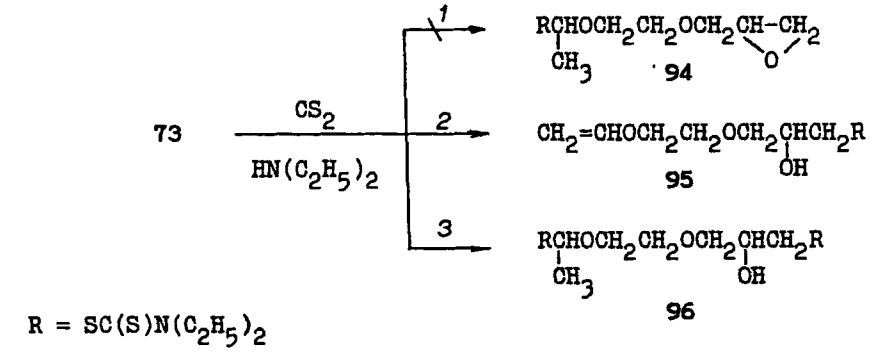
The ^1H NMR chemical shifts of **89–93** are shown in Table 11.

The products obtained are colored liquids with a moderate characteristic odor, soluble in most organic solvents and scarcely soluble in water (their water solubility decreases with increasing sulfur content), stable upon storage.

2.5.2.4. *With Dithiocarbamates*

2.5.2.4.1. *With the secondary amine-CS_2 system* The reaction of dialkyldithiocarbamic acids, generated *in situ* from carbon disulfide and dialkylamine, with vinyl ethers, which leads to 1-alkoxyethyl esters of dialkyldithiocarbamic acid seems to have been reported only once.[140] However, the products of this reaction, especially with functionally substituted vinyl ethers, are of great interest as objects of biological studies, and as reagents and intermediates.

Recently, the reaction of vinyl epoxy ether **73** with *N,N*-diethyldithiocarbamic acid was studied.[141–144] The interaction might be expected to follow three major directions to give the monoadducts **94** and **95**, the diadduct **96** or their mixture.



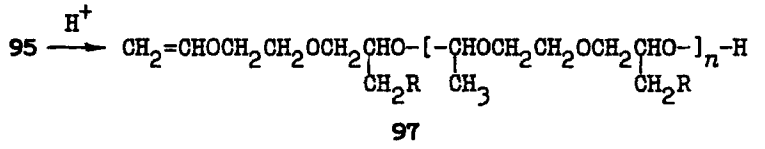
Scheme 53

TABLE 11 ^{1}H Chemical shifts and n_D^{20} values of bis(2-vinyloxyalkoxymethyl) sulfides and polysulfides **89–93**[136]

Cpd. No.	n_D^{20}	Chemical shift, δ (ppm)						
		=CHO, q	$=CH_2$, *cis*, dd	$=CH_2$, *trans*, dd	OCH_2CH_2O m	CH_2S, m	CH_2O, m	OH, s
89	1.4994	6.33	3.87	4.03	3.67	2.58	3.42	4.60
90	1.5245	6.33	3.86	4.06	3.66	2.61	3.43	—
91	1.5455	6.35	3.82	4.05	3.67	2.71	3.39	—
92	1.4960	6.35	3.85	4.03	3.68	2.60	3.37	5.91
93[a]	1.5040	6.33	3.86	4.04	3.53	2.58	3.38	7.21

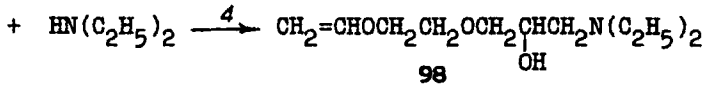
[a]Chemical shift of the acetal moiety, $OCH(CH_3)O$, 4.64 q, 1.21 d.

Independent of the reaction conditions (temperature and duration, the ratio of reagents, the order and rate of their addition, solvents and catalysts), only routes 2 and 3 were operative. With two- or threefold excess of carbon disulfide and diethylamine (80 °C, 3 h), the diadduct **96** was the only reaction product. It is only when use was made of an acid catalyst (30 °C, 2 h, 2% CF_3COOH) that the ^1H NMR spectrum of the reaction mixture showed a signal of the methine proton of the acetal fragment $OCH(CH_3)O$ (δ, CH 4.75 ppm) which belongs to the oligomer **97**.



Scheme 54

Upon mixing the reagents in the order: ether **73**—diethylamine—carbon disulfide (55 °C, 10 h) 6-vinyloxy-2-hydroxy-1-diethylamino-4-oxahexane **98** was not observed among the reaction products, although reaction 4 may even be preferred under these conditions.[1] This implies that the rate of the formation of *N,N*-diethyldithiocarbamic acid greatly exceeds the rate of reaction 4.



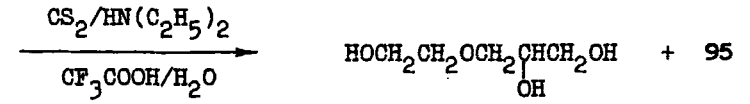
Scheme 55

The highest yield (95%) of 6-vinyloxy-2-hydroxy-1-diethyldithiocarbamoyl-4-oxahexane **95** is achieved when diethylamine is slowly introduced into a cooled (within a range from −20 to −10 °C) mixture of **73** with 2-fold excess carbon disulfide. Under the conditions studied (from −20 to +90 °C, 1–10 h, benzene, hexane, 0–2% CF_3COOH), the reaction path does not change, the yield of the adduct **95** changing to a lesser extent than could be expected.[141]

The epoxy acetal **94** was not obtained, even in the presence of catalytic amounts of trifluoroacetic acid which specifically activates the regioselective addition of protic reagents to the double bonds of vinyl epoxy ethers.[145,146] In this case, together with the adduct **95** a considerable quantity of the oligoacetal **97** is formed by electrophilic polyaddition of the "hydroxyl to the vinyloxy group". Heating of the adduct **95** (120 °C, 2 h) in the presence of trifluoroacetic acid (1%) leads to a viscous light-yellow polymer. The ^1H NMR spectrum of the latter shows clearly defined signals of the acetal moiety: δ 4.83 (CH), δ 1.24 (CH_3) ppm with correspondingly lower intensity of the vinyloxy proton signals. The element composition, refraction index, IR and ^1H NMR spectra of the oli-

gomers, both specially synthesized and isolated from the reaction mixture, are practically the same. IR spectra taken during the oligoacetal **97** formation show that the concentration of vinyloxy groups decreases 2 times as fast as that of hydroxyl groups. This was attributed to hydrolytic cleavage of some of the oligomer terminal vinyloxy groups by traces of water.[141]

The hydrolytic instability of vinyl epoxy ethers is well known.[147] In the presence of a mixture of *N,N*-diethyldithiocarbamic acid and a weak acid such as diethylammonium trifluoroacetate, the hydrolysis of **73** proceeds readily even at low temperature (from −2 to −3 °C). Thus, when aqueous diethylamine and trifluoroacetic acid were used (1%, 1 h, hexane), together with the adduct **95** glycerol hydroxyethyl ether was isolated (~50% yield):



Scheme 56

Thus, vinyl epoxy ethers do not add selectively *N,N*-diethyldithiocarbamic acid to the double bond owing to the higher sensitivity of the epoxide ring compared to that of the vinyloxy group to proton donors of this type. Traces of diethylamine which seem to be always present in the reaction mixture favor this reaction course by inhibiting the electrophilic addition to the double bond.

The dithiocarbamate **95** is a light-yellow liquid with a slight odor, well-soluble in benzene, carbon tetrachloride and other organic solvents. The isolation and purification of **95** is effected by high vacuum distillation. Its ^{1}H NMR spectrum shows proton signals of the vinyloxy group as quartets in the region 6.47 (=CH), 4.18, and 4.00 ($=CH_2$), the SCH_2 moiety at 3.40 and 3.60 ppm, and CH_3 groups as a double triplet at 1.27 ppm. The signals of the remainly protons are multiplets at 4.0 and 3.8 ppm. The doubling of the methyl signal is caused by hindered rotation about the C—N bond. The integral ratios in the ^{1}H NMR spectrum are as expected for **95**.

The IR spectrum of **95** retains the set of fundamental absorption bands occurring in the spectrum of the starting vinyl epoxy ether corresponding to the vinyloxy group vibrations: 3120, 3065 [υ_{as} ($=CH_2$)], 1640, 1620 (υ (CH=CH_2)], 1325 [(δ (CH), flat], 1208 [υ_{as} (=C—O—C)], 1050 cm^{-1} [υ_s (=C—O—C)], CH_2 groups [υ_s (CH_2)]: 2880 and 2930 cm^{-1} and C—O—C bonds (broad band in the 1090–1140 cm^{-1} region). The low-wavenumber wagging vibrations of the $=CH_2$ group in the vinyl epoxy ether **73** (825 cm^{-1}) seem to overlap with a more intense absorption band caused by CH_2 groups deformational vibrations of ethyl groups (840 cm^{-1}), which is indicated by a markedly distorted shape of this band. In the spectrum of the diadduct **96** (without vinyloxy groups) the δ CH_2 vibrations give rise to a narrow, very intense band (850 cm^{-1}) of perfect shape. The char-

acteristic signals of the epoxy ring at 3010 [υ (CH)], 1250 (υ_s epoxy ring) and 912 cm^{-1} (υ_{as} epoxy ring) are absent. In the epoxy ether **73** and 3060 cm^{-1} band [υ (CH_2 in $\overset{\diagdown}{CH}—CH_2O$)] overlaps with the band of the $=CH_2$ asymmetrical stretching vibrations. The weakening of this band in the spectrum of the adduct **95** may be regarded as evidence for the absence of contributions from the epoxy ring CH_2 stretching vibrations to the absorption in this region.

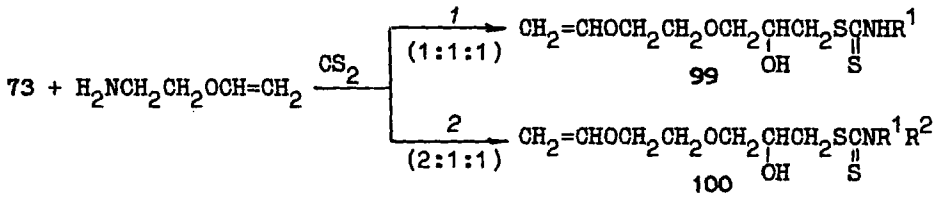
The sharp weakening of the 965 cm^{-1} band intensity in the spectrum of **95** (visible as a shoulder on the 1000 cm^{-1} band) and the retention and even strengthening of this band in the spectra of the diadduct **96** and oligoacetal **97** may be indicative of the fact that the presence of this band is caused by CSS asymmetrical stretching vibrations rather than by out-of-plane CH deformational vibrations in $=CH_2$ and $=CH$ groups.[148] Relying upon assignments made in Ref. 148 the intense absorption band at 930 cm^{-1} occurring in the spectra of **95–97** can also be ascribed to υ_{as} (CSS). The 560, 840, 930, 1280, 1300, 1365, 1395, 1430, 1465, and 1500 cm^{-1} bands arise from bond vibrations in the diethyldithiocarbamate fragment.[149] The C—O and C=S bonds absorb in the region 1000–1250 cm^{-1} and manifest themselves as a set of 1000, 1025, 1090, 1120, and 1170 cm^{-1} bands. The bands corresponding to OH deformational vibrations occur in the same region. The broadened band at 3450 cm^{-1} is related to the associated hydroxyl group stretching vibrations.

The intense absorption band at 1500 cm^{-1}, also present in the spectra of the diadduct **96** and the oligoacetal **97**, can be assigned[148] to stretching vibrations of the C—N bond in the C(S)-N moiety.

2.5.2.4.2. *With the primary amine-CS_2 system* The interaction of vinyl epoxy ether **73** with *N*-monosubstituted dithiocarbamic acids has been studied and new functionally substituted vinyl ethers have been synthesized.[142–144,150,151]

The dithiocarbamic acids were obtained *in situ* from carbon disulfide and 2-(vinyloxy)ethylamine, ethylene-, *m*-phenylene- and *p*-xylylenediamine. In the case of 2-(vinyloxy)ethylamine, together with the monoadduct **99** the trivinyl ether **100** is formed.[142,150]

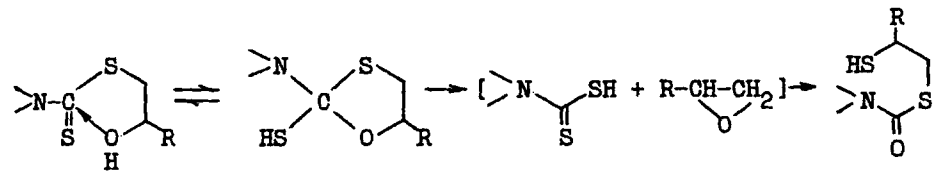
Even with very slow addition of 2-(vinyloxy)ethylamine to an equimolar mixture of carbon disulfide and the ether **73** the reaction is accompanied by a strong exothermic effect (heating up to 90–95 °C). After removal of unreacted starting material by heating the reaction mixture under reduced pressure (60 °C, 1 *mm* Hg) the monadduct **99**, 6-vinyloxy-2-hydroxy-1-(2-vinyloxyethyl)dithiocarbamoyl-4-oxahexane, was obtained in 97% yield. In its IR spectrum the vinyloxy group is represented by a standard[141] set of bands: 3150, 3050, 1640, 1620, 1325, 1200, 1060 (shoulder at the 1100 cm^{-1} band), 830 cm^{-1}. Weak bands in the 540, 600, 640, 700, 770, 900 cm^{-1} region, a broadened band with maxima at 1100 and 1160 cm^{-1} (C—O—C, C=S) in combination with bands of intermediate intensity at 1400 and 1470 cm^{-1} and strong bands at 980 (υ_{as} CSS) and 3260 (NH) cm^{-1} correspond to the dithiocarbamate moiety. The O—H stretching vibrations occur at 3450 cm^{-1}.



$R^1 = CH_2CH_2OCH{=}CH_2$, $R^2 = CH_2CH(OH)CH_2OCH_2CH_2OCH{=}CH_2$

Scheme 57

The marked weakening of the band at 1500 cm^{-1}, normally very intense,[141,148] (in the IR spectrum of **95**) related to stretching vibrations of the C—N bond of the dithiocarbamate moiety N—C(S)S (1540 cm^{-1}), along with the appearance of a band at 1670 cm^{-1} of comparable intensity (υ C=O), are likely to be a result of the base-initiated alkoxide-thiolate rearrangement known with many disubstituted aliphatic compounds of dicoordinate sulfur, which proceeds *via* the formation of a 1,3-oxathiolane ring.[105,107,152]

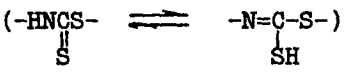


$R = CH_2OCH_2CH_2OCH{=}CH_2$

Scheme 58

For 2-hydroxyalkyl esters of dithiocarbamic acids, rearrangements of this kind had not been reported before the cited work.[105,150] An additional support of this fact is provided by the observed,[100–102, 104] (but not explained before the cited work[105]) formation of *S*-epithio esters of thiolcarbamic acids instead of the expected corresponding *S*-glycidyl esters of dithiocarbamic acids in the reaction of epichlorohydrin with dialkyldithiocarbamic acids and their salts.

The weak band at 1750 cm^{-1} (C=N) in the IR spectrum of **99** was attributed to thione-thiol tautomerism:[150]



Scheme 59

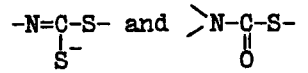
In the ^1H NMR spectrum of the adduct **99**, signals of epoxy ring protons are

absent. The vinyloxy group gives rise to the usual quartets in the 6.37 ppm region (=CHO) and at 4.20 and 4.00 ppm ($=CH_2$, *trans*- and *cis*-protons, respectively). The signals of other protons are present as a broad multiplet in the 3.8–3.3 ppm region.

With an ether **73**-amine-carbon disulfide ratio of 1:1:2 the adduct **99** was isolated as well.[150]

The addition of the monoadduct **99** to the ether **73** (125 °C, 3–5 h) gives **100** in quantitative yield. Use of a two-fold molar excess of **73** in the reaction with *N*-(2-vinyloxyethyl)dithiocarbamic acid (pathway 2) also leads to **100**. In this case, however, the reaction is carried out with a gradual increase in temperature.

The absence of the NH absorption band in the IR spectrum of **100** as well as the weakening of the bands at 1540, 1470, and 1400 cm^{-1} and appearance of intense bands at 1670 and 1765 cm^{-1} indicates not only the addition of a second molecule of **73** to **99** (the element composition of the reaction product perfectly corresponds to **100**), but also a considerable contribution from the structures



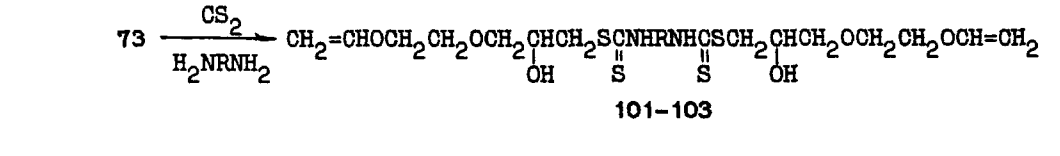
Scheme 59a

The former is possible due to the tautomerism known for *N*-monosubstituted thiocarbamates,[133] whereas the latter is produced by the above-mentioned alkoxide-thiolate rearrangement, accelerating upon heating.[105]

With two-fold (with respect to amine) molar excess of vinyl ether **73** and carbon disulfide the adduct **100** was isolated.[150]

The structure of **100** is also supported by the ^1H NMR spectrum (δ, ppm): 6.36 q, 4.22 dd, 4.00 dd ($OCH=CH_2$), 3.75–3.50 m (other protons); the integral intensity of signals corresponds to **100**.

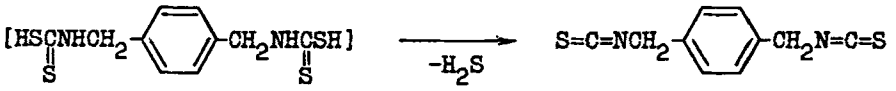
Bis-dithiocarbamic acids derived from primary diamines react with vinyl epoxy ether **73** to afford the adducts **101–103** in quantitative yield.



Scheme 60

When the order of mixing of the reagents is changed, especially when **73** is

added to *N,N'*-bis-xylylenedithiocarbamic acid heated to 80 °C, the IR spectrum of the product **102** shows (together with fundamental bands) a band of moderate intensity at 1740 cm^{-1} (−N=C) and two weak bands 2100 and 2180 cm^{-1}, corresponding to the isothiocyanate moiety —N=C=S which is formed according to Scheme 61:



Scheme 61

Unlike compound **102**, the IR spectrum of the adduct **101** exhibits two strong bands at 1660 (C=O) and 1720 cm^{-1} (—N=C) of nearly equal intensity and a band of moderate intensity at 1520 cm^{-1} [NHC(S)]. The intensity ratio of these bands changes gradually in favor of the first two ones.

Upon storage **99** cross-links spontaneously.

2.5.3. *Reactions of 2-(vinyloxy)ethoxymethylthiirane with amines* The reactions of thiiranes with amines are fairly well understood, *e.g.*[107,126,131,132,153,154] Nevertheless, the interest in these reactions has not diminished and the number of publications in this field is still increasing due to the wide applications of amino thiols in medicine and engineering, *e.g.*[107,135,154]

Epithioglycidol ethers held a modest position in the total volume of publications concerning the reaction of thiiranes with amines. The list of epithio ethers involved in this reaction is scanty. The yields of β-amino thiols are moderate, as a rule, whereas the reaction temperature is high (100–200 °C).[132]

The reaction of vinyloxyorganylthiiranes with amines is mentioned only briefly in Refs. 1, 125. The first representative of vinyl ethers containing a β-amino thiol fragment was synthesized in 48% yield by reaction of 2-(vinyloxy)ethoxymethylthiirane **86** with two-fold excess diethylamine (boiling water bath temperature, 3 h).[125] The product turned out to be quite stable and, in spite of the presence in its molecule of both mercapto and vinyloxy groups, practically without tendency towards polyaddition and cyclization, as was the case in the synthesis of 2-(vinyloxy)ethanethiol.[119]

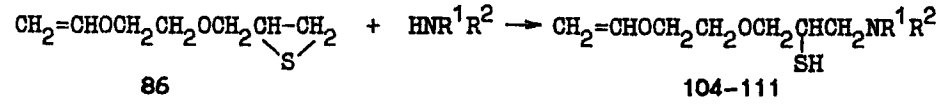
In order to obtain additional 3-(2-vinyloxyethoxy)-1-aminopropane-2-thiols, i.e., **104–111**, and to gain a clearer understanding of this reaction the authors of Refs. 143, 155, 156 examined the addition of various primary and secondary amines to 2-(vinyloxy)ethoxymethylthiirane **86**. The reaction conditions and results are presented in Table 12.

Normally, for the suppression of thiirane polymerization it is possible to use excess amine or non-polar solvents or to carry out the reaction without solvent.[157,158]

TABLE 12 The reaction conditions (equimolar mixture of reagents, benzene, 3 h), constants, yields of the amino thiols **104–111**[155]

Cpd. No.	Reaction temperature, °C	Yield, %	B.p., °C (*mm* Hg)	n_D^{20}	d_4^{20}
104	100	78	92(1)	1.4740	0.9851
105	110	78	120(3)	1.4705	0.9497
105[a]	110	30			
106	100	32	105(3)	1.4840	
107	102	50	105(1)	1.4950	1.0858
107[a]	102	27			
108	105	76	111(3)	1.4972	1.0467
109[a]	110[b]	21	136(1)	1.5355	
110	105	72	87(1)	1.4920	1.0289
110[a]	135	45			
111	107	73	132(3)	1.4987	1.0886

[a]Without solvent.
[b]Reaction time 8 h.



$R^1 = R^2 = n\text{-}C_3H_7$ (104), $n\text{-}C_4H_9$ (105); $R^1 = H$, $R^2 = t\text{-}C_4H_9$ (106), $CH_2CH_2OCH{=}CH_2$ (107), $CH_2CH{=}CH_2$ (108), $CH_2C_6H_5$ (109); R^1, $R^2 = (CH_2)_5$ (110), $(CH_2)_2O(CH_2)_2$ (111)

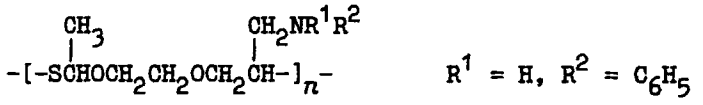
Scheme 62

As seen from Table 12, with benzene as a solvent (stoichiometric ratio of reagents), the yields of β-amino thiols are fairly high in most cases (70–80%). Without solvent, on the contrary, the yields of the adducts **104–111** drop abruptly (approximately by a factor of two) due to polymerization of the starting thiirane **86**.

Elimination of sulfide from 2-(vinyloxy)ethoxymethylthiirane, sometimes observed in the reaction of thiiranes with amines,[159] does not occur under these conditions. In the ^1H NMR spectra of the reaction mixtures there are not even traces of allyloxy group signals. The absence of the thioacetal signals, $OCH(CH_3)S$, as well as the full intensity of the vinyloxy group signals confirm the stability of the 3-(2-vinyloxyethoxy)-1-aminopropane-2-thiols **104–111** under the conditions studied.[155]

Unlike aliphatic and arylaliphatic amines, aniline in the reaction with the thiirane **86** without solvent (120–125 °C, 6 h) forms a viscous orange-red product, in the IR and ^1H NMR spectra of which there are no absorptions attributable the vinyloxy group and the thiirane ring.[155] At the same time, the presence in the ^1H NMR spectrum of two triplets in the region 7.14 (H_m in C_6H_5) and 6.66 ppm ($H_{o,p}$), a quartet (4.82 ppm) and a doublet (1.49 ppm), corresponding to the

protons of the methine and methyl groups of the thioacetal moiety, and a multiplet centred at 3.57 ppm (other protons) indicate that the final reaction product, 3-(2-vinyloxyethoxy)-1-phenylaminopropane-2-thiol, undergoes polyaddition ("head-to-tail" type) to form the polythioacetal **112**.[155]



112 $R^1 = H$, $R^2 = C_6H_5$

Scheme 63

A decrease in the reaction temperature and time (105 °C, 3 h) and use of solvent (benzene) do not stop the polymerization, but decelerate the reaction: thiirane **86**: upon distillation of the reaction mixture the starting material is recovered, and a resinous product (*ca.* 15%) remains.

The amino thiols **104–111** are colorless mobile liquids well soluble in normal organic solvents.

In the IR spectra of **104–111** the absorption band at 620 cm^{-1}, characteristic of the thiirane ring, disappears and a band at 2560 cm^{-1}, corresponding to the SH group stretching vibrations, appears. In the spectra of **106** and **109** the intensity of this band is uncommonly high. The vinyloxy group is represented by a normal set of characteristic frequencies (800–820, 960–980, 1190–1200, 1310, 1600–1650, 3100 cm^{-1}) which remain in the spectra of all compounds. The Raman spectra show an intense absorption band in the 2549–2560 cm^{-1} region, corresponding to SH vibrations. The yields and constants of the amino thiols **104–111** are given in Table 12, IR and Raman spectra are presented in Table 13 and ^1H NMR spectra in Table 14.

TABLE 13 IR and Raman spectra of the amino thiols **104–111**[155]

Cpd. No.	IR, cm^{-1}	Raman (SH), cm^{-1}
104	680, 730, 800, 860, 950, 990, 1030, 1120, 1180, 1220, 1305, 1350, 1440, 1600, 1620, 2570, 2830, 2850, 2935, 3110	2570
105	680, 725, 800, 865, 945, 990, 1030, 1075, 1120, 1180, 1225, 1310, 1345, 1445, 1600, 1625, 2565, 2725, 2800, 2850, 2915, 2950, 3110	—
106	680, 735, 800, 820, 850, 890, 940, 1020, 1115, 1180, 1220, 1305, 1340, 1380, 1440, 1600, 1620, 2565, 2855, 2920, 2950, 3110	—
107	700, 810, 880, 955, 1035, 1080, 1125, 1200, 1240, 1315, 1350, 1450, 1615, 1635, 2565, 2800, 2865, 2920, 3120	2570
108	560, 710, 800, 850, 920, 980, 1030, 1080, 1200, 1260, 1325, 1360, 1430, 1460, 1620, 1640, 2570, 2820, 2900, 2950, 2975, 3100, 3130, 3330	—
109	580, 690, 745, 810, 850, 955, 1030, 1130, 1200, 1250, 1320, 1350, 1450, 1615, 1635, 2565, 2800, 2850, 2920, 3020, 3120, 3300	2549
110	700, 770, 820, 880, 950, 990, 1035, 1125, 1250, 1270, 1325, 1350, 1375, 1450, 1620, 1640, 2500, 2800, 2850, 2935, 3120	2576
111	700, 820, 845, 885, 910, 950, 990, 1030, 1055, 1110, 1135, 1215, 1335, 1380, 1475, 1635, 1650, 2575, 2700, 3110, 3150	2545

TABLE 14 The ^{1}H NMR spectra of **104–111**[155] $CH_2=CHOCH_2CH_2OCH_2CH(SH)CH_2NR^1R^2$

Cpd. No.	R^1	R^2	Chemical shift, δ, ppm							
									R^1, R^2	
			=CHO, q	$=CH_2$, *trans*, dd	$=CH_2$, *cis*, dd	OCH_2CH_2O, m	CH_2CHS, m	CH_2N, m	CH_2, m	CH_3
104	*n*-C_3H_7	*n*-C_3H_7	6.47	4.18	3.98	3.72	3.13	2.33	1.47	0.86 t
105	*n*-C_4H_9	*n*-C_4H_9	6.47	4.16	3.99	3.79	3.14	2.38	1.34	0.90 t
106	H	*t*-C_4H_9	6.47	4.17	4.00	3.76	2.85	2.35	1.69	1.08 s
107	H	$CH_2=CHOCH_2CH_2$	6.48	4.18	4.00	3.78	2.89	2.09	1.43	—
108	H	$CH_2=CHCH_2$	6.48	4.18	3.78	3.78	3.23	2.76	1.74	5.84 m, 5.24 d, 5.07 m[a]
109	H	$C_6H_5CH_2$	6.45	4.16	4.00	3.58	3.20	2.49	1.50	7.30[b]
110		$(CH_2)_5$	6.42	4.12	3.93	3.72	3.14	2.39	1.50	—
111		$(CH_2)_2O(CH_2)_2$	6.47	4.18	4.00	3.69	3.20	2.47	1.49	—

[a] $CH_2=CH$ in R^2.
[b] C_6H_5 in R^2.

The amino thiols **104–111** are purified by distillation at reduced pressure. The residues are viscous liquids, colored from bright orange to dark brown, which were proved to be mixtures of 2-(vinyloxy)ethoxymethylthiirane homopolymer and oligomers **112**, the latter prevailing.[155] This conclusion is confirmed by elemental analysis and spectral characteristics. In the ^{1}H NMR spectrum of the still residue of amino thiol **109**, for example, the signals of the vinyloxy group occur as traces, instead of them, the thioacetal signals appear (4.78 q and 1.28 d ppm).

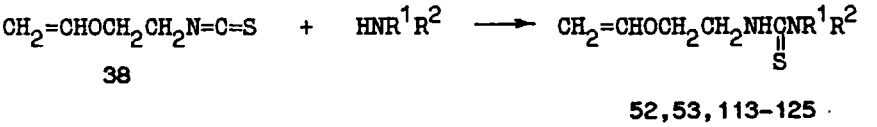
Upon storage the amino thiols **104–111**, purified by distillation, undergo slow polymerization. After about three months their viscosity is increased and in six months on average they completely lose fluidity.[155]

2.6. *Reactions of 2-(Vinyloxy)ethyl Isothiocyanate*

2.6.1. *With Amines*

2.6.1.1. *With aliphatic amines* Reactions of isothiocyanates with amines have been investigated both preparatively and kinetically, *e.g.*[93,95,160] The most important results of the kinetic studies are covered in a review.[161] The growing interest in this reaction is caused by its great synthetic and applied value as well as by the wide spectrum of biological activities of substituted thioureas.[160,162–164]

Reaction of 2-(vinyloxy)ethyl isothiocyanate **36**[55,58,63,66,67,70,73,78,85] with ammonia, primary and secondary amines gave the earlier unknown *N*-(2-vinyloxyethyl)thioureas **52, 53, 113–125** (Table 15).



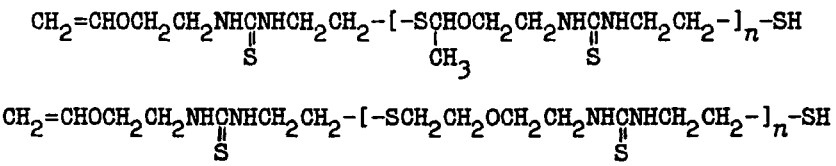
Scheme 64

N-(2-Vinyloxyethyl)-*N'*-(2-mercaptoethyl)thiourea **117** containing groups sensitive to each other (thiol and vinyloxy) oligomerizes partially or cyclizes already during its synthesis. In the ^{1}H NMR spectrum of the product along with signals of the target compound **117** small signals of the thioacetal moiety $OCH(CH_3)S$ are observed (1.54 d and 4.83 q ppm). Upon storage (for about one month) the product loses its fluidity turning into a transparent, weakly coloured, viscously-tough odorless essentially polymeric substance soluble in acetone, dimethyl sulfoxide, *etc*. This material proved to result from the polyaddition in a "head-to-tail" manner, both according to and against the Markovnikov rule. From the ^{1}H NMR signal intensities the polymer contains nearly equal quantities of Markovnikov and anti-Markovnikov blocks:

TABLE 15 Characteristics of the thioureas **52, 53, 113–127**[58,66]

Cpd. No.	R^1	R^2	M.p., °C	n_D^{20}	d_4^{20}
52	H	H	38	—	—
53	H	CH_2=$CHOCH_2CH_2$	52–54	—	—
113	H	CH_3	78	—	—
114	H	CH_2=$CHCH_2$	—	1.5623	1.0927
115	H	*i*-C_4H_9	—	1.5318	1.0304
116	H	CH_2CH_2OH	—	1.5685	1.1754
117	H	CH_2CH_2SH	—	1.6100	1.2144
118	H	$C_4H_9SCH_2CH_2OCH_2CH_2$	—	1.5444	1.1039
119	CH_3	CH_3	—	1.5562	1.0655
120	C_2H_5	C_2H_5	—	1.5425	1.0547
121	*n*-C_4H_9	*n*-C_4H_9	—	1.5140	0.9860
122	CH_2CH_2OH	CH_2CH_2OH	—	1.5530	1.2018
123	CH_3	*cyclo*-C_6H_{11}	—	1.5502	1.0674
124	-$(CH_2)_5$-		—	1.5639	1.1057
125	-$(CH_2)_2O(CH_2)_2$-		47	—	—
126[a]	-$(CH_2)_2O(CH_2)_2$-		—	1.5566	1.1434
127[b]	-$(CH_2)_2O(CH_2)_2$-		—	1.4576	1.3923

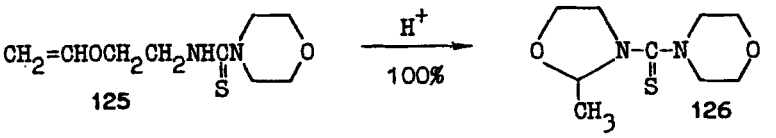
[a]Product of intramolecular cyclization of thiourea **125**.
[b]Adduct of thiourea **125** with $H(CF_2)_4CH_2OH$.



Scheme 65

The other thioureas (**113–116, 118–125**) are fairly stable, undergoing no visible change during a long time. Upon distillation the liquid products partially decompose which is apparent from the appearance of a weak isothiocyanate absorption in the IR spectra. The ^{1}H NMR parameters of the thioureas **53, 114, 117, 122** are summarized in Table 16.

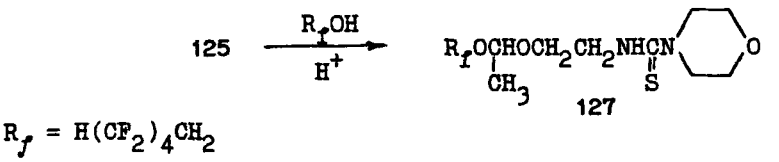
The capacity of *N*-(2-vinyloxyethyl)thioureas to undergo typical reactions of vinyl ethers is illustrated by their intramolecular cyclization into 1,3-oxazolidines and their alcohol addition. Thus, thiourea **125** in the presence of catalytical amounts of perfluorobutyric acid at 50–60 °C for 5–10 min smoothly and quantitatively cyclizes into 2-methyl-3-[(1-morpholyl)thiocarbonyl]-1,3-oxazolidine **126**.



Scheme 66

This synthesis seems to be the first example of the addition of a thiourea to a vinyl ether. The ^{1}H NMR (δ, ppm) spectrum of **126**: 5.78 q (OCHN), 1.47 d (CH_3), 3.53 m, 3.69 m (OCH_2CH_2N).

The acid-catalyzed reaction of thiourea **125** with 2,2,3,3,4,4,5,5-octafluoropentan-1-ol (0.5% of C_3F_7COOH, 50–60 °C, 5 min) leads to *N*-(4-methyl-7,7,8,8,9,9,10,10-octafluoro-3,5-dioxadecylthiocarbamoyl)morpholine **127**.



Scheme 67

In the ^{1}H NMR spectrum of the reaction mixture (after the reaction is completed), together with signals of the acetal moiety in the compound **127** [1.35 d (CH_3), 4.84 q (OCHO) ppm], signals of the oxazolidine **126** (*ca.* 15–20%) are

TABLE 16 ^{1}H Chemical shifts in the NMR spectra of thioureas **53, 114, 117, 122** (δ, ppm, $CDCl_3$)[58,66]

Cpd. No.	=CHO, q	$=CH_2$, *trans*, dd	$=CH_2$, *cis*, dd	OCH_2, NCH_2, m	NH, s	R^1, R^2
53[a]	6.25	4.07	3.91	3.41		
114	6.41	4.19	4.03	3.82	6.99	5.82 m (=CH), 5.18 m ($=CH_2$), 4.03 m (NCH_2)
117	6.46	4.21	4.06	3.82	7.02	2.76 t (SCH_2), 3.75 m (NCH_2)
122	6.44	4.17	4.01	3.81	7.85	4.51 s (OH) 3.81 m (NCH_2CH_2O)

[a] C_6D_6.

present (1.47 d (CH_3), 5.80 q (OCHN) ppm]. Signals of remaining protons: 3.75 m (OCH_2CH_2N), 6.57 t, 5.54 t [$H(CF_2)_4$]. When the reaction is carried out in a solvent (benzene, 0.5% of $C_3F_7CO_2H$, 58–60 °C, 1 h), the product contains no oxazolidine **126**.

2.6.1.2. *With aromatic amines* The high synthetic potential of 2-(vinyloxy)ethyl isothiocyanate **38** as a CH_2=CHO carrier in a one-pot synthesis of functionally substituted thioureas has been demonstrated for the first time in[55] with the reaction of (2-hydroxyethyl)- and 2-(vinyloxy)ethylamines, which leads to promising and earlier unknown *N*-(2-hydroxyethyl)- and *N,N'*-bis(2-vinyloxyethyl)thioureas in quantitative yield. The reaction of 2-(vinyloxy)ethyl isothiocyanate **38** with aliphatic amines has been described in Refs. 58, 63, 66, 67, 70, 85.

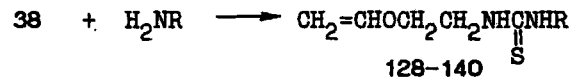
The reaction of 2-(vinyloxy)ethyl isothiocyanate **38** with aromatic amines leading to high yields of earlier unknown *N*-(2-vinyloxyethyl)-*N'*-aryl (heteroaryl) thioureas **128–140** has been reported in Refs. 64, 67, 77, 85. The *N*-(2-vinyloxyethyl)-*N'*-phenylthiourea **132** was obtained previously by addition of 2-(vinyloxy)ethylamine to phenyl isothiocyanate.[165]

The reaction is carried out without solvents and catalysts with stoichiometric quantities of reagents. Normally the reaction proceeds with a mild exothermic effect (30–40 °C) and is completed within 2–5 min. Only in a few cases, usually upon addition of less basic or sterically hindered amines such as 3,4-dichloroaniline, 2-aminoacetophenone, 2-amino-4-methylpyridine (Table 17), it required moderate (30–50 °C) short (5–30 min) heating of the reaction mixture.

TABLE 17 The reaction of 2-(vinyloxy)ethyl isothiocyanate **38** with aromatic amines[77]

Reaction temperature (self-heating), °C	Reaction time, min	Product	Yield, %	M.p., °C
(40)	2–3[a]	**128**	90	71–73
(35)	2–3[a]	**129**	95	82
30	60	**130**	95	94
50	15	**130**	90	94
50	5	**131**	95	75
(30)	3–5[a]	**132**	95	138–140
40–45	15–20	**133**	65	88
(35–38)	2–3[a]	**134**	95	72–74
(40)	2–3	**135**	100	82–84
38–40	2–3	**136**	100	62
50	0.5 h	**137**	100	65
60	15	**138**	75	130–132
30	0.5 h	**139**	100	106
(38)	2–3	**140**	100	127

[a]Without additional heating.



R = 2,4-$(CH_3)_2C_6H_3$ (128), 3-ClC_6H_4 (129), 3,4-$Cl_2C_6H_3$ (130), 2-$CH_3COC_6H_4$ (131), 2-naphthyl (132), 5-CH_3-2-pyridyl (133), C_6H_5 (134), 2-$CH_3C_6H_4$ (135), 2-$CH_3OC_6H_4$ (136), 3-$C_2H_5OC_6H_4$ (137), 4-$CH_3CONHC_6H_4$ (138), 2-pyridyl (139), 4-BrC_6H_4 (140)

Scheme 68

Unlike primary amines, secondary aromatic amines, in particular, diphenylamine and phenothiazine, failed to add to the isothiocyanate **38** neither by heating nor in the presence of triethylamine (Table 17).

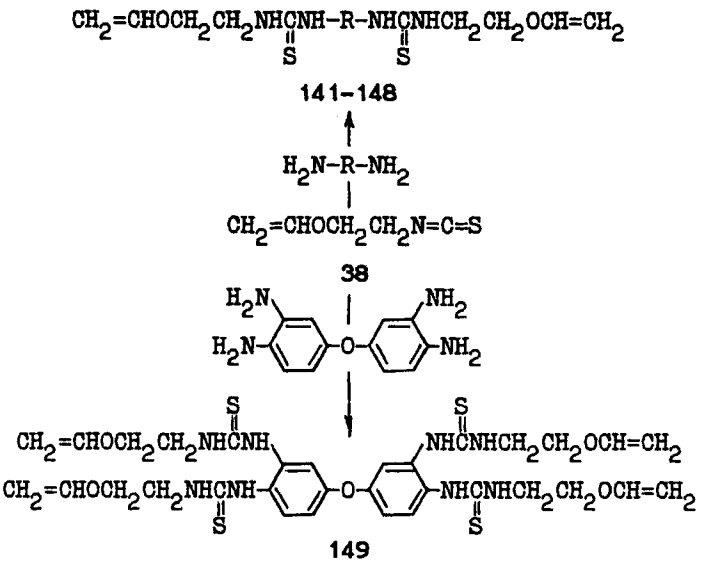
The representative spectral characteristics of the thioureas **128–134** are exemplified in Table 18.

In their IR spectra the set of characteristic absorption bands related to the vinyloxy group (810–830, 1180–1200, 1600–1640 cm^{-1}) remains unchanged, the broad split band corresponding to the isothiocyanate group (2100–2200 cm^{-1}) disappears and bands caused by vibrations of the thioamide NHC(S) (1500–1530 cm^{-1}) appear. In the ^1H NMR spectra of the thioureas **128–134** the vinyloxy group gives rise to signals 6.40–6.56 q, 4.17–4.28 dd, 3.92–4.00 dd, the (OCH_2CH_2N) part to signals 3.86–4.13 m and the NH proton to signals 8.52–12.00 s, 5.93–9.43 s (ppm).

2.6.1.3. *With diamines* The work described in Ref. 81 deals with the reaction of 2-(vinyloxy)ethyl isothiocyanate **38** with primary di- and tetraamines, which leads to quantitative yields of earlier unknown di- and tetra-(2-vinyloxyethyl)di- **142–148** and -tetrathioureas **149**. The synthesis was carried out by simple mixing of stoichiometric quantities of reagents without solvents and catalysts. The addition of aliphatic diamines to the isothiocyanate **38** is accompanied by a strong exothermic effect and ceases nearly instantly.[81] As should be expected, aromatic diamines react more calmly, while with 3,3′,4,4′-tetraaminodiphenyl ether moderate heating of the reaction mixture ($CHCl_3$, 50 °C, 1 h) is needed. The order of addition of the reactants does not affect the reaction result appreciably.[81]

TABLE 18 ^{1}H Chemical shifts in the NMR spectra of the thioureas **128–139**[77]

Cpd. No.	Chemical shift, δ (ppm), $CDCl_3$					
	=CHO, q	$=CH_2$, *trans*, dd	$=CH_2$, *cis*, dd	OCH_2, NCH_2, m	NH, s	R
128	6.46	4.20	3.95	3.87	8.52, 6.97	2.29 s (CH_3), 2.20 s (CH_3), 7.07 m (C_6H_3)
129	6.51	4.23	3.98	3.91	9.04, 7.50	7.14 m (H^4), 7.35 m ($H^{5,6}$), 7.71 m (H^2)
130	6.51	4.24	3.99	3.90	9.14, 7.60	7.93 d (H^2), 7.48 d (H^6), 7.45 dd (H^5)
131	6.51	4.25	3.96	4.59	9.91, 5.93	1.60 s (CH_3), 7.49 dd (H^6), 7.30 td (H^3), 7.10 m ($H^{4,5}$)
132	6.40	4.17	3.92	3.86	9.07, 7.07	7.53–7.58 m (H^{3-6}), 7.83–8.05 m ($H^{2,7,8}$)
133	6.56	4.28	4.00	3.96	12.0, 9.43	7.02 d (H^3), 6.90 d (H^5), 8.08 d H^6), 2.33 s (CH_3)
134	6.50	4.24	3.98	3.90	8.98, 7.30	7.12 m ($H^{2,6}$), 7.49 m (H^{3-5})
137	6.36	4.17	4.00	3.84	8.82	7.22 (H_m), 6.79 ($H_{o,o',p}$), 3.84 (OCH_2), 1.36 (CH_3)
139	6.51	4.26	4.05	4.00	9.00	8.17 d (H^6), 7.63 (H^4), 6.87 ($H^{3,5}$)

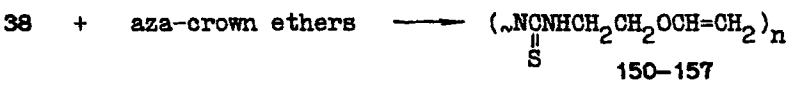


R = $(CH_2)_2$ (141), CH_2CHCH_3 (142), $(CH_2)_4$ (143), 1,4-$CH_2C_6H_4CH_2$ (144), 1,3-C_6H_4 (145), 2,4-$C_6H_3CH_3$ (146), 1,4-$C_6H_3COCH_3$-2 (147), 2,3-$C_{10}H_6$ (148)

Scheme 69

The melting points and spectral (IR) characteristics of the thioureas **141–148** are presented in Table 19.

2.6.1.4. *With aza-crown ethers* A new group of functionally substituted aza-crown ethers with highly active vinyloxy and thiocarbamoyl functions have been prepared quantitatively by the reaction of aza-crown ethers (aza-12-crown-4, aza-15-crown-5, aza-18-crown-6, benzoaza-15-crown-5, 1,7-diaza-12-crown-4, 1,7-diaza-15-crown-5, 1,10-diaza-18-crown-6, 1,4-dioxa-7,10,13-triaza-15-crown-5) with 2-(vinyloxy)ethyl isothiocyanate **38**.[166]



Scheme 70

n is the number of NH groups in the ether (see Table 20).

Compound **38** is useful for the functionalization of a large number of aza-crown ethers and other macroheterocyclic structures containing NH groups.

Such macrocyclic compounds are of interest as phase transfer catalysts, com-

TABLE 19 Melting points and spectral (IR) characteristics of the thioureas **141–149**[81]

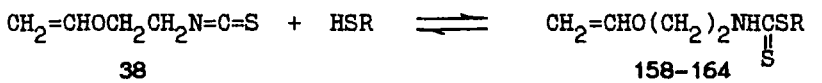
Cpd. No.	M.p., °C	ν, cm^{-1}
141	115–125	540, 560, 610–670, 730, 770, 790, 830–850, 910, 960–990, 1020, 1090, 1130–1140–1160–1190–1210–1250, 1300–1310–1320–1360, 1490, 1510–1520–1570–1620, 2860–2940–3100, 3200
142	115	560, 660–690, 820, 960, 1010, 1080, 1200, 1280, 1310–1340–1370, 1460, 1500–1520–1550, 1620–1640, 2870, 2930–2960, 3060, 3250
143	108	500, 550, 640, 690–700, 820, 910, 960, 970, 1020, 1050–1060–1080, 1140–1180, 1220, 1250, 1280–1300–1330–1350–1370, 1420–1450, 1520–1540, 1610, 2840–2860, 2920, 3040, 3240–3300
144	80	500–510–540–580, 680, 790–810, 910, 950, 1010, 1070, 1180, 1280, 1310, 1320, 1370, 1420, 1450, 1530–1550, 1610, 2850, 2910, 3050, 3220, 3400
145	140–148	520–600, 650, 700, 720, 790, 810, 880, 910, 980, 1040, 1090, 1190, 1300–1330–1350–1370, 1460, 1530–1540, 1580, 1610–1640, 2850, 2920, 3070, 3450
146	140–142	550, 610–640, 710, 800, 860, 940–960, 990, 1010, 1060, 1120, 1180, 1240, 1270, 1300, 1330, 1360–1380, 1440, 1500–1520–1530–1570, 1600, 2850–2910–2950, 3150, 3250, 3350
147	130–132	510–540, 600, 700, 820, 960–970, 1010–1030, 1070, 1260, 1300–1330, 1370, 1400, 1510–1540, 1620–1640, 2850, 2910, 3050, 3250
148	88–90	460, 550, 630, 730, 820–840–870, 1010, 1060, 1180, 1270, 1310–1330–1350, 1430, 1510–1540, 1600, 2860–2920, 3250

plexing agents, monomers, cross-coupling agents, intermediates, and objects for biological research.

The NMR spectra of **150–157** are shown in Table 21.

2.6.2. *With thiols* The thiylation of isothiocyanates has mainly been studied as a simple method for the preparation of *N*-monosubstituted dithiocarbamates.[93] However, no data concerning the reaction of thiols with isothiocyanates possessing a second reactive centre not indifferent to SH function, in particular, with 2-(vinyloxy)ethyl isothiocyanate **38**[52] have been available for a long time.

Recently,[89,90] the reaction of 2-(vinyloxy)ethyl isothiocyanate with thiols (ethane-, propane-, butane-, pentane-, hexane-, heptanethiol, benzyl mercaptan) in the presence of triethylamine, to give the *S*-organyl *N*-(2-vinyloxyethyl)dithiocarbamates **158–164** has been investigated (Tables 22–25).

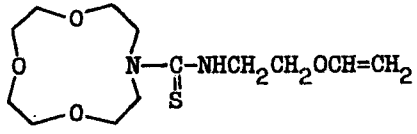
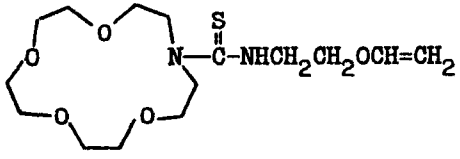
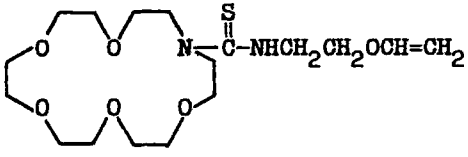
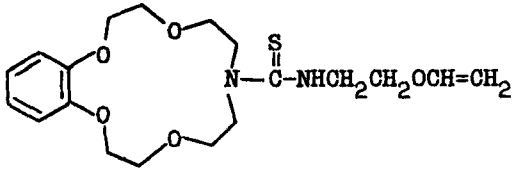


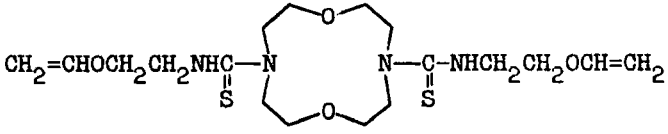
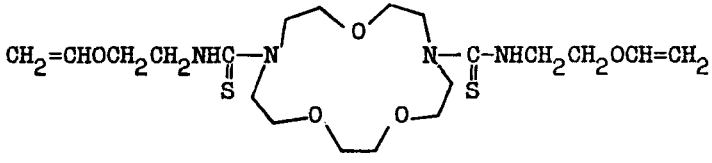
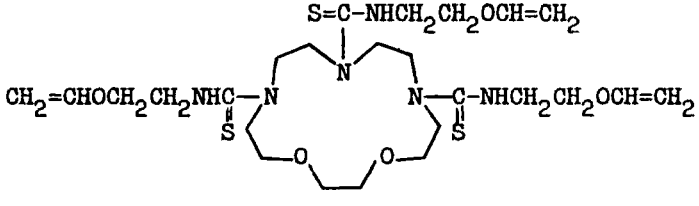
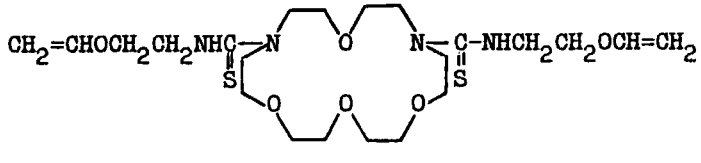
38 **158–164**

R = C_2H_5 (**158**), C_3H_7 (**159**), n-C_4H_9 (**160**), C_5H_{11} (**161**), n-C_6H_{13} (**162**), n-C_7H_{15} (**163**), $C_6H_5CH_2$ (**164**)

Scheme 71

TABLE 20 Reactions of 2-(vinyloxy)ethyl isothiocyanate **38** with aza-crown ethers[166]

Cpd. No.	Formula	Reaction temperature, °C[a]	Time, min	M.p., °C
150		60	5–10	56
151		70	5–10	52
152		53	5–10	*b*
153		40	5–10	68

154		90	5–10	142
155		70	60	88
156		100	5–10	162
157[c]		60	120	86

[a]Exothermic effect.
[b]n_D^{20} 1.5280.
[c]In $CHCl_3$ at room temperature.

TABLE 21 ^{1}H NMR (δ, ppm) spectra of **150–157**[166]

Cpd. No.	OCH=, q	CH_2=, *cis*, dd	CH_2=, *trans*, dd	CH_2N, *endocycl*, *m*	δ-CH_2O, *endocycl*, *m*	CH_2O,[a] *endocycl*, *m*	CH_2O, *exocycl*, *m*	CH_2N, *exocycl*, *m*	NH, s
150	6.43	4.00	4.19	3.78–4.00[b]	3.59	3.78–4.00[b]	3.59	3.59	7.91
151	6.45	4.00	4.18	3.87	3.63[c]	3.87	3.56	3.56	7.94
152	6.45	3.99	4.18	3.87	3.65[d]	3.87[e]	3.63	3.63	7.86
153[f]	6.44	4.00	4.21	3.85–3.90	4.11[g]	3.85–3.90	3.78	3.78	7.80
154	6.43	4.01	4.18	3.87	3.87	3.87	3.63	3.63	7.34
155	6.44	4.03	4.20	3.85	3.85	3.85	3.62	3.62	7.62
156	6.47	4.01	4.21	3.94	3.94	3.94	3.62	3.62	8.04–8.21
157	6.46	4.02	4.18	3.84	3.84	3.84	3.63	3.63	7.65

[a]Remaining CH_2O groups.
[b]Complicated multiplet.
[c]δ,ϵ-OCH_2, 8H.
[d]ϵ,o-OCH_2, 8H.
[e]12H.
[f]6.86 s (4H in C_6H_4).
[g]λ,δ′-OCH_2, 4H.

TABLE 22 Effect of the reaction conditions on the yields of the dithiocarbamates **158–164** (equimolar ratio of reagents, 0.01 mol)[89,90]

Cpd. No.	$(C_2H_5)_3N$, %	T, °C	Time, min	Yield of **158–164**, %[b]
158	0.8	(40)[a]	5–10	60
158	0.6	85 (79)[a]	30	100
158	0.6	100	4 h	80[c]
158	0.6	20–25 (46)[a]	3 d	100
159	0.5	(79)[a]	1–2	100
160	0.5	(77)[a]	1–2	100
161	0.5	(59)[a]	1–2	100
162	0.5	(55)[a]	1–2	100
163	0.5	(57)[a]	1–2	100
164	0.5	(100)[a]	1–2	100

[a]In brackets, the temperature reached by spontaneous heating is given.
[b]From IR spectra.
[c]A fairly intense N=C=S absorption band appears in the IR spectrum of the reaction mixture.

TABLE 23 Yields and characteristics of *S*-organyl *N*-(2-vinyloxyethyl)dithiocarbamates **158–164** and 2-methyl-3-[1-thioorganyl)thiocarbony]-1,3-oxazolidines **165, 166**[89,90]

Cpd. No.	Yield, %	B.p., °C (*mm* Hg)	n_D^{20}	d_4^{20}
158	63[a]	134–136 (7)	1.5678	1.1384
159	73[a]	125–126 (1)	1.5660	1.1032
160	80[a]	110–112 (0.05)	1.5578	1.0852
161[b]	100		1.5508	1.0549
162[b]	100		1.5447	1.0345
163[b]	100		1.5354	1.0146
164[b]	100		1.6200	
165	100[a]	145–146 (7)	1.5644	1.1157
166	100[a]	147–148 (0.07)	1.6242	1.2162

[a]Isolated by distillation.
[b]Undistilled product.

TABLE 24 IR spectra of dithiocarbamates **158–164** and 1,3-oxazolidines **165, 166**[89,90]

Cpd. No.	cm^{-1}
158	730, 800, 860, 940, 1000, 1060, 1100, 1170, 1210, 1250–1270, 1300, 1360, 1440, 1490–1500, 1600–1630, 2850, 2900, 3250
159	820, 880, 960, 1040, 1070, 1130, 1190, 1240, 1280, 1320, 1375, 1440, 1460, 1500–1520, 1620, 2875, 2935, 2965, 3300
160	800, 870, 945, 1030, 1070, 1160, 1100, 1170, 1260, 1300, 1360, 1445–1480, 1600, 2860, 2920, 2950, 3260
161	800, 870, 950–960, 1010, 1070, 1105, 1180, 1260, 1300, 1370, 1420, 1440–1450, 1490, 1605–1620, 2840–2860, 2920, 2950, 3280
162	820, 880, 970, 1020, 1080, 1115, 1190, 1220, 1280, 1310, 1390, 1460, 1500, 1610–1620, 2860–2880, 2920, 3300
163	800, 880, 950, 1005, 1060, 1100, 1180, 1260, 1300, 1370, 1450, 1490, 1600–1620, 2840–2860, 2910, 2950, 3270
164	470, 545, 560–600, 700, 770, 840, 890, 920, 970, 1040, 1080, 1140, 1200, 1245, 1290, 1325, 1400, 1460, 1500, 1635, 2890, 2945, 3010, 3040, 3070, 3090, 3120, 3300
165	470, 545, 650, 690, 735, 765, 800, 820, 850, 890, 920, 940, 965, 980, 1030, 1060–1080–1100, 1160–1175, 1230, 1310, 1335, 1360, 1400, 1430, 1440, 2850, 2940
166	500, 540, 560, 700, 750, 765, 810, 850, 880, 910, 940, 960, 1000, 1010, 1030, 1040, 1060, 1090–1100–1120, 1190–1210, 1220, 1240, 1290, 1340–1350, 1360, 1380, 1430, 1450, 1470, 1500, 1570, 1600, 2920, 2975, 3010, 3040, 3060

TABLE 25 ^1H NMR spectra of the dithiocarbamates **158–164**, $CH_2{=}CHOCH_2CH_2NHC(S)SR$,[a] and the 1,3-oxazolidines **165, 166**[89,90]

Cpd. No.	δ, ppm
	R
158	1.32 t (CH_3), 3.24 q (CH_2S)
159	0.98 *t* (CH_3), 1.69 m (CH_2), 3.20 *t* (CH_2S)
160	0.91 *t* (CH_3), 1.50 m ($(CH_2)_2$), 3.24 *t* (CH_2S)
161	0.92 *t* (CH_3), 1.38 m, 1.72 m ($(CH_2)_3$), 3.28 *t* (CH_2S)
162	0.87 *t* (CH_3), 1.30 m, 1.62 m ($(CH_2)_4$), 3.24 *t* (CH_2S)
163	0.86 *t* (CH_3), 1.28 m, 1.66 m ($(CH_2)_5$), 3.24 *t* (CH_2S)
164[b]	7.27 m (C_6H_5), 4.51 d (CH_2S)
165	5.94 q (OCHN), 1.57 d (CH_3), 4.18 m (CH_2O), 3.78 m (CH_2N), 0.92 m (CH_3), 3.28 *t* (CH_2S)
166	5.90 q (OCHN), 1.57 d (CH_3), 4.11 m (CH_2O), 3.83 m (CH_2N), 7.29 m (C_6H_5), 4.53 d (CH_2S)

[a]The ^1H NMR spectra of the compounds of **158–164** show the vinyloxy group protons as a quartet in the region of δ = 6.41–6.48 ppm (OCH=) and as a quartet at δ = 4.19–4.23 ppm (the *trans* to oxygen proton of CH_2=), δ = 4.05–4.09 ppm (the *cis* to oxygen proton of CH_2=).
[b]Only small amounts of 1,3-oxazolidines **166** are observed: their weak signals appear at 1.57 d (CH_3) and 5.89 q (OCHN) ppm.

A radical addition of thiols to the vinyloxy group of **38** has been assumed to be impossible.[1] As known,[167] the radical thiylation of vinyl sulfides is not inhibited in the presence of bases (*e.g.* during the vinylation of thiols with acetylene[167]). However, under the conditions studied (Table 22) thiol adducts to the vinyloxy group have not been identified.

The reaction course was monitored by IR and ^{1}H NMR spectra.[89,90] Account was taken of intensity changes in the absorption bands and signals corresponding to the vinyloxy group (IR, cm^{-1}: 820, 1200, 1320, 1610–1630, 3100; ^{1}H NMR, δ, ppm: 6.45 q, 4.20 dd, 4.00 dd) and to the isothiocyanate group (IR, cm^{-1}: 2100–2200) as well as of the chemical shifts of the CH_2S moiety [^{1}H NMR, δ, ppm: 2.47–2.50 q in the thiol, 3.20–3.24 m in the dithiocarbamates **158–164**, 2.59–2.61 m and 2.71 t in the α- and the β-adducts, respectively, to the vinyloxy group], OCH_2CH_2N [^{1}H NMR, δ, ppm: 3.82 m in **38**, 3.92–3.97 m in dithiocarbamates, 3.65–3.67 m in adducts to the C=C bond]. The process was carried out without solvent with a stoichiometric ratio of reagents.

The time during which the reaction mixture reaches room temperature is, as a rule, sufficient for the quantitative addition of thiols to **38**, mild and short (40–60 °C) heating being permissible. As the temperature rises (up to 100 °C) and the reaction time increases (to 7 h) the N=C=S group absorption band (2100–2200 cm^{-1}) again appears in the IR spectrum of the reaction mixture. The intensity of the band depends on the reaction conditions and the structure of the thiol, the band being most intense with ethanethiol. This is due to a relatively low (especially in the presence of bases) thermal stability of dithiocarbamates which normally decompose to isothiocyanate and thiol. The thermolysis of dithiocarbamates obtained by condensation of alkyl halides with the salts of dithiocarbamic acids furnishes one of the routes to isothiocyanates[99] including 2-(vinyloxy)ethyl isothiocyanate.[76]

Upon distillation of the reaction mixtures the decomposition is intensified and the IR spectra of all distillates contain an N=C=S absorption of moderate intensity [especially with **158** and **159**]. Besides, distillation is accompanied by intramolecular cyclization of dithiocarbamates to the corresponding 1,3-oxazolidines.[76] In this case the cyclization is enhanced with increasing bulk of R. Thus, during distillation, the dithiocarbamates **160** and **164** undergo quantitative cyclization to the 2-methyl-3-[(1-thioorganyl)thiocarbonyl]-1,3-oxazolidines **165** and **166**.

R = *n*-C_4H_9 (165), $C_6H_5CH_2$ (166)

Scheme 72

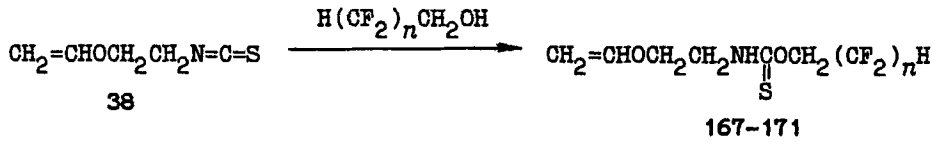
In the IR spectra of **165** and **166** there remain no absorption bands of $CH_2=CHO$ and NH groups. The absorption in the 2100–2200 cm^{-1} is also absent. The structures of the oxazolidines **165** and **166** is proven by the presence of $OCH(CH_3)N$ signals in their ^1H NMR spectra: 1.57 d (CH_3), 5.90 q (OCHN).[58,66,76] Signals of the vinyloxy group have not been observed.[52]

It is remarkable that the intramolecular addition of NH to the vinyloxy group takes place even in the presence of triethylamine* (normally even small admixtures of bases are enough for partial or complete inhibition of electrophilic reactions of vinyl ethers). Moreover, amines are commonly used as stabilizers of vinyl ethers.[169] An analogous cyclization in the presence of base (1% KOH) was first observed with *S*-methyl *N*-(2-vinyloxyethyl)dithiocarbamate[76] during the elaboration of an alternative process for the preparation of 2-(vinyloxy)ethyl isothiocyanate.[55,59–61]

To avoid thermal destruction and cyclization of the target products it is reasonable, after the reaction is completed, to remove volatile impurities of the reaction mixture *in vacuo* without distillation. Physico-chemical characteristics of **158–166** are listed in Table 23. The purity and identity of the undistilled products was confirmed by elemental analysis, IR and ^1H NMR spectra (Tables 24 and 25).[89,90]

2.6.3. *With polyfluoroalkanols* In the presence of bases (tertiary amines, alkali metal hydroxides and alkoxides) isothiocyanates are known to add alcohols and phenols to form *N*-monosubstituted thiocarbamates.[170,171] However, prior to the research of Refs. 53–55 the reaction of isothiocyanates with fluorinated alcohols, which differ much in their reactivity from their nonfluorinated analogs,[172] has not been reported.

Polyfluoroalkyl esters of ethylthiocarbamic *O*-acid **167–171** (Tables 26–29) have been prepared in high yields from 2-(vinyloxy)ethyl isothiocyanate **38** and polyfluoroalkanols.[69]



n = 2 (167), 4 (168), 6 (169), 8 (170), 10 (171)

Scheme 73

Taking into account the high reactivity of isothiocyanates with respect to nucleophiles and, on the contrary, the higher ability of fluoroalkanols to act as electrophiles (due to their higher acidity), it might be expected that the superposition of the two effects would inhibit the reaction. However, unlike alkanols

*The dithiocarbamates were distilled without being washed free of triethylamine.

TABLE 26 Yields and conditions of the reactions of polyfluoroalkanols $H(CF_2)_nCH_2OH$ with 2-(vinyloxy)ethyl isothiocyanate **38**[69]

n	$(C_2H_5)_3N$, %	Temperature, °C	Reaction time, h	Reaction product (yield, %)
2	None[a]	20–25	0.5	**167** (51)
2	0.3	80	1.7	**167** (34)
2	0.3	80–90	2.5	**167** (46)
2	0.8	80–85	3	**167** (71)
4	0.5	80–85	2	**168** (79)
4	0.8	70–90	4.5	**168** (94)
6	None	80	0.1	**169** (100)[b]
8	2.5	80–90	3	**170** (37)[b]
8[c]	0.7	55–60	3	**170** (100)[b]
10	4.5	60–70	6	**170** (90)[b]

[a]Polyfluoroalkanol stored for a long time over K_2CO_3 without further distillation.
[b]Yield of crude reaction product.
[c]With two-fold excess of **38**.

TABLE 27 Isolated yields and constants of polyfluoroalkyl esters of 2-(vinyloxy)ethylthiocarbamic *O*-acid **167–170**[69]

Cpd. No.	Yield, %	B.p., °C (1 *mm* Hg)	n_D^{20}	d_4^{20}
167	71	95–99	1.4660	1.3262
168	94	102–103	1.4310	1.4224
169	81	110–113	1.4085	1.5643
170	50	130	1.3980	1.5968

TABLE 28 IR Spectra of the polyfluoroalkyl esters of 2-(vinyloxy)ethylthiocarbamic *O*-acid **167–171**[69]

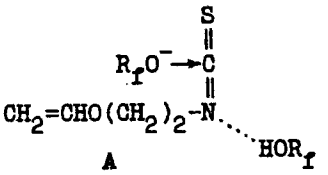
Cpd. No.	IR,[a] cm^{-1}
167	540, 580, 640–650, 730, 770, 815, 920, 930, 940, 960, 1000, 1050, 1080, 1100, 1140, 1165, 1220, 1255, 1300, 1315, 1350, 1395, 1400, 1430–1450, 1500, 1610–1620, 2880, 2940, 2975, 3050, 3110, 3280–3390
168	540, 600, 650, 710, 780, 790, 805, 900, 965, 975, 1025, 1070, 1120, 1175, 1195, 1250, 1290, 1320, 1330, 1400, 1450, 1515, 1620–1640, 2880, 2950, 3050, 3110, 3280, 3300, 3400
169	520, 590, 630, 680, 700, 720, 750, 780, 810, 840, 900, 950–960, 1010, 1060, 1115, 1180, 1200, 1255, 1310, 1320, 1370, 1395, 1430, 1510, 1610–1630, 2880, 2940, 3050, 3110, 3300, 3400
170	520, 600, 630, 685, 715, 750, 805, 930, 940, 960, 1005, 1060, 1110, 1200, 1260, 1305, 1320, 1400, 1440–1450, 1500, 1530, 1600–1620, 2860, 2930, 2970, 3050, 3100, 3280, 3390
171	510, 520, 620, 680, 710, 805, 880, 930, 960, 1000, 1060–1120–1180, 1260, 1300, 1330, 1390, 1450, 1500, 1600–1620, 2860, 2930, 2960, 3050, 3110, 3300–3400

[a]Film.

TABLE 29 ^{1}H NMR Spectra of the polyfluoroalkyl esters of 2-(vinyloxy)ethylthiocarbamic *O*-acid **167–171**[69]

Cpd. No.	Chemical shift, δ, ppm, $CDCl_3$						
	OCH=, q	CH_2= *trans*, dd	CH_2= *cis*, dd	$(CF_2)_nH$, tt	OCH_2, NCH_2, m	$(CF_2)_nCH_2O$, t	NH, s
167	6.42	4.17	4.04	5.86	3.84	4.79	6.96
168	6.45	4.20	3.96	6.04	3.87	4.95	6.82
169	6.44	4.19	3.96	6.05	3.87	4.95	6.81
170	6.44	4.18	4.06	6.04	3.84	4.94	
171	6.45	4.19	4.06	6.04	3.84	4.95	

which add to **38** with difficulty even in the presence of strong base, polyfluoroalkanols react readily under mild conditions (equimolar ratio of reagents, no solvents, 0.3–4.5% of tertiary amine, 60–90 °C, 0.1–6 h).* This may be due to a concerted process when in the reaction complex **A** the attack on the N=C bond by the polyfluoroalkoxide anion is accompanied by simultaneous proton transfer from the second polyfluoroalkanol molecule.

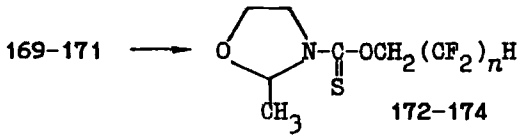


Scheme 74

The markedly increased yield and the milder reaction conditions with higher polyfluoroalkanols (*e.g.*, n = 6) compared with those for polyfluoroalkanol (n = 2) are in agreement with the above scheme.

As seen from Table 26, the polyfluoroalkanol (n = 6) quantitatively adds to **38** without catalyst upon short heating to 80 °C. The reaction mixture contained no starting material as judged by GLC, IR spectroscopy and heating *in vacuo* (62 °C, 1 *mm* Hg).[69] Identical data were obtained by elemental analysis of the unreacted and distilled product. However, during the distillation some of **169** was lost (81% preparative yield) due to high-temperature cyclization to the substituted 1,3-oxazolidine **172**. The elemental composition of the residue was identical to that of the thiocarbamate **169**.

*Normally, the reaction of isothiocyanates with alcohols is carried out in a solvent (*p*-xylene, for example) or with large excess (to ten-fold) of the starting alcohol at 100 °C and higher.[171]



n = 6 (172), 8 (173), 10 (174)

Scheme 75

Upon vacuum distillation (4 *mm* Hg) **170** and **171** undergo complete cyclization to the corresponding oxazolidines **173** and **174**. Pure **170** were isolated in preparative yield (50%) by vacuum distillation (0.7 *mm* Hg).[69]

No cyclization of the thiocarbamates **167–169** to the corresponding 1,3-oxazolidines takes place under these conditions which is indicated by the absence of proton signals of the $NCH(CH_3)O$ fragment in the ^1H NMR spectra of the reaction mixtures and crude products.

When the reaction of the polyfluoroalkanol (n = 8) is carried out with twofold excess of **38** the yield of **170** becomes quantitative (Table 26). Excess **38** is readily removed by vacuum distillation.[69]

When use was made of the polyfluoroalkanol with n = 2 stored for a long time over K_2CO_3 without further distillation, the reaction occurred at room temperature in the absence of tertiary amine (Table 26). Evidently, in this case the catalytic effect is produced by trace amounts of either potassium hydroxide or the corresponding alkoxide which may be present in the K_2CO_3-treated alcohol.

In the electron absorption spectrum of the thiocarbamate **167** in ethanol there are two bands of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electron transitions (λ_{max} 307, log ϵ 1.8 and 245 nm, log ϵ 4.9). For methyl *N*-alkylthiocarbamates in cyclohexanol the corresponding bands occur at λ_{max} 288–292 (log ϵ 2.1–1.5) and 242–247 nm (log ϵ 4.02–3.48).[173]

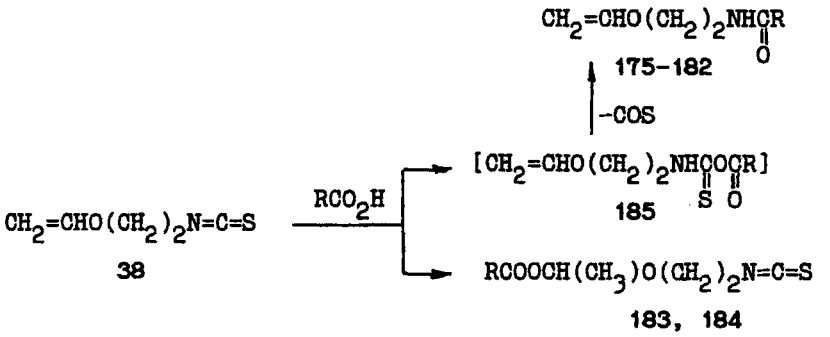
2.6.4. *With carboxylic acids* The reaction of carboxylic acids with 2-(vinyloxy)ethyl isothiocyanate **38** may involve addition of the acid to the vinyloxy group[80,82,84,86,91] and intramolecular cyclization of the amide formed to a 2-methyl-1,3-oxazolidine (intramolecular NH addition to the vinyloxy group[58,66,76,94,174–176]).

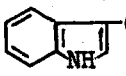
In order to synthesize new amides with highly reactive vinyloxy groups and to acquire supplementary information concerning the reactivity of 2-(vinyloxy)ethyl isothiocyanate **38** the authors of Ref. 92 have investigated its reaction with carboxylic acids and found them to add smoothly to the N=C bond forming alkyl-*N*-(2-vinyloxyethyl)amides **175–182** in quantitative yield (Table 30).

TABLE 30 Yields and conditions for the reaction of 2-(vinyloxy)ethyl isothiocyanate **38** with carboxylic acids (equimolar mixture of reagents)

$(C_2H_5)_3N$, %	T, °C	Time, h	Products (yield, %)[a]
15	75–80	2.5	*ca.* 100 (**175**)
10	60	4	*ca.* 100 (**175**)
5	60	5.5	*ca.* 100 (**185**)
5	60–65	8	*ca.* 80 (**175**), 20 (**183**)
15	55–65	0.5	*ca.* 100 (**176**)
15	75–80	2.5	*ca.* 100 (**177**)
15	45–50	1	*ca.* 100 (**178**)
15	65–75	3	*ca.* 100 (**179**)
15	45–50	1	*ca.* 100 (**180**)
15[b]	75–80	23	*ca.* 60 (**181**, 10 (**184**)
15[c]	40–45	4	*ca.* 100 (**182**)
15	65–75	1.5	[d]
5	85–90	1	*ca.* 50
15	60–65	5.5	*ca.* 100 (**188**)
15	55	2.5	*ca.* 15 (**188**), 85 (**192**)
Equimolar	(52)[e]	1	[d]
15	45–50	0.25	*ca.* 25 (**189**)
15	60–65	6	*ca.* 100 (**189**)
15[b]	40–45	2.5	*ca.* 100 (**190**)

[a]From ^{1}H NMR and IR spectra.
[b]In benzene.
[c]In $CHCl_3$.
[d]Polymer of unidentified structure.
[e]The temperature reached by spontaneous heating of the reaction mixture.



R = Me (**175**, **183**), Et (**176**), *i*-Pr (**177**), *n*-Bu (**178**), *t*-Bu (**179**), C_7H_{15} (**180**), Ph (**181**, **184**), 

(**182**)

Scheme 76

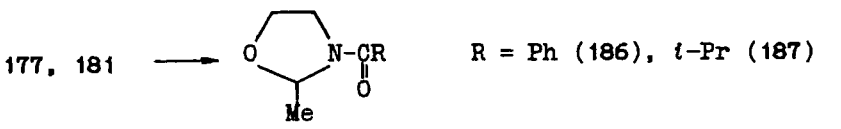
The reaction is carried out in the presence of triethylamine, without solvent, with a stoichiometric ratio of reagents, a slight exothermic effect (24–40 °C) being observed upon mixing.[92]

The reaction course was monitored by IR and ^{1}H NMR spectra of the reaction mixtures (changes in the N=C=S, CH_2=CHO, OH, NH absorption band intensities and the vinyloxy group integral intensity signals: 6.44–6.47 q, 4.17–4.19 dd, 4.00–4.03 dd ppm. The appearance of the signals of acylal, C(O)OCH(CH_3)O [5.88–6.15 q (CH), 1.39–1.58 d (CH_3)] and oxazolidine fragments [5.35–5.49 q (CH), 1.35–1.40 d (CH_3)] in ^{1}H NMR spectra showed the reaction to involve the vinyloxy group.

The reaction occurs under comparatively mild conditions and is accompanied by a simultaneous and nearly complete elimination of COS from the intermediate **185**. This is confirmed by elemental analysis of crude products (sulfur content below 1.5–2%).

The influence amount of the catalyst on the reaction time and the yield was studied. For the reaction of **38** with ethanoic acid, with triethylamine concentrations reduced from 15 to 5%, the reaction time increased from 3 to 5.5 h, the intermediate **185** (R = CH_3) being the major reaction product, as shown by the presence of an intense absorption line at 1700 cm^{-1} and elemental analysis (no absorption band of the isothiocyanate group was observed).[92] Thus, triethylamine activates not only addition, but elimination reactions as well. The ^{1}H NMR spectrum of the same reaction mixture displays signals of the acylal fragment (5.88 q, 1.39 d) as soon as one hour after the start of the reaction.[92] This means that in the presence of 5% of triethylamine ethanoic acid adds partially at the vinyloxy group as well (~20% of acylal **183** after 8 h). A small admixture of acylal **184** (~10%) was also found (^{1}H NMR) in the products of the reaction of **38** with benzoic acid.[92]

The dependence of both the yield of amides and of the reaction course on the structure of the acid (in the series of alkanoic acids) is less essential. In general, acids with unbranched substituents add to the N=C bond more readily than acids with branched substituents.[92] On going from ethanoic to octanoic acid the reaction time decreases. Benzoic acid adds to **38** much more slowly than aliphatic acids do. In this case, the ^{1}H NMR spectra of the distillation products show not only signals of the amide **181** and acylal **184** (~30%) but also those of the oxazolidine **186** [5.49 q (OCHN), 1.40 d (CH_3)]. The corresponding oxazolidine **187** (~35%) was identified by its ^{1}H NMR spectrum [5.35 q (OCHN), 1.35 d (CH_3)] and in the residue of distillation of the adduct of **38** with 2-methylpropanoic acid.[92]

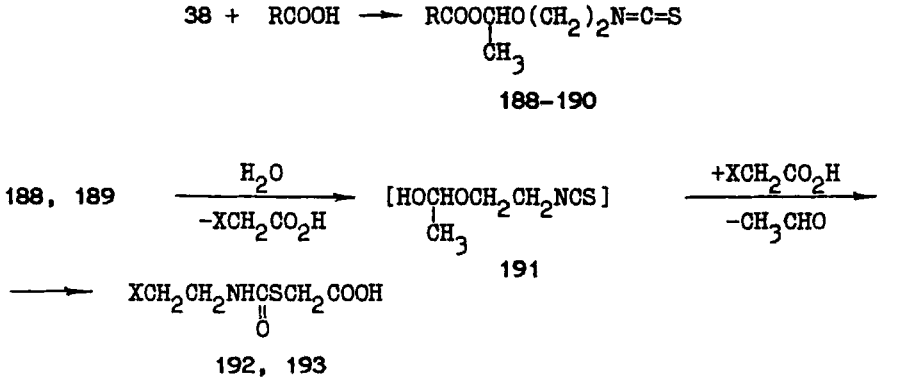


186, 187

Scheme 77

Haloalkanoic acids (2-chloro-, 2-bromo, and trifluoroethanoic acid) add to 2-(vinyloxy)ethyl isothiocyanate solely at the vinyloxy group to give acylals **188–190**,[82,84,86,91] even in the presence of amine.[92] Going from ethanoic to trifluoroethanoic acid, *i.e.*, with an increase in the acidity and, consequently, a decrease in the nucleophilicity of the corresponding anion, the rate of addition to the isothiocyanate group is reduced and that to the vinyloxy group increased.[92] An increase in the triethylamine concentration up to equimolar leads to strong resinification of the reaction mixture, the intensity of the isothiocyanate band not being changed much.

When exposed to moisture (on storage or during synthesis), the acylals **188** and **189** undergo rearrangement to the acids **192** and **193**.



Scheme 78

This unusual rearrangement has been described in more detail in Refs. 82, 84, 86, 91. In the ^{1}H NMR spectrum of the reaction mixture no signals of the vinyloxy group are observed. Instead, there are signals corresponding to the acylal **188** [6.01 q (OCHO), 1.47 d (CH_3), 4.10 s (CH_2Cl), 3.70 m (OCH_2CH_2N)], the acetal **191** (5.40 q, 1.45 d), 2-chloroethanoic acid [4.25 s (CH_2Cl)], acetaldehyde (2.14 d), and the acid **192** [4.00 s (CH_2S); the $ClCH_2CH_2N$ signal overlaps with the broadened multiplet of OCH_2CH_2N].

No cyclization of the amides **175–182** to the corresponding 2-methyl-1,3-oxazolidines occurred under the conditions studied.

The addition of acrylic and methacrylic acid occurs at the N=C bond but more slowly.[92] The reaction with acrylic acid was completed with the formation of a solid polymer. The vinyloxy group signals in the ^{1}H NMR spectrum of this polymer do not disappear, the signals of the corresponding acylal and oxazolidine have not been identified.

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