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# SULFUR DERIVATIVES OF VINYL ETHERS

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Syntheses of functional sulfides (by thiylation of vinyl ethers), isothiocyanates, 1,3-oxazolidine-2-thione and open-chain thiocarbamates (by electrophilic alcohol and carboxylic acid addition to 2-(vinyloxy)ethyl isothiocyanate), thiiranes (by electrophilic alcohol addition to 2-(vinyloxy)ethoxymethylthiirane) as well as their reactivity are reviewed.

*Key words:* Vinyl ethers, acetals, acylals, sulfides, thiiranes, haloalkoxyethenes, isothiocyanates, vinyloxyorganyl carboxylates, 2-(vinyloxy)ethoxymethyloxirane, 2-(vinyloxy)ethoxymethylthiirane, 2-(vinyloxy)ethyl isothiocyanate.



## CONTENTS



## 1. INTRODUCTION

The interest in the chemistry of vinyl ethers has been undiminished through many decades (initiated by fundamental research by Favorsky and Shostakovsky). A new fruitful area in the synthetic chemistry of vinyl ethers developed by the

authors of this review, proved to be selective additions of mono- and multiprotic reactants (alcohols, thiols, carboxylic acids) to the vinyloxy group of bifunctional members of the series, particularly to divinyl, epoxy- and epithiovinyl ethers of diols, 2-(vinyloxy)ethyl isothiocyanate, and the like. This general approach was demonstrated to be a simple and versatile route to a new group of highly active monomers, reagents and technically applicable products (including new generation epoxy, thiirane, and cycliccarbonate resins).

The utilization of available sulfur addends and substrates (vinyl ethers with isothiocyanate and thiirane functions) in these reactions gives access to novel sulfides, isothiocyanates, and thiiranes (with epoxy, acetal, acylal, and thioacetal groups) as well as to other important sulfur-organic compounds.

## 2. SYNTHESIS OF SULFUR DERIVATIVES OF VINYL ETHERS

### 2.1. *Thiylation of Vinyl Ethers*

2.1.1. *Divinyl ethers* The starting point of recent research on radical reactions of divinyl ethers of diols with thiols is known work[1–4] on the thiylation of the simplest vinyl ethers.

With a thiol:divinyl ether (**1–4**) molar ratio of 1:3 double addition and telomerization are noticeably suppressed and the yield of monoadducts (**5–15**) exceeds 70% (Scheme 1).[5–7]

$$\underset{\textbf{1–4}}{CH_2{=}CHOXOCH{=}CH_2} + R^1SH \rightarrow \underset{\textbf{5–15}}{CH_2{=}CHOXOCH_2CH_2SR^1} +$$

$$+ \underset{\textbf{16}\ (<5\%)}{CH_2{=}CHOXOCH(CH_3)SR^1} + \underset{\textbf{17, 18}}{R^1SCH_2CH_2OXOCH_2CH_2SR^1} + \text{telomer}$$

X = $(CH_2)_2$ (**1**), $R^1$ = Et (**5**), *n*-Pr (**6, 17**), *n*-Bu (**7**), *t*-Bu (**8**), *n*-$C_5H_{11}$ (**9**), Ph (**10**); X = $(CH_2)_3$ (**2**), $R^1$ = *n*-Pr (**11**); X = $(CH_2)_4$ (**3**), $R^1$ = *n*-Pr (**12**); X = $(CH_2)_2O(CH_2)_2$ (**4**), $R^1$ = Et (**13**), *n*-Pr (**14, 18**), *n*-Bu (**15**)

SCHEME 1

The thiylation is carried out either in the presence of azobisisobutyronitrile (AIBN) as initiator, by exposure to UV irradiation, or by thermal initiation (Table 1).[5,6] The highest yield (76%) of 1:1 adducts was obtained in the case of ethylene glycol divinyl ether (**1**) and non-catalytic addition. The use of UV irradiation considerably shortens the reaction time (3 h or less instead of 12–35 h), the yield of monoadduct remaining rather high (40–60%). The use of AIBN as a catalyst increases the yield of oligomer. With the divinyl ether of 1,4-butanediol (**3**) or of diethylene glycol (**4**) this leads to the formation of transparent colorless insoluble (benzene, $Et_2O$, $CCl_4$) polymers containing sulfur (up to 9%). Unlike alkyl vinyl ethers,[8,9] the ethers **3** and **4** are readily polymerized in the presence of the above initiator to form colorless homopolymers of different consistency (from gels to solid glasses) depending on the polymerization time (2–12 h, 70–

TABLE 1 Thiylation conditions for divinyl ethers **1–4**[6]

| $R^1$ | Initiator | T, °C | Time, h | Ether:thiol molar ratio | Yield of 1:1 adduct, % |
|---|---|---|---|---|---|
| | | $CH_2$=CHO$(CH_2)_2$OCH=$CH_2$ (**1**) | | | |
| Et | None | 40–45 | 10 | 2:1 | 50 |
| *n*-Pr | None | 40–55 | 6 | 1:1 | 45 |
| *n*-Bu | BP | 60–65 | 6 | 2:1 | No reaction |
| *n*-Bu | AIBN | 60–65 | 8 | 3:1 | 53 |
| *n*-Bu | UV | 20–25 | 6 | 3:1 | 44 |
| *n*-Bu | UV | 20–25 | 3 | 2:1 | 72 |
| *n*-$C_5H_{11}$ | None | 60–70 | 25 | 2:1 | 76 |
| *n*-$C_5H_{11}$ | AIBN | 60–70 | 25 | 2:1 | 44 |
| Ph | UV | 20–25 | 2 | 3:1 | 55 |
| Ph | None | 60–65 | 25 | 3:1 | 57 |
| *t*-Bu | UV | 20–25 | 3 | 2:1 | 29 |
| | | $CH_2$=CHO$(CH_2)_3$OCH=$CH_2$ (**2**) | | | |
| *n*-Pr | UV | 20–25 | 3 | 2:1 | 43 |
| | | $CH_2$=CHO$(CH_2)_4$OCH=$CH_2$ (**3**) | | | |
| *n*-Pr | UV | 20–25 | 3 | 2:1 | 47 |
| | | $CH_2$=CHO$(CH_2)_2$O$(CH_2)_2$OCH=$CH_2$ (**4**) | | | |
| Et | None | 40–50 | 13 | 2:1 | 64 |
| *n*-Pr | None | 60–65 | 12 | 3:1 | 64 |
| *n*-Pr | None | 50–60 | 12 | 1.5:1 | 42 |
| *n*-Pr | AIBN | 60–65 | 12 | 3:1 | 0 |
| *n*-Bu | None | 60–65 | 12 | 3:1 | 73 |
| *n*-Bu | AIBN | 60–65 | 12 | 3:1 | 0 |



80 °C). In the presence of 1% benzoyl peroxide (BP) neither addition nor polymerization occur (Table 1).

In order to elucidate the relative reactivity of divinyl ethers in the thiylation, a series of runs with 1-propanethiol was carried out[5,6] under comparable conditions (Table 2). Judging by the extent of conversion, there is some tendency towards increasing reactivity in the order **4** < **1** < **3** < **2**; however, the yield of the 1:1 adduct varies in the opposite manner. Upon going from systems with a β-array of oxygen atoms (**1** and **4**) to γ- and δ-systems (**2** and **3**), respectively,

TABLE 2 The relative reactivity of divinyl ethers **1–4** in thiylation[a6]

| Divinyl ether | Yield[b] of 1:1 adduct, % | Total yield of bisadduct and oligomers, % | Conversion of **1–4**, % |
|---|---|---|---|
| **1** | 55 | 38 | 56 |
| **2** | 43 | 46 | 64 |
| **3** | 47 | 45 | 57 |
| **4** | 63 | 28 | 50 |

[a]Thiol *n*-PrSH, UV irradiation, 20–25 °C, 3 h, ether-thiol molar ratio = 2:1. [b]Based on consumed divinyl ether.

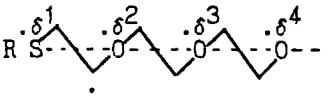
the selectivity decreases abruptly. In fact, if the ratio of the yield of monoadduct to the total yield of bisadduct and oligomers is conventionally taken as a measure of selectivity, it can be seen that the selectivity in the reaction with divinyl ethers of 1,3-propane- and 1,4-butanediol (**2** and **3**) is nearly the same (0.9 and 1.0), whereas with divinyl ethers of ethylene glycol and diethylene glycol (**1** and **4**) it is considerably higher (1.5 and 2.2, respectively). Such a "β-effect" was previously unknown.[5,6] If this effect is assumed to be completely due to differences in the inductive influence on the reactivity centre, this does not explain the strong difference in selectivity between **1** and **4**, in which the inductive influence on the vinyloxy group should be nearly equal. On the other hand, the observed differences in selectivity are indicative of a change in stabilization of the intermediate radical **19** (Scheme 2).

$$[RS\text{-}CH_2\dot{C}H\text{-}OR \longleftrightarrow RSCH_2CH{=}\dot{O}R]$$

**19**

SCHEME 2

From the experiment it follows that compared with **2** and **3** the systems with a β-array of oxygen atoms (**1**, **4**) are more advantageous for additional stabilization of the intermediate **19**. It is suggested[5,6] that stabilization of this kind involves partial electron-transfer to the $O_\beta$ atom and, finally, to the second double bond. The interaction may occur through space in a spiral conformation of the polyethylene glycol chain (Scheme 3).




SCHEME 3

A similar electron-transfer effect in vicinal systems was found by Voevodsky *et al.*[10,11] in a study of the ESR spectra of some aromatic radical anions. The electron has been assumed to be transferred along the σ-bond chain. Later on, however, this point of view was criticized.[12] The enhanced ability of systems with β-alternating oxygen atoms to transfer substituent effects has also been recognized in a kinetic examination of electrophilic reactions of vinyl ethers.[5,13–16] Among the ethers studied (Table 2) the divinyl ether of diethylene glycol should give the most stable radical with a reduced ability to initiate polymerization, which is in agreement with the experimental data.

The isomeric purity of the sulfides **5–15** was proven by $^1$H NMR an IR spectroscopy, TLC, and chemical functional group analysis.[6] In accordance with the structure adopted for **14**, in its $^1$H NMR spectrum there is no $CH_3$ group doublet and no quartet of the $OCH(CH_3)$ methine proton; however, signals due to $CH_2O$ protons are present. Comparison of the IR spectra of the sulfides **8**, **14** and $CH_2{=}CHOXOCH(CH_3)SR^1$ (**16**) shows a marked structural difference. In the spectrum of **8** three methyl groups are represented by an intense band at 1360

$cm^{-1}$. In the spectra of **16** (two methyl groups), the band at 1374 $cm^{-1}$ is less intense, and in the spectrum of **14** there is only a weak absorption in this region (one methyl group). Besides, the spectrum of **16** contains fairly intense bands at 630 and 670 $cm^{-1}$, absent in the spectra of **8** and **14** (apparently, stretching vibrations of the C–S bond in the α-alkoxyethylthio group). The vinyloxy group is unambiguously identified in the spectra of all monoadducts **5–16** with the wave numbers: 815–820, 965–975, 1200–1205, 1320, 1615–1620, 1635–1640, 3040–3050, 3100–3120 $cm^{-1}$. TLC ($Al_2O_3$) showed no α-isomers (Table 3) of the adducts **7, 11, 12, 14, 15**. In fact, the corresponding α- and β-isomers of the sulfides **14** and **16** differ much in their $R_f$ values. An analysis of the isomeric composition of the sulfides **5–15** with $HgCl_2$ turned out to be inadequate because the vinyloxy group was partly involved in the reaction to liberate the acid.[17] Therefore use was made of hydrolytic oximation which provided additional support for the β-addition scheme (Table 3).

Physical data of **5–18** are listed in Table 4. The ability of the monoadducts obtained to form polymers under the effect of cationic catalysts ($BF_3$ etherate,

TABLE 3 Hydrolytic oximation of the adducts of divinyl ethers **1–4** with thiols[6]

| Ether | Thiol | Initiator | Adduct | m[a] |
|---|---|---|---|---|
| **1** | *n*-PrSH | None | **6** | 1.04 |
| **1** | *n*-BuSH | UV | **7** | 0.96 |
| **1** | PhSH | UV | **10** | 0.99 |
| **2** | *n*-PrSH | UV | **11** | 0.96 |
| **3** | *n*-PrSH | UV | **12** | 1.00 |
| **4** | *n*-PrSH | None | **14** | 1.00 |
| **4** | *n*-BuSH | None | **15** | 1.01 |
| **4** | *n*-PrSH | $SOCl_2$ | **16** | 1.90 |

[a]Number of moieties (vinyloxy or thioacetal) hydrolyzed with liberation of acetaldehyde.

TABLE 4 Adducts of divinyl ethers **1–4** with thiols[5,6]

| Cmpd No. | Formula | B.p., °C (*mm* Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| **5** | $CH_2{=}CHO(CH_2)_2O(CH_2)_2SEt$ | 73 (2) | 1.4721 | 0.9893 |
| **6** | $CH_2{=}CHO(CH_2)_2O(CH_2)_2SPr$-*n* | 72–72.5 (1) | 1.4723 | 0.9728 |
| **7** | $CH_2{=}CHO(CH_2)_2O(CH_2)_2SBu$-*n* | 84.5–85 (1) | 1.4710 | 0.9631 |
| **8** | $CH_2{=}CHO(CH_2)_2O(CH_2)_2SBu$-*t* | 88–88.5 (1.5–2) | 1.4686 | 0.9559 |
| **9** | $CH_2{=}CHO(CH_2)_2O(CH_2)_2SC_5H_{11}$ | 101–101.5 (1) | 1.4705 | 0.9543 |
| **10** | $CH_2{=}CHO(CH_2)_2O(CH_2)_2SPh$ | 121–122 (1) | 1.5460 | 1.0825 |
| **11** | $CH_2{=}CHO(CH_2)_3O(CH_2)_2SPr$-*n* | 88–90 (1) | 1.4693 | 0.9571 |
| **12** | $CH_2{=}CHO(CH_2)_4O(CH_2)_2SPr$-*n* | 109–109.5 (1.5) | 1.4699 | 0.9541 |
| **13** | $CH_2{=}CHO[(CH_2)_2O]_2(CH_2)_2SEt$ | 99 (1) | 1.4730 | 1.0118 |
| **14** | $CH_2{=}CHO[(CH_2)_2O]_2(CH_2)_2SPr$-*n* | 110 (1) | 1.4723 | 1.0018 |
| **15** | $CH_2{=}CHO[(CH_2)_2O]_2(CH_2)_2SBu$-*n* | 126.5 (1.5) | 1.4711 | 0.9893 |
| **16** | $CH_2{=}CHO[(CH_2)_2O]_2CH(CH_3)SPr$-*n* | 113–115 (1.5) | 1.4700 | 0.9943 |
| **17** | *n*-$PrS[(CH_2)_2O]_2(CH_2)_2SPr$-*n* | 135.5–137 (1.5) | 1.4876 | 0.9969 |
| **18** | *n*-$PrS[(CH_2)_2O]_3(CH_2)_2SPr$-*n* | 170–172 (1.5) | 1.4851 | 1.0186 |

$SnCl_4$) was checked with **6** and **7**. Viscous polymeric liquids were obtained at room temperature.[5,6]

2.1.2. *Acid-induced radical thiylation of butoxyethene and 2-(vinyloxy)-ethoxymethyloxirane* Vinyl ethers are known to add hydrogen sulfide and thiols to their double bond, both with an electrophilic and a radical mechanism to form the corresponding Markovnikov (α-)[18–20] or *anti*-Markovnikov (β-)[21,22] adducts or their mixtures,[2,23] depending on the reaction conditions.

The formation of β-adducts under the influence of acids is usually explained by interference of a concurrent radical mechanism which sometimes cannot be suppressed efficiently when traces of oxygen are present in the reaction mixture. However, if this is true, in the presence of acids a decrease in the yield of the β-isomer should always be observed.

Studying the addition of thiols to the vinyl ethers **20** and **21** the present authors[24–29] encountered an unexpected increase in the yield of the β-isomers **22–31** when acids ($C_3F_7CO_2H$, *p*-$MeC_6H_4SO_3H$) were introduced into the reaction mixture (Scheme 4).

$$\underset{\textbf{20,21}}{CH_2{=}CHOR^1} + HSR^2 \longrightarrow \underset{\textbf{22–31}}{R^2SCH_2CH_2OR^1} + \underset{\textbf{32}}{R^2SCH(CH_3)OR^1}$$

$R^1$ = *n*-Bu (**20**, **22**); $(CH_2)_2OCH_2\overline{CH\text{-}CH_2O}$ (**21**); $R^2$ = Et (**23**), *n*-Pr (**24**), *i*-Pr (**25**), *n*-Bu (**26**), *t*-Bu (**27**), $C_{12}H_{25}$ (**28**), $CH_2{=}CHCH_2$ (**29**), $PhCH_2$ (**30**), Ph (**31**)

SCHEME 4

Inspecting the data of Table 5, where typical results of the addition of *n*-butanethiol to *n*-butoxyethene **20** are collected, one can see that both the total yield and the isomer ratio **22**:**32** depend on the content and nature of the acid

TABLE 5 Conditions and results of the addition of *n*-butanethiol ($R^2$ = *n*-Bu) to *n*-butoxyethene **20** (0.125 mol of *n*-butanethiol, 0.125 mol of **20**, ambient temperature, 4 h)[25]

| Catalyst, % | | Total yield of **22** + **32**, % | Isomer content, %[a] **22** | **32** |
|---|---|---|---|---|
| None | | 6 | 93 | 7 |
| $C_3F_7COOH$ | 1.00 | 20 | ~100 | *traces*[b] |
| $C_3F_7COOH$ | 2.10 | 42 | 90 | 10 |
| $C_3F_7COOH$ | 2.10 | 59[c] | ~100 | *traces*[b] |
| $C_3F_7COOH$ | 5.00 | 50[d] | 30 | 70 |
| *p*-$MeC_6H_4SO_3H$ | 0.16 | 41 | 45 | 55 |
| *p*-$MeC_6H_4SO_3H$ | 0.30 | 47 | 23 | 77 |
| *p*-$MeC_6H_4SO_3H$ | 0.46 | 50 | 8 | 92 |
| *p*-$MeC_6H_4SO_3H$ | 1.17 | 60 | ~100 | *traces*[b] |

[a]Here, and in Tables 6–8, from $^1H$ NMR spectra. [b] Here and in Tables 6–8 this is to mean that no detectable signals of the corresponding isomer were found in the $^1H$ NMR spectrum of the reaction mixture. [c]The reaction was carried out at 78 °C for 3 h. [d]The reaction lasted 2 h.

used for the catalysis. Mostly, the yield of the β-isomer (**22**) in the acid-catalyzed reaction is higher than that in a non-catalytic one, though, sometimes, the relative content of the α-isomer (**32**) increases in the former case. However, at low acid concentrations the reaction may become regiospecific relative to the isomer **32**, while at a higher acid percentage the **22:32** ratio decreases with increasing acid content, indicating an expected acceleration of the electrophilic counterpart of the reaction. Thus, a stronger acid such as *p*-$MeC_6H_4SO_3H$ exhibits a stronger acceleration of the electrophilic pathway: the ratio **22:32** decreases rapidly with increasing acid concentration.[24,25]

For 2-(vinyloxy)ethoxymethyloxirane (**21**) the acceleration and selectivity of the *anti*-Markovnikov (radical) addition in the presence of acids is remarkable as illustrated by Table 6. Unlike **20**, under the influence of *p*-toluenesulfonic acid **21** adds *n*-butanethiol exothermically to give the β-isomer **26** almost exclusively. This seems to originate from the lowering of an excessive acid concentration by reaction with the epoxide group.[24,25]

The effect of the thiol structure on the product yield and the regioselectivity of this double-faced addition is expected to be a rather sophisticated one involving facilitation of H–S bond homolysis, the ionization potential of the thiol, its acidity, steric requirements, *etc.* This is well reflected by Table 7, and the following rough trend can be recognized: bulky thiols give lower total yields and a higher content of the β-isomer at a larger difference between the yield of catalytic and non-catalytic addition in favor of the former.[25]

As Table 8 shows, typical inhibitors of radical processes such as hydroquinone and phenyl-β-naphthylamine slow down the acid-induced addition, increasing the content of the Markovnikov isomer.

It is remarkable that no evidence of acid-induced homolytic addition to vinyl ethers has been presented prior to this work.[24,25] An earlier observed acceleration of the *anti*-Markovnikov addition of hydrogen sulfide to *n*-butoxyethene in the presence of 0.1% HCl-dioxane solution was ascribed by the authors[2,23] to the action of unknown peroxides contained in the catalyst. Since in Refs.[24,25] freshly distilled reagents and specially purified catalysts were used and peroxide tests always were negative, any role of this "mysterious peroxide" can be ruled out.

TABLE 6 The addition of *n*-butanethiol to **21** (equimolar ratio of reagents)[25]

| Catalyst, % | | T, °C | Time, h | Total yield of **26** + **32**, % | Isomer content, %[a] **26** | **32** |
|---|---|---|---|---|---|---|
| None | | 20–25 | 4 | 9.5 | ~100 | *traces* |
| None | | 140 | 3 | 72.6 | ~100 | *traces* |
| $C_3F_7COOH$ | 0.5 | 20–25 | 4 | 9.7 | 93 | 7 |
| $C_3F_7COOH$ | 2.2 | 20–25 | 3 | 43.0 | 75 | 25 |
| $C_3F_7COOH$ | 3.0 | 20–25 | 4 | 63.3 | 80 | 20 |
| $C_3F_7COOH$ | 2.1 | 140 | 3 | 72.6 | 67 | 33 |
| *p*-$MeC_6H_4SO_3H$ | 0.2 | 20–25 (60)[a] | 4 | 75.9 | ~100 | *traces* |
| *p*-$MeC_6H_4SO_3H$ | 0.5 | 20–25 (75)[a] | 2 | 65.2 | ~100 | *traces* |

[a]Rise of temperature after addition of the catalyst.

TABLE 7 The effect of thiol structure on the yield and isomer ratio in the catalytic and non-catalytic additions to **21** (equimolar ratio of reagents, 60 °C, 4 h)[25]

| Thiol | Total yield, % | Isomer content, % | |
|---|---|---|---|
| | | **23–31** | **32** |
| EtSH | 65.0[a] | 75 (**23**) | 25 |
| | 53.3[b] | ~100 (**23**) | *traces* |
| *i*-PrSH[c] | 40.5[a] | 65 (**25**) | 35 |
| | 27.8[b] | ~100 (**25**) | *traces* |
| *t*-BuSH[d] | 46.0[a] | 95 (**27**) | 5 |
| | 27.0[b] | ~100 (**27**) | *traces* |
| $CH_2$=$CHCH_2SH$[d] | 36.4[a] | 75 (**29**) | 25 |
| | 17.9[b] | ~100 (**29**) | *traces* |
| $PhCH_2SH$ | 50.8[a] | 93 (**30**) | 7 |
| | 25.8[b] | ~100 (**30**) | *traces* |
| PhSH | 39.0[a] | 95 (**31**) | 5 |
| | 14.5[b] | ~100 (**31**) | *traces* |

[a]In the presence of 2.1% of $C_3F_7COOH$. [b]In the absence of acid. [c]Reaction time 5 h. [d]Reaction temperature 70 °C.

TABLE 8 The effect of inhibitors on the yield and isomer ratio in the acid-induced addition of *n*-butanethiol to **21** (equimolar ratio of reagents, ambient temperature, 2.1% $C_3F_7COOH$, 3 h)[25]

| Inhibitor, % | | Total yield of **26** + **32**, % | Isomer content, %[a] | |
|---|---|---|---|---|
| | | | **26** | **32** |
| No inhibitor and catalyst | | 7.5 | ~100 | *traces* |
| No inhibitor | | 49.6 | 80 | 20 |
| Hydroquinone | 0.042 | 31.7 | 50 | 50 |
| Phenyl-β-naphthyl-amine | 0.021 | 7.7 | 50 | 50 |

The following plausible mechanism of the acid-induced radical addition of thiols to the C=C double bond can be considered: the intermediate carbenium ion **33** or the proton of the acid taken for the catalysis captures an electron from the thiolate anion in a single-electron transfer fashion to afford a radical pair which then gives rise to a radical chain addition (Scheme 5).[25]

$$CH_2{=}CHOR^1 + H^+ \longrightarrow [\overset{+}{M}eCHOR^1 \longleftrightarrow MeCH{=}\overset{+}{O}R^1] \quad (\mathbf{33})$$

$$HSR^2 \rightleftharpoons H^+ + {}^-SR^2$$

$$\mathbf{33} + {}^-SR^2 \longrightarrow Me\dot{C}HOR^1 + \dot{S}R^2$$

$$H^+ + {}^-SR^2 \longrightarrow \dot{H} + \dot{S}R^2$$

$$CH_2{=}CHOR^1 + \dot{S}R^2 \longrightarrow R^2SCH_2\dot{C}HOR^1$$

$$R^2SCH_2\dot{C}HOR^1 + HSR^2 \longrightarrow (\mathbf{22\text{-}31}) + \dot{S}R^2 \longrightarrow etc.$$

$$Me\dot{C}HOR^1 + HSR^2 \longrightarrow \mathbf{32} + \dot{H} \longrightarrow etc.$$

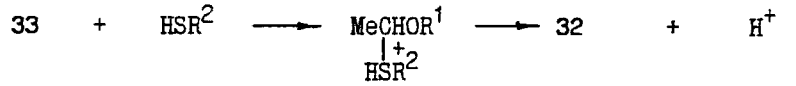
SCHEME 5

This scheme is strongly supported by the fact that this acid-induced reaction could be shown to be inhibited just like a typical radical one (Table 8).[24,25]

It is well known that the so-called non-catalytic addition of an SH function to multiple bonds resulting in *anti*-Markovnikov adducts is actually a radical chain process initiated by traces of oxygen commonly present in the reagents (larger amounts of oxygen may inhibit the process).

The above thiol-to-cation one-electron transfer mechanism initiated in the presence of acids appears to be a general (but until recently obscure) source of *anti*-Markovnikov adducts in acid-catalyzed thiol additions to unsaturated compounds.[25]

The concurrent electrophilic path should be susceptible to a branching of the thiol molecule in its stage of "quenching" of the cationic intermediate **33** in a two-electron transfer fashion (Scheme 6):

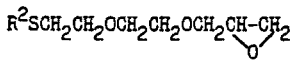


SCHEME 6

The bulkier the substituents $R^1$ and $R^2$ are the more preferable should the one-electron transfer "quenching" of the cation **33** become, being less demanding in its steric requirements. One may see that these speculations are in keeping with all the experimental data available (Tables 5–7). Thus, the higher selectivity of the acid-catalyzed *anti*-Markovnikov addition in the case of **21** may not only result from a partial uptake of the acid by the epoxide function, but from more rigid steric conditions for the capture of the thiol by cation **33** as well. Similarly, the above trend (Table 7) implying that a radical mode of addition in the presence of acid becomes more preferable with increased branching of the thiol molecule, is in good agreement with the rationalization proposed.[25]



TABLE 9 Yields and characteristics of adducts **23–31**[25]



| Cmpd No. | $R^2$ | Yield, % | B.p., °C (*ca.* 1 *mm* Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|---|
| **23** | Et | 53.3 | 110–112 | 1.4760 | 1.0665 |
| **24** | *n*-Pr | 81.0 | 114–116 | 1.4760 | 1.0460 |
| **25** | *i*-Pr | 72.6 | 132 | 1.4730 | 1.0253 |
| **26** | *n*-Bu | 27.8 | 118 | 1.4760 | 1.0469 |
| **27** | *t*-Bu | 27.0 | 120–122 | 1.4680 | 1.0120 |
| **28** | $C_{12}H_{25}$ | 65.3 | 195–197 | 1.4720 | 0.9623 |
| **29** | $CH_2{=}CHCH_2$ | 17.9 | 116–118 | 1.4860 | 1.0735 |
| **30** | $PhCH_2$ | 25.8 | 170–172 | 1.5340 | 1.1302 |
| **31** | Ph | 14.5 | 160–162 | 1.5665 | 1.1838 |

2.1.3. *Vinyloxyorganyl carboxylates* Until the sixties vinyloxyalkyl esters of unsaturated and aromatic acids had not been studied much. The list of the known members of this series seems to have long been confined to vinyloxymethyl acetate,[30] 2-(vinyloxy)ethyl acetate,[31,32] 2-(vinyloxy)ethyl benzoate,[33] and mono- and diglycerol vinyl ethers,[31,32] mentioned only briefly in the above references. Only in the late sixties a number of acetates **34–36** and corresponding benzoates **37, 38** have been obtained by acylation of vinyloxyalkyl esters and examined in detail (Scheme 7).[13,34]

$$CH_2{=}CH(OCH_2CH_2)_nOH + RCOCl \xrightarrow{(C_2H_5)_3N} \underset{\textbf{34–38}}{CH_2{=}CH(OCH_2CH_2)_nOCOR}$$

R = Me, $n$ = 1 (**34**), 2 (**35**), 3 (**36**); R = Ph, $n$ = 2 (**37**), 3 (**38**)

SCHEME 7

Ethanethiol adds to the vinyl ethers **35** and **36** at room temperature in the absence of catalysts. Normally this reaction seems to be initiated by trace amounts of oxygen or peroxides present in the starting acetate ("peroxide effect"), since under these conditions the addition is *anti*-Markovnikov.[13]

$$\underset{\textbf{35,36}}{CH_2{=}CHO(CH_2CH_2O)_nCOCH_3} + C_2H_5SH \longrightarrow \underset{\textbf{39,40}}{C_2H_5SCH_2CH_2O(CH_2CH_2O)_nCOCH_3}$$

$n$ = 2 (**39**), 3 (**40**)

SCHEME 8

According to Refs.[13,34] the ethyl sulfides **39** and **40** are contaminated with as small as 0.8–1.1% of the "normal" addition product. By alcoholysis of the acetates **39** and **40** in alcoholic alkali solution it is possible to obtain the corresponding oxy sulfides with a tri- or tetraethylene glycol chain (Scheme 9).[13,34]

$$\textbf{39} \xrightarrow[KOH]{C_2H_5OH} \underset{\textbf{41}}{C_2H_5S(CH_2CH_2O)_3H}$$

SCHEME 9

The constants of these sulfur-containing vinyloxyorganyl carboxylate derivatives are given in Table 10.

2.1.4. *Haloalkoxyethenes* A study of the reactivity of haloalkoxyethenes has shown[13,35] that, analogously to alkyl vinyl ethers, these compounds are very prone to electrophilic addition to the vinyloxy group.

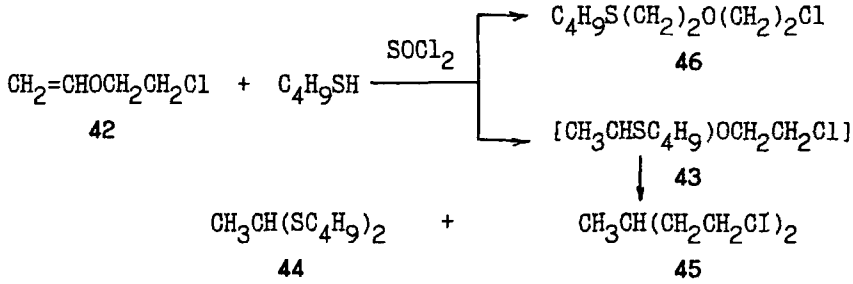
The $SOCl_2$-catalyzed addition of *n*-butanethiol to 2-chloroethyl vinyl ether **42**

TABLE 10 Sulfides derived from vinyloxyorganyl carboxylates[13]

| Cmpd No. | Formula | Yield, % | B.p., °C (*mm* Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|---|
| **39** | $C_2H_5S[(CH_2)_2O]_3COCH_3$ | 72 | 125 (2) | 1.4655 | 1.0641 |
| **40** | $C_2H_5S[(CH_2)_2O]_4COCH_3$ | 84 | 144 (2) | 1.4720 | 1.0760 |
| **41** | $C_2H_5S[(CH_2)_2O]_3H$ | 56 | 131 (4) | 1.4795 | 1.0597 |
| **46** | $C_4H_9S(CH_2)_2O(CH_2)_2Cl$ | 52 | 109–110 (6) | 1.4800 | 1.0393 |

proceeds exothermally; however, the expected mercaptal **43** could not be isolated by distillation due to its disproportionation (Scheme 10).[13]

This transformation is likely to be favored by the presence of sulfonium salts which are normally formed from chlorine-containing sulfides upon heating.[36–38]




SCHEME 10

Under uncatalyzed conditions the electrophilic mechanism fails to compete with the radical mechanism and this leads to butyl (2-chloroethoxy)ethyl sulfide **46** (Table 10). The latter was separated from the mercaptal (6%) by boiling in acidic aqueous dioxane.[35,39]

2.1.5. *Silicon-containing vinyl ethers* In the absence of catalysts, the silicon-containing vinyl ethers **47–49** add ethanethiol to form the corresponding organosilicon sulfides **50–52** (Table 11) in almost quantitative yield (Scheme 11). The Markovnikov products have not been found in this case.[13,40]

$$CH_2{=}CHOXOSi(CH_3)_3 + C_2H_5SH \rightarrow C_2H_5SCH_2CH_2OXOSi(CH_3)_3$$
**47–49** **50–52**

X = $(CH_2)_2$ (**47, 50**), $(CH_2)_2O(CH_2)_2$ (**48, 51**), $(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**49, 52**)

SCHEME 11

2.1.6. (*Polyfluoroalkoxy*)*ethenes* By radical non-catalytic addition of *n*-butanethiol to the ether **53** (UV, 3 h) 1-(2,2,3,3-tetrafluoropropyloxy)-2-(butylthio)ethane **54** was obtained in 95% yield (Scheme 12).[41,42]

TABLE 11 Sulfides derived from silicon-containing vinyl ethers[13]

| Cmpd No. | Formula | B.p., °C (*mm* Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| **50** | $C_2H_5S(CH_2CH_2O)_2Si(CH_3)_3$ | 81 (4) | 1.4505 | 0.9380 |
| **51** | $C_2H_5S(CH_2CH_2O)_3Si(CH_3)_3$ | 112 (3) | 1.4525 | 0.9615 |
| **52** | $C_2H_5S(CH_2CH_2O)_4Si(CH_3)_3$ | 142 (3) | 1.4569 | 0.9872 |

$$\underset{\mathbf{53}}{HCF_2CF_2CH_2OCH{=}CH_2} + HSC_4H_9 \longrightarrow \underset{\mathbf{54}}{C_4H_9SCH_2CH_2OCH_2CF_2CF_2H}$$

SCHEME 12

In the $^1H$ NMR spectrum of the sulfide **54** there are signals of the protons of the fluoroalkyl (δ 5.84, 3.87 ppm) and the butyl group (δ 0.85, 1.43 ppm) and of methylene groups attached to sulfur and oxygen atoms (δ 2.44, 2.56 and 3.60 ppm); signals of $CHCH_3$ groups (due to a probable presence of α-adduct) are not observed.[42]

## 2.2. *Electrophilic Reactions of Vinyl Ethers With Alcohols*

### 2.2.1. *Reactions of 2-(Vinyloxy)ethyl Isothiocyanate*

2.2.1.1. *With alkanols and phenols* Electrophilic addition of alcohols to vinyl ethers, thoroughly and systematically studied (*e.g.*,[13,43]), provides a simple, mild and convenient synthesis of acetals, important starting materials and practically valuable products (*e.g.*,[44-46]). Acetals are also interesting as biologically active compounds (*e.g.*,[44,47]) playing a substantial role in the chemistry of living matter (*e.g.*,[48,49]).

However, data on the preparation and properties of acetals containing an isothiocyanato group as well as on the addition of isothiocyanato alcohols to vinyl ethers were missing in the literature until Refs.[50-54] though such a study could be of use in the search for new pesticides and pharmaceuticals.

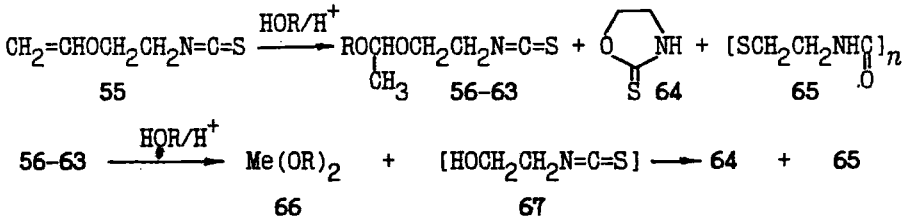
In Refs.[53,54] the addition of alkanols (methanol, 1-propanol, 2-propanol, 1-butanol, cyclohexanol, 2-propyn-1-ol, benzyl alcohol) and phenol to 2-(vinyloxy)ethyl isothiocyanate (**55**) catalyzed by trifluoroethanoic, heptafluorobutanoic, or *p*-toluenesulfonic acid is described. Under mild conditions, alcohols add to **55** exclusively across the vinyloxy group, *i.e.* regiospecifically, to form earlier unknown acetals **56–63** containing isothiocyanato groups (Scheme 13);[50-54] the reaction conditions and the yields being listed in Table 12.

Among the alcohols ROH (R = Me, *n*-Pr, *n*-Bu) the best acetal yield is observed for methanol (58%). Under comparable conditions, for 1-propanol and 1-butanol, the acetal yield falls to 33 and 15%, respectively (Table 12, entries 1, 3, 10). 2-Propanol, 2-propyn-1-ol, and phenol give a quantitative yield of the corresponding acetals **58**, **62**, and **63**.[53,54]

TABLE 12 Yields of the acetals **56–63** and the thione **64** (and its polymer **65**) in dependence of the ROH structure and the reaction conditions[53,54]

| Run | Acetal | R | Molar ratio **36**:ROH | T, °C | Time, h | $C_3F_7CO_2H$, % | Total yield of **64** and **65**, % | Yield of **56–63**, % |
|---|---|---|---|---|---|---|---|---|
| 1 | **56** | Me | 1:1[c] | 45–50 | 2 | 0.35 | 10 | 58 |
| 2 | **56** | Me | 1:2[d] | 53 | 1 | 0.41 | 68 | 11 |
| 3 | **57** | *n*-Pr | 1:1[c] | 40–45 | 2 | 0.30 | 32[e] | 33 |
| 4 | **57** | *n*-Pr | 1:1.5[d] | 35–65 | 1.5 | 0.43 | 53 | *f* |
| 5 | **57** | *n*-Pr | 1:2[d] | 70 | 0.3 | 0.38 | 60 | 19 |
| 6 | **57** | *n*-Pr | 1:2[d] | 60–80 | 0.7 | 0.38 | 66 | 6 |
| 7 | **57** | *n*-Pr | 1:2[d] | 78–80 | 0.75 | 1.32 | 78 | *f* |
| 8 | **58** | *i*-Pr | 1:1 | 70 | 2 | 0.10 | 0[g] | 0[g] |
| 9 | **58** | *i*-Pr | 1:1 | 50 | 2 | 0.30 | *traces*[h] | ~100 |
| 10 | **59** | *n*-Bu | 1:1[c] | 45 | 2.25 | 0.37 | 18 | 15 |
| 11 | **59** | *n*-Bu | 1:1 | 20–25 | 2 day | 0.50 | 69 | *f* |
| 12 | **59** | *n*-Bu | 1:1 | 60–70 | 2 | 0.30[i] | 24 | 31 |
| 13 | **59** | *n*-Bu | 1:1 | 40–50 | 1 | 0.50[i] | *f,j* | *f* |
| 14 | **59** | *n*-Bu | 1:1 | 50–60 | 1 | 0.10[k] | 76[l] | *f* |
| 15 | **59** | *n*-Bu | 1:1 | 50 | 1 | 0.50[k] | | ~95 |
| 16 | **59** | *n*-Bu | 1:2[d] | 50–55 | 2 | 0.41 | 65 | 11 |
| 17 | **60** | *cyclo*-$C_6H_{11}$ | 1:1[d] | 70 | 1 | 0.50 | 17 | 39 |
| 18 | **61** | $PhCH_2$ | 1:1[d] | 30–40 | 1 | 0.50 | 31[f] | 34 |
| 19 | **62** | $CH{\equiv}CCH_2$ | 1:1[d] | 50–65 | 5 | 0.50 | | ~100 |
| 20 | **62** | $CH{\equiv}CCH_2$ | 1:2[d] | 45–64 | 2[m] | 0.50 | 6 | 94 |
| 21 | **63** | Ph | 1:1[d] | 45–70 | 4 | 0.50 | | ~100 |

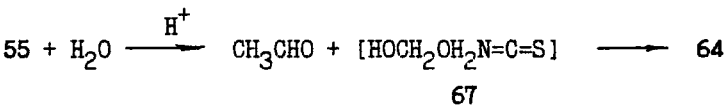
[a]Freshly distilled alcohols were used without special drying. [b]Based on the isothiocyanate **55** taken. [c]Alcohol was added very slowly to the isothiocyanate **55** containing the catalyst. [d]Catalyst was introduced in the reactant mixture stirred at ambient temperature. [e]The reaction mixture was analyzed after two days. [f]The yield was not determined. [g]No reaction was observed. [h]According to the IR spectrum the product is a mixture of thione **64** and polymer **65**. [i]$CF_3CO_2H$. [j]Polymer **65**, m.p. 140 °C. [k]*p*-$MeC_6H_4SO_3H$. [l]The product contains an admixture of polymer **65**, m.p. 225–230 °C. [m]After 70 min the isothiocyanate **55** was absent from the reaction mixture.



SCHEME 13

For the definition of R see Table 12.

However, the unsymmetric acetals **56–61** are not the only products of the reaction. In these cases, 1,3-oxazolidine-2-thione **64**[51] and its polymer **65** have been isolated in a yield up to 40% along with the above unsymmetric acetals **56–63** and corresponding symmetric acetals **66**. A probable pathway of the reaction leading to **64** is shown in Scheme 13. It implies the alcoholysis of the initially formed unsymmetric acetals **56–61** by a second molecule of the alcohol to produce 2-(hydroxy)ethyl isothiocyanate **67** which further undergoes ring closure. Symmetric dialkyl acetals **66** have been detected among the reaction products by GLC analysis using authentic samples. In the case of an equimolar ratio of reactants the reaction mixtures always consists of some amounts (15%) of unconsumed **55** (GLC), supporting the proposed mechanism. When commercial grade 1-butanol (without preliminary drying and distillation) was employed, the yield of thione **64** increased up to 76% (Table 12, entries 11 and 14) and the reaction mixture did not contain unconsumed **55**. In this case, an additional contribution to the formation of **64**, which results in an increase of the yield over the stoichiometrically possible one, comes from the hydrolysis of **55** due to the presence of moisture in the 1-butanol.[53,54]



SCHEME 14

A mild hydrolysis of the ether **55** (12 mmol of **55**, 30 ml of $H_2O$, 0.5% of $CF_3COOH$, 50 °C, 2 h) shows the major product of the reaction to be 1,3-oxazolidine-2-thione (apart from acetaldehyde).[53,54] When a 1.5-2-fold excess of alcohol is employed, a remarkable fall in the yield of unsymmetric acetals and, correspondingly, an increase in the yield of the thione **64** (up to 78%) takes place (Table 12, entries 2, 4–7, 16), again in agreement with the above scheme. When the reaction is carried out in 1-butanol at ambient temperature (10 days), the yield of the thione **64** is close to 100%. Interestingly, even after standing overnight the reaction mixture contains unreacted 2-(vinyloxy)ethyl isothiocyanate **55** and only traces of the unsymmetric acetal **59**, this shows that the alcoholysis rate exceeds that of the addition reaction. From the acetal **59** containing 8% 1-butanol, upon storage at ambient temperature over several months, crystals

of the thione **64** precipitate. The same thione **64**, together with dibutyl acetal, has been obtained by heating of distilled butyl 2-(isothiocyanato)ethyl acetal **59** with 1-butanol (40 °C, 2 h, 0.3% $C_3F_7COOH$). Unlike alkanols, 2-propyn-1-ol and phenol add to the ether **55** without side formation of the thione **64** even with longer reaction times (up to 5 h). An especially clear-cut picture of the effect of the alcohol structure upon the yield of unsymmetric acetals and thione **64** is observed in the reaction with an equimolar ratio of reactants. Here the following trend is noticed: the higher the acidity of the alcohol (and, therefore, its reactivity in the electrophilic addition) the lower the yield of the thione **64**.[53,54] Thus, in the series MeOH, *n*-PrOH, and *n*-BuOH the lowest yield of the thione **64** is observed for methanol and in the case of 2-propyn-1-ol and phenol the thione **64** is not formed at all, this is consistent with the $pK_a$ values of the alcohols:

| | |
|---|---|
| *n*-PrOH,[55] *n*-BuOH[55] | 16.10 |
| MeOH[55] | 15.09 |
| $HC{\equiv}CCH_2OH$[56] | 13.60 |
| PhOH[57] | 9.95 |

Apparently, methanol, 2-propyn-1-ol, and phenol add to the vinyloxy group much faster than the alcoholysis of the unsymmetric acetals proceeds. Indeed, the rate of methanol addition to *n*-butoxyethene is 3.7 and 7.6 times higher than that of 1-propanol and 1-butanol, respectively.[58] On the other hand, the reactivity of the acetals **56, 62**, and **63** in the alkoxy group exchange (alcoholysis) should be decreased as compared with their *n*-propyl and *n*-butyl analogs due to a lower

$$[RO\text{-}\overset{+}{C}H\text{-}CH_3 \longleftrightarrow RO\text{=}\overset{+}{C}H\text{-}CH_3]$$

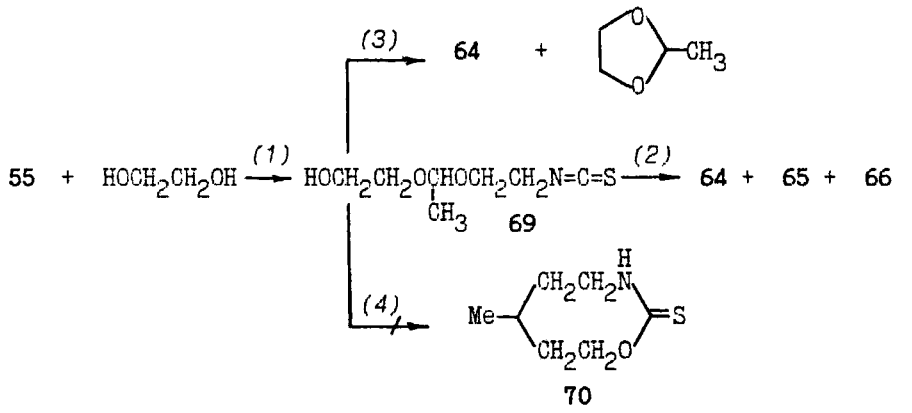
**68**

stabilization of the intermediate carbocation **68** in the former case in accordance with a decreasing electron-donating power of R after the Taft $\sigma^*$ scale:[53,54]

| R | $\sigma^*$ | R | $\sigma^*$ |
|---|---|---|---|
| Me | 0.0 | $HC{\equiv}CCH_2$ | +0.468 |
| *n*-Pr | −0.115 | Ph | +0.60 |
| *n*-Bu | −0.125 | | |

Under the conditions employed, on going to 2-propanol, the thione **64** is practically not formed, in spite of the fact that the rate of 2-propanol addition to vinyl ethers is lower than that of normal alkanols and, hence, in the reaction mixture free alcohol is always present, even at a stoichiometric ratio of the reactants. Apparently, this is a result of steric inhibition of the alcoholysis of acetal **58**.[53,54]

In the reaction of 2-(vinyloxy)ethyl isothiocyanate with 1,2-ethanediol, apart from the acetal **69**, the symmetric acetal **66**, and the thione **64**, one could expect the macrocyclic thione **70** to be formed (Scheme 15, direction 4).[54]



SCHEME 15

However, the thione **70** has not been identified. The major product of the reaction is the thione **64**. The unusually high yield of the thione **64** (> 90%) most probably results from reaction along path 3 (Scheme 15), *i.e.*, from intramolecular alcoholysis of the acetal **69**. In the $^1$H NMR spectrum of the liquid fraction signals of two acetal moieties, 4.69 q, 1.35 d (major) and 4.75 q, 1.14 d (minor) are present.[54]

TABLE 13 Acetals **56–63**, thione **64**, and polymer **65** prepared by addition of alcohols to 2-(vinyloxy)ethyl isothiocyanate[51,53,54]

| Cmpd[a] No. | B.p., °C (*mm* Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|
| **56** | 73 (2) | 1.4920 | 1.0521 |
| **57** | 99 (4) | 1.4822 | 1.0364 |
| **58** | 60 (0.1) | 1.4860 | 1.0299 |
| **59** | 105–110 (4) | 1.4754 | 1.0160 |
| **60** | 90–100 (5) | 1.4954 | 1.0388 |
| **61** | 120 (0.3) | 1.5466 | 1.1219 |
| **62** | 90–91 (5) | 1.5063 | 1.0868 |
| **63** | 130–140 (0.5) | 1.5538 | 1.1577 |
| **64** | 96[b] | | |
| **65**[c] | 160[b], 210[b] | | |

[a]Good or satisfactory elemental analyses (C, H, N, S) have been obtained for all the adducts. [b]M.p. [c]Soluble in DMSO.

In some runs (upon variation of the reaction conditions), the formation of polymeric thione **64** (**65**) has been observed, though only as a minor admixture to the thione **64**. The polymer **65** is insoluble in water and most organic solvents (except DMSO); therefore these products (**64** and **65**) are readily separated. Generally, the polymerization of thione **64** is favored by long reaction times and high concentrations of catalyst (at a relatively low rate of the major reaction).

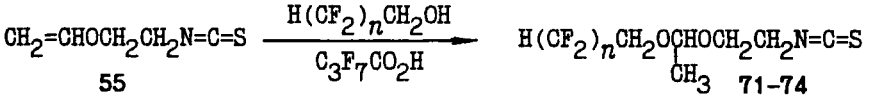
When the stronger *p*-toluenesulfonic acid is used as catalyst in low concentrations (Table 12, entry 14) the major product is the thione **64** (with a small admixture of

polymer **65**). Upon an increase of the catalyst concentration from 0.1 to 0.5% (by mass), the acetal **59** becomes practically the only product (Table 12, entry 15).[53,54]

Physico-chemical characteristics and spectra of the acetals **56–63** are listed in Tables 13–15. All properties of 1,3-oxazolidine-2-thione **64** (m.p., solubility, IR, $^1H$, $^{13}C$ NMR, and mass spectra) were identical to those of an authentic sample synthesized according to Refs.[51,59]

2.2.1.2. *With polyfluoroalkanols* The selective addition of polyfluoroalkanols to functional vinyl ethers has been investigated with diol divinyl[60] and epoxy vinyl[60–62] ethers. The reaction of the isothiocyanate **55** with polyfluoroalkanols was first mentioned briefly in Refs. [63,64] and later experimental details of this reaction were published.[65]

It was shown[65] that under electrophilic conditions **55** smoothly adds polyfluoroalkanols to the vinyloxy group to form isothiocyanates with a polyfluoro acetal moiety **71–74** (Scheme 16, Tables 16–18).




*n* = 2 (**71**), 4 (**72**), 6 (**73**), 8 (**74**)

SCHEME 16

TABLE 14 The IR spectra (film) of acetals **56–63**, thione **64**, and polymer **65** (KBr)[51,53,54]

| Cmpd No. | $cm^{-1}$ |
|---|---|
| **56** | 500, 620, 810–820, 900–930, 980, 1020–1080–1110–1150–1190, 1260, 1310–1340, 1380, 1420–1450, 1510, 2100–2200, 2820, 2880–2940–2990 |
| **57** | 500, 640, 890, 940, 980, 1010–1040–1070–1100–1110–1140–1210, 1300, 1330, 1370, 1430–1480–1500, 2100–2200, 2870–2920–2960 |
| **58** | 500, 640, 880, 920, 960, 1050–1100–1130–1200, 1260, 1300, 1350, 1420–1470–1500, 2100–2200, 2840–2900–2940 |
| **59** | 910, 940, 965, 1020–1050–1080–1130–1146–1180, 1340, 1365–1390, 1430–1450, 1460, 2100–2200, 2860–2920–2950, 2980 |
| **60** | 500, 610, 870, 880–900, 960, 1000–1020–1070–1110–1140, 1300–1320–1330–1370, 1430, 1500, 2100–2200, 2840–2920–2970 |
| **61** | 460, 530, 600, 650, 700, 830, 930, 960, 970, 1030–1040–1070–1100–1140–1165, 1200, 1280, 1330, 1340, 1370, 1400, 1460, 1465, 1500, 1535, 2120–2200, 2880–2900–2940–3000, 3040, 3100 |
| **62** | 640–670, 850, 980, 1000–1010–1040–1060–1100–1140, 1250, 1275, 1320, 1350, 1360, 1400, 1450, 2100–2200, 2900 |
| **63** | 500, 600, 640, 685, 750, 800, 820, 880–930–950, 1000–1020–1040–1070–1120–1140, 1170, 1230, 1280, 1340, 1370–1380, 1440–1450, 1460–1480, 1590–1600, 2100–2200, 2870–2940–3000, 3040, 3050 |
| **64** | 490, 610, 685, 890, 920, 940, 1150, 1260, 1300, 1360, 1430, 1510, 3200 |
| **65** | 600, 800, 1180, 1500, 1640, 2900, 3000, 3260 |

TABLE 15 The $^1$H NMR spectra ($CDCl_3$, δ, ppm) of acetals **56–63**, thione **64**, and its polymer **65**[51,53,54]

| Cmpd No. | R | OCHO, q | $CH_3$, d | $OCH_2CH_2N$, m | R |
|---|---|---|---|---|---|
| **56** | Me | 4.71 | 1.31 | 3.67 | 3.33 s ($CH_3$) |
| **57** | *n*-Pr | 4.71 | 1.26 | 3.63, 3.40 | 0.86 t ($CH_3$), 1.50 t, 1.72 t ($CH_2CH_2$) |
| **58** | *i*-Pr | 4.80 | 1.29 | 3.65 | 1.14 t ($CH_3$), 3.88 s (CH) |
| **59** | *n*-Bu | 4.74 | 1.25 | 3.61 | 0.88 t ($CH_3$), 1.36 m, 1.50 m ($CH_2CH_2$), 3.74 m ($CH_2O$) |
| **60** | *cyclo*-$C_6H_{11}$ | 4.88 | 1.29 | 3.66 | 1.80 m, 1.50 m |
| **61** | $PhCH_2$ | 4.90 | 1.42 | 3.61 | 7.31 s ($C_6H_5$), 4.60 d |
| **62** | $CH{\equiv}CCH_2$ | 4.95 | 1.37 | 3.70 | 4.23 d ($CH_2$), 2.45 t (CH≡) |
| **63** | Ph | 5.44 | 1.50 | 3.58, 3.80, 3.67 | 7.27 t, 7.04 d, 6.96 q |
| **64**[a] | | 4.72 t ($CH_2O$), 3.81 t ($CH_2N$), 8.01 s (NH) | | | |
| **65**[b] | | 2.85 t ($CH_2S$), 3.21 t ($CH_2N$), 8.36 s (NH) | | | |

[a]The $^{13}$C NMR (DMSO-$d_6$, δ, ppm): 188.87 (C=S), 69.86 (C-O), 43.83 (C-N). Molecular ion: [$M^+$.] = 103. [b]DMSO-$d_6$.

TABLE 16 The addition of polyfluoroalkanols $H(CF_2)_nCH_2OH$ to 2-(vinyloxy)ethyl isothiocyanate **55**[65]

| *n* | Amount of $C_3F_7CO_2H$, % | T, °C | Time, min | Reaction product (yield, %)[a] |
|---|---|---|---|---|
| 2 | 0.73 | 75–80 | 20 | **71** (80) |
| 2 | 0.58 | 45 | 240 | **71** (90), (100)[b] |
| 2 | 0.44 | ~85 | 10 | **71** (67) |
| 2 | 0.36 | ~70 | 5 | **71** (46) |
| 4 | 0.50 | 50–55 | 20 | **72** (54) |
| 4 | 0.52 | 55–65 | 75 | **72** (61) |
| 4 | 0.52 | 60–65 | 10 | **72** (73) |
| 4 | 0.42 | ~70 | 5 | **72** (66), (100)[b] |
| 6 | 0.41 | ~80 | 10 | **73** (80) |
| 6 | 0.41 | 80–90 | 120 | **73** (100)[b] |
| 8 | 0.34 | 45–50 | 60 | **74** (100)[b] |

[a]Preparative yield calculated basing on consumed **55**. [b]GLC.

TABLE 17 Polyfluoroalkyl (2-isothiocyanato)ethyl acetals **71–74**[65]

| Cmpd No. | Yield, % | B.p., °C (1 *mm* Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| **71** | 90 | 99–100 | 1.4410 | 1.2352 |
| **72** | 66 | 107 | 1.4148 | 1.3838 |
| **73** | 80 | 120–123 | 1.3980 | 1.5108 |
| **74** | 100 | 130 | 1.3856 | 1.5855 |



The reaction was performed without solvent with an equimolar ratio of reagents in the presence of 0.3–0.7% heptafluorobutanoic acid and at 70–80 °C, as a rule being completed in a few minutes. The addition was controlled by IR spectroscopy and GLC of the reaction mixture: the absence of absorption bands of vinyloxy and hydroxy groups in the IR spectrum (with retention of the isothiocyanate group absorption) and the absence of the starting materials in the chromatograms (the only peak of the reaction product, that of the unsymmetrical acetal being present) indicated that the reaction was over.[65]

Factors such as the order and rate of introduction of the reagents and the catalyst, which considerably influence the reaction of alkanols with the isothiocyanate **55**,[53,54] play no noticeable role in the addition of polyfluoroalkanols to the same isothiocyanate.

Also, in contrast to their unfluorinated analogs,[53,54] the addition of polyfluoroalkanols to **55** proceeds without complications. In particular, no symmetrization of the polyfluoro acetals **71–74** was observed, neither in the course of the synthesis nor upon distillation. Only in one case where the reaction mixture was allowed to stand for 24 h 1,3-oxazolidine-2-thione **64** appeared in a small amount (< 1%). This compound was obtained in approximately the same yield from the acetal **71** upon storage for seven months.[65]

TABLE 18 IR and $^1H$ NMR spectra of acetals **71–74**[65]

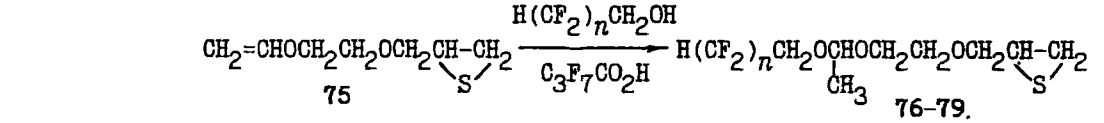
| Cmpd No. | $cm^{-1}$ | δ, ppm, $CDCl_3$ | | | | |
|---|---|---|---|---|---|---|
| | | OCHO, q | $CH_3$, d | $H(CF_2)_n$, tt | $OCH_2$, t | $OCH_2CH_2N$, m |
| **71** | 460, 540, 570, 650, 690, 710, 740, 830, 860, 930, 1010, 1050–1150, 1200, 1230, 1270, 1300, 1340, 1370, 1400, 1440, 1450, 2100, 2200, 2880, 2940, 2990 | 4.90 | 1.37 | 5.90 | 3.96 | 3.68 |
| **72** | 450, 520, 540, 600, 630, 700, 740, 750, 800, 860–890–920–950–985, 1050–1240, 1280, 1340, 1380, 1390, 1440, 1450, 2100, 2200, 2875, 2935, 2980 | 4.93 | 1.38 | 6.06 | 4.03 | 3.69 |
| **73** | 450, 520, 540, 600, 670, 700, 730, 740, 750, 770, 815, 830, 840, 910, 940, 1010, 1040, 1140–1190–1250, 1280, 1330, 1365, 1380, 1430, 1440, 2100, 2200, 2880, 2940, 2985 | 4.91 | 1.39 | 6.04 | 4.02 | 3.67 |
| **74** | 460, 500, 540, 560, 640, 690, 705, 710, 750, 790, 810, 860, 930, 980, 1010, 1050–1260, 1265, 1340, 1370, 1390, 1440, 1450, 2100, 2200, 2880, 2940, 2980 | 4.93 | 1.39 | 6.04 | 4.02 | 3.68 |

The differences in addition of polyfluoroalkanols and alkanols, under identical reaction conditions, to the vinyl ether **55** are likely to be of the same nature as those observed between 1-propanol (or 1-butanol) and phenol (or propargyl alcohol),[53,54] and can be rationalized likewise.

On one hand, analogously to phenol and propargyl alcohol, the rate of addition of polyfluoroalkanols to the vinyloxy group of **55** is so high that the reaction mixture after a short time contains no starting alcohol or phenol (with an equimolar ratio of reagents), showing that no alcoholysis takes place. On the other hand, the reactivity of the polyfluoro acetals **71–74** in alcoholysis compared with the propyl or butyl analogs,[53,54] is reduced due to the lower stability of the intermediate cation $[ROCHCH_3 \leftrightarrow RO{=}CHCH_3]$, caused by a decrease in the electron-donating power of the substituent R in going from R = *n*-$C_3H_7$, *n*-$C_4H_9$ to $H(CF_2)_nCH_2$. The enhanced stability of fluoro acetals has already been encountered previously[66] in an unsuccessful attempt to add bis(2,2,3,3-tetrafluoropropyl) acetal to 2-(vinyloxy)ethoxymethyloxirane in spite of variation of the reaction conditions in a wide range (extreme conditions were as follows: 2% cationic catalyst, 140 °C, 5 h).

2.2.2. *Reactions of 2-(vinyloxy)ethoxymethylthiirane* Previously, the addition of alcohols (including polyfluorinated ones[60–62]) and phenols to vinyloxy epoxides leading to high yields of epoxy acetals has been reported.[67–71] In the presence of perfluorocarboxylic (trifluoroethanoic, heptafluorobutanoic) acids and their acylals (adducts with alkyl vinyl ethers) the reaction was shown[69–71] to proceed selectively at the vinyloxy group without affecting the epoxy entity.

In Refs.[72,73] the acid-catalyzed reaction of 2-(vinyloxy)ethoxymethylthiirane **75** with polyfluoroalkanols was shown to be a convenient route to promising and earlier unknown epithiofluoro acetals **76–79** (Scheme 17).




*n* = 2 (**76**), 4 (**77**), 6 (**78**), 8 (**79**)

SCHEME 17

The reaction conditions and results are presented in Table 19.

The reaction was $^1H$ NMR controlled to detect changes in the integral intensities of the signals corresponding to the vinyloxy group [6.47 q (OCH=), 4.20 dd, 4.01 dd ($CH_2$=)], acetal [4.86–4.91 q (OCHO), 1.33–1.36 d ($CH_3$)] and the thiirane [3.06 q (CHS), 2.49–2.50 d, 2.19–2.20 d ($CH_2S$)].[73]

Taking into account the considerable and equal distance separating the oxirane and the thiirane entities from the vinyloxy group, one might expect a minor and approximately equal ring effect on the electron distribution and reactivity of the vinyloxy group in 2-(vinyloxy)ethoxymethyloxirane **21** and its thio analog **75**.

TABLE 19 The yields of thiiranes **76–79** in dependence of the reaction conditions (Scheme 17, benzene, equimolar ratio of reagents)[73]

| *n* | $C_3F_7CO_2H$, % | T, °C[a] | Time, h | Conversion of thiirane **75**, % | Yield, %[b] Thiirane (**76–79**), %[b] | Yield, %[b] Polymer, %[b] |
|---|---|---|---|---|---|---|
| 2[c] | 0.5 | 60 | 1 | 35 | **76** (5) | 30 |
| 2[c] | 1.0 | 20–22 (37) | 24 | 100 | **76** (50) | 50 |
| 2[c] | 6.0 | (92) | 0.3 | 100 | **76** (40) | 60[d] |
| 2[c] | 7.0 | 20–22 (87) | 24 | 100 | **76** (0) | 100[e] |
| 2 | 0.5 | 48–50 | 2 | 32 | **76** (28) | 4 |
| 2 | 0.5 | 90 | 2 | 44 | **76** (40) | 4 |
| 2 | 1.0 | 60 | 4 | 100 | **76** (68) | 32 |
| 2[f] | 1.0 | 95–100 | 3 | 60 | **76** (45) | 15 |
| 2 | 2.0 | 63 | 2 | 100 | **76** (80) | 20 |
| 2 | 2.0 | 92 | 3 | 100 | **76** (60) | 40 |
| 4[c] | 1.0 | 60 | 2.5 | 58 | **76** (35) | 23 |
| 4[g] | 1.0 | 60 | 2 | 91 | **77** (80) | 11 |
| 4 | 1.0 | 90 | 3 | 93 | **77** (79)[h] | 14 |
| 6[c] | 1.0 | 20–22 | 2 | 58 | **78** (28) | 30 |
| 6 | 0 | 90 | 3 | 17 | **78** (0) | 17 |
| 6 | 0.8 | 90 | 3 | 88 | **78** (80)[h] | 8 |
| 6 | 1.0 | 60 | 2 | 81 | **78** (72) | 9 |
| 6 | 1.0 | 60 | 3 | 81 | **78** (67) | 14 |
| 8 | 1.0 | 60–63 | 2 | 89 | **79** (87) | 2 |
| 8 | 1.0 | 90 | 3 | 76 | **79** (72)[h] | 4 |
| 8 | 2.0 | 60–63 | 2 | 92 | **79** (76) | 16 |

[a]In brackets self-heating temperature of the reaction mixture is given. [b]Based on **75** consumed. [c]Without solvent. [d]Mixture of homopolymers (or copolymers) of **75** or **76** in the ratio 20:80 (elemental analysis, $^1$H NMR spectrum). [e]Homopolymer of **76**. [f]Two-fold excess of fluoro alcohol. [g]In $CH_3CN$. [h]In the $^1$H NMR spectrum signals of the allyloxy group are identified.



Indeed, the analysis of their photoelectron spectra (Table 20) shows a superposition of poorly excited spectra of the fragmentary compounds (oxirane **80**, ethyl methyl ether **81**, ethyl vinyl ether **82**, and dimethyl sulfide **83**). The only essential feature is the overlapping of the thiirane and vinyloxy bands, implying a competition between the vinyloxy group and the thiirane entity with respect to electrophiles.[73]

In this connection it should be noted that the behavior of the thiirane **75** and its oxygen analog **21** differs much under the reaction conditions studied. Thus, when the reaction is carried out without solvent in the presence of 0.5% heptafluorobutanoic acid, the oxirane **21** adds polyfluoroalkanols with a strong exothermic effect to form the corresponding acetals in quantitative yield.[62] Under identical conditions (24 °C, 25 min) the analogous thiirane **75** gives a polymer in only 16% yield. With increasing temperature (up to 60 °C) and reaction time (up to 1 h) the yield of the thiirane **76** becomes as low as 5% (Table 19), the polymer yield reaching 30%. When the reaction was carried out without solvent the highest yield of **76** was achieved at room temperature in the presence of 1% catalyst for 24 h (Table 19). At a higher concentration of the catalyst (7%), the reaction mixture is quantitatively polymerized already at room temperature.[73]

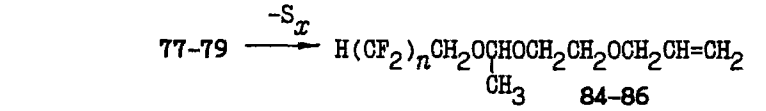
TABLE 20 Vertical ionization potentials of 2-(vinyloxy)ethoxymethyloxirane **21**, its thio analog **75** and fragmentary compounds[73]

| Cmpd No. | Formula | Ionization energy, eV | | | | |
|---|---|---|---|---|---|---|
| **21** | $CH_2=CHOCH_2CH_2OCH_2CH(O)CH_2$ | 9.01 ($\pi_4$)[a] | 9.64 ($\pi_3$) | 10.56 ($\pi_2$) | 11.60 ($n_o$)[b] | 12.02 ($\pi_1$) |
| **80**[c] | $CH_2(O)CH_2$ | | | 10.57 ($\pi_1$)[a] | 11.85 ($n_o$) | |
| **81**[d] | $CH_3CH_2OCH_3$ | | 9.86 ($\pi_1$)[a] | | 11.60 ($n_o$) | |
| **82** | $CH_2=CHOCH_2CH_3$ | 9.10 ($\pi_2$)[a] | | | 11.61 ($n_o$) | 11.97 ($\pi_1$) |
| **83**[d] | $CH_3SCH_3$ | 8.72 ($\pi_1$)[a] | | | 11.30 ($n_s$) | |
| **75** | $CH_2=CHOCH_2CH_2OCH_2CH(S)CH_2$ | 8.96 ($\pi_4$)[a]<br>9.00 ($\pi_3$) | 9.95 ($\pi_2$) | | 11.08 ($n_s$)<br>11.65 ($n_o$)[e] | 12.00 ($\pi_1$)[b] |

[a]$\pi$-Like orbitals were not taken into consideration in numbering MO. [b]Shoulder. [c]Ref.[74]. [d]Ref.[75] [e]Overlapping bands. The observed maximum position is presented.

The general tendency for reactions without solvent with increasing temperature, reaction time, and catalyst concentration is a parallel or selective increase in the yield of the polymeric product.[73] The use of a solvent (benzene, acetonitrile) not only inhibits polymerization, but simultaneously accelerates the addition of the fluoro alkanol to the vinyloxy group, which is consistent with the data.[13] At the same time, use of a two-fold excess of alkanol (Table 19) leads neither to an increase in **76** yield nor to the formation of the diadduct, the product of addition of a second molecule of alcohol to the thiirane ring.[73]

When the reaction is run above 90 °C the addition of the fluoroalkanol (with the exception of 2,2,3,3-tetrafluoro-1-propanol) is accompanied by partial (7–10%) desulfurization of the thiiranes **77–79**: in their $^1$H NMR spectra (Table 23) weak signals of the allyloxy group are present. The corresponding allyl ethers **84** and **85**, the products of the desulfurization of the thiiranes **77** and **78**, were isolated by preparative GLC (Scheme 18).[73]




$n$ = 4 (**84**), 6 (**85**), 8 (**86**)

SCHEME 18

The fluorothiiranes **76–79** are transparent colorless liquids with a faint specific odor. Their physical constants, elemental analyses, and spectral characteristics are presented in Tables 21–23. The thiiranes **76–79** can be purified by vacuum distillation. The stillages (at modest catalyst concentrations and moderate temperature) are, as a rule, homopolymers of the initial thiirane **75** (according to elemental analysis and spectral data). At a higher catalyst concentration the polymerized reaction mixture and the stillage are mainly or completely polymers of the thiirane **76** (Table 19). Under normal conditions the thiirane **76**, purified by distillation, is stable for about one month, then it slowly polymerizes to form a solid transparent polymer. The thiiranes **77–79** are more stable compounds.[73]

TABLE 21 Thiiranes **76–79**[73]

| Cmpd No. | Yield, % | B.p., °C (*mm* Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| **76** | 80 | 135 (10) | 1.4285 | 1.2663 |
| **77** | 80 | 120–122 (4) | 1.4050 | 1.3864 |
| **78** | 80 | 135–138 (4) | 1.3824 | 1.4894 |
| **79** | 87 | 148–158 (5) | 1.3750 | 1.5884 |

TABLE 22 The IR spectra of thiiranes **76–79**[73]

| Cmpd No. | $\nu$, $cm^{-1}$ |
|---|---|
| **76** | 530, 600, 680, 735, 790, 850, 880, 920, 940, 1090, 1140, 1265, 1375, 1440, 2850, 2920, 2975 |
| **77** | 525, 600, 680, 740, 780, 875, 920, 950, 1100, 1160, 1230, 1265, 1360, 1440, 1600, 2855, 2920, 2980 |
| **78** | 525, 600, 690, 740, 780, 880, 920, 940, 1100, 1150, 1240, 1270, 1370, 1450, 2870, 2940, 2980 |
| **79** | 535, 615, 650, 700, 730, 760, 800, 870, 930, 960, 1020, 1140, 1200, 1300, 1325, 1340, 1400, 1465, 2890, 2950, 3010 |

## 2.3. *Reactions of Sulfur-Containing Vinyl Ethers With Carboxylic Acids*

### 2.3.1. *Reactions of 2-(vinyloxy)ethyl isothiocyanate*

2.3.1.1. *With alkanoic acids* In the presence of catalytic amounts (0.3–0.5%) of heptafluorobutanoic acid the addition of carboxylic (ethanoic, butanoic, pentanoic, benzoic, acrylic, and methacrylic) acids to the vinyl ether **55** proceeds smoothly and with high selectivity at the vinyloxy group to give earlier unknown isothiocyanates **87–92** with an acylal moiety (Scheme 19, Tables 24–27).[76]

$$\underset{\mathbf{55}}{CH_2{=}CHOCH_2CH_2N{=}C{=}S} + RCOOH \longrightarrow RCOOCHOCH_2CH_2N{=}C{=}S$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3 \quad \mathbf{87\text{–}92}$$

SCHEME 19

The definitions of R are presented in Table 24.

The reaction course was followed by IR and $^1H$ NMR spectroscopy. The completion of the reaction was indicated by disappearance of the absorption bands corresponding to the hydroxyl (2700–3600 $cm^{-1}$) and vinyloxy (3100, 1620–1610, 1320, 1200, 820 $cm^{-1}$) groups in the IR spectrum, appearance of a broadened band of acetals and acylals in the 1000–1190 $cm^{-1}$ region and a band at 2960–2990 $cm^{-1}$ ($CH_3$) with remaining absorption bands of groups not affected in the reaction course: 2100–2200 $cm^{-1}$ (N=C=S) and 1700–1780 $cm^{-1}$ (C=O).

When the reaction is over, in the $^1H$ NMR spectrum of the reaction mixture there are no signals of the vinyloxy group (6.45 q, 4.19 dd, 4.00 dd) and signals of the $OCH(CH_3)O$ fragment appear in the 5.94–6.17 q (CH), 1.42–1.54 d ($CH_3$) ppm regions.[76]

Acrylic and methacrylic acid add to **55** without catalyst (Table 24). The use of catalysts with these acids decreases the reaction temperature and time and increases the yield of the adduct **91** up to quantitative (Table 24). To avoid resinification the reaction with benzoic and methacrylic acids should be carried out in an organic solvent (*e.g.*, benzene).[76]

The isothiocyanates **87–92** are colorless or slightly colored liquids with a spe-

TABLE 23 The $^1H$ NMR spectra of thiiranes **76–79**[73]

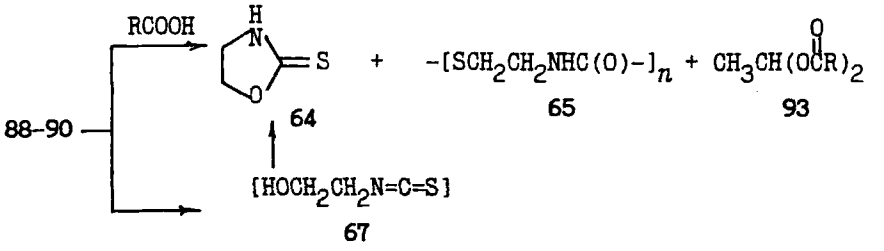
| Cmpd No. | $HCF_2$, tt | $CH_2O$, s | OCHO, q | $CH_3$, d | $OCH_2CH_2OCH_2$, m | CHS, q | $CH_2S$, d | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | *trans* | *cis* |
| **76** | 6.47 5.93 5.39 | 3.90 | 4.86 | 1.33 | 3.66 | 3.06 | 2.49 | 2.19 |
| **77** | 6.58 6.05 5.53 | 4.01 | 4.91 | 1.35 | 3.66 | 3.06 | 2.50 | 2.19 |
| **78** | 6.55 6.04 5.52 | 4.02 | 4.91 | 1.35 | 3.67 | 3.06 | 2.50 | 2.19 |
| **79** | 6.52 6.05 5.51 | 4.00 | 4.91 | 1.36 | 3.68 | 3.07 | 2.49 | 2.20 |

TABLE 24 Addition of carboxylic acids, RCOOH, to 2-(vinyloxy)ethyl isothiocyanate **55** (equimolar ratio of reagents)[76]

| Adduct | R | $C_3F_7CO_2H$, % | T, °C | Time, h | Yield,[a] %[b] |
|---|---|---|---|---|---|
| **87** | $CH_3$ | 0.5 | 40–45 | 1 | ~100 |
| **88** | $n$-$C_3H_7$ | 0.5 | 40–45 | 0.75 | ~100 |
| **89** | $n$-$C_4H_9$ | 0.5 | 40–45 | 0.67 | ~100 |
| **90** | $C_6H_5$ | 0.5 | 60–70 | 1.5 | ~100 |
| **90** | $C_6H_5$ | 0.3 | 50 | 3 | ~100 |
| **91** | $CH_2$=CH | None | 50 | 5 | ~100 |
| **91** | $CH_2$=CH | 0.3 | 20–22 | 5 | ~100 |
| **92** | $CH_2$=C($CH_3$) | None | 50–60 | 5 | ~50 |
| **92** | $CH_2$=C($CH_3$) | 0.5 | 40–45 | 1 | 85 |
| **92** | $CH_2$=C($CH_3$) | 0.3 | 60 | 3 | ~100 |

[a]From $^1$H NMR spectra. [b]Based on consumed **55**. [c]In benzene.

cific pleasant odor, soluble in most organic solvents, fairly stable and capable of purification by vacuum distillation. In this case only a small portion of the product residue is lost due to decomposition. As reported in Ref. [77] among the products of thermodestruction of simpler acylals, the starting reagents, the alcohol corresponding to the vinyl ether, the symmetrical acetal and traces of acetaldehyde are normally identified. From the undistilled acylals **88–90** after storage and removal of the first distillate (enriched with free acid) a small amount of a colorless crystalline substance corresponding to the 1,3-oxazolidine-2-thione **64** or its polymer **65** (elemental analysis, IR, $^1$H NMR, mass spectra, m.p.) was isolated.[51,53,54] The formation of the thione **64** in the electrophilic reaction of alcohols with **55** was proven experimentally[53,54] to result from the alcoholysis of the initially formed unsymmetrical acetals. The reaction conditions for the preparation of 1,3-oxazolidine-2-thione **64** in quantitative yield have been found.[51] The formation of the thione **64** from **88–90** may be explained by either their acidolysis with a second molecule of the acid or cyclization of the unstable 2-(hydroxy)ethyl isothiocyanate **67** as one of the possible products of the thermolysis of these acylals (Scheme 20).[76]




SCHEME 20

The acylal **90**, the adduct of benzoic acid to **55**, is less stable and normally crystallizes soon after synthesis. The crystalline substance isolated by TLC ($Al_2O_3$, diethyl ether-ethanol, 1:2) was also 1,3-oxazolidine-2-thione **64** (IR, $^1$H NMR spectroscopy).[76]

Bis[(2-isothiocyanato)ethyl] acetal, $CH_3CH(OCH_2CH_2N{=}C{=}S)_2$ **94**, probably from the disproportionation of the acylals **87–92**, has been isolated from the distilled acylal **92** (identified by IR and $^1H$ NMR spectroscopy). The formation of **94** could hardly be explained by addition of 2-(hydroxy)ethyl isothiocyanate **67** to **55**, since in all the experiments where formation of the alcohol **67** was expected (in particular, in electrophilic reactions of **55** with alcohols[53,54]) 1,3-oxazolidine-2-thione was isolated, the product of the cyclization of **67**. An attempt[59] to synthesize 2-(hydroxy)ethyl isothiocyanate also led to **64** instead of the expected product. Although unsymmetrical acylals are not prone to disproportionation,[77] in this case the formation of the acetal **94** could only be explained by the transformation: 2 **92** → **93** + **94**.

Trace amounts of the acetal **94** are also present in the undistilled product **92** as evident from the $^1H$ NMR spectrum: 4.87 q (OCHO), 1.38 d ($CH_3$). The IR spectrum of **94** shows a strong absorption at 2100–2200 $cm^{-1}$, which corresponds to the N=C=S group, and an intense broadened absorptions of acetal [1050, 1070, 1100, 1130 $cm^{-1}$ (O–C–O), and 2970 $cm^{-1}$ ($CH_3$)]. The $^1H$ NMR spectrum of the acetal **94** (δ, ppm): 4.85 q (OCHO), 1.36 d ($CH_3$), 3.71 m ($OCH_2CH_2N$) corresponds to its structure.

When use is made of freshly distilled reactants taken in strictly stoichiometric quantities, the acylals **87–92** do not need distillation.[76]



TABLE 25 Isothiocyanates **87–92**[76]

| Cmpd No. | B.p., °C (4 *mm* Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|
| **87** | 95 | 1.4930 | 1.1350 |
| **88** | 105–107 | 1.4800 | 1.0569 |
| **89** | 130 | 1.4800 | 1.0607 |
| **90**[a] | | 1.5455 | 1.1676 |
| **91**[a] | | 1.5075 | 1.1434 |
| **92** | 80–83[b] | 1.4984 | 1.0995 |

[a]Undistilled product. [b]At 0.055 *mm* Hg.

TABLE 26 The IR spectra of the isothiocyanates **87–92**[76]

| Cmpd No. | ν, $cm^{-1}$ |
|---|---|
| **87** | 450, 600–640, 830, 920, 1000–1030–1080–1120–1160, 1240, 1330, 1360, 1440, 1730, 2100–2200, 2720, 2870–2920–2970 |
| **88** | 450, 650, 830, 920, 1020–1090–1120–1190, 1250, 1730, 2100–2200, 2750, 2870–2930–2960 |
| **89** | 510, 830, 910, 1010–1060–1110–1130–1150, 1200–1240, 1320, 1370, 1430–1440, 1710, 2100–2200, 2850, 2910–2930–2960 |
| **90** | 650–690–710, 810–840, 930, 1020–1030–1080–1140–1160, 1270, 1310, 1350–1390, 1440, 1590–1600, 1710, 2100–2200, 2870–2930–2990, 3060 |
| **91** | 430, 510, 620, 790, 820, 910, 990, 1010, 1050, 1100, 1130–1150, 1280, 1300, 1330, 1360, 1420, 1610–1620, 1700, 2100–2200, 2850–2910–2970 |
| **92** | 430, 510, 640, 690, 710, 760–790–830, 860, 920, 1020, 1070, 1110–1150–1220, 1330, 1380, 1430, 1780, 2100–2200, 2870–2920–2980 |

TABLE 27 The $^1H$ NMR spectra of the isothiocyanates **87–92**, $R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\,\overset{\overset{CH_3}{|}}{C}\,HOCH_2CH_2N{=}C{=}S$[76]

| Cmpd No. | R | δ, ppm, $CDCl_3$ | | | | |
|---|---|---|---|---|---|---|
| | | OCHO, q | $CH_3$, d | $OCH_2CH_2N$, m | | R |
| **87** | $CH_3$ | 5.94 | 1.42 | 3.78 | 3.68 | 2.09 s ($CH_3$) |
| **88** | $n$-$C_3H_7$ | 5.96 | 1.42 | 3.74 | 3.66 | 0.95 t ($CH_3$), 1.65 s (β-$CH_2$), 2.33 t (α-$CH_2$) |
| **89** | $n$-$C_4H_9$ | 5.94 | 1.42 | 3.78 | 3.68 | 0.92 t ($CH_3$), 1.4–1.6 m (β, γ-$CH_2$), 2.34 t (α-$CH_2$) |
| **90** | $C_6H_5$ | 6.17 | 1.54 | 3.81 | 3.63 | 7.49 ($H_m$, $H_p$), 8.06 ($H_o$) |
| **91** | $CH_2{=}CH$ | 6.00 | 1.45 | 3.75 | 3.66 | 6.07 dd (CH), 6.45 dd ($CH_2=$, *trans*), 5.85 dd ($CH_2=$, *cis*) |
| **92** | $CH_2{=}C(CH_3)$ | 6.00 | 1.47 | 3.76 | 3.68 | 1.93 d ($CH_3$), 5.62 dd, 6.17 d ($CH_2=$) |

2.3.1.2. *With haloalkanoic acids* In order to prepare new functional isothiocyanates, which are promising monomers, synthetic intermediates and potentially bioactive substances, as well as to examine the structural effect of the acid on the stability of the acylals, the reaction of 2-(vinyloxy)ethyl isothiocyanate **55** with haloalkanoic acids (2-chloro-, 2-bromo-, trifluoro- and trichloroethanoic, 3-bromopropanoic acid) has been investigated.[78–81]

These haloalkanoic acids were found to add smoothly to the vinyloxy group of **55** thus leading quantitatively to the acylals **95–99** (Scheme 21).[81]

$$\underset{\mathbf{55}}{CH_2{=}CHOCH_2CH_2N{=}C{=}S} + RCOOH \longrightarrow \underset{\mathbf{95\text{–}99}}{RCOOCH(CH_3)OCH_2CH_2N{=}C{=}S}$$

SCHEME 21

The definitions of R and the reaction conditions are presented in Table 28.

The addition was controlled by IR and $^1$H NMR spectroscopy. The reaction was over when IR absorption bands (820, 1200, 1320, 1610–1620, 3100 $cm^{-1}$) and NMR signals (6.45 q, 4.18 dd, 4.00 dd ppm) corresponding to the vinyloxy group had disappeared from the spectrum of the reaction mixture.

In contrast to simpler alkanoic acids,[76] the considerably stronger haloalkanoic acids react with **55** without any catalyst or special heating of the reaction mixture (Table 28).



TABLE 28 The reaction of haloalkanoic acids, RCOOH, with 2-(vinyloxy)ethyl isothiocyanate **55** (equimolar ratio of reactants, 0.1–0.2 mol, yields[a] of **95–99** are nearly quantitative)[81]

| Cmpd No. | R | T, °C[b] | Time, min |
|---|---|---|---|
| **95** | $CH_2Cl$ | 37 | 3–5 |
| **96** | $CH_2Br$ | 45 | 3–5 |
| **97** | $(CH_2)_2Br$ | 20–22 | 300 |
| **98** | $CF_3$ | 65 | 5 |
| **99** | $CCl_3$ | $-5 \div -3$[c] | 15 |

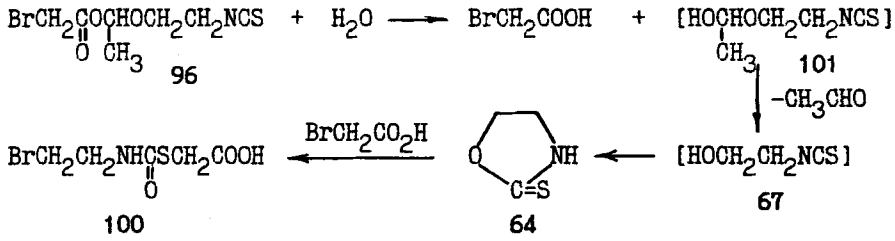
[a]From $^1$H NMR spectra. [b]Self-heating temperature of the reaction mixture. [c]Maintained by cooling of the reaction mixture.

The acylals **95–99** are slightly colored liquids with a faint odor; upon distillation they decompose (the acylals **95** and **96** undergo partial decomposition).[81]

On storage under normal conditions the undistilled acylal **96** gradually rearranges to give a crystalline product (over 2–4 days). In the $^1$H NMR spectrum ($C_2D_5OD$) of the rearrangement product there are signals at 3.73 s ($CH_2S$), 3.53 t ($CH_2Br$), 3.66 q ($CH_2N$), 7.76 s (NH), 11.10 s (COOH). $^{13}$C NMR ($C_3D_5OD$): 172.79 [C(O)OH], 168.44 [C(O)S], 44.46 ($CH_2N$), 31.09 ($CH_2Br$), 33.06 ($CH_2S$). The IR spectrum (KBr) displays intense absorption bands 1630, [NHC(O)], 1670 [OC(O)], 3280, 1500 (NH), 3400 (COOH).[78–81]

From the elemental and spectral analysis the rearrangement product was assigned the structure of 7-bromo-5-aza-4-oxo-3-thiaheptanoic acid **100**.

The suggestion[81] that the destabilizing effect on the acylal **96** is produced by moisture possibly present in the initial acid (or in the atmosphere) which induces slow hydrolysis of **96**, followed by transformation of the products of hydrolytic decomposition, looks reasonable (judging by the chemical properties of acylals[77]), as shown in Scheme 22.

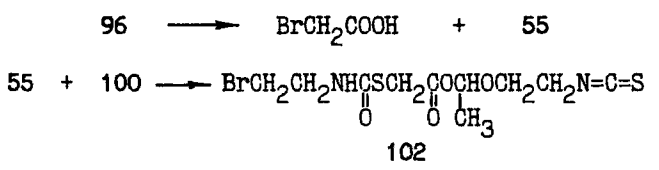



SCHEME 22

Indeed, an equimolar amount of water deliberately added to the acylal **96** markedly accelerated its rearrangement (the process was complete after 12–15 h at room temperature).[81]

The $^1$H NMR spectrum of the reaction mixture (the reaction was carried out in a spectrometer ampoule in deuteroacetone) displayed, besides the signals of the rearrangement products (7.72 s, 3.72 s, 3.56 m), those of acetaldehyde [2.12 d ($CH_3$), 9.72 q (CH)], 2-bromoethanoic acid (3.98 s, 10.6 s) and of the $OCH(CH_3)O$ moiety (5.05 q, 1.23 d), the appearance of which is postulated in the above hydrolytic scheme. It should be noted, that the position of the methine proton signal (5.05 ppm) indicates that the latter cannot be assigned to an acetal (4.7 ppm)[53] nor an acylal (~6.0 ppm) and is likely to correspond to the structure **101**.

Upon heating (100 °C) in deuterodimethylformamide (without special addition of water) the acylal **96** undergoes quantitative rearrangement in 1.5 h (the reaction was carried out in a spectrometer ampoule). Ten minutes after the beginning of heating the spectrum exhibited the signals of acetaldehyde, 2-bromoethanoic acid, the rearrangement product (3.67 s, 3.54 m) and a vinyloxy group (6.48 q, 4.28 dd, 4.16 dd), as well as traces of the second acylal whose signals overlapped with signals of the acylal **96**. The acylal methine proton signal is split and slightly shifted from 6.00 to 5.97–5.93 ppm. Methyl groups give rise to signals in the 1.38–1.41 ppm region. The concentration of vinyloxy groups is about 35–40% of that of acylal groups. The appearance of vinyloxy groups is most likely to be due to thermal decomposition common to acylals, which occurs at the same time leading, as known,[77] to carboxylic acid and vinyl ether (to 2-bromoethanoic acid and ether **55** in this case). Subsequent reaction between the ether **55** and the acid **100** affords compound **102** with an acylal fragment $C(O)OCH(CH_3)O$ showing signals nearly in the same region as those of the acylals **95–99** (Scheme 23).[81]

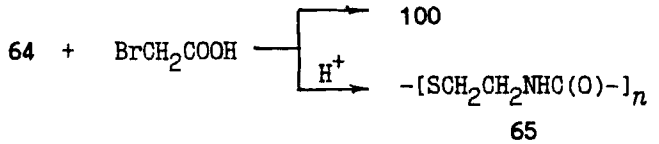


SCHEME 23

Being hydrolyzed under reaction conditions analogous to those for the acylal **96**, the adduct **102** gives the same products, *i.e.*, acetaldehyde, thione **64** and the rearrangement product **100**. The hydrolytic decomposition of the ether **55** is also possible under these conditions.[54] In fact, after 1 h the signals of the major (**96**) and the intermediate (**102**) acylals are of nearly equal intensity whereas in the $^1$H NMR spectrum recorded after 1.5 h only the signals of the rearrangement product **100** are present.[81]

At the same time, the hydrolysis of the acylal **96** should lead to 1,3-oxazolidine-2-thione **64**, the subsequent reaction of which with 2-bromoethanoic acid, if it occurs (the reaction of 1,3-oxazolidine-2-thione with haloalkanoic acids has not been described in the literature), could give the acid **100**.[81]

However, the signals of the thione **64** [4.69 t ($CH_2O$), 3.79 t ($CH_2N$)][51] have not been found in the $^1$H NMR spectra of the reaction mixtures in the above tests.[81] Moreover, a specially carried out reaction of 2-bromoethanoic acid with the thione **64** (benzene, equimolar mixture of reagents, 20–25 °C, 5 h) did not lead to the acid **100**. Under these conditions the thione **64** is polymerized to form poly(ethylene thiolcarbamate) **65** (Scheme 24).[53,54]



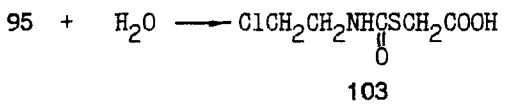
SCHEME 24

Along with the signals of unreacted **64** (4.56 t, 3.73 t) in the $^1$H NMR spectrum [$(CD_3)_2SO$] of the reaction mixture there were observed the signals of polymer **65** [3.25 t ($CH_2N$), 2.89 t ($CH_2S$)][53] which became more intense with increasing reaction time. The polymer **65** was obtained also by reaction of the acylals **95**, **98**, and **99** with water.[81]

The formation of thione **64** upon heating (110 °C) the acylal **96** in deuterodimethylformamide with 15–20% of $D_2O$ (in a spectrometer ampoule) has been detected.[81] In this case, as early as 5–7 min after the beginning of heating, in the $^1$H NMR spectrum there were neither signals of the initial acylal **96** nor signals of the vinyloxy group and the second acylal **102**. Instead, together with signals of the rearrangement product (**100**), acetaldehyde, and 2-bromoethanoic acid, one could clearly observe signals of the thione **64** (4.63 t, 3.68 t). In the $^1$H NMR spectrum recorded 30 min later at room temperature only signals of the acid **100** and acetaldehyde occurred.[81]

In the $^1H$ NMR spectrum of a solution of specially prepared 1,3-oxazolidine-2-thione[59] and 2-bromoethanoic acid in DMFA-$d_7$ 20 min after the start of heating (110 °C) the signals of the starting materials disappeared and there were only signals of compound **100** (3.68 s, 3.55 m).[81]

When heated in DMFA-$d_7$ (110 °C), the acylal **95** behaves in an analogous manner, although the hydrolysis rate is much lower in this case (Scheme 25). 7-Chloro-5-aza-4-oxo-3-thiaheptanoic acid **103** can be identified by the signals 3.67 s ($CH_2S$), 3.61 m ($ClCH_2CH_2N$), 12.01 s (COOH).[81]

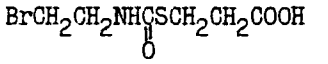



103

SCHEME 25

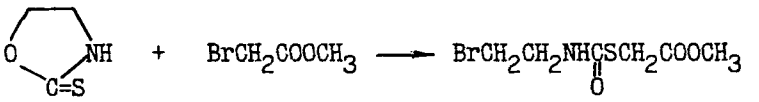
The same compound is formed in the reaction of thione **64** with 2-chloroethanoic acid (DMFA-$d_7$, 110 °C, 80 min).[81-83]

Under identical conditions the reaction of the thione **64** with 3-bromopropanoic acid proceeds more slowly (35 and 75% conversion for 30 and 65 min, respectively).[81-83] Upon storage the acylal **97** gradually rearranges, like acylal **96**, to form 9-bromo-6-aza-5-oxo-4-thiaoctanoic acid **104** (isolated).[81]




104

Unlike 2-chloro- and 2-bromoethanoic acid and 3-bromopropanoic acid, ethanoic, trifluoro- and trichloroethanoic, benzoic, 2-chlorobenzoic, and oxalic acid do not react with **64** under identical conditions, which provides supplementary evidence for the fact that monohaloalkanoic acids act as haloalkylating reagents in this case, *i.e.*, the reaction involves the $CH_2$-halogen bond rather than the carboxy group.[81-83] This conclusion is supported by reaction of the thione **64** with esters of monohaloalkanoic acids which leads to new esters of carboxylic acids possessing thiocarbamate groups. Thus, the methyl ester of 2-bromoethanoic acid reacts quantitatively with 1,3-oxazolidine-2-thione (DMFA-$d_7$, 110 °C, 10 min) to give the previously unknown methyl ester of 7-bromo-5-aza-4-oxo-3-thiaheptanoic acid **105** (Scheme 26).[81,82]

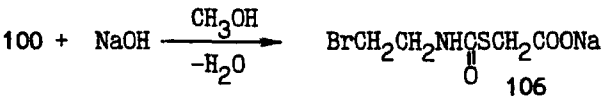



64 105

SCHEME 26

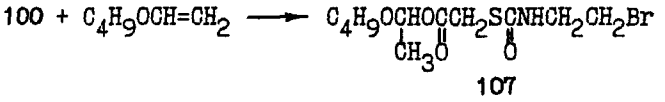
The pH and $pK_a$ values for aqueous solution of **100** were determined as ~3 and 3.58, indicating a strong acidity of this acid.[81]

In the $^1H$ NMR spectrum ($(CD_3)_2SO$] of the product of titration of the acid **100** with an NaOH solution in methanol there are two signals, 3.48 m ($BrCH_2CH_2N$, $CH_2S$), 9.34 s (NH), which is in agreement with the formula **106** (Scheme 27).[81]



SCHEME 27

The acid **100** readily and quantitatively adds to butyl vinyl ether, without catalysts, under mild conditions (benzene, 50 °C, 1 h) to give the acylal **107** (according to its $^1H$ NMR spectrum) (Scheme 28).[81]



SCHEME 28

The physical constants and spectral data for **95–107** are presented in Tables 29 and 30.

TABLE 29 Physico-chemical constants of **95–100, 104, 107**[81]

| Cmpd No. | B.p., °C (*mm* Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|
| **95** | 98 (0.1) | 1.5070 | 1.2414 |
| **96** | 117–120 (4) | 1.5240 | 1.4628 |
| **97**[a] | | 1.5220 | 1.3748 |
| **98**[a] | | 1.4455 | 1.2634 |
| **99**[a] | | 1.5162 | 1.3820 |
| **100** | 115–116[b] | | |
| **104**[c] | 124[d] | | |
| **107** | | 1.4805 | |

[a]Undistilled product. [b]M.p. (from acetone). [c]Isolated by TLC ($Al_2O_3$, benzene-chloroform-ethanol, 4:20:1). [d]M.p., colorless bright crystals.

TABLE 30 The $^1H$ NMR spectra (ppm)[a] of the acylals **95–99**, $RCOOCH(CH_3)OCH_2CH_2N{=}C{=}S$, and **104–107**[81]

| Cmpd No. | R | OCHO, q | $CH_3$, d | $CH_2O$, t | $CH_2N$, q | R |
|---|---|---|---|---|---|---|
| **95** | $CH_2Cl$ | 6.02 | 1.51 | 3.85 | 3.68 | 4.12 s |
| **96** | $CH_2Br$ | 5.96 | 1.47 | 3.85 | 3.79 | 3.89 s |
| **97** | $(CH_2)_2Br$ | 6.01 | 1.46 | 3.87 | 3.65 | 3.70 t, 2.97 t |
| **98** | $CF_3$ | 6.09 | 1.60 | 3.85 | 3.73 | |
| **99** | $CCl_3$ | 6.05 | 1.59 | 3.86 | 3.73 | |
| **104**[c] | | 3.56 m ($BrCH_2CH_2N$), 3.06 t ($CH_2S$), 2.63 t ($CH_2COO$), 7.55 s (NH) | | | | |
| **105**[d] | | 3.54 m ($BrCH_2CH_2N$), 3.70 s ($CH_3O$), 3.65 s ($CH_2S$), 8.05 s (NH) | | | | |
| **106**[b] | | 9.34 s (NH), 3.48 m ($CH_2S$, $CH_2Br$, $CH_2N$) | | | | |
| **107** | | 5.88 1.30 3.70 s ($CH_2S$), 3.55 m ($BrCH_2CH_2N$), 7.69 s (NH), 0.89 t, 1.44 m, 3.44 m ($C_4H_9$) | | | | |

[a]$CDCl_3$. [b]$(CD_3)_2SO$. [c]$(CD_3)_2CO$. [d]DMFA-$d_7$. $^{13}C$ NMR [$(CD_3)_2CO$, δ, ppm]: 170.37, 166.36 (C=O), 52.76 ($CH_3O$), 43.72 ($CH_2N$), 31.99, 31.80 ($CH_2S$, $CH_2Br$).

TABLE 31 The IR spectra (KBr, $cm^{-1}$) of **104–107**[81]

| Cmpd No. | $\nu$, $cm^{-1}$ |
|---|---|
| **104** | 1640 [NHC(O)], 1680 [OC(O)], 1530, 3310 (NH), 3400 (COOH) |
| **105**[a] | 840, 900, 1160, 1200, 1300, 1360–1385, 1440, 1520, 1660, 1740, 2840–2920–2940–3000, 3300 |
| **106**[b] | 450–550–670, 780, 830, 900, 920, 980–1060, 1190, 1300, 1500, 1560, 1630, 2900–2950–3000, 3300–3400 |
| **107**[a] | 550, 680, 810, 900, 960, 980, 1000–1030–1060–1100–1140–1180, 1270, 1360, 1430, 1490, 1660, 1700, 2850, 2920, 2940, 3320 |

[a]Thin layer. [b]Soluble in water, methanol, DMSO; swells in pyridine, insoluble in diethyl ether, acetone, acetonitrile.



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