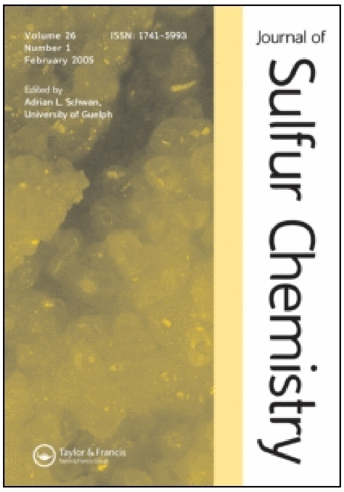

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DIVINYL SULFOXIDE: SYNTHESIS, PROPERTIES, AND APPLICATIONS

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The present review deals with the synthesis, reactions, structure, physico-chemical properties, and applications of divinyl sulfoxide, a new promising synthon and reagent for the preparation of fine organic chemicals.

Key words: Divinyl sulfoxide, oxidation, hydrogen peroxide, nucleophilic addition.

CONTENTS

I. INTRODUCTION

The discovery of the reaction of acetylene with hydrated sodium sulfide in the early seventies and the development of a commercial process for the preparation of divinyl sulfide (DVS) on the basis of this reaction[1-6] allowed a comprehensive investigation of this compound and its derivatives to be started. One of the most promising trends in this field is the inception of the chemistry of divinyl sulfoxide (DVSO), which previously was a difficultly accessible and, therefore, neglected reagent.

At present sulfoxides are extensively studied as heavy-metal extractant,[7-9] special complexing agents,[10] detergents,[11,12] polymer clarifiers,[13] and bioactive substances.[4,14,15] Functionally substituted sulfoxides are of special interest in this respect. However, their synthesis encounters certain difficulties. DVSO whose reactivity only recently has become the object of systematic studies in connection with the development of a convenient route to this compound by the oxidation of DVS with aqueous hydrogen peroxide solutions,[16-18] offers new simple approaches to these sulfoxides.

The DVSO double bonds add, under mild conditions and in most cases quantitatively, various nucleophiles such as amines, alcohols, thiols, and CH acids. These reactions can be carried out either selectively at one double bond to give new functionally substituted vinyl sulfoxides or exhaustively at both double bonds to yield diadducts. In this way, nearly any compound with a labile hydrogen atom can be converted to the corresponding vinyl sulfoxide or, more exactly, to a vinylsulfinylethyl derivative. By analogy with cyanoethylation, this series of reactions may be called vinylsulfinoethylation.

The present paper reports also data on the reactions of DVSO with bifunctional nucleophilic reagents (diamines, glycols, dithiols), with halogens, and hydrogen halides as well as the use of DVSO in Diels-Alder reactions and high-temperature conversions of this sulfoxide.

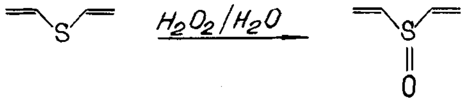
II. SYNTHESIS OF DIVINYL SULFOXIDE

The development of methods for the preparation of vinyl organyl sulfoxides is treated in a considerable number of publications.[19-24] However, information concerning the synthesis of DVSO is scarce. DVSO was first prepared by the oxidation of DVS with perbenzoic acid at − 5 to − 10°C in ether.[25] The yield, purity of DVSO and conversion of DVS were not reported. The preparation of DVSO by dehydroiodination[26] of di(2-iodoethyl) sulfoxide with excess triethylamine at 20 °C in anhydrous benzene (reaction time 8 days) and by dehydrochlorination[27] of di(2-chlorethyl) sulfoxide with boiling aqueous sodium carbonate have been published. The DVSO yield by methods[26,27] is 75–80%.

Since the preparative possibilities of the known synthetic routes to DVSO were unsatisfactory (inefficiency and explosivity of the process,[25] expensive and toxic raw materials, the di(2-haloethyl) sulfoxides[26,27]) it was worthwhile to develop a convenient method for preparing this sulfoxide.

It is thought[27] that DVSO cannot be obtained by oxidation of DVS with 30% hydrogen peroxide in acetone or acetic acid (other reaction conditions are not reported), though it is known[19,20] that vinyl organyl sulfides can effectively be oxidized with hydrogen peroxide of various concentrations (30–90%) in organic solvents (acetone, acetic acid anhydride, acetic acid).

The oxidation of DVS with 30% hydrogen peroxide has been studied under different conditions.[16,17] When carried out in acetic anhydride or acetone, the reaction leads to comparatively low (51–53%) yields of DVSO (Table 1, runs 1 and 2). Until this work,[17] no data had been reported concerning the possibility of oxidation of vinyl sulfides with hydrogen peroxide in an aqueous medium. DVS was shown to be effectively oxidized with dilute aqeuous H_2O_2 solutions (Table 1, run 3) free of organic solvents.



Scheme 1

When the reaction is performed in the presence of emulsifying agents (such as higher alkyl sulfates and sulfonates, salts of higher carboxylic acids, polyacetals of different structure) an increase in both the yield of DVSO and the conversion of DVS is observed (Table 1, runs 4–6).

As seen from Table 1, the exclusion of organic solvents from the reaction mixture allows reasonably pure (95–97%) DVSO to be prepared. As a concomitant impurity, acetic acid was identified, the product of the oxidation of acetaldehyde resulting from the competing hydrolysis of DVS. This process in H_2O_2 should be accompanied by increasing acidity of the reaction mixture and, consequently, display an autocatalytic character (since the hydrolytic cleavage of vinyl sulfides is acid catalyzed).[27] Aqueous hydrogen peroxide is a weak acid ($K_a\,1.78 \cdot 10^{-12}$).[28] In order to prevent the hydrolysis of DVS it is reasonable to carry out its oxidation in an alkaline medium. Any information concerning the possibility of the oxidation of organic sulfides with hydrogen peroxide at $pH > 7$ is likely to be absent in the literature. Moreover, it was generally accepted[29] that this reaction requires an acidic medium.

The experiments[16,17] have shown that DVS can be oxidized to DVSO with 30% H_2O_2 at pH 8–9 (in the presence of K_2CO_3, Table 1, run 7). Under these conditions the side processes were suppressed, thus increasing the DVSO purity to 99%. However, the reproducibility of the oxidation of DVS in the presence of K_2CO_3 was unsatisfactory (the conversion of DVS and the yield of DVSO vary considerably). The introduction of sodium tetraborate as a buffer (pH 8–9) overcame this drawback and a reliable 76% yield of DVSO of 99.9% purity was achieved.

It should be noted that the oxidation of DVS with a substoichiometric amount of 30% hydrogen peroxide (H_2O_2:DVS molar ratio = 1:1.2) proceeds selectively in both organic solvents and water (Table 1), although it is known[19] that under comparable conditions vinyl organyl sulfides are oxidized to form along with sulfoxides small quantities of the corresponding sulfones. The higher, as compared with DVSO, susceptibility to oxidation of vinyl organyl sulfoxides is likely due to their lower ionization

Table 1. Oxidation of Divinyl Sulfide with 30% Aqueous Hydrogen Peroxide (molar ratio DVS:H_2O_2 = 1.2:1, 60–65 °C, 5–6 h)[17]

Run, No.	Co-solvent or additive (% of the DVS mass)	DVS conversion, %	DVSO yield,[a] %	DVSO purity, %	Undistilled residue, % of the DVS mass
1[b]	Acetic acid anhydride (200)	82	51	99.5[c]	46.5
2	Acetone (200)	62	53	91	32.5
3	None	64	65	95	25
4	Synthetic detergent "Novost" (higher alkyl sulfates and sulfonates) (1.5)	74	70	96	21
5	$C_{17}H_{35}COONa$ (1.5)	84	72	97	19
6	$[CH(CH_3)O(CH_2)_2O]_7$ (3)	77	79	96	11
7	K_2CO_3 (2)	70–90	58–76	99.5	21–28
8	$Na_2B_4O_7 \cdot 10\,H_2O$ (2)	65	76	99.9	13

[a] The yield was calculated with respect to the DVS consumed. [b] The run was carried out at room temperature. [c] Determined after treatment of the reaction mixture with a saturated aqueous K_2CO_3 solution.

potential (the ionization potentials were determined from the UV spectral data for complexes of the above sulfoxides with tetracyanoethylene[17]).

Vinyl organyl sulfoxide	Ionization potential, eV
Vinyl ethyl sulfoxide	8.93
Vinyl propyl sulfoxide	8.81
Divinyl sulfoxide	9.10

For the optimization of the reaction conditions a mathematical planning of the experiment was undertaken.[17] The yield of DVSO expressed as per cent of the theoretical value, y_1, and the conversion of DVS, y_2, were taken as optimization parameters. Using the replica 2^{5-2} of the full factor plan 2^5 the effect of the following factors was studied: temperature (x_1), reaction time (x_2), concentration of hydrogen peroxide (x_3), concentration of $Na_2B_4O_7 \cdot 10\,H_2O$, % of the DVS mass ($x_4$), molar ratio H_2O_2:DVS (x_5). The experimental conditions and results are listed in Table 2. A linear model was employed for a steep ascent along the response surface y_1 where $y_1 = 87\%$ with $y_2 = 98\%$ was achieved (Table 3, runs 3 and 4). After refining the models, the equations fitting the experimental data for y_1 and y_2 were derived.

The isolines of the yield of DVSO and of the conversion of DVS, constructed by these equations in the coordinates x_1 and x_5 (with the constants $x_2 = x_3 = x_4 = 1$ more favorable values can be selected) have shown (see Figure 1) that a higher yield of DVSO can be obtained in another region of the factor space: low x_1 values (reaction tem-

Table 2. Optimization of the DVSO Synthesis. Planning Matrix and Experimental Results[17]

	x_1		x_2		x_3		x_4		x_5		y_1	y_2
Run, No.	°C	Arbitrary units	h	Arbitrary units	%	Arbitrary units	%	Arbitrary units	Molar ratio	Arbitrary units	%	%
1	70	1	6	1	38	1	8	1	1.2	1	62.00	91
2	70	1	4	−1	15	−1	2	−1	0.6	−1	65.10	45
3	30	−1	4	−1	38	1	8	1	0.6	−1	48.52	16
4	30	−1	6	1	15	−1	2	−1	1.2	1	60.10	15
5	30	−1	4	−1	38	1	2	−1	1.2	1	65.93	26
6	30	−1	6	1	15	−1	8	1	0.6	−1	41.70	37
7	70	1	6	1	38	1	2	−1	0.6	−1	67.24	53
8	70	1	4	−1	15	−1	8	1	1.2	1	47.90	60

Table 3. Optimization of the DVSO Synthesis. Motion in the Gradient Direction[17]

Run, No.	x_1, °C	x_2, h	x_3, %	x_4, %	x_5, molar ratio	y_1, %	y_2, %
1	50	5	30	2.0	0.9	67.8	58
2	60	5	43	1.8	1.0	80.9, 81.8, 79.0	96, 96, 97
3	70	4	43	0.2	1.2	85.0, 88.6	97, 98
4	80	5	43	0.2	1.2	87.0	98
5	90	3	43	0.2	1.2	78.0	100

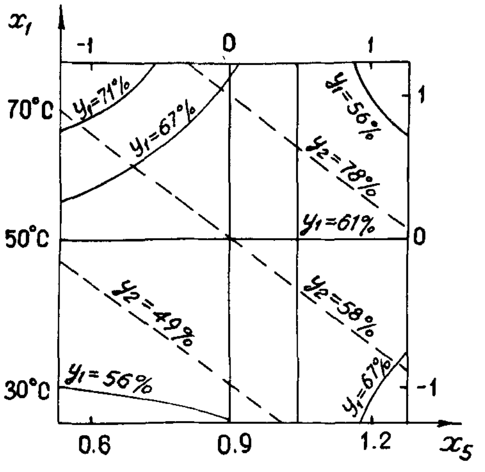


Figure 1. The isolines of the yield of DVSO (y_1) and of the conversion of DVS (y_2) with $x_2 = x_3 = x_4 = 1$

Table 4. Optimization of the DVSO Synthesis. Supplementary Runs[17]

Run, No.	x_1, °C	x_2, h	x_3, %	x_4, %	x_5, molar ratio	y_1, %	y_2, %
1	35	5	38	8	1.0	55.0	50
2	33	6	38	8	1.0	70.7	57
3	35	6	38	8	1.2	80.5	55
4	37	6	38	11	1.5	73.0	96
5	35	6	38	11	1.5	71.0	95

perature) and high x_5 values (molar ratio H_2O_2:DVS). Therefore some additional calculations and tests (Table 4) supporting these conclusions have been carried out.

The results obtained show that the oxidation of DVS can effectively be performed at comparatively low temperatures (35–38 °C), which is of special importance when dealing with peroxidized compounds, to afford DVSO in 73% yield at a DVS conversion of 98% (Table 4, runs 4 and 5). However, when the reaction is carried out with a 1.5-fold excess of H_2O_2 and the borax content increases to 11%, the formation of considerable amounts of divinyl sulfone (up to 5% in crude DVSO) and polymeric products (19% of the DVS mass) takes place. A slight increase in the reaction temperature (to 53–55 °C) and use of 2% borax with a small excess (1.2-fold) of aqueous 38% H_2O_2 lead to $y_1 = 89\%$ and $y_2 = 80\%$. Under these conditions the divinyl sulfone contamination in the crude main product is 0.5%. By a single vacuum distillation it is possible to obtain DVSO with a purity of as much as 99.95%.[17]

An attempt to employ dimethyl sulfoxide as a DVS oxidant under the conditions offered previously for the transoxidation of dialkyl sulfides[30] was no success: upon prolonged boiling (145–170 °C) of the starting reagents only small quantities of tarry products were formed.[31]

The known method of liquid-phase oxidation of dialkyl sulfides to the corresponding sulfoxides using heteropolyacids turned also out to be unsuitable for the synthesis of

DVSO.[32] The reaction of DVS with heteropolyacids $H_{3+n}PMo_{12-n}V_nO_{40}$, n = 2-8 (temperature range 20-96°C, acetic acid or acetonitrile as the solvent, under air or argon) proceeds instantly (as judged by the appearance of a blue color characteristic of reduced forms of the starting acid), but only leads to the formation of polymeric products. The reaction of DVS with salts of the above acids occurs more slowly: the reaction rate drops with increasing substitution of Na^+ for H^+ in the acid and upon addition of sodium acetate which reduces the acidity of the reaction system. Under these conditions divinyl sulfoxide and divinyl sulfone are indeed formed, but in a total yield not exceeding 3% (with 100% conversion of DVS).[17]

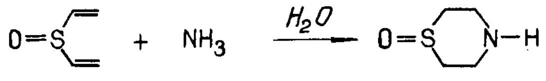
Thus, the oxidation of DVS with aqueous hydrogen peroxide solutions constitutes a convenient and efficient route to DVSO,[16-18] pilot scale batches of which have been produced by this method .

III. PROPERTIES, REACTIONS, AND APPLICATIONS OF DIVINYL SULFOXIDE

III.1. Reactions of Divinyl Sulfoxide with Ammonia and Amines

DVSO has been reported[26] not to react with ammonia (no reaction conditions were specified). The accomplishment of this reaction, however would provide some new information concerning the reactivity of α,β-unsaturated sulfoxides and would offer further synthetic routes to previously unknown and technically interesting nitrogen-containing sulfoxides.

Recently it was shown that DVSO readily reacts with aqueous ammonia to form 1,4-perhydrothiazine 1-oxide **1**[33] not described in the literature before.



1

Scheme 2

To ascertain the preparative possibilities of this reaction the effect of the reaction conditions (reagent ratio, temperature) on the yield of **1** has been studied.

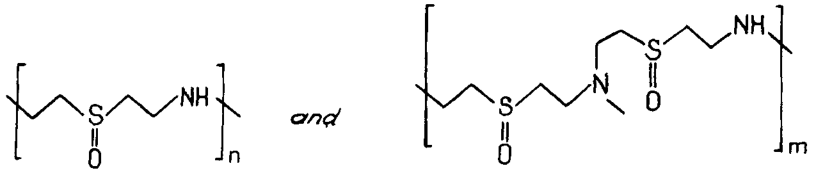
As seen from Table 5, the highest yield of the thiazine oxide **1** is achieved with a considerable excess (14-fold) of ammonia and at 50 °C (run 1). To carry out the reaction

Table 5. The Yield-Conditions Relationship in the Reaction of Divinyl Sulfoxide with Ammonia[33]

Run, No.	Molar ratio DVSO:NH_3	t, °C	Time, h[a]	Yield of **1**, %	Undistilled residue, % of the DVSO mass
1	1:14	50	5	53	23
2	1:14	30	6	48	25
3	1:11.3	50	5	45	33
4	1:1.9	20-25	4	15	64
5	1:1.5	30	8	30	47
6	1:1.5	20-25	4	traces	100
7	1:25	80-85	4	49	47

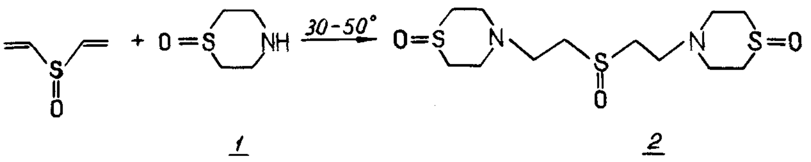
[a] In runs 1-6 the time (3 h) of the DVSO addition to the ammonia solution at 20-25 °C is not taken into account.

at a higher temperature (80–85 °C) and with a 25-fold excess of ammonia is unreasonable since the yield of the heterocycle **1** is not increased (Table 5, run 7). A decrease in the reaction temperature and especially in the ammonia excess with respect to DVSO leads to a drop of the yield of the thiazine oxide **1**. The conversion of DVSO is nearly complete (90–100%) in all runs. When the reaction is carried out at room temperature and with a slight excess of ammonia (Table 5, run 6) the heterocycle **1** is not formed. Instead, a mixture of undistillable products, also formed in smaller quantities in the other runs, is obtained. Among these, some oligomers of linear and branched structure seem to be present.[33]



Scheme 3

An attempt to isolate individual compounds from this mixture (by fractionation or column chromatography) was unsuccessful. To identify at least some of the components and to elucidate the character of possible side reactions, the reaction of thiazine oxide **1** with DVSO was investigated and bis[2-(1-oxo-1,4-perhydro-4-thiazinyl)ethyl] sulfoxide **2** was found to form.[33]

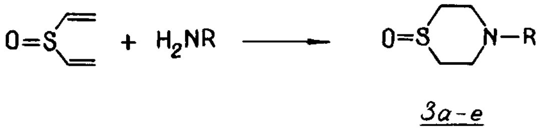


Scheme 4

The adduct **2** is also formed in the direct reaction of DVSO with ammonia. TLC analysis of the reaction mixture confirmed the presence of a compound identical as judged by R_f (retention time) with the sulfoxide **2**.[33]

From DVSO and primary amines (methylamine, isopropylamine, cyclohexylamine) the corresponding 4-organyl-1,4-perhydrothiazine 1-oxides **3** have been prepared in about 50% yield by heating the reagents in ethanol.[34]

A more thorough investigation of this reaction has uncovered conditions[35,36] which allow the perhydrothiazine oxides **3** to be obtained in 90–95% yield. This is achieved at 65–75 °C (3–5 h) by slow introduction of the army into the DVSO bulk.

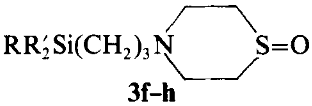


R = n-Bu (3a), s-Bu (3B), cyclo-C_6H_{11} (3c),
Bz (3d), n-$C_{18}H_{37}$ (3e).

Scheme 5

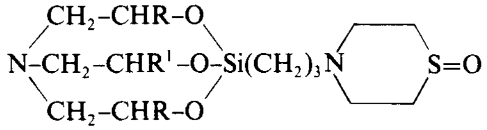
It was considered as rather promising, especially from the viewpoint of pharmacology, to introduce into this reaction functionally substituted amines, organosilicon amines, for example, as well as amino alcohols and amino acids which were already known to be bioactive compounds.[37–40]

In this context a synthesis of the 4-(3-trialkylsilylpropyl)perhydrothiazine 1-oxides **3f–h**[41] and the 1-[3′-(1″, 4″-perhydrothiazinyl-1″-oxo)propyl]silatranes **3i–l**[42] was performed by the reaction of DVSO with 3-aminopropylalkylsilanes and 1-(3′-aminopropyl)-silatranes.



3f-h

R = R′ = Me (**3f**); R = R′ = Et (**3g**); R = Me, R′ = *n*-Bu (**3h**)

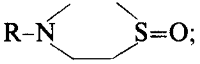


3i-l

R = R′ = H (**3i**); R = H, R′ = Me (**3k**); R = R′ = Me (**3l**)

The yield of the thiazine oxides **3f–l** is 67–92%.[41,42]

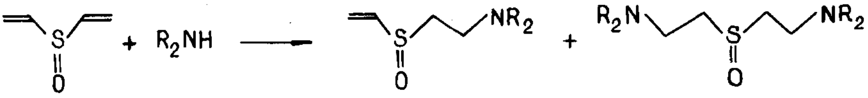
Ethanolamine and the corresponding vinyl ether as well as γ-aminobutyric and ε-aminocaproic acid react with DVSO in an aqueous or alcoholic medium on heating (55–75°C) to give the corresponding functionally substituted 1,4-perhydrothiazine 1-oxides **4a–d** in 82–89% yield.[43,44]



4a-d

R = $(CH_2)_2OH$ (**4a**), $(CH_2)_2OCH{=}CH_2$ (**4b**), $(CH_2)_3COOH$ (**4c**), $(CH_2)_5COOH$ (**4d**)

Secondary amines add readily to DVSO to form 2-(*N*,*N*-dialkylamino)ethyl vinyl sulfoxides **5a–c** and bis[2-(*N*,*N*-diorganylamino)ethyl] sulfoxides **6a,b,d,e**.[45–47]



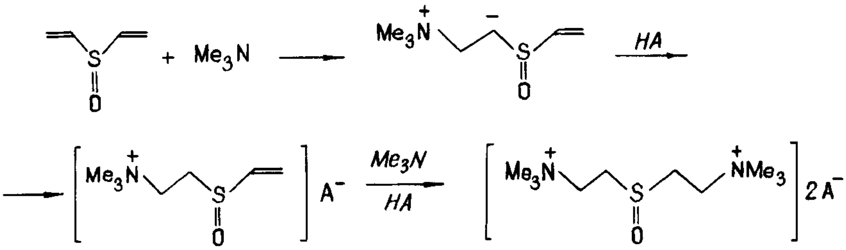
5a-c 6a,b,d,e

R= Me (a), Et (b), n-Pr (c), s-Bu (d), Ph(e).

Scheme 6

The process is carried out by short heating of the reagents (1–3 h, 35–50 °C for aliphatic and 65–80 °C for aromatic amines). The reaction can be directed towards predominant formation either of mono- or of diadducts. The monoadducts **5** are obtained in 80–98% yield with a considerable (4–5-fold) molar excess of DVSO with respect to the amine in ethanol or without solvent. In this case the order of mixing of the reagents is very important: the amine should be added dropwise to DVSO. To obtain the diadducts **6** (yield 70–94%) the reaction is performed in ethanol with stoichiometric amounts of the initial reagents. Aromatic amines add to DVSO in the presence of alkali metal alkoxides.

DVSO has been found[35,48,49] to react smoothly with trimethylamine in the presence of hydrohalic acids at a temperature from − 10°C to 0°C to form diquaternary salts, the bis[(trimethylammonio)ethyl] sulfoxide dihalides **7a,b** in 71–76% yield. The reaction proceeds as a nucleophilic addition of trimethylamine to DVSO with a simultaneous stabilization of the carbanionic center by a proton to form a quaternary ammonium salt.



A= Br (7a), Cl (7b).

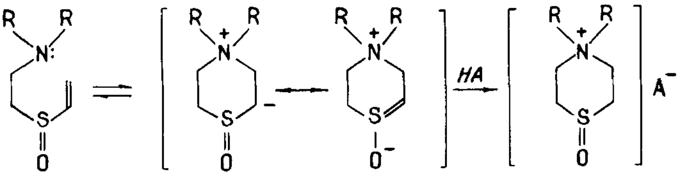
7a,b

Scheme 7

Other trialkylamines, such as triethylamine, for example, are considerably less reactive in this reaction. Under the above conditions they fail to add to DVSO and do not form the corresponding trialkylammonium halides. This seems to indicate a higher nucleophilicity (along with lower basicity) of trimethylamine as compared to other trialkylamines.

The salt **7b** was prepared by independent synthesis, i.e., quaternization of bis[(2-(*N*,*N*-dimethylamino)ethyl] sulfoxide with methyl iodide, followed by treatment of the salt with hydrochloric acid.

Upon treatment of the 2-(*N*,*N*-dialkylamino)ethyl vinyl sulfoxides **5** with acids some previously unknown salts of 4,4-dialkyl-1,4-perhydrothiazinium 1-oxides **8a-f** were isolated.[49–51] The structure of the heterocycle (1,4-perhydrothiazine rather than 1,3-thiazolidine) shows that the salt formation is preceded by nucleophilic cyclization to the intermediate zwitterion. The formation of the salts **8a-f** proceeds exothermally and, in most cases, quantitatively (yield 85–93%).



5a-c

8a-f

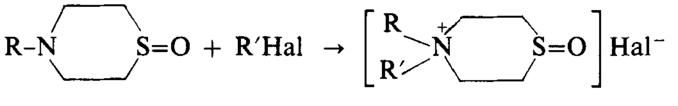
R=Me, A=J (8a), Cl (8b), CO$_3$ (8c), p-MeC$_6$H$_4$SO$_3$ (8d);
R= Et, A=Cl (8e); R= n-Pr, A=Cl (8f).

Scheme 8

The ability of the sulfoxide **5a** to form the salt **8c** is so high that even in air it transforms spontaneously to its carbonate by absorbing atmospheric CO_2 and moisture.

As compared with the dimethyl derivative **5a**, the 2-(*N*,*N*-diethylamino)- and 2-(*N*,*N*-dipropylamino)ethyl vinyl sulfoxides **5b,c** under analogous conditions undergo a considerably slower cyclization to the corresponding salts **8e,f**.

4,4-Diorganyl-1,4-perhydrothiazinium 1-oxide salts including those containing different substituents at the nitrogen atom, can be effectively prepared by the quaternization of the 4-organylperhydrothiazine 1-oxides **9a–h**.

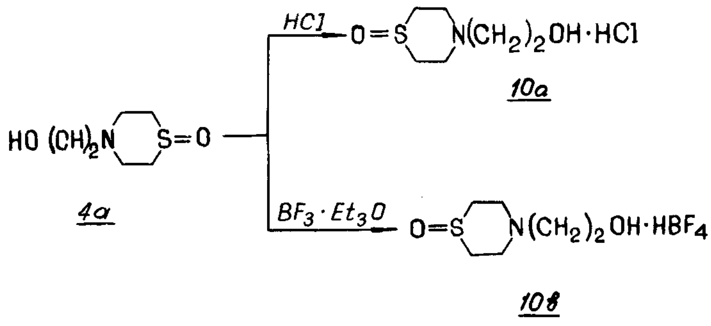


9a–h

R = *i*-Am, R′ = Me, Hal = I (**9a**); R = Me, R′ = $CH_2{=}CHCH_2$, Hal = Br (**9b**); R = Me, R′ = $CH \equiv CCH_2$, Hal = Cl (**9c**); R = Me, R′ = Et, Hal = Br (**9d**); R = Me, R′ = *n*-Pr, Hal = Br (**9e**); R = Me, R′ = Bz, Hal = Cl (**9f**); R = *cyclo*-C_6H_{11}, R′ = Bz, Hal = Cl (**9g**); R = *n*-$C_{18}H_{37}$, R′ = *n*-Bu, Hal = Br (**9h**)

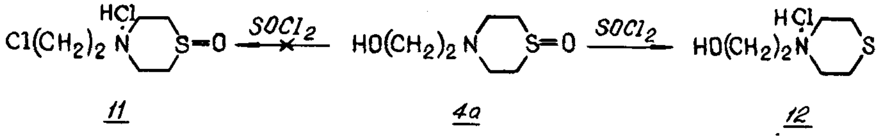
The reaction proceeds in 2–3 h either at 30–40 °C (for compounds 9a–e) or at 60–70 °C (synthesis of the salts **9f–h**). Depending on the alkyl halide, the quaternization is carried out in ethanol (**9f,g**), acetonitrile (**9b,c**), or nitromethane (**9d,e,h**). The yield of the main products is 86–96%.

In the reaction of the thiazine oxide **4a** with hydrogen chloride or boron trifluoride etherate (in an aqueous medium) under mild conditions (5–20°C) the corresponding salts **10a** and **10b** have been obtained.[52]



Scheme 9

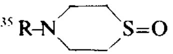
It has been found[53] that the reaction of the heterocycle **4a** with thionyl chloride affords, instead of the expected 4-(2-chloroethyl)-1,4-perhydrothiazine 1-oxide hydrochloride **11**, the product of the reduction of **4a** at the sulfoxide group, 4-(2-hydroxyethyl)-1,4-perhydrothiazine **12** in 84% yield.

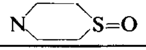
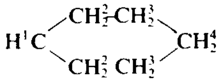


Scheme 10

The characteristic data of compounds **1**, **3–8** are listed in Tables 6–8.

Table 6. Characteristic Data of 1,4-Perhydrothiazine 1-oxides[35] R-N S=O



Compound	R	Yield, %	B.p. °C (mm), m.p., °C (solvent)	^1H NMR, δ, ppm R	^1H NMR, δ, ppm N S=O 
1	H	53	127–129 (1)[a]	1.83 s (NH)	2.75 m ($CH_2S{=}O$), 3.46 m (CH_2N)
3a	$CH_2^1CH_2^2CH_2^3CH_3^4$	95	107 (6.6 10^{-3})	(H^1)[b], 1.52 m (H^2), 1.24 m (H^3), 0.94 t (H^4)	2.25–3.31 m
3b	$CH^1(CH_3^2)CH_2^3CH_3^4$	92	125–126 (1)[c]	2.78 m (H^1), 1.10 m (H^3), 0.91 d (H^2), 0.88 t (H^4)	2.60 m
3c	 H^1C CH_2^2-CH_2^3 CH_2^4 CH_2^2 CH_2^3	90	68 (heptane)	3.03 m (H^1), 1.73 m (H^2), 1.12 m (H^3, H^4)[d]	2.60 m
3d	$CH_2^1C_6H_5^2$	90	154 (8 10^{-3})	7.47 m (H^2), 3.47 s (H^1)	2.73 m
4a	$CH_2^1CH_2^2OH$	89	165 (5 10^{-2})	3.62 m (H^2), (H^1)[b]	2.80 m
4b	$CH_2^1CH_2^2OCH^3{=}CH_2^4$	80	51 (ethanol)	6.54 q (H^4), 4.37 d and 4.18 d (H^3), 3.96 m (H^2), (H^1)[b]	
4c	$CH_2^1CH_2^2CH_2^3COOH$	82	134 (ether)	2.54 t (H^1), 2.29 t (H^3), 1.79 m (H^2)	2.94 m

[a] d_4^{20} 1.2438, n_D^{20} 1.5524. [b] The (H^1) proton signals overlap with the thiazine ring methylene proton signals. [c] d_4^{20} 1.0618, n_D^{20} 1.5400. [d] The (H^3) and (H^4) proton signals overlap.

Table 7. Characteristic Data of Amino Sulfoxides Derived from DVSO[35]

	Compound	Yield, %	B.p., °C (mm), m.p., °C (solvent)	d_4^{20}	n_D^{20}	^{1}H NMR, δ, ppm (J, Hz)	IR, ν, cm^{-1}
5a	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4N(CH_3^5)_2$	80	82 (1)	1.0221	1.4900	6.88 q (H^2), 5.93 d (H^1) (16.1), 5.84 d (H^1) (10.2), 2.78 m (H^3, H^4), 2.20 s (H^5)	1040–1060 (S=O), 1605 (C=C), 3040 (HC=)
5b	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4N(CH_2^5CH_3^6)_2$	90	105 (2)	0.9680	1.4920	6.87 q (H^2), 5.94 d (H^1) (15.9), 5.84 d (H^1) (10.1), 2.77 m (H^3, H^4), 2.50 q (H^5), 1.0 t (H^6)	1035–1070 (S=O), 1590 (C=C), 3030 (HC=)
6a	$[(CH_3^1)_2NCH_2^2CH_2^3]_2S(O)$	94	130 (2)	0.9720	1.4900	2.78 m (H^2, H^3), 2.20 s (H^1)	1040–1060 (S=O)
6b	$[(CH_3^1CH_2^2)_2NCH_2^3CH_2^4]_2S(O)$	80	135 (1.3)	0.9709	1.4860	2.78 m (H^3, H^4), 2.50 q (H^2), 1.0 t (H^1)	1040–1060 (S=O)
6d	$\{[CH_3^1CH_2^2CH^3(CH_3^4)]_2NCH_2^5CH_2^6\}_2S(O)$	76	175 (1.3)	1.1089	1.4940	2.94 m (H^3), 2.84 (H^5, H^6), 1.34 m (H^2), 0.92 d (H^4), 0.87 t (H^1)	1040–1060 (S=O)
6e	$[(C_6H_5^1)_2NCH_2^2CH_2^3]_2S(O)$	70	94–96 (CCl_4)	–	–	7.0 m (H^1), 4.19 t (H^2), 2.86 t (H^3)	1050–1070 (S=O)
7a	$\{[(CH_3^1)_3\overset{+}{N}CH_2^2CH_2^3]_2S(O)\}2\ Br^-$	71	134–136 (acetone)	–	–	4.15–3.36 m (H^2, H^3), 3.22 s (H^1)	1040–1060 (S=O)
7b	$\{[(CH_3^1)_3\overset{+}{N}CH_2^2CH_2^3]_2S(O)\}2\ Cl^-$	76	236 (acetone)	–	–	4.20–3.38 m (H^2, H^3), 3.21 s (H^1)	1040–1060 (S=O)

Table 8. Characteristic Data of the Salts[35] $[R_2\overset{+}{N}\langle\,\rangle S{=}O]\,A^-$

Compound	R	A	Yield, %	M.p., °C (acetone)	¹H NMR, δ, ppm	
					R	$\overset{+}{N}\langle\,\rangle S{=}O$
8a	CH_3	I	85	296–300	3.23 s	3.06–4.04 m
8b	CH_3	Cl	93	290–295	3.24 s	3.01–4.45 m
8c	CH_3	CO_3	88	280–285	3.21 s	2.74–4.35 m
8d	CH_3	$MeC_6H_4SO_3$	93	300	3.26 s	2.97–4.23 m
8e	$CH^1_3CH^2_2$	Cl	45	190	0.94 t (H^1), (H^2)[a]	2.99–4.55 m
8f	$CH^1_3CH^2_2CH^3_2$	Cl	41	138	0.93 m (H^1), 1.75 m (H^2), (H^3)[a]	3.10–4.77 m

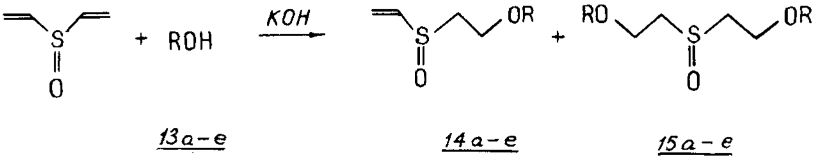
[a] The H proton signals overlap with the thiazine ring methylene proton signals.

III.2. Base-Catalyzed Addition of Alcohols and Thiols to Divinyl Sulfoxide and Thermolysis of the Adducts

It is known[26] that boiling of DVSO in anhydrous methanol or ethanol in the presence of alkali alkoxides leads to 2,2′-dimethoxy- and 2,2′-diethoxydiethyl sulfoxide, respectively. Evidence for the structure of the compounds obtained as well as any information concerning their yield and purity has not been reported.

It has briefly been reported[54] that cysteic and *o*-mercaptobenzoic acid comparatively readily (50 °C, catalyst $KHCO_3$) add to DVSO with their mercapto groups to give the adducts: $[HOOCCH(NH_2)CH_2SCH_2CH_2]_2S(O)$ and $(o\text{-}HOOCC_6H_4SCH_2CH_2)_2S(O)$, respectively.

Recently it has been established[55] that the alcohols **13** add to DVSO in the presence of catalytic amounts of potassium hydroxide at 45–70 °C to form 2-(alkoxy)ethyl vinyl sulfoxides **14** and 2,2′-di(alkoxy)diethyl sulfoxides **15**.



R= Me (a), Et (b), n-Pr (c), i-Pr (d), t-Bu (e).

Scheme 11

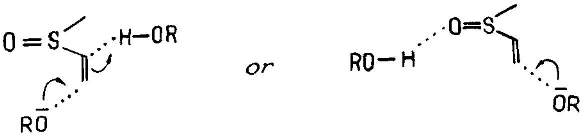
The vinyl sulfoxides **14** were obtained by slow introduction of the alcohol to a 2-molar excess of DVSO. For the synthesis of diadducts a two-fold stoichiometric excess of alcohol with respect to DVSO is usually employed.

A comparative study of the reactivity of alcohols **13** in the reaction with DVSO (45–50 °C, 5% KOH, DVSO: alcohol molar ratio 2:1) shows their reactivity to drop in the order HOMe ≃ HOEt ≃ HOPr-*n* > HOPr-*i* > HOBu-*t*.[55]

Alcohol	Conversion of alcohol, %	Sulfoxide formed	Yield of **14**, %
MeOH	100	**14a**	82
EtOH	100	**14b**	86
i-PrOH	60	**14d**	56
t-BuOH	39	**14e**	21

The comparatively low reactivity of isopropyl and *t*-butyl alcohol in the reaction with DVSO is in keeping with the relative nucleophilicities of the methoxide, ethoxide, isopropoxide and *t*-butoxide ions of 0.82, 1.0, 0.4 and 0.04, respectively,[56]

An alternative reason for the lower reactivity of the branched alcohols **13d,e** might be a concerted character of the reaction.

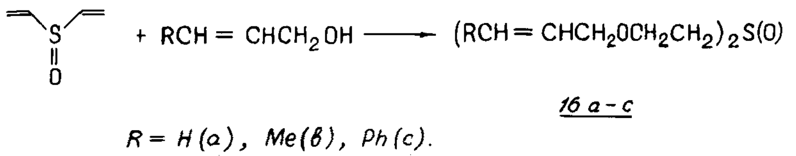


Scheme 12

In these transition states the ion addition is accompanied and facilitated by a simultaneous proton transfer. If the reaction follows this concerted mechanism the reaction rate would depend on not only the nucleophilicity of the anion, but on the ability of the medium to release the proton. Isopropyl and *t*-butyl alcohol are known[56] to possess less mobile protons as compared with normal alcohols **13a,b**.

It is possible to add the alcohols **13d,e** to DVSO nearly quantitatively, too, if the reaction is performed at 65–70 °C.[55]

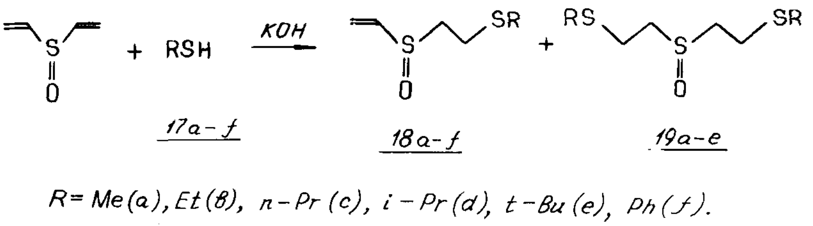
The use of superbasic catalytic system (potassium *t*-butoxide-DMSO) enables allyl alcohols to add to DVSO. As a result bis(2-alkenyloxyethyl) sulfoxides **16** were obtained in 76–95% yield, seemingly without the probable prototropic isomerization of the allylic moiety.[57]



Scheme 13

The yields, physico-chemical constants and spectral characteristics of the alkoxy sulfoxides **14–16** are compiled in Table 9.

It has been established[58] that the organic thiols **17** in the presence of catalytic amounts of potassium hydroxide enter readily (at 35–40°C, only with PhSH an elevated temperature of 50–55°C is required) the nucleophilic addition to DVSO to form 2-(organylthio)ethyl vinyl sulfoxides **18** and 2,2′-di(organylthio)diethyl sulfoxides **19**.



Scheme 14

Using a slow addition of the thiols to a 1.5 molar excess of DVSO the reaction can be stopped nearly completely at the stage of the formation of vinyl sulfoxides **18**. For preparing the diadducts **19** it is necessary to use 1.1–1.2 times as much as the stoichiometric amount of thiol with respect to DVSO. The characteristics of the sulfoxides **18** and **19** are listed in Tables 10 and 11, respectively. The yields of the monoadducts **18** and the diadducts **19** are 72–79 and 86–95%, respectively.[58] Together with the vinyl sulfoxides **18** the alkyl vinyl sulfides **20** were isolated as by-products in 9–20% yield.

$CH_2{=}CHSR$, R = Me (a), Et (b), *n*-Pr (c), *i*-Pr (d), *t*-Bu (e)

20a-e

A GLC analysis of the reaction mixture indicates that the vinyl sulfides **20a–e** do not form in the course of the reaction of DVSO with thiols. The sulfides **20a–e** are obtained

Table 9. Yields and Characteristics of Alkoxy Sulfoxides Derived from DVSO[53,57]

	Compound	Yield, %	B.p., °C (mm)	d_4^{20}	n_D^{20}	^{1}H NMR, δ, ppm (J, Hz)	IR (ν, cm^{-1})
14a	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4OCH_3^5$	82	90 (1.5)	1.1125	1.4930	6.94 q (H^2), 6.09 d (H^1) (16.0), 5.90 d (H^1) (9.6), 3.70 m (H^4), 3.31 s (H^5), 2.86 m (H^3)	1610 (C=C) 1050 (S=O)
14b	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4OCH_2^5CH_3^6$	86	110 (1.5)	1.0744	1.4832	6.90 d (H^2), 5.97 d (H^1) (16.5), 5.87 d (H^1) (10.2), 3.55 m (H^4), 3.48 d (H^5), 2.87 m (H^3), 1.14 t (H^6)	1605 (C=C) 1060 (S=O)
14d	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4OCH^5(CH_3^6)_2$	80	87 (1)	1.0563	1.4795	6.52 d (H^2), 5.96 d (H^1) (16.4), 5.85 d (H^1) (9.9), 3.60 d (H^5), 3.56 m (H^4), 2.88 m (H^3), 1.13 d (H^6)	1595 (C=C) 1060 (S=O)
14e	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4OC(CH_3^5)_3$	71	110 (1)	1.0328	1.4705	6.78 d (H^2), 6.02 d (H^1) (16.4), 5.72 d (H^1) (9.9), 3.58 m (H^4), 2.87 m (H^3), 1.10 s (H^5)	1610 (C=C) 1060 (S=O)
15a	$(CH_3^1OCH_2^2CH_2^3)_2S(O)$	93	98 (0.5)	1.1347	1.4820	3.50 m (H^2), 3.30 s (H^1), 2.63 m (H^3)	1060 (S=O)

15b	$(CH_3^1CH_2^2OCH_2^3CH_2^4)_2S(O)$	85	120 (1)	1.0520	1.4680	3.69 m (H^3), 3.45 d (H^2), 2.83 m (H^4), 1.12 t (H^1)	1045 (S=O)
15c	$(CH_3^1CH_2^2CH_2^3OCH_2^4CH_2^5)_2S(O)$	80	137 (1)	1.0237	1.4610	3.70 m (H^4), 3.34 t (H^3), 2.82 m (H^5), 1.52 m (H^2), 0.86 t (H^1)	1050 (S=O)
15d	$[(CH_3^1)_2CH^2OCH_2^3CH_2^4]_2S(O)$	83	125 (1)	1.0072	1.4643	3.71 m (H^3), 3.55 q (H^2), 2.83 m (H^4), 1.22 d (H^1)	1060 (S=O)
15e	$[(CH_3^1)_3COCH_2^2CH_2^3]_2S(O)$	74	140 (1)	1.0058	1.4603	3.66 m (H^2), 2.72 m (H^3), 1.01 s (H^1)	1040 (S=O)
16a	$(CH_2^1{=}CH^2CH_2^3OCH_2^4CH_2^5)_2S(O)$	76	159 (2)	1.0701	1.4939	5.88 m (H^2), 5.17 m (H^1), 3.97 m (H^3), 3.76 m (H^4), 2.90 m (H^5)	1045 (S=O)
16b	$(CH_3^1CH^2{=}CH^3CH_2^4OCH_2^5C$-$H_2^6)_2S(O)$	81	150 (1 10^{-1})	1.0438	1.4938	5.46 m (H^2, H^3), 3.95 m (H^4), 3.70 t (H^5), 2.83 m (H^6), 1.70 d (H^1)	1050 (S=O)
16c	$(C_6H_5^1CH^2{=}CH^3CH_2^4OCH_2^5$-$CH_2^6)_2S(O)$	93	169 (1 10^{-2})	1.1567	1.5920	7.18 m (H^1), 6.15 m (H^2, H^3), 4.01 d (H^4), 3.73 t (H^5), 2.85 m (H^6)	1050 S=O)

Table 10. Yields and Characteristics of Vinyl Organylthio Sulfoxides Derived from DVSO[58]

	Compound	Yield, %	B.p., °C (mm), m.p., °C	d_4^{20}	n_D^{20}	^{1}H NMR, ppm (J, Hz)	IR (ν, cm^{-1})
18a	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4SCH_3^5$	69	102 (3)	1.1588	1.5469	6.83 q (H^2), 5.98 d (H^1) (14.4), 5.93 d (H^1) (11.3), 2.77 m (H^3, H^4), 2.12 s (H^5)	1610 (C=C) 1060 (S=O)
18b	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4SCH_2^5CH_3^6$	77	114 (1.5)	1.1543	1.5420	6.82 q (H^2), 5.99 d (H^1) (16.5), 5.92 d (H^1) (9.40), 2.84 m (H^3, H^4), 2.53 q (H^5), 1.23 t (H^6)	1596 (C=C) 1060 (S=O)
18c	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4SCH_2^5CH_2^6CH_3^7$	78	115 (1)	1.1054	1.5350	6.82 q (H^2), 5.99 d (H^1) (16.7), 5.93 d (H^1) (9.4), 2.82 m (H^3, H^4), 2.52 t (H^5), 1.60 m (H^6), 0.97 t (H^7)	1610 (C=C) 1060 (S=O)
18d	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4SCH^5(CH_3^6)_2$	79	110 (1)	1.0834	1.5320	6.73 q (H^2), 6.02 d (H^1) (16.3), 5.92 d (H^1) (9.65), 2.78 m (H^3, H^4, H^5), 1.27 d (H^6)	1610 (C=C) 1060 (S=O)
18e	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4SC(CH_3^5)_3$	72	105 (0.4)	1.0097	1.5230	6.78 q (H^2), 6.00 d (H^1) (16.4), 5.90 d (H^1) (9.9), 2.79 m (H^3, H^4), 1.31 s (H^5)	1596 (C=C) 1060 (S=O)
18f	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4SC_6H_5^5$	74	65–66	–	–	7.21 m (H^5), 6.61 q (H^2), 5.99 d (H^1) (16.0), 5.86 d (H^1) (9.5), 3.06 m (H^3, H^4)	1600 (C=C) 1045 (S=O)

Table 11. Yields and Characteristics of Di(organylthio)diethyl Sulfoxides Derived from DVSO[58]

	Compound	Yield, %	M.p., °C	^1H NMR, ppm	IR (ν, cm^{-1})
19a	$(CH_3^1SCH_2^2CH_2^3)_2S(O)$	95	40–41	2.85 m (H^2, H^3), 2.31 s (H^1)	1038 (S=O)
19b	$(CH_3^1CH_2^2SCH_2^3CH_2^4)_2S(O)$	93	46–47	2.89 m (H^3, H^4), 2.54 q (H^2), 1.24 t (H^1)	1030 (S=O)
19c	$(CH_3^1CH_2^2CH_2^3SCH_2^4CH_2^5)_2S(O)$	95	50–51	2.83 m (H^4, H^5), 2.52 t (H^3), 1.61 m (H^2), 0.98 t (H^1)	1035 (S=O)
19d	$[(CH_3^1)_2CH^2SCH_2^3CH_2^4]_2S(O)$	86	45	2.84 m (H^2, H^3, H^4), 1.28 d (H^1)	1045 (S=O)
19e	$[(CH_3^1)_3CSCH_2^2CH_2^3]_2S(O)$	87	44	2.82 m (H^2, H^3), 1.34 s (H^1)	1040 (S=O)

by vacuum fractionation of the reaction mixture as the products of thermolysis of the sulfoxides **18** (the reaction mixture is heated to 220–290 °C, depending on the boiling points of the products).[58]

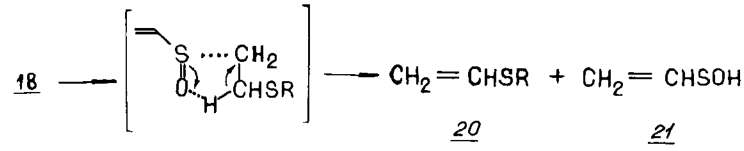
Indeed, it has been shown with the individual monoadducts **18b,d** as an example that sulfoxides of this type can be cleaved upon heating to give the corresponding vinyl sulfides **20b,d**. Contrary to the base-catalyzed cleavage of aliphatic sulfoxides[29] the pyrolysis of the vinyl sulfoxides **18b,d** is inhibited by bases (240–250 °C, 1.5 h) so that the yield of the vinyl sulfides **20b,d** decreases.[58]

Sulfoxide	Pyrolysis conditions	Vinyl sulfide formed	Yield of vinyl sulfide, %
18b	Without alkali	**20b**	32
18d	Without alkali	**20d**	42
18b	2% KOH	**20b**	10
18d	2% KOH	**20d**	25

Upon vacuum distillation of the reaction products of DVSO with 1-butanethiol **17g** it was not possible to isolate the expected 2-(butylthio)ethyl vinyl sulfoxide **18g** since the latter is completely decomposed (the temperature of the mixture reaching 300–320 °C). The yield of butyl vinyl sulfoxide **20g** is 75% in this case.[58]

At the same time, the preparation of the sulfoxides **18f** and **19a–e**, crystalline products isolated by recrystallization, i.e. under conditions excluding their thermolysis, does not involve the formation of the vinyl sulfides **20a–f**.

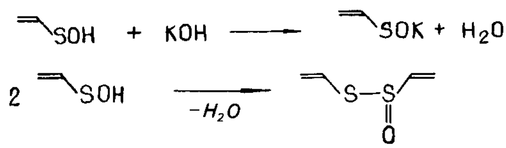
The pyrolysis of the monoadducts **18** seems to follow the scheme previously described for dialkyl sulfoxides.[29]



Scheme 15

The inhibitory effect of alkali on this process has been explained by the known solvation interaction between the alkali cations and the sulfoxide oxygen[59] impeding the achievement of the cyclic transition state mentioned. Like alkanesulfenic acids,[29] ethenesulfenic acid seems to undergo a number of transformations, of which polymerization is the most probable. This suggestion is in agreement with broad absorption bands with an overrated background in the IR spectrum and elemental analysis of a nondistillable polymeric residue obtained by vacuum fractionation of the DVSO-1-butanethiol reaction products. Besides, the pH of the reaction mixture formed in the pyrolysis of the sulfoxides **18** is 5–6 which is likely due to the presence of ethenesulfenic acid or its polymers.[58]

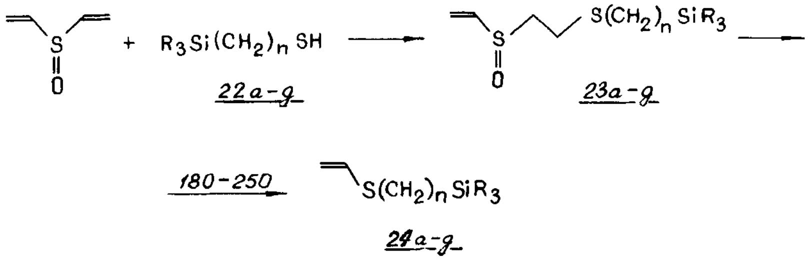
The thermolysis of the sulfoxides **18** involves the formation of small amounts of water (1–7% of the total reaction mixture weight). The formation of water is explained either by the neutralization of ethenesulfenic acid (when the pyrolysis is carried out in the presence of KOH) or by its dehydration dimerization.[58]



Scheme 16

The latter reaction has been described for 2-methyl-2-propanesulfenic acid.[29] It should be noted that acetylene, the product of possible thermolysis of the sulfoxides **18** at the C–S bond in the vinyl sulfinyl group, has not been identified (negative qualitative reaction with the Ilosvay reagent[59]).

As established[60] the reaction of DVSO with the triorganylsilylalkanethiols **22** proceeds in the presence of KOH to give at first monoadducts, vinyl (β-triorganylsilylalkylthioethyl) sulfoxides **23**, which decompose upon vacuum distillation (bath temperature 180–250 °C) to form vinyl (triorganylsilylalkyl) sulfides **24** in 50–60% yield.



R, n: Me, 3 (a); Et, 1 (b); Et, 2(c); Et, 3(d);
MeO, 1 (e); MeO, 2 (f); MeO, 3 (g).

Scheme 17

The decomposition of the adducts **23** also takes place during GLC analysis at 190–220 °C.

The reaction was studied in more detail with 3-(trimethylsilyl)-1-propanethiol **22a**.[60] The analysis of the reaction mixture obtained with the trimethylsilylpropanethiol (after repeated treatment with water to complete the removal of DVSO) using IR, ^1H NMR and mass spectrometry provides evidence for the presence of the vinyl sulfoxide **23a** the heating of which at 170–180 °C for 10 min leads to vinyl sulfide **24a** (up to 50%), according to ^1H NMR data. Thus, thiol addition to DVSO is accompanied by the pyrolysis of the resulting vinyl sulfoxides, which involves cleavage of the C_α–S bond and abstraction of the β-hydrogen under the action of the sulfoxide oxygen.[60]

The formation of ethenesulfenic acid in the course of the reaction is indicated by PGLC isolation of vinyl 3-(trimethylsilylpropyl) disulfide **25** from higher boiling reaction products, which is likely to result from the following transformation:[60]

$$CH_2{=}CHSOH + Me_3Si(CH_2)_3SH \rightarrow \underset{\mathbf{25}}{CH_2{=}CHSS(CH_2)_3SiMe_3} + H_2O$$

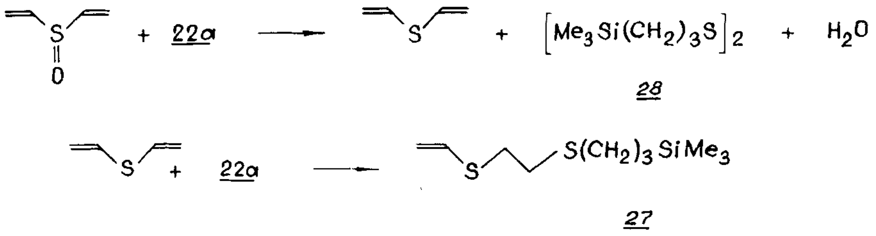
The possibility of an interaction of this kind between sulfenic acids and alkanethiols is known.[61]

The addition of triorganylsilylalkanethiols to DVSO involves a series of by-processes occurring at high temperatures. Thus, vacuum distillation of the reaction mixture obtained by the reaction of DVSO with 3-(trimethylsilyl)-1-propanethiol gave a fraction (b.p. 80–140°C, 2–3 mm Hg) from which 1,1-bis(trimethylsilylpropylthio)ethane **26** and vinyl [2-(trimethylsilylpropylthio)ethyl] sulfide **27** were isolated by PGLC.[60]

The mercaptal **26** appears to be the product of the electrophilic addition of thiol **22a** to vinyl sulfide **24a** catalyzed by sulfenic acid.

$$\underset{\mathbf{24a}}{Me_3Si(CH_2)_3SCH{=}CH_2} + \underset{\mathbf{22a}}{Me_3Si(CH_2)_3SH} \xrightarrow{H^+} \underset{\mathbf{26}}{[Me_3Si(CH_2)_3S]_2CHMe}$$

The formation of the vinyl sulfide **27** was explained in terms of the addition of the thiol **22a** to divinyl sulfide, the product of DVSO reduction under the action of the thiol (similar reactions have been reported for aliphatic sulfoxides).[62]



Scheme 18

Bis(3-trimethylsilylpropyl) disulfide **28** was found among the reaction products by mass spectrometry.

We were able to prepare, isolate and characterize the monoadducts **23** and the bis[2-(triorganylsilylalkylthio)ethyl] sulfoxides **29** by keeping the reaction mixture at a temperature below 50 °C.[63] The yields of these sulfoxides range from 71 to 77%. The constants and parameters of the IR and ^1H NMR spectra of these compounds are shown in Table 12.

The ability of the monoadducts **23** to form vinyl sulfides upon thermolysis is now used

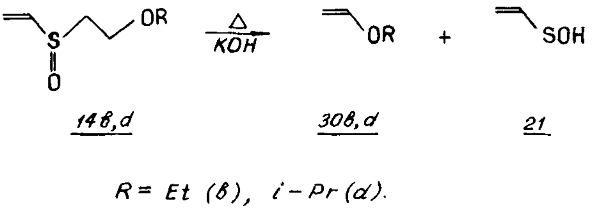
Table 12. Yields and Characteristics of (Triorganylsilylalkylthio)ethyl Sulfoxides and (Trialkylsilylalkoxy)ethyl Sulfoxides[63]

	Compound	Yield, %	B.p., °C (mm)	d_4^{20}	n_D^{20}	^{1}H NMR, ppm (J, Hz)	IR (ν, cm^{-1})
23a	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4SCH_2^5CH_2^6CH_2^7Si(CH_3^8)_3$	71	[a]	1.0067	1.5130	6.70 d (H^2), 5.96 d (H^1) (16.5), 5.58 d (H^1) (9.5), 2.75 m (H^3, H^4), 2.50 m (H^5), 1.60 m (H^6), 0.53 m (H^7), 0.0 s (H^8)	1595 (C=C) 1055 (S=O)
23b	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4SCH_2^5Si(CH_2^6CH_3^7)_3$	76	[a]	1.1020	1.5190	6.73 d (H^2), 5.96 d (H^1) (16.5), 5.88 d (H^1) (9.5), 2.85 m (H^3, H^4), 1.80 s (H^5), 0.85 m (H^7), 0.56 m (H^6)	1595 (C=C) 1060 (S=O)
23e	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4SCH_2^5Si(OCH_3^6)_3$	77	[a]	1.2106	1.5105	6.80 d (H^2), 6.08 d (H^1) (16.5), 5.50 d (9.5), 3.65 s (H^6), 2.91 m (H^3, H^4), 1.68 s (H^5)	1580 (C=C)
29c	$[(CH_3^1CH_2^2)_3SiCH_2^3CH_2^4SCH_2^5CH_2^6]_2S(O)$	72	[a]	0.9933	1.5160	2.80 m (H^4, H^5, H^6), 0.85 m (H^1), 0.55 m (H^2, H^3)	1070 (S=O)
31a	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4OCH_2^5Si(CH_2^6CH_3^7)_2CH_3^8$	55	146	0.9531	1.4815	6.69 d (H^2), 5.93 d (H^1) (16.6), 5.73 d (H^1) (9.6), 3.63 m (H^4), 3.09 s (H^5), 2.74 m (H^3), 0.84 m (H^7, H^8), 0.54 m (H^6)	1060 (S=O)
31b	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4OCH_2^5CH_2^6CH_2^7Si(CH_2^8CH_3^9)_2C$-$H_3^{10}$	61	158 (2)	0.9321	1.4845	6.73 d (H^2), 6.00 d (H^1) (16.4), 5.83 d (H^1) (9.5), 3.74 m (H^4, H^5), 2.79 m (H^3), 1.55 m (H^6), 0.90 m (H^9, H^{10}), 0.51 m (H^7, H^8)	1600 (C=C) 1055 (S=O)
31c	$CH_2^1{=}CH^2S(O)CH_2^3CH_2^4OCH_2^5CH_2^6CH_2^7Si(CH_3^8)_3$	57	136 (3)	0.9434	1.4780	6.81 d (H^2), 5.99 d (H^1) (16.5), 5.86 d (H^1) (9.5), 3.74 m and 3.39 m (H^4, H^5), 2.85 m (H^3), 1.55 m (H^6), 0.50 m (H^7, H^8)	1595 (C=C) 1060 (S=O)
32	$[(CH_3^1)_3SiCH_2^2CH_2^3CH_2^4OCH_2^5CH_2^6]_2S(O)$	66	203 (2)	0.9365	1.4685	3.73 m and 3.43 m (H^4, H^5), 3.05 m (H^6), 1.59 m (H^3), 0.45 m (H^2)	1070 (S=O)

[a] B.p. (°C) was not determined.

for the preparation[64-66] of the vinyl (trialkoxysilylalkyl) sulfides **24e–g** which cannot be synthesized by direct vinylation of thiols.[67]

It has been shown with the sulfoxides **14b,d** as an example[55,68] that [2-(alkoxy)ethyl] vinyl sulfoxides, like their sulfur analogs, undergo pyrolysis at 280–290 °C, i.e., under more severe conditions. Among the products of thermolytic cleavage of the sulfoxides **14b,d** acetaldehyde in a yield of 85 and 93%, respectively, and small amounts of water were isolated. Heating of the sulfoxides **14b,d** in the presence of KOH leads to the alkyl vinyl ethers **30b,d** in 71 and 65% yield, respectively.

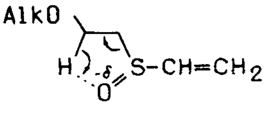


Scheme 19

The acetaldehyde formed by pyrolysis in the absence of alkali seems to be the product of acid hydrolysis of alkyl vinyl ethers[69] catalyzed by ethenesulfenic acid.

$$CH_2{=}CHOR + H_2O \xrightarrow{H^+} MeCHO + ROH$$

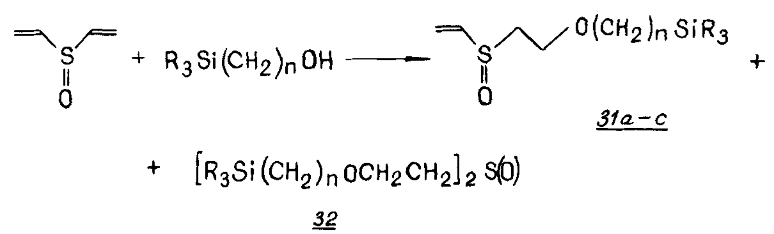
As with [2-(alkylthio)ethyl] vinyl sulfoxides the elimination of ethenesulfenic acid is inhibited in the presence of alkali. This implies an intramolecular non-catalytic character of the process.



Scheme 20

The retarded elimination, as compared with the sulfur analogs, is due to a destabilizing effect of the oxygen atom with respect to the carbanion formed (repulsion between the charge and the neighboring oxygen lone electron pairs). This is usually manifested as inhibition of the abstraction of hydrogen halide by strong bases from β-haloalkyl ethers.[69] The sulfur atom, on the contrary, stabilizes the negative charge in the α-position on account of low-lying vacant orbitals and the ability of sulfur to expand its valence shell.[70] Since the vinyl ethers formed from the vinyl sulfoxides **14** have a stronger conjugation than vinyl sulfides,[71] the oxygen-assisted destabilization of the carbanion-like state upon thermolysis is likely to cover considerably this difference in the conjugation energies of the final products.

Unlike (triorganylsilyl)alkanethiols, the nucleophilic addition to DVSO of their oxygen analogs, (trialkylsilyl)alkanols, is not complicated by any side-processes of thermal cleavage. Owing to this fact the vinyl [2-(trialkylsilylalkoxy)ethyl] sulfoxides **31** and the bis[2-(trialkylsilylalkoxy)ethyl] sulfoxides **32** formed can be isolated by vacuum distillation at 140–200°C.[63] The adduct yields of 55–66% and their characteristics are collected in Table 12.

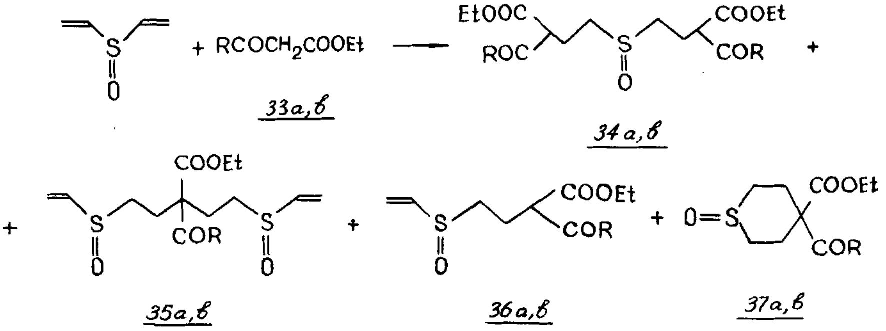


$R_3Si = MeEt_2Si$, $n = 1$ (31a); $R_3Si = MeEt_2Si$, $n = 3$ (31b);
$R = Me$, $n = 3$ (31c); $R = Me$, $n = 3$ (32).

Scheme 21

III.3. Reaction of Divinyl Sulfoxide with CH Acids

It has been established[72,73] that DVSO reacts with acetoacetic **33a** and malonic **33b** esters upon heating to 45–65 °C in THF (or without solvent) under the action of catalytic amounts of base to form the following compounds: 3,3′-di(acetyl)-3,3′-di(carbethoxy)dipropyl sulfoxide **34a**, 3,3,3′,3′-tetra(carbethoxy)dipropyl sulfoxide **34b**, 1,5-di(vinylsulfinyl)-3-acetyl-3-carbethoxypentane **35a**, 1,5-di(vinylsulfinyl)-3,3-di(carbethoxy)pentane **35b**, 1-vinylsulfinyl-3-acetyl-3-carbethoxypropane **36a**, 1-vinylsulfinyl-3,3-di(carbethoxy)propane **36b**, 4-acetyl-4-carbethoxythiacyclohexane 1-oxide **37a**, and 4,4-di(carbethoxy)thiacyclohexane 1-oxide **37b**. The formation of the heterocycles **37a** and **37b** from DVSO and the esters **33a,b** is likely to result from intramolecular cyclization of the monoadducts **36a,b**.



R = Me (a), OEt (b).

Scheme 22

As seen from Table 13 (runs 1–4) the reaction of DVSO with acetoacetic ester is quite efficient (79–84% total yield of the sulfoxides **34a**–**37a**, 86–90% conversion) at 45–50 °C in THF in the presence of sodium methoxide. The replacement of the latter by KOH, other conditions being equal, leads to a considerable decrease (by a factor of ~ 1.7) of both the yield of the final products and the conversion of the starting reagents (Table 13, run 5).[72]

It turned out, at the same time, that KOH is a fairly efficient catalyst for the reaction of DVSO with malonic ester (Table 13, runs 1 and 2). A somewhat higher reactivity of this ester as compared with acetoacetic ester is also indicated by a greater conversion of the former in this process.[72]

Table 13. Conditions of the Synthesis of the Sulfoxides **34a**-**37a** (45-50 °C, 5 h, MeONa 0.2 g, THF 20-25 ml)[72]

Run, No.	Amount of reagents, mole		Yield,[a] %				Conversion, %	
	DVSO	**33a**	**34a**	**35a**	**36a**	**37a**	DVSO	**33a**
1	0.1	0.3	70	-	9	-	86	b
2	0.3	0.1	-	68	16	-	b	85
3	0.1	0.1	-	-	65	15	90	86
4[c]	0.1	0.1	-	-	29	52	88	84
5[d]	0.1	0.1	-	-	40	5	52	54

[a] In runs 1 and 3-5 the product yields are calculated for a given amount of DVSO, in run 2 for a given amount of the ester **33a**.
[b] The conversion of the above reagents was not determined, since in these runs they were used in excess.
[c] The run was carried out at 65 °C, THF 100 ml.
[d] KOH (0.2 g) was employed as a catalyst.

The yields of the reaction and especially its regioorientation depend also on the ratio of the initial reagents, the order of their mixing, the temperature of heating and even the amount of THF used as solvent. Thus, the highest yields of the diadducts **34a,b** (70 and 90%, respectively) were achieved upon slow addition of DVSO to a 1.5-fold molar excess of acetoacetic or malonic ester (Table 13, run 1; Table 14, run 1) whereas the inverse order of mixing of the reagents and of their molar ratio are required for the synthesis of the diadducts **35a,b** (Table 13, run 2; Table 14, run 3). The yield of the sulfoxides **35a** and **35b** is 68 and 86%, respectively, in this case.[72]

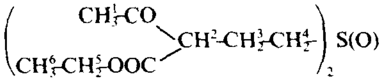
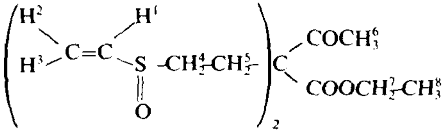
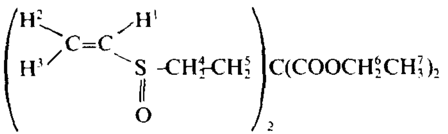
The monoadducts **36a,b** and the heterocycles **37a,b** are formed in good yields (50-85%) when the reagents are present in stoichiometric quantities. It should be noted that a comparative analysis of the data obtained shows the monoadduct **36a** to be less prone to cyclization (Table 13, runs 1-3, 5) than the monoadduct **36b** (Table 14, runs 1-4). However, the reaction of DVSO with acetoacetic ester can be directed towards the predominant formation of the heterocycle **37a** by increasing the reaction temperature to

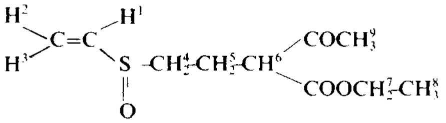
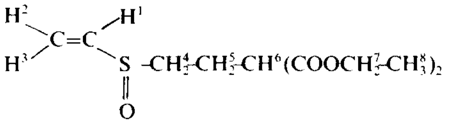
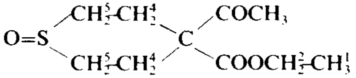
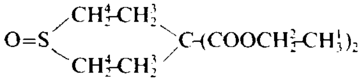
Table 14. Conditions of the Synthesis of the Sulfoxides **34b**-**37b** (45-50 °C, 5 h, KOH 0.2 g, THF 25-30 ml)[72]

Run, No.	Amount of reagents, mole		Yield,[a] %				Conversion, %	
	DVSO	**33b**	**34b**	**35b**	**36b**	**37b**	DVSO	**33b**
1	0.1	0.3	90	-	-	7	100	b
2[c]	0.1	0.3	94	-	-	5	100	b
3	0.3	0.1	-	86	-	8	b	100
4	0.1	0.1	7	traces	-	85	98	98
5[d]	0.1	0.1	20	15	50	10	99	98

[a] In runs 1 and 3-5 the product yields are calculated for a given amount of DVSO, in run 2 for a given amount of the ester **33b**.
[b] The conversion of the above reagents was not determined, since in these runs they were used in excess.
[c] MeONa was used as a catalyst.
[d] The run was carried out without THF.

Table 15. Characteristics of the Sulfoxides **34–37**, Adducts of CH-Acids to DVSO[72]

	Compound	Yield, %	M.p., °C (ether)	^{1}H NMR, ppm; J, Hz	IR, ν, cm^{-1}		
					C=C	S=O	C=O
34a	 $\left(\begin{matrix}CH^1_3\text{-}CO\\CH^6_3\text{-}CH^5_2\text{-}OOC\end{matrix}>CH^2\text{-}CH^3_2\text{-}CH^4_2\text{-}\right)_2S(O)$	70	a	4.11 q (H^5), 3.61 t (H^2), 2.02-2.60 m (H^3, H^4), 2.18 s (H^6), 1.19 t (H^1)	–	1045	1720
34b	$[(CH^1_3\text{-}CH^2_2\text{-}COO)_2CH^3CH^4_2\text{-}CH^5_2\text{-}]_2S(O)$	90	a	4.17 q (H^2), 3.55 t (H^3), 2.26-2.71 m (H^4, H^5), 1.25 t (H^1)	–	1050	1730
35a		68	a	6.58 dd (H^1), 5.97 d (H^3), 5.91 d (H^2), 4.11 q (H^7), 2.60 m (H^4, H^5), 2.18 s (H^6), 1.19 t (H^8); $J_{H^1H^2}$ 9.2, $J_{H^1H^3}$ 15.6	1590	1045	1735
35b		86	138	6.58 dd (H^1), 6.06 d (H^3), 5.99 d (H^2), 4.21 q (H^6), 2.74 m (H^5), 2.21 m (H^4), 1.26 t (H^7); $J_{H^1H^2}$ 9.4, $J_{H^1H^3}$ 15.8	1605	1060	1720

36a		65	a	6.64 dd (H^1), 6.08 (H^3), 6.00 d (H^2), 4.24 q (H^7), 2.80–2.60 m (H^4, H^5), 3.69 t (H^6), 2.20 s (H^9); $J_{H^1H^2}$ 9.2, $J_{H^1H^3}$ 15.6	1590	1040	1740
36b		50	a	6.55 dd (H^1), 6.02 d (H^3), 5.92 d (H^2), 4.40 q (H^7), 3.5 t (H^6), 2.69 m (H^5), 2.22 m (H^4), 1.2 t (H^8)	1610	1050	1720
37a		52	a	4.23 q (H^2), 2.27–2.58 m (H^4, H^5), 2.19 c (H^3), 1.28 t (H^1)	–	1045	1725
37b		85	130	4.12 q (H^2), 2.65 m (H^3), 2.15 m (H^4), 1.18 t (H^1)	–	1060	1725

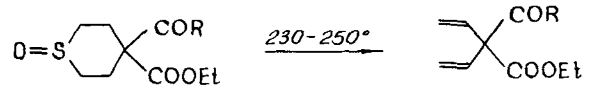
[a] A viscous oil.

65 °C and diluting the reaction mixture with THF (Table 13, run 4). Under these conditions the yields of the sulfoxides **37a** and **36a** are 52 and 29%, respectively.

On the other hand, it was possible to slow down the cyclization of the monoadduct **36b** and to obtain this monoadduct in 50% yield only when THF was excluded from the reaction mixture (Table 14, run 5).[72]

The physicochemical constants and spectral characteristics of **34a,b–37a,b** are given in Table 15.

It is known that the synthesis of dienes can be performed by pyrolysis of acyclic sulfoxides. Thus, 3,3-di(carbethoxy)-1,4-pentadiene was prepared in 63% yield by heating (180 °C) 1,5-di(4-chlorophenylsulfinyl)-3,3-di(carbethoxy)pentane.[74] It has been found[72,75,76] that this process may also involve cyclic sulfoxides such as 4-acetyl-4-carbethoxythiacyclohexane 1-oxide **37a** and 4,4-di(carbethoxy)thiacyclohexane 1-oxide **37b** which undergo thermolysis to afford 3-acetyl-3-carbethoxy-1,4-pentadiene **38a** or 3,3-di(carbethoxy)-1,4-pentadiene **38b**.



37a,b 38a,b

R= Me (a) , OEt (b)

Scheme 23

The cleavage occurs at 230–250 °C, the yields of the dienes **38a** and **38b** being 63 and 54%, respectively.[75]

Thus, DVSO is a convenient $CH_2{=}CH$ synthon to convert alcohols, thiols and CH acids into vinyl and divinyl derivatives.[55,58,60,75]

III.4. Reactions of Divinyl Sulfoxide with Halogens, Hydrogen Halides, and Triorganylsilanes

Information concerning the reactions of DVSO with halogens and hydrogen halides is rather scarce. Chlorine and bromine have been reported[26,77,78] to add to both DVSO bonds with the formation of the corresponding bis(dihaloethyl) sulfoxides **39a,b**.

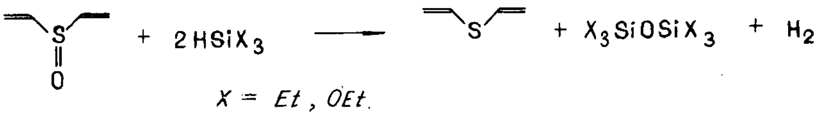
$$CH_2 = CHS(O)CH = CH_2 + 2\,X_2 \rightarrow \underset{\textbf{39a,b}}{XCH_2XCHS(O)CHXCH_2X}$$

$$X = Cl\ (a),\ Br\ (b)$$

The reaction is carried out under cooling in a CCl_4 medium. The yield of the sulfoxides **39a,b** is about 50%.[26,77] The use of ethanol as a solvent in the chlorination of DVSO has led to an increase in the yield of the bis(dichloroethyl) sulfoxide **39a** up to 85%.[78]

It has briefly been reported[26] that DVSO does not react with hydrogen chloride, gives insoluble polymeric products with hydrogen bromide, and is decomposed in the presence of hydrogen iodide.

It has been shown[79] that upon heating (150°C, 40–48 h) of DVSO with triethyl- or triethoxysilane in the presence of catalytic amounts of $H_2PtCl_6{\cdot}6H_2O$, $NiCl_2$ or $Ni(acac)_2$ with or without toluene, instead of the expected hydrosilylation reduction of DVSO takes place leading to the corresponding disiloxanes $X_3SiOSiX_3$ (X = Et, yield 40%; X = OEt, yield 2–5%).



Scheme 24

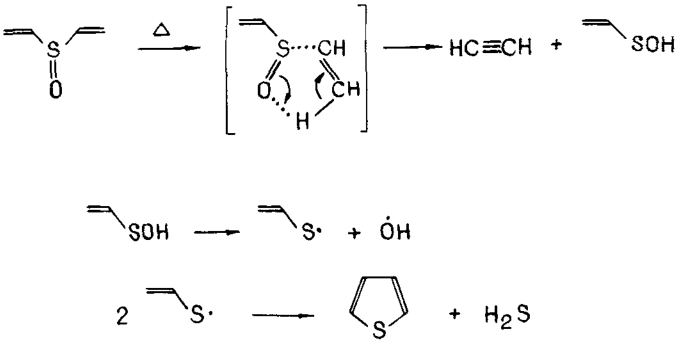
The hydrogen formed in the reaction was identified by GC.[79]

DVSO is reduced with silanes in the absence of catalysts as well; however, in this case the conversion of $HSiX_3$ is decreased by a factor of two. The yield of DVS is negligible (1-3%) in all the cases; this seems to be due to its polymerization.[79]

III.5. Gas Phase Pyrolysis of Divinyl Sulfoxide

The gas phase pyrolysis of DVSO was studied in the temperature range 350-450 °C in a stream of nitrogen.[80,81] The main reaction product is thiophene, obtained in the highest yield at 400 °C (Table 16). Simultaneously water, acetaldehyde, paraldehyde, hydrogen sulfide, and acetylene were formed. Above 450 °C DVSO undergoes thermodegradation to afford considerable amounts of gaseous products.

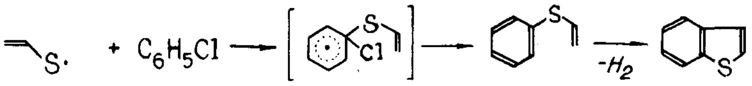
The formation of acetylene suggests DVSO in the gas phase to eliminate ethenesulfenic acid according to a synchronous cyclic scheme. Thiophene was assumed to be the product of the thermolysis of this acid, involving loss of the OH group and formation of the vinylthio radical. The latter was assumed to undergo further intramolecular cyclization.[80,81]



Scheme 25

This scheme was considered proven by co-pyrolysis of DVSO with chlorobenzene which acts as a "trap" for vinylthio radicals to give benzothiophene according to the scheme below.[82]

Indeed, the co-pyrolysis of DVSO in excess chlorobenzene at 500-600 °C leads to benzothiophene the yield of which increases with the temperature, the yield of thiophene decreasing (Table 17).[81]



Scheme 26

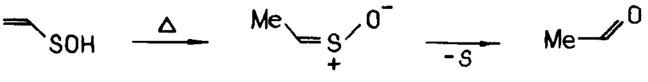
Table 16. Gas Phase Pyrolysis of Divinyl Sulfoxide[80,81]

Reaction temperature, °C	Reaction time, min	Contact time, sec	DVSO, g	Pyrolysate, g	Conversion of DVSO, %	Main pyrolysis products and yields, %	
						Thiophene	Paraldehyde
350	4	62	2.14	1.3	89.2	26.1	19.5
380	9	68	4.8	2.7	96.3	42.8	1.8
380	13.5	88	4.5	2.5	97.3	36.5	3.2
400	6	69	3.2	2.4	87.5	60.0	2.4
420	4.5	66	2.4	1.2	94.2	33.5	3.2
450	17.5	97	4.7	1.8	100.0	34.6	1.7

Table 17. Co-Pyrolysis of Divinyl Sulfoxide with Chlorobenzene (1:2 molar ratio)[81]

Reaction temperature, °C	Contact time, sec	Condensate composition, wt %				
		C_6H_5Cl	Benzene	Thiophene	Benzthiophene	Diphenyl sulfide
500	53	82.6	-	5.7	0.5	1.3
550	50	87.8	0.9	8.4	2.6	0.2
600	47	85.3	1.4	7.6	4.9	0.8
630	45	82.7	0.9	2.9	11.1	2.4

Acetaldehyde in the pyrolysis of DVSO is likely to be formed by the isomerization of ethenesulfenic acid to methylsulfine. Such transformations were observed in the impulse pyrolysis of *t*-butyl vinyl sulfoxide.[83]

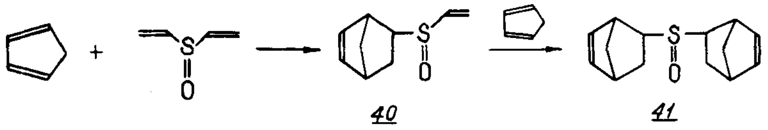


Scheme 27

The impulse pyrolysis is completely inhibited in the presence of chlorobenzene. In the course of the reaction diphenyl sulfide, the product of interaction of chlorobenzene and hydrogen sulfide, is formed[82] which also agrees with the scheme. At 450 °C and above ethenesulfenic acid can decompose to give SO_2.[82]

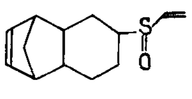
III.6. Diels-Alder Reactions

It has been shown[84] that DVSO can be used as dienophile in the Diels-Alder reaction. With cyclopentadiene either the monoadduct **40** or the diadduct **41** is formed in 90 and 72% yield, respectively, depending on the reagent ratio.



Scheme 28

The formation of the vinyl sulfoxide **42** is also possible.[85]

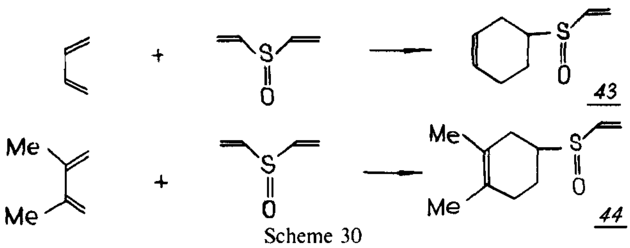


42

Scheme 29

However, neither data concerning the isolation nor evidence for the structure of this compound have been reported.[85]

The reaction of DVSO with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, even with excess of the latter and at comparatively high temperatures, only leads to the monoadducts **43** and **44**.[85]



Scheme 30

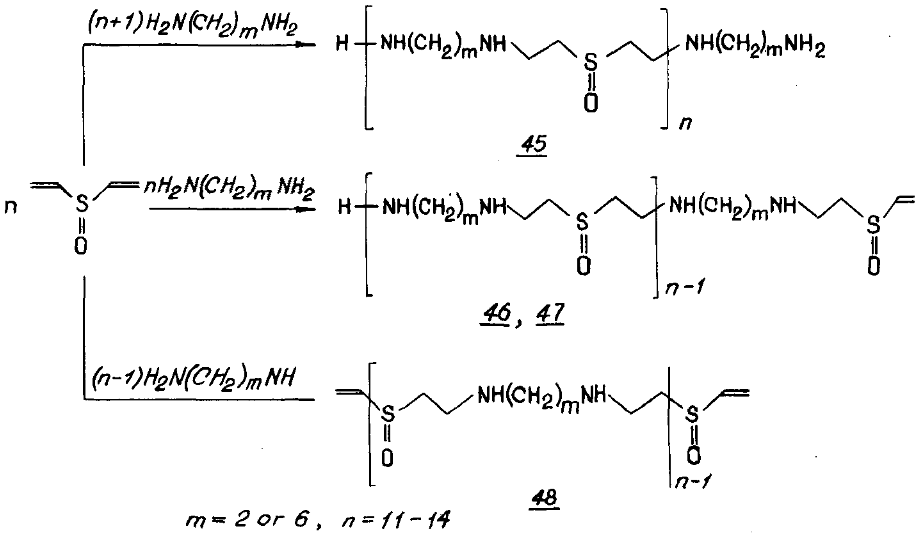
III.7. *Reaction of Divinyl Sulfoxide with Bifunctional Addends*

Great possibilities for the application of DVSO are provided by the addition of various bifunctional compounds such as diamines, dithiols, alkali sulfides, and glycols. By these reactions quite new polymers (including water-soluble ones) displaying a wide range of useful properties can be prepared.[4,86,87]

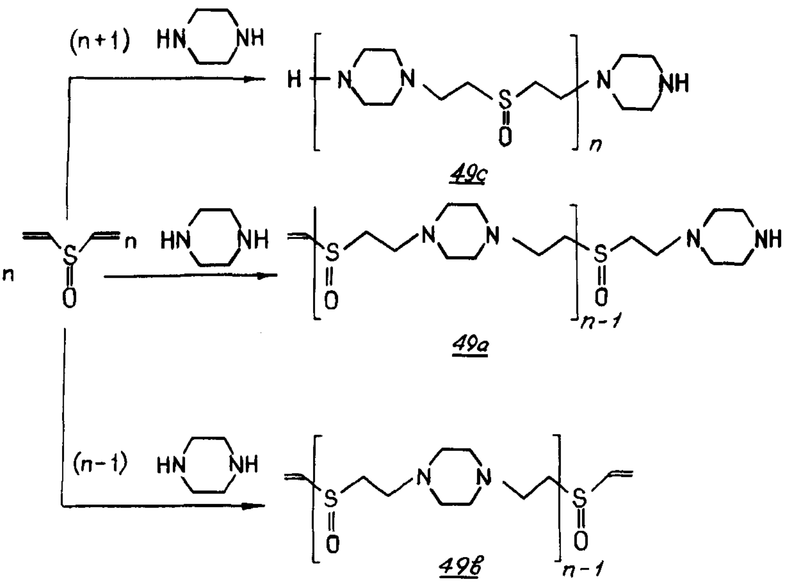
Polysulfoxides are usually synthesized by oxidation of the corresponding sulfides with nitric acid[88] or hydrogen peroxide,[89] by polycondensation of monomeric dihydroxydiaryl sulfoxides or by low-temperature polymerization of alkyl vinyl sulfoxides.[90,91] Recently, polymers containing regularly alternating sulfoxide groups and a heteroatom in the backbone chain and terminal reactive vinyl amino, mercapto, or hydroxy groups, have been studied.

It has been shown[92,93] that DVSO enters readily into polyaddition with diaminoalkanes as well as with piperazine to give oligoamino sulfoxides **45–49** in high yield (90–98%). The polyaddition reaction can be selectively directed towards the formation of either oligomers **45**, **49c**, or **46**, **47**, **49a**, or **48**, **49b** using a DVSO:diamine molar ratio of 1:2.3, or 1:1, or 2.2:1, respectively (Table 18).

When carried out at 20–60 °C (2–3 h) in ethanol or without solvent (in the latter case the polyaddition can be performed in a sealed vessel), the reaction affords oligomers (Mm 1000–10000), readily soluble in water, alcohol, acetone, and chloroform.[92]



Scheme 31



n = 53(49a), 6(49b), 6(49c).

Scheme 32

The presence of amino (**45**, **49c**) or vinyl groups (**48**, **49b**) or both (**46**, **47**, **49a**) as terminals provides potentialities for many applications by modification and curing of the oligomers **45**–**49**.

In the reaction of DVSO with 2*H*,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine **50**, the product of heterocyclization of divinyl sulfide with thiourea,[3] one could expect from[35] either the dithiazine **50** to add DVSO at the double bonds forming mono- and diadducts or the above reagents to react according to an addition-heterocyclization giving a perhydrothiazine ring. However, heating (65–75 °C) of equimolar quantities of DVSO and the dithiazine **50** in ethanol or acetonitrile led to oligomeric products, viscous or solid resins (Mm 1500–4800) soluble in methanol, acetone, and chloroform. The for-

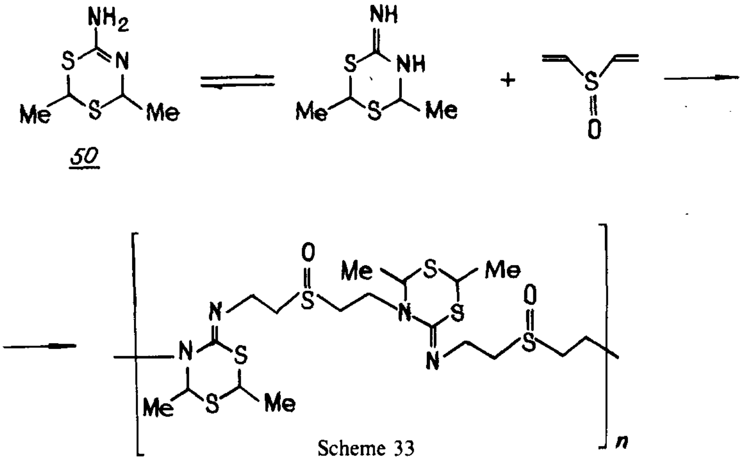
Table 18. The Synthesis Conditions of Oligoamino Sulfoxides[92]

Oligomer	m	Degree of oligomerization	Molecular mass[a]	Yield, %	Reaction temperature, °C[b]	DVSO: diamine ratio, mol
45	2	12	2000	97	45–50	1:2.3
46	2	11	1800	98	45–50	1:1
47	6	13	3000	92	20–25 (ethanol)	1:1
48	6	14	3200	98	45–50 (ethanol)	2.2:1
49a		53	10000	97	50–55 (ethanol)	1:1
49b		6	1100	90	55–60	2.2:1
49c		6	1200	94	50–55 (ethanol)	1:2.2

[a] The molecular mass was determined isopiestically.

[b] The reaction time in all runs was 3 h.

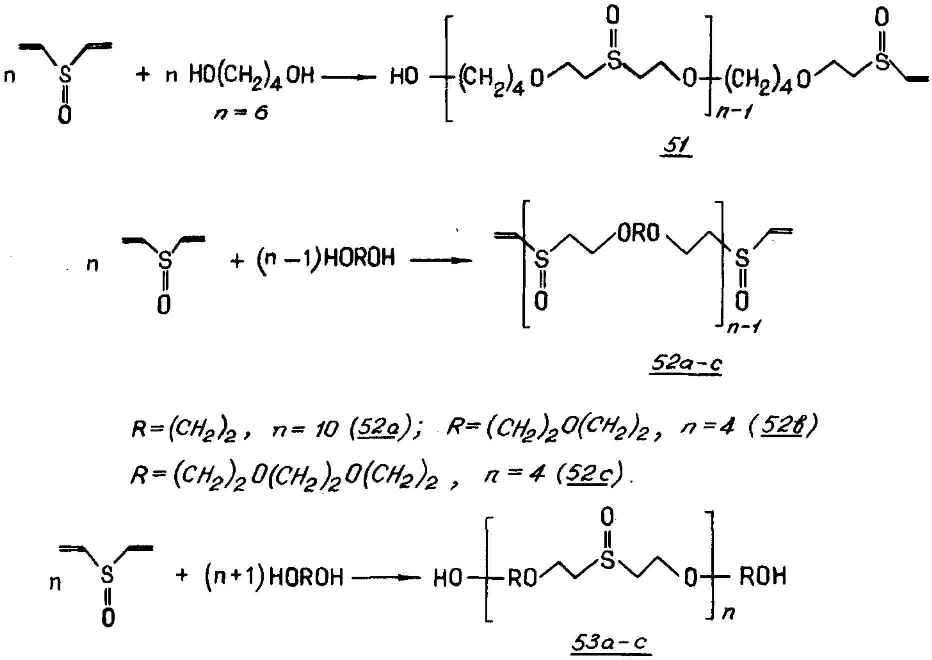
mation of oligomers suggests the heterocycle **50** to be involved in the reaction predominantly in its imino form.[94]



50

Scheme 33

It has been found[95,96] that DVSO and glycols smoothly enter the polyaddition reaction to quantitatively form the low-molecular (Mm 500–1500) viscous oligomers **51–53**, readily soluble in water and most organic solvents (alcohols, acetone, DMSO, chloroform) and insoluble in ether and CCl_4.



51

52a–c

$R = (CH_2)_2$, $n = 10$ (52a); $R = (CH_2)_2O(CH_2)_2$, $n = 4$ (52b)

$R = (CH_2)_2O(CH_2)_2O(CH_2)_2$, $n = 4$ (52c).

53a–c

$R = (CH_2)_2$, $n = 3$ (53a); $R = (CH_2)_2O(CH_2)_2$, $n = 4$ (53b);

$R = (CH_2)_2O(CH_2)_2O(CH_2)_2$, $n = 2$ (53c).

Scheme 34

Table 19. The Synthesis Conditions of the Oligosulfoxides **51**–**53**[96]

Oligomer	Degree of oligomerization	Molecular mass[a]	Yield, %	Reaction temperature, °C[b]	DVSO: glycol ratio, mol	Catalyst
51	6	1500	96	80	1:1	KOH
52a	8-9	1500	93	60	3:1	NaOH
52b	3	750	90	60	3:1	NaOH
52c	2-3	750	97	65	3:1	NaOH
53a	2-3	500	90	60	1:3	$Bu_4\overset{+}{N}\overset{-}{O}H$
53b	4	1000	98	60	1:3	NaOH
53c	2	750	75	65	1:3	NaOH

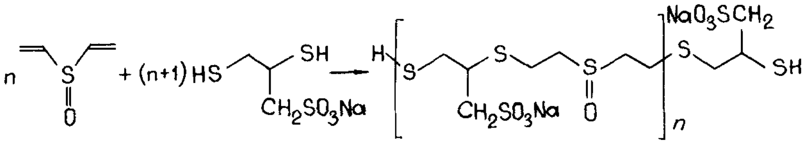
[a] The molecular mass was determined isopiestically.

[b] The reaction time is 3 h (synthesis of **51**) and 5 h (synthesis of **52** and **53**).

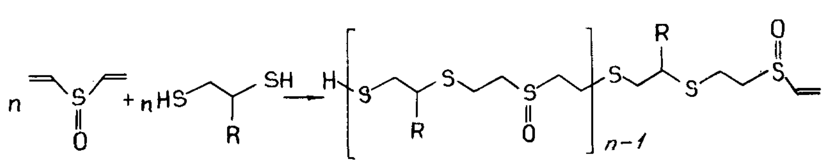
The reaction proceeds at 20–80 °C (3–5 h) in the presence of alkali metal hydroxides or a quaternary ammonium base (tetrabutylammonium hydroxide) in an amount of 0.5–5% by weight and allows sulfoxides with active terminal (hydroxy or vinyl) groups to be prepared in one step (Table 19).

A glycol:DVSO molar ratio of 1:1 leads to oligomer **51** bearing both vinyl and hydroxyl groups. Variation of the molar ratio of the above reagents from 3:1 to 1:3 makes it possible to direct the reaction towards the formation of the sulfoxides **52** and **53**, respectively (Table 19).[95,96]

On the basis of nucleophilic addition of dithiols to DVSO a novel general synthetic route[97,98] to heterochain oligoethylthio sulfoxides with active terminal vinyl and/or mercapto groups has been developed. DVSO under mild conditions (20–40 °C, 3 h) with sodium 2,3-dimercaptopropane-1-sulfonate (unithiol), 1,2-dimercaptoethane, and 2,3-dimercaptopropanol forms the oligoethylthio sulfoxides **54a–c**, **55**, and **56** in high yields (87–98%). The condensation is performed in water in the presence of sodium hydroxide (Table 20). The reaction can selectively be directed towards the formation of oligomers bearing either terminal mercapto groups (with excess dithiol), or terminal vinyl fragments (with excess DVSO) or both vinyl and mercapto groups (stoichiometric ratio of reagents).

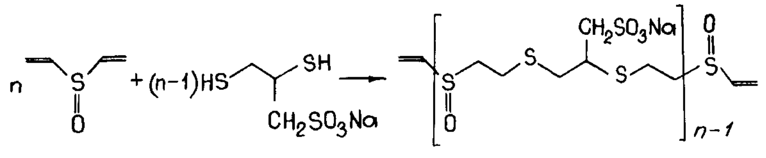


54в



54a 55 56

$R = CH_2SO_3Na$, $n = 4$ (54a); $R = H$ (55); $R = CH_2OH$ (56).



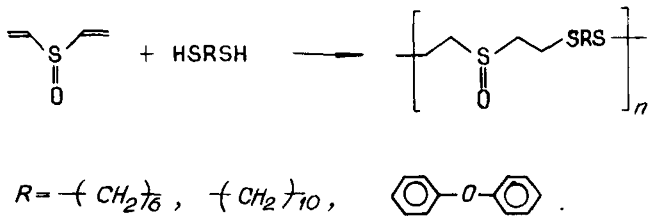
n = 4

Scheme 35

54c

The oligomers **54**–**56** are rubber-like or, more frequently, powdery low-molecular (Mm 1100–1300) products; some of them (**54a**–**c**) are well soluble in water and DMSO. The oligothio sulfoxides **55** and **56** are insoluble in organic solvents and water which makes the determination of their physical constants and the assignment of spectral parameters more difficult.

Polyalkylene(arylene)thio sulfoxides were obtained (in 88–99% yield) in a similar manner.[99]



Scheme 36

The reaction proceeds in HMPA or DMSO in the presence of Et_3N at a temperature not exceeding 90 °C.

III.8. *Physico-Chemical Properties of Divinyl Sulfoxide*

There is no single view of the electronic and molecular structure of sulfoxides at present. In a study of the dipole moments of vinyl sulfoxides[100] it was concluded that in the ground state any marked manifestation of the $S{=}O$ group—$C{=}C$ bond conjugation is not observed. At the same time, in [101] a bathochromic shift in the UV spectra of vinyl

Table 20. Synthesis of the Oligothio Sulfoxides **54**–**56**[98]

Oligomer	M.p., °C (decomp.)	Molecular mass[a]	Yield, %	Reaction temperature, °C[b]	DVSO:dithiol:NaOH ratio, mol
54a	85	1300	90	30	1:1:0.24
54b	82	1300	88	30	1:24:0.4
54c	83	1100	86.5	40	1:0.33:0.13
55	158–163	c	98	20	1:1:2.4
56	150	c	97	20	1:1:2.4

[a] The molecular mass was determined isopiestically; characteristic viscosity of **54a**–**c**: 0.03.
[b] Reaction time 3 h in all runs.
[c] The oligomers are insoluble in organic solvents and water.

sulfoxides is explained by weak conjugation between the double bond and the sulfoxide group.

In[102] the UV spectra of dialkyl and vinyl sulfoxides have been analysed and the presence of three absorption bands in the regions 227, 213–208 and 200–196 nm in the spectra of the latter has been revealed. The first two bands may be assigned, on the basis of solvent effects and non-empirical calculation of the model H_2SO, to the transitions localized mainly on the SO group. The bathochromic shifts of these bands with respect to the spectra of dialkyl sulfoxides are 4000 and 1000 cm^{-1}. The expected interaction of the double bond π-electrons with vacant orbitals of the sulfur atom, due to an increase in the negative charge on sulfur, should lead, on the contrary, to short-wavelength shifts. Consequently, this interaction alone cannot account for the spectral pattern observed. The conjugation of vinylic π-electrons with sulfur lone pairs looks more probable. This interaction should give rise to a bathochromic shift due to an $(n) \rightarrow \pi^*$ transition.[102]

A hypsochromic shift of the long-wavelength band in the spectrum of divinyl sulfoxide as compared with dialkyl and alkyl vinyl sulfoxides may be explained by a conformational nonequivalence of the vinyl groups and their different orientation relative to the lone pairs of the sulfur atom. This seems to lead to an alternating difference in conjugational mechanism of each of the unsaturated groups with the sulfoxide fragment. That of the vinyl groups which at present displays an orientation disadvantageous for the p-π-conjugation, retains a possibility for interaction with vacant orbitals of the sulfur atom or the whole fragment. Conformational analysis[3] provides evidence for the hypothesis of an alternating non-identity of the vinyl groups in the DVSO molecule.

Due to the high sensitivity of ^{13}C screening to charge distribution and conformational features of the molecular structure ^{13}C (δ C) chemical shifts are convenient parameters for investigating the intramolecular structures of molecules.

In studying alkyl vinyl ethers and sulfides by ^{13}C NMR spectroscopy it has been established[103,104] that the ^{13}C screening of the vinyl group involves considerable contributions from the polarization of double-bond π-electrons by polar alkoxy and alkylthio groups, steric interaction of the vinyl group with alkyls, as well as from the delocalization of electron pairs of oxygen and sulfur by a p-π-conjugational mechanism. The latter two effects are interrelated since an increase in the alkyl size leads to an increase in both its steric interaction with the vinyl fragment and the weight of less conjugated non-planar conformations.

In alkyl vinyl sulfoxides of the Type $H_2^{\beta}C{=}C^{\alpha}HS(O)R$ (R = Me, Et, *i*-Pr, *t*-Bu) the Alk variation leads to smaller changes in δ C than in ethers and sulfides, and is accompanied by a shielding of the $^{\alpha}C$ nuclei and a deshielding of the vinylic $^{\beta}C$.[105]

The influence of Alk in these compounds is of two main types: the polarization of double bond π-electrons which is nearly independent of the size of the substituents, and the steric effect related directly to alkyl group size.

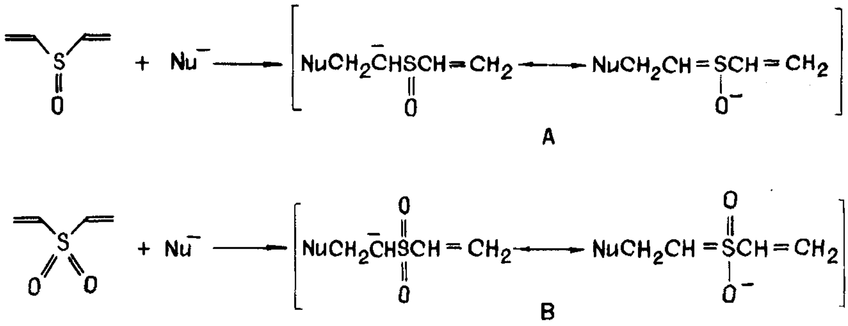
^1H, ^{13}C, ^{17}O, ^{77}Se and ^{125}Te NMR spectral parameters of vinyl chalcogenides and their derivatives $CH_2{=}CHXCH{=}CH_2$ (X = O, S, SO, SO_2, Se and Te) have been obtained.[106] The effective electronegativities and reasonance constants of $XCH{=}CH_2$ groups have been evaluated. It has been shown that in the reaction with the unsaturated moiety at the VIA group hetero atoms the π-donating effect decreasing in the series O > S > Se > Te is predominant whereas a π-withdrawing interaction occurs in the series of sulfoxides and sulfones.

At the same time, in the above series the electron density on the C_β atom is higher than that on the C_α atom not only in divinyl ether, divinyl sulfide and divinyl selenide which is in agreement with their susceptibility to electrophilic addition, but in divinyl sulfoxide and divinyl sulfone as well.

^{13}C Chemical Shifts (ppm) in $(H_2C_\beta{=}C_\alpha H)_2X$

X	C_α	C_β
O	148.56	92.72
S	129.88	114.34
Se	125.52	118.90
SO	140.98	119.38
SO_2	136.94	129.63

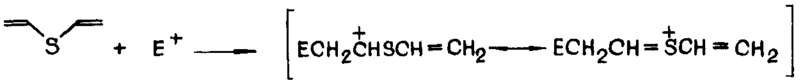
The high reactivity of DVSO (as well as that of divinyl sulfone) in nucleophilic addition reactions can be explained by the properties of the transition states of the reactions or by the intermediates formed in the reaction course rather than the ground state of DVSO and divinyl sulfone.



Scheme 37

In fact, the carbanions A and B should be stable due to a stabilizing effect of the neighboring electron-withdrawing sulfinyl and sulfonyl groups.

For divinyl sulfide, on the contrary, electrophilic addition reactions are more common[3] since the intermediate carbocations are well stabilized by the lone pairs of the sulfur atom:



Scheme 38

Investigations devoted to the properties of organic sulfoxides as bases are scarce and far from systematic.[107-110]

It has been reported[111] that the thermodynamic properties of the hydrogen bonding of phenols with sulfoxides depend on the substitutent attached to the sulfoxide group and, first of all, upon the inductive effect of this substituent. The basicity of vinyl organyl sulfoxides has not been considered in the literature until recently. In[112] the basicity of sulfoxides was estimated by the shift of ($\Delta\nu_{OH}$) of phenol H-bonded with sulfoxides.

Table 21. Comparison of DVSO Relative Basicity ($\Delta\nu_{OH}$) with that of Other Sulfoxides and Substituent Constants[112]

Sulfoxide	$\Delta\nu_{OH}$, cm^{-1}	σ^*	E_s^0	n
$CH_2{=}CHS(O)Me$	315	0.59	0.25	3
$CH_2{=}CHS(O)Et$	318	0.49	−0.02	2.4
$CH_2{=}CHS(O)Pr$-n	321	0.475	−0.29	2.4
$CH_2{=}CHS(O)Pr$-i	324	0.40	−0.6	1.8
$CH_2{=}CHS(O)Bu$-n	325	0.46	−0.34	2.4
$CH_2{=}CHS(O)Bu$-i	326	0.465	−0.89	2.4
$CH_2{=}CHS(O)Bu$-t	328	0.29	−1.88	1.2
$CH_2{=}CHS(O)Am$-n	325	0.47	−0.35	2.4
$CH_2{=}CHS(O)C_6H_{13}$-*n*	324	0.425	−0.35	2.4
$CH_2{=}CHS(O)C_6H_{11}$-*cyclo*	335	0.33	−0.94	1.8
$CH_2{=}CHS(O)Ph$	285	1.19	0.50	1.8
MeS(O)Me	350	0	0	6
EtS(O)Et	373	−0.2	−0.54	4.8
n-PrS(O)Pr-*n*	378	−0.23	−1.12	4.8
i-PrS(O)Pr-*i*	382	−0.38	−1.70	3.6
n-PrS(O)Et	378	−0.215	−0.83	4.8
i-BuS(O)Bu-*i*	392	−0.25	−2.26	4.8
i-BuS(O)Et	384	−0.225	−1.4	4.8
t-BuS(O)Bu-*t*	403	−0.60	−4.28	2.4
n-AmS(O)Am-*n*	387	−0.24	−1.2	2.4
i-PrS(O)Ph	329	0.41	−0.6	3
$CH_2{=}CHS(O)CH{=}CH_2$	284	1.18	0.50	1.8

Some pair and multiple correlations for $\Delta\nu_{OH}$ with inductive (σ^*), steric (E_s^0) and hyperconjugative (Δn) constants of substituents have been obtained (Table 21).[112]

A general equation is written as

$$\delta\nu = 346(\pm 9.8) - 62.2(\pm 7.3)[\pm 2.4]\Sigma\sigma^* - 3.7(\pm 2.6)[\pm 0.6]\Sigma E_s^0 + {}$$
$$+\ 2.7(\pm 1.7)[\pm 0.3]\Sigma\Delta n$$
$$r = 0.99,\ s_0 = 6.2$$

The uncertainties of the regression coefficients are given in parentheses, the contributions from experimental errors within $\pm 3\,\mathrm{cm}^{-1}$ are shown in square brackets.

The comparison of the regression coefficient and uncertainties shows that the sulfoxide basicity is mainly determined by the inductive effect of the substituents. The steric and hyperconjugative contributions proved to be low and statistically indefinite. The results for the series as a whole imply that the dependence of the basicity on the substituents at the sulfoxide group may be well approximated by a linear equation with the sum of inductive constants as the only argument:

$$\Delta\nu = 359.7(\pm 3.4) - 72.7(\pm 9.5)\Sigma\sigma^*$$
$$r = 0.98,\ s_0 = 6.7$$

The $\Delta\nu_{OH}$ values decrease with increasing substituent electronegativity.[112]

For a better understanding of the chemical properties of sulfoxides in general and DVSO in particular it is important to know the site of the highest basicity since in these molecules the lone pairs of both the sulfur and oxygen atoms may serve as the basic site.

Quantum chemical calculations of H_2SO[113] and DMSO[114] have shown that the lowest ionization potential is displayed by molecular orbitals whose contributions are from the oxygen lone pairs, therefore it is the oxygen atom that may be considered to be the basic site in sulfoxides. This is also consistent with a supplementary, specially developed criterion for determining the basic site in sulfoxides by means of orthosubstituted phenols.[115,116]

III.9. Applications of Divinyl Sulfoxide and Its Derivatives

The toxicity parameters of DVSO were determined upon intraperitoneal administration of a DMSO solution to cross-bred male and female white mice weighing 20–24 g. The LD_{50} estimated by the Kerber method is 87 mg/kg.

Investigations of the anticoagulation properties of a series of nitrogen-containing sulfoxides have revealed that the *N*-substituted 1,4-perhydrothiazine 1-oxides **4** and their salts **10** can be used to induce hemostasis.[52] The investigations were carried out with blood plasma taken from the auricular marginal vena of rabbits and stabilized by a 9:1 sodium citrate solution. The citrate plasma was incubated for 3 min at 37 °C in the presence of **4** and **10** (concentration range 5000–30 μg/ml), then the recalcification time was measured as an indicator of the direct anticoagulation effect. The lytic effect of **4** and **10** on XIIIa factor-stabilized fibrin has also been studied.[117] The results were recorded 2, 24 and 48 h after the fibrin clots had been treated with **4** and **10** solutions.

The incubation of **4** and **10** in doses of 5–2.5 mg/ml in blood plasma in the presence of Ca^{2+} accelerates moderately (from 10 to 20%) the coagulation reaction. In lower concentrations (1000–30 μg/ml) the above compounds do not produce any significant effect on coagulation. Similar results were obtained when these substances were introduced into native blood for automatic registration of hemocoagulation by means of a thromboelastogram.[52]

The lytic effect of compounds **4** and **10** on fibrin was studied *in vitro*. Compounds **4a** and **10a,b** increase the total and non-fermentative activity of blood plasma. With **4a** the maximum fermentative activity measured by the lysis area of non-stabilized fibrin lamellas is increased to 105 ± 7.8 mm^2.[52]

Research carried out with the fibrin momomer f-dez-AABB free from plasminogen impurities and polymerized in a neutral medium (pH 7.4) at 37°C has shown that a 1% solution of **10a** produces a lytic effect on non-stabilized fibrin of 28.7 ± 4.2% for 2 h; with **10a,b** (1% solution) the lytic effect on the fibrin clot achieved for as long as 48 h is considerably less (by 10–13%).[52]

The ability of **4,10** to dissolve fibrin stabilized by the XIIIa factor was confirmed on a fibrinogen preparation free from plasminogen on lysine-sepharose. It has been established that **4a** (1% solution) causes lysis of 49.3 ± 3.9% of fibrin for 2 h and after 24 h a 100% lysis of the fibrin clot is achieved. Solutions (1%) of **10a,b** are responsible for lysis of 32.5 ± 2.6% and 30.3 ± 3.5% fibrin, respectively, after 48 h.[52]

In a search for new effective inhibitors of plant growth the quaternary ammonium salts **8** and **9** have been studied. The 4,4-dimethyl-1,4-perhydrothiazinium 1-oxide chloride **8b** has been found to possess a clearly expressed retardant property.[118,119]

The growth controlling activity of **8b** was estimated in comparison with the known retardant chlorocholine chloride (CCC) according to the effect of the latter on the growth of "Skala" wheat. The wheat was cultivated in a hydroponic culture on keramsite with the Hogland-Arnon nutrient and under phytotron conditions (25 °C in the day time, 20 °C in the night, artificial illumination with filament lamps). After ten days the chloride **8b** and CCC were introduced into the nutrient. The keramsite was treated with the nutrient thrice a day. The treatment was ceased a week before harvest. Each vessel of 21 cm diameter contained 10–12 plants. The tests were repeated in triplicate.[119]

As seen from Table 22, the salt **8b** inhibits the elongation of the wheat stem and stimulates, unlike CCC, the bushiness of the plants, thus increasing the wheat yield.[119]

It should be emphasized that the retardant activity is also shown by other salts of 4,4-dimethyl-1,4-perhydrothiaziniumm 1-oxide bromide and iodide **8a**.[118] At the same time, replacement of the methyl groups at the nitrogen atom in these compounds by other alkyl (**9a,d,e**), unsaturated (**9b,c**), cyclic (**9g**), or aromatic (**9f**) groups leads to an abrupt decrease in the retardant activity of the above salts as shown in a biotest with bean sprouts.[118]

At present alkali xanthogenates are widely employed as collectors in the flotation processes in dressing mills.[120,121] However, the effectivity and selectivity of the metal recovery do not meet the requirements of modern production, especially under the conditions of constantly decreasing metal contents of crude ores and the involvement of hard-milling ores. This necessitates the search for new reagents in hydrometallurgy.

With this aim in view the floatation properties of DVSO and of a number of DVSO derivatives have been studied. It has been established that DVSO is an effective collector[122] and the sulfoxide **34b** can be used as a foaming agent in the floatation of sulfide lead-zinc ores.[123]

Laboratory tests of DVSO and **34b** were carried under conditions corresponding to commercial lead-zinc ore processing. The grinded ore was treated on a mechanical floatation plant of 0.75 l size according to a selective scheme in an open cycle.

The comparative data obtained from the floatation of polymetallic ores with parallel use of DVSO and a 2:1 mixture of potassium ethyl and butyl xanthogenates show the total recovery of metals to be 172.2 and 163.6%, respectively (Table 23). Besides, the use of DVSO leads to higher indexes of selectivity and metal recovery of the process and decreases the metal loss in tails.[122]

The sulfoxide **34b** was tested as a frother for the floatation of polymetallic ores in comparison with a commercial reagent, dimethyl phthalate (DMEP). The maximum total recovery of metals with **34b** is 172.4% (reagent consumption 30 g/t) and that with DMEP is 163.2% (45 g/t). Besides, the use of the sulfoxide **34b** also gave higher grade crude concentrates with 22.9% Pb (10.8% with DMEP) and a zinc-bearing concentrate with 30.2% Zn (17.9% with DMEP).[123]

The maintenance of water resources and environmental protection make it necessary to decrease run-off pollution as much as possible. That is why one of the most important problems of national economy is the intensification of industrial waste water (WW) purification. During the latest years the floatation method has been widely employed for this purpose. However, the floatation recovery of hydrophilic slime-lignine precipitates without collectors is ineffective. In the floatation cleaning of industrial waste water collectors are known to increase considerably the quality of the purified water and to reduce the operating time.[124]

In this connection, the possibility of floatation cleaning of WW from the Baikalian

Table 22. The Effect of CCC and Chloride **8b** on Plant Height and Wheat Productivity

Compound	Concentration, mg/l	Stem length, cm	Bushiness	Total production	Number of grains (per 1 vessel)	Grain weight, g		Straw weight, g/vessel
						per 1 vessel	per 1000 grains	
Control	–	76.0	3.7	3.1	883	24.5	27.8	35.1
CCC	100	64.8	3.7	3.3	864	22.6	26.2	28.6
8b	250	54.6	5.0	4.2	1096	25.3	23.1	30.6
8b	500	54.3	5.4	4.7	1370	29.6	21.6	35.8

Table 23. Summarized Data on the Total Recovery of Metals and the Average Lead and Zinc Contents of Crude Concentrates

Total recovery		Average contents of lead product		Average contents of zinc product		Collector and its consumption, g/t
Lead	Zinc	Lead	Zinc	Lead	Zinc	
80.25	83.32	29.07	8.46	3.02	24.76	Potassium butyl and ethyl xanthate, 142
80.74	91.5	34.2	4.05	2.14	29.09	Divinyl sulfoxide, 500

Pulp and Paper Plant (PPP) has been studied using 4-butyl-4-octadecyl-1,4-perhydrothiazinium 1-oxide bromide **9h** as a collector.[125,126]

The WW cleaning was performed in a glass floatation column of 400 ml with a Schott filter No. 4 serving as the column bottom. Air was supplied (0.9 l/min) from below through a porous plate. The samples were prepared with aluminium sulfate (18.4 mg/l, based on Al^{3+} consumed) and polyacrylamide (PAA, 0.38 mg/l). The pH value of the medium was adjusted to 5.8 using 0.1 N H_2SO_4. The collector **9h** was introduced into the system as an aqueous solution. The foam product formed in the floatation process was mechanically removed.

The use of this reagent has been shown to increase significantly the quality of the cleaned water as compared with the current standards.[125,126] The best results were achieved with a reagent consumption of $3.54 \cdot 10^{-4}$ mol/l, oxygen absorption 30 mg/l (normal 55–60 mg/l), color 40 degr. (normal 60 degr.), suspended substances 3.5 mg/l (normal 7.5 mg/l); it means that the purification grade is increased by a factor of 1.5–2 (Table 24). It is rather essential that the bromide **9h** considerably improves the indexes of purified water even without treating with WW coagulant (aluminium sulfate) and flocculant (polyacrylamide). In this case, with a **9h** consumption of $3.54 \cdot 10^{-4}$ mol/l and a floatation time of 4 min the yield of cleaned water is 85% (see Table 24).[125,126]

It has been found that the DVSO-modified polyacrylamide (PAA) considerably reduces (as compared with pure PAA) the water loss of polymeric drilling fluid used in sample boring for the stabilization of borehole walls.[127]

Table 24. Floatation Cleaning of Baikalian PPP Wastes Using the Bromide **9h** as the Collector

			Indexes of Cleaned Water Quality		
Run, No.	Consumption of **9h**, 10^{-4}, mol/l	Yield of froth product, %	O_2 absorption mg/l	color, degr.	suspended substances, mg/l
1[a]	3.11	7.5	50	60	5.0
2[a]	3.54	15.0	30	40	3.5
3[b]	3.11	5.0	50	40	2.0
4[b]	3.54	15.0	40	30	1.0
5[b]	3.89	17.0	40	30	1.0

[a] In runs 1 and 2 the samples were pretreated with aluminium sulfate and PAA. [b] In runs 3–5 floatation was performed without pretreatment.

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