

EQUILIBRIA OF *cis-trans*-ISOMERS OF UNSATURATED SULFIDES

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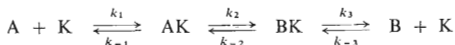
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In the paper the preparation and *cis-trans*-isomerisations of 1,2-disubstituted ethenes of the  $RS-CH=CH-X$  type, where  $X = Br, Cl$  and  $OC_2H_5$  and  $R = CH_3, C_2H_5, (CH_3)_2CH$  and  $(CH_3)_3C$  are investigated in dependence on temperature and polarity of the medium. In the series of 1-chloro-2-alkylthioethenes *cis*-isomers are more stable, while in the series of 1-ethoxy-2-alkylthioethenes the *trans*-isomers are more stable; the equilibrium position is dependent on the polarity of the medium. For the series of 1-bromo-2-alkylthioethenes the authors were unable to find suitable conditions for isomerisation with respect to polymerisation.

The question of the relative stability of geometrical isomers of 1,2-disubstituted ethenes became interesting when it was observed that in some types of these substances the *cis*-isomers are more stable. A series of such systems was found<sup>1-3</sup> even though the experimental conditions usually differed. The majority of authors discuss this phenomenon from a qualitative point of view only and agrees in the conclusion that its basis is attractive dipolar or dispersion interaction. Hill<sup>4</sup> and Mark<sup>5</sup> treated this problem quantitatively for 2-butenes under utilisation of empirical potential functions and achieved a good agreement with experiments.

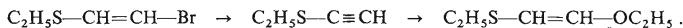
Therefore we now investigated the *cis-trans*-isomery in the series of 1-halogeno-2-alkylthioethenes and 1-ethoxy-2-alkylthioethenes. In view of the large range of hardly accessible thermodynamical information which is necessary for the comparison of the calculated data with those measured we only dealt with temperature dependences and with the discussion of energy factors. The kinetics of non-catalysed and catalysed *cis-trans*-isomerisations was followed to a larger extent, and in the case of the catalysed isomerisation it comprises the following sequence of equilibria:



where K is a catalytically active particle. Two cases are known: a)  $k_1, k_3 \gg k_2, k_{-1}, k_{-3} \gg k_{-2}$  found in the system  $I-CH=CH-I/I_2$  by Noyes and Dickinson<sup>6</sup>, and b)  $k_1, k_3 \sim k_2, k_{-1}, k_{-3} \sim k_{-2}$  found in the system  $C_6H_5S-CH=CH-C_6H_5/C_6H_5S$  (ref.<sup>7</sup>).

1-Bromo-2-alkylthioethenes were prepared in the known manner<sup>8</sup>. According to gas chromatographic analysis the reaction products generally contain 2 substances only, *i.e.* *cis*- and *trans*-isomers of the corresponding 1-bromo-2-alkylthioethene. 1-Bromo-1-alkylthioethenes are not formed at all or only in a negligible amount. The *cis*-isomer always prevails and it is possible to isolate it in a purity higher than 97% by simple distillation. The content of the *cis*-isomer in the reaction mixture increases in the following order:  $R = \text{CH}_3 < \text{C}_2\text{H}_5 < (\text{CH}_3)_2\text{CH} < (\text{CH}_3)_3\text{C}$ . The yields of bromination and the representation of the *cis*- and *trans*-isomers are given in Table I. The structure of substances was confirmed by IR and NMR spectroscopy.

1-Ethoxy-2-alkylthioethenes are mentioned in paper<sup>9</sup> in which a mixture of 1-ethoxy-2-ethylthioethene isomers was prepared in the following manner:



We simplified the whole procedure by carrying out the reaction in one step. We also proved that the reaction sequence is an elimination-addition one in which elimination takes place very rapidly. Alkylthioethyne, formed as an intermediate, was identified on the basis of retention data, by comparison with an authentic sample. The addition takes place slowly and it is stereoselective; the content of the *cis*-isomer was always above 90%. The structure of the compounds was also confirmed by IR and NMR spectroscopy.

From literature several methods of preparation of 1-chloro-2-alkylthioethenes<sup>10,11</sup> are known, but none of them is sufficiently general. Using the described procedures we prepared only *cis*-1-chloro-2-isopropylthioethene, *cis*-1-chloro-2-tert-butylthioethene and *trans*-1-chloro-2-ethylthioethene. We now developed a new procedure consisting of low-temperature addition of chlorine to alkyl vinyl sulfide and subsequent elimination of hydrogen chloride in the presence of a tertiary amine. According to gas chromatographic analysis the yields are generally low and their de-

TABLE I  
Yields of Bromination of Alkyl Vinyl Sulfides

Compound	Yield, %	<i>cis</i> , %	<i>trans</i> , %
$\text{CH}_3\text{S}-\text{CH}=\text{CH}-\text{Br}$	28	75	24
$\text{C}_2\text{H}_5\text{S}-\text{CH}=\text{CH}-\text{Br}$	72	87	13
$(\text{CH}_3)_2\text{CHS}-\text{CH}=\text{CH}-\text{Br}$	75	88	12
$(\text{CH}_3)_3\text{CS}-\text{CH}=\text{CH}-\text{Br}$	42	98	2

pendence on the alkyl group is the same as in the series of 1-bromo-2-alkylthioethenes. The addition of chlorine is strongly exothermic and it is accompanied both by the fragmentation of the molecule under formation of low-boiling products, and by elimination of hydrogen chloride during which the 1-chloro-2-alkylthioethene formed gives on chlorine addition and subsequent elimination of hydrogen chloride higher chlorinated products, mainly 1,1-dichloro-2-alkylthioethenes. The content of these substances in the reaction mixture increases with the rate of chlorination and with the decrease of the alkyl group size in the sequence  $R = \text{CH}_3 > \text{C}_2\text{H}_5 > > (\text{CH}_3)_3\text{C}$ . The results of chlorination are summarised in Table II.

The prevalence of the *cis*-isomer in the reaction mixture and the dependence of the relative representation of the isomers on the alkyl group can be explained on the

TABLE II  
Yields of the Synthesis of 1-Chloro-2-alkylthioethenes

Starting compound	g	Yield, g	<i>cis</i> , %	<i>trans</i> , %	$\text{RS}-\text{CH}=\text{CCl}_2$ %
$\text{CH}_3\text{S}-\text{CH}=\text{CH}_2$	16.7	5	63	10	24
$\text{C}_2\text{H}_5\text{S}-\text{CH}=\text{CH}_2$	22	13	75	8	15
$(\text{CH}_3)_2\text{CHS}-\text{CH}=\text{CH}_2$	26	19 <sup>a</sup>	47	2.5	43
$(\text{CH}_3)_3\text{CS}-\text{CH}=\text{CH}_2$	19	9	84	4	10

<sup>a</sup> Higher rate of chlorination.

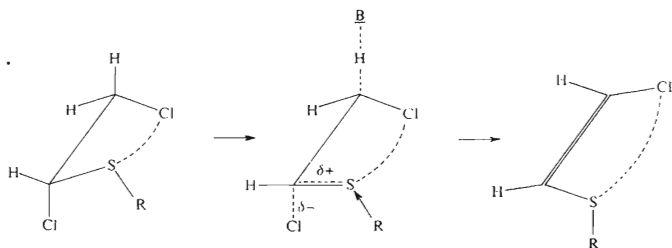


FIG. 1  
Transition State of the Elimination (B means base)

basis of the model of the transition state (Fig. 1). Evidently, elimination does not take place by a synchronous mechanism and it is shifted to the E1 type in view of the activation of the  $\alpha$ -position by participation of the sulphur atom electrons on the reaction centre. At the same time the formation of the *cis*- and *trans*-isomers is kinetically directed because the isomerisation rate is negligible under the conditions of the reaction. The advantage of the *cis*-arrangement of the transition state is probably given by two factors. Dispersion interactions S...Cl are attractive as may be inferred from

TABLE III  
Thermodynamic Data of 1-Chloro-2-alkylthioethenes

$T, K$	$K_c^a$	$\Delta F^b$	$\Delta U^b$	$\Delta S^b$	$K_{ex}^a$
1-Chloro-2-methylthioethene					
433.5	$1.77 \pm 0.02$	-0.49	$-3.07 \pm 0.09$	$-5.9 \pm 0.2$	1.78
443.7	$1.63 \pm 0.03$	-0.43			1.65
453.9	$1.48 \pm 0.03$	-0.36			1.49
464.2	$1.40 \pm 0.02$	-0.31			1.41
1-Chloro-2-ethylthioethene					
433.5	$2.03 \pm 0.03$	-0.61	$-3.16 \pm 0.02$	$-5.8 \pm 0.03$	2.00
443.7	$1.92 \pm 0.02$	-0.58			1.89
453.9	$1.71 \pm 0.02$	-0.49			1.70
464.2	$1.61 \pm 0.02$	-0.44			1.59
1-Chloro-2-isopropylthioethene					
433.5	$2.17 \pm 0.04$	-0.67	$-3.74 \pm 0.1$	$-7.1 \pm 0.1$	2.18
443.7	$1.99 \pm 0.03$	-0.61			1.98
453.9	$1.81 \pm 0.03$	-0.54			1.81
464.2	$1.63 \pm 0.03$	-0.45			1.62
1-Chloro-2-tert-butylthioethene					
433.5	$2.03 \pm 0.04$	-0.61	$-4.31 \pm 0.01$	$-8.5 \pm 0.05$	2.01
443.7	$1.79 \pm 0.02$	-0.52			1.80
453.9	$1.64 \pm 0.01$	-0.45			1.65
464.2	$1.45 \pm 0.05$	-0.34			1.44

<sup>a</sup>  $K_c$  value obtained from kinetic data;  $K_{ex}$  limit value of the *cis-trans* ratio; <sup>b</sup>  $\Delta F$ ,  $\Delta U$  in kcal  $mol^{-1}$ ,  $\Delta S$  in cal.  $mol^{-1} deg^{-1}$ .

the results of isomerisation of 1-chloro-2-alkylthioethenes. The asymmetric position of the electron-deficient region with respect of the C—C bond, given by the participation of the electrons of the sulfur atom on the reaction centre, leads to the preference of the *cis*-arrangement, because in that case the dipolar interactions of C—Cl and RS—C bonds are most favourable. This explanation enables the interpretation of the alkyl group R, because with increasing polarisability [ $\text{CH}_3 < \text{C}_2\text{H}_5 < (\text{CH}_3)_2\text{CH} < (\text{CH}_3)_3\text{C}$ ], the effects of both phenomena are deepened. The above

TABLE IV  
Kinetic Data of 1-Chloro-2-alkylthioethenes

<i>T</i> , K	$k_1 \cdot 10^4$ <sup>a</sup>	$k_2 \cdot 10^4$ <sup>b</sup>	$E_1$ <sup>a</sup>	$E_2$ <sup>b</sup>	$\log P_1$ <sup>a</sup>	$\log P_2$ <sup>b</sup>
1-Chloro-2-methylthioethene						
433.5	1.83 ± 0.08	3.22 ± 0.11	18.34	15.31	5.505	4.068
443.7	3.01 ± 0.21	4.90 ± 0.41				
453.9	4.25 ± 0.26	6.27 ± 0.27				
464.2	7.82 ± 0.25	10.97 ± 0.42				
1-Chloro-2-ethylthioethene						
433.5	0.64 ± 0.05	1.29 ± 0.10	32.18	29.02	12.041	10.763
443.7	1.67 ± 0.08	3.21 ± 0.13				
453.9	3.39 ± 0.17	5.80 ± 0.13				
464.2	7.80 ± 0.11	12.56 ± 0.32				
1-Chloro-2-isopropylthioethene						
433.5	0.65 ± 0.05	1.40 ± 0.07	27.62	23.84	10.00	7.897
443.7	1.45 ± 0.07	2.69 ± 0.10				
453.9	2.80 ± 0.20	5.08 ± 0.48				
464.2	5.32 ± 0.43	8.67 ± 0.91				
1-Chloro-2-tert-butylthioethene						
433.5	1.07 ± 0.14	2.06 ± 0.12	22.38	18.72	7.342	5.778
443.7	2.19 ± 0.03	3.93 ± 0.08				
453.9	3.49 ± 0.27	5.80 ± 0.48				
464.2	6.19 ± 0.12	8.90 ± 0.71				

<sup>a</sup>  $k_1$ ,  $E_1$  and  $P_1$  rate constant ( $\text{s}^{-1}$ ), activation energy ( $\text{kcal}\cdot\text{mol}^{-1}$ ) and frequency factor of the reaction *cis* → *trans*; <sup>b</sup>  $k_2$ ,  $E_2$  and  $P_2$  the same parameters for the reaction *trans* → *cis*.

mentioned conclusions may be applied directly to the series of 1-bromo-2-alkylthioethenes because the results of dehydrobrominations are entirely similar.

The isomerisations in the series of 1-bromo-2-alkylthioethenes were followed at  $-3^{\circ}$  to  $120^{\circ}\text{C}$  in benzene, acetone, chlorobenzene and dioxan under catalysis with iodine and thermally. In all instances a rapid polymerisation took place without regard to the inert atmosphere (argon) or the addition of hydroquinone as inhibitor. On the basis of these facts and in view of the observed sensitivity of the substances

TABLE V  
Thermodynamic Data of 1-Ethoxy-2-alkylthioethenes

$T, \text{K}$	$K_{ex}^a$	$\Delta F$ $\text{kcal} \cdot \text{mol}^{-1}$	$\Delta U$ $\text{kcal} \cdot \text{mol}^{-1}$	$\Delta S^b$ $\text{cal} \cdot \text{mol}^{-1} \cdot \text{deg}^{-1}$
1-Ethoxy-2-methylthioethene				
433.6	$1.42 \pm 0.03$	-0.30	$-2.38 \pm 0.07$	$-4.8 \pm 0.1$
443.7	$1.36 \pm 0.03$	-0.27		
453.9	$1.27 \pm 0.03$	-0.22		
464.2	$1.19 \pm 0.02$	-0.16		
1-Ethoxy-2-ethylthioethene				
433.5	$1.51 \pm 0.02$	-0.36	$-1.80 \pm 0.05$	$-3.32 \pm 0.1$
443.7	$1.45 \pm 0.02$	-0.33		
453.9	$1.38 \pm 0.04$	-0.29		
464.2	$1.32 \pm 0.02$	-0.26		
1-Ethoxy-2-isopropylthioethene				
433.5	$1.98 \pm 0.03$	-0.59	$-1.48 \pm 0.02$	$-2.05 \pm 0.04$
443.7	$1.91 \pm 0.02$	-0.57		
453.9	$1.83 \pm 0.02$	-0.55		
464.2	$1.77 \pm 0.03$	-0.53		
1-Ethoxy-2-tert-butylthioethene				
433.5	$3.01 \pm 0.05$	-0.95	$-0.58 \pm 0.02$	$+0.84 \pm 0.03$
443.7	$2.94 \pm 0.02$	-0.95		
453.9	$2.91 \pm 0.03$	-0.96		
464.2	$2.87 \pm 0.02$	-0.97		

<sup>a</sup>  $K_{ex}$  limit value of the *trans/cis* ratio. <sup>b</sup> For the given experimental arrangement the values of mixed entropy ranged from 0.09 to 0.24  $\text{cal} \cdot \text{mol}^{-1} \cdot \text{deg}^{-1}$ .

to traces of acids we consider that in this case an acid catalysed polymerization is in operation where hydrogen bromide split off from the thermolabile starting compound functions as a catalyst. In the series of 1-chloro-2-alkylthioethenes isomerisations were carried out in dioxan under catalysis with iodine in the 160–190°C temperature range. The results of measurements are given in Tables III and IV. As the unequal rate of polymerisation of isomers could distort the final results we eliminated this effect by not including in the calculation the samples in which the total loss of substances by polymerization exceeded 10%. The equilibrium constants were obtained in two ways, *i.e.* either by computation from kinetic data or by extrapolation from the dependence  $K_{A/B} = K(t)$ . From the results it is evident that the agreement is good. The rate constants were obtained by linearisation of the exponential function using the method of three points and the model *a*) described in the introduction, and the agreement of the measured values with those computed confirmed this idea. The  $\Delta U$  and  $\Delta S$  values were obtained from the relation  $\Delta F = \Delta U - T\Delta S$  using the method of least squares. In addition to polymerisation which becomes manifest by the darkening of the reaction mixture we also observed in the case of 1-chloro-2-tert-butylthioethene a weak fragmentation detectable from the presence of two unidentified low-boiling substances. In the series of 1-ethoxy-2-alkylthioethenes isomerisations were carried out in dioxan at the same temperature range as above. The question of the choice of the catalyst was solved only after a series of experiments, because it was observed that iodine gives side reactions the products of which were separable from both isomers only with difficulty. We found dialkyl disulfides (primarily di(tert-butyl) disulfide) to be effective and inert catalysts, the activity of which in thermal isomerisations was not known so far. Analysing the kinetic curves of the catalysis with di(tert-butyl) sulfide we found that the dependence  $c_A = f(t)$  agrees with the theory, but the equilibrium constants<sup>1</sup> calculated

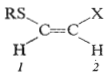
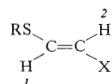
TABLE VI

Dependence of the Equilibria on the Polarity of the Medium for the System  $C_2H_5S-CH=CH-OC_2H_5$  ( $t-C_4H_9$ )<sub>2</sub>S<sub>2</sub>

Solvent	<i>T</i> , °K	$K_{ex}^a$
Acetonitrile	453.9	1.07 ± 0.02
Ethyl formate	453.9	1.26 ± 0.07
Acetone	453.9	1.32 ± 0.02
Dioxan	453.9	1.39 ± 0.02
Cyclohexane	453.9	1.54 ± 0.02

<sup>a</sup>  $K_{ex}$  limit value of the *trans/cis* ratio.

TABLE VII  
NMR Spectra

R	X	H <sub>1</sub> , p.p.m.	H <sub>2</sub> , p.p.m.	J <sub>12</sub> , Hz
<p><i>cis</i>-Isomers</p> 				
C <sub>2</sub> H <sub>5</sub> <sup>a</sup>	Br	6.74	6.15	6.5
(CH <sub>3</sub> ) <sub>2</sub> CH	Br	6.76	6.14	6.5
(CH <sub>3</sub> ) <sub>3</sub> C	Br	6.84	6.15	6.5
CH <sub>3</sub>	Cl	6.20	6.00	6.5
C <sub>2</sub> H <sub>5</sub>	Cl	6.27	6.01	6.5
(CH <sub>3</sub> ) <sub>2</sub> CH	Cl	6.33	6.01	6.5
(CH <sub>3</sub> ) <sub>3</sub> C	Cl	6.40	6.03	6.5
CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	4.70	6.10	5.5
C <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	4.71	6.13	5.5
(CH <sub>3</sub> ) <sub>2</sub> CH <sup>a</sup>	OC <sub>2</sub> H <sub>5</sub>	4.93	6.27	5.5
(CH <sub>3</sub> ) <sub>3</sub> C <sup>a</sup>	OC <sub>2</sub> H <sub>5</sub>	5.00	6.23	5.6
<p><i>trans</i>-Isomers</p> 				
C <sub>2</sub> H <sub>5</sub> <sup>a</sup>	Br	6.75	6.10	13.0
(CH <sub>3</sub> ) <sub>2</sub> CH	Br	6.78	6.10	13.0
(CH <sub>3</sub> ) <sub>3</sub> C	Br	6.88	6.08	13.0
CH <sub>3</sub>	Cl	6.30	5.95	13.0
C <sub>2</sub> H <sub>5</sub>	Cl	6.34	5.95	13.0
CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	5.13	6.58	12.0
C <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	5.15	6.60	12.2
(CH <sub>3</sub> ) <sub>2</sub> CH <sup>a</sup>	OC <sub>2</sub> H <sub>5</sub>	5.33	6.68	12.2
(CH <sub>3</sub> ) <sub>3</sub> CH <sup>a</sup>	OC <sub>2</sub> H <sub>5</sub>	5.36	6.68	12.1
CH <sub>3</sub>	Cl <sub>2</sub>	6.52	—	—
C <sub>2</sub> H <sub>5</sub>	Cl <sub>2</sub>	6.57	—	—
(CH <sub>3</sub> ) <sub>2</sub> CH	Cl <sub>2</sub>	6.65	—	—

<sup>a</sup> Measured on a Varian HA 100 (100 Mc) apparatus in chloroform with tetramethylsilane as internal reference. Other values were measured on a Tesla BS-487 (80 Mc) apparatus in tetrachloromethane with hexamethylsiloxane as internal reference.



with the use of the chosen model did not agree completely with experimental values. In this reaction the catalytically active particle is probably the  $RS'$  radical because when passing from acetonitrile to cyclohexane the isomerisation rate did not change substantially (measured for  $(t-C_4H_9)_2S_2$ ). The kinetics may be described within the frame of model *b*). The  $\Delta U$  and  $\Delta S$  values were again obtained by the method of least squares. Of the side reactions fragmentation of 1-ethoxy-2-tert-butylthioethene took place to a certain extent, while polymerisation was negligible. The results are given in Tables V and VI.

The mere fact that the *cis*-isomers of the 1-chloro-2-alkylthioethene series are more stable is probably the consequence of the effect of non-bonding interactions, and in view of the drawbacks of the theory it is not directly deducible from molecular parameters. The effect of two factors may be deduced from the temperature dependence for the observed dependence of isomerisation free energies on the alkyl group, *i.e.* an energetic and an entropic one. The difference of internal energies of *cis*- and *trans*-isomers increases in the series of alkyls, methyl < ethyl < isopropyl < tert-butyl, and it evidently depends on the increase of polarisability of alkyl groups in the same order, which has the deepening effect of both of dispersion and dipolar interactions as consequence even though that is a secondary effect. The entropy member displays an opposite dependence, *i.e.* in the reaction  $A_{cis} \rightarrow A_{trans}$  the entropy of the system increases and simultaneously the change of the entropy during the isomerisation increases in the order  $R = CH_3 < C_2H_5 < (CH_3)_2CH < (CH_3)_3C$ . This phenomenon is understandable taking into account that in the *trans*-isomer the system  $R-S-C=C$  may assume two energetically favourable positions, *i.e.* *s-cis*- and *s-trans*-form, while in the *cis*-isomer the *s-cis*-form is at a disadvantage by the non-bonding interactions of the alkyl group with the chlorine atom. The dependence on the volume of the alkyl group is then understandable and it also explains the larger entropy change for the transition from isopropyl to tert-butyl group, which was observed.

The results obtained in the series of 1-ethoxy-2-alkylthioethenes indicate that the *trans*-isomers are here generally more stable and that the dependence of the equilibrium constant on the nature of the alkyl group is monotonous and increases in the  $R = CH_3 < C_2H_5 < (CH_3)_2CH < (CH_3)_3C$  sequence. This dependence is again a consequence of the combination of energy and entropy factors although their interpretation is difficult in this case. The changes of internal energy (in absolute value) decrease in the order  $R = CH_3 > C_2H_5 > (CH_3)_2CH > (CH_3)_3C$  and therefore they are not substantially affected by steric interactions of the alkyl group. The changes of entropy during the reaction  $A_{trans} \rightarrow A_{cis}$  are positive, contrary to expectations, for the first three members although their values decrease slowly. The transition from isopropyl to tert-butyl is connected with the change of the sign of the isomerisation entropy which may be interpreted as a consequence of increased steric requirements of the tert-butyl group. The circumstance that the *cis*-isomers

are entropically favoured for three alkyl groups is not clear and its interpretation in the frame of *s-cis*- and *s-trans*- forms is not viable in view of the complexity of the whole system. The investigated dependence of the equilibrium constant on the polarity of the medium is in agreement with the finding that in substances of this type *cis*-isomers have higher dipole moments than the corresponding *trans*-isomers.

## EXPERIMENTAL

Isomerisations were carried out in sealed glass ampoules of 70–80  $\mu$ l volume, the volume of the liquid phase was always 9  $\mu$ l. The concentrations of substances ranged between 10 and 17% by weight, concentration of the catalyst: iodine 0.3% (weight), di(*tert*-butyl) disulfide 1% (weight). Analyses were carried out by gas chromatography (CHROM 31, Laboratorní pístroje, Prague), the stationary phases used: SE 52, 7% on porovina 0.2–0.3 mm, column 1.20 m/6 mm for 1-chloro-2-alkylthioethenes, poly(ethylene glycol adipate), 4% on Chromaton NAW-DMCS, 0.2–0.25 mm, column 2.40 m/6 mm for 1-ethoxy-2-alkylthioethenes. In all instances we worked up integration records because the response of the FID was the same for corresponding *cis*- and *trans*-isomers within the accuracy of the injection and the integrator (1%).

### 1-Chloro-2-isopropylthioethene

A solution of 13.3 ml of liquid chlorine in 140 ml of dichloromethane cooled to  $-45^{\circ}\text{C}$  (the chlorine solution was introduced by nitrogen gas overpressure through a capillary into the reaction mixture) was added to a mixture of 26 g of isopropyl vinyl sulfide and 50 ml of dichloromethane under stirring and cooling at  $-30^{\circ}\text{C}$  over 50 minutes. The mixture was stirred at  $-10^{\circ}\text{C}$  for 30 minutes and 40 g of dimethylaniline and 40 g of tributylamine were then added. After two hours refluxing the mixture was chilled, extracted with two 70 ml portions of 2.5M-HCl and 50 ml of 20%  $\text{K}_2\text{CO}_3$ , dried over anhydrous sodium sulfate. Dichloromethane and the lower boiling products were distilled through a 20 cm Vigreux rectification column and the residue was distilled in a vacuum under nitrogen to yield 19 g of a mixture of b.p.  $60.5-70^{\circ}\text{C}/15$  Torr, which was separated by preparative gas chromatography (5 m SE 301, 10% on Chromaton NAW-DMCS, column temperature  $130^{\circ}\text{C}$ ). The following products were obtained: *cis*-1-Chloro-2-isopropylthioethene: For  $\text{C}_5\text{H}_9\text{ClS}$  (136.65) calculated: 43.92% C, 6.64% H, 23.48% S; found: 44.08% C, 6.73% H, 23.27% S. 1,1-Dichloro-2-isopropylthioethene: For  $\text{C}_5\text{H}_8\text{Cl}_2\text{S}$  (171.1) calculated: 18.72% S, 41.49% Cl; found: 19.02% S, 41.87% Cl. 1,2-Dichloro-1-isopropylthioethene: For  $\text{C}_5\text{H}_8\text{Cl}_2\text{S}$  (171.1) calculated: 18.72% S, 41.49% Cl; found: 18.91% S, 41.15% Cl.

### 1-Chloro-2-ethylthioethene

Into a solution of 22 g of ethyl vinyl sulfide in 40 ml of dichloromethane gaseous chlorine mixed with nitrogen was introduced under stirring at  $-40^{\circ}\text{C}$ . The degree of conversion was followed by gas chromatography as the decrease in concentration of ethyl vinyl sulfide. After introduction of 6 l of chlorine (150 min) all unsaturated sulfide had reacted (calculated 5.6 l). Dimethylaniline (38 g) and tributylamine (30 g) was then added to the mixture which was worked up as in the preceding case. A mixture was obtained (13 g) of b.p.  $46-57^{\circ}\text{C}/15$  Torr which was separated by preparative gas chromatography (5 m SE 301, 10% on Chromaton NAW-DMCS, column temperature  $120^{\circ}\text{C}$ ). The following compounds were obtained: *cis*-1-Chloro-2-ethylthioethene: For  $\text{C}_4\text{H}_7\text{ClS}$  (122.6) calculated: 39.25% C, 5.76% H, 26.15% S; found: 39.33% C, 5.80% H, 26.30% S. 1,1-Dichloro-2-ethylthioethene: For  $\text{C}_4\text{H}_6\text{Cl}_2\text{S}$  (157.1) calculated: 20.45% S, 44.90% Cl; found: 20.38% C, 45.11% Cl.

## 1-Chloro-2-methylthioethene

From 16.7 g of methyl vinyl sulfide 5 g of mixture were obtained, b.p. 50–67°C/25 Torr, which was separated by preparative gas chromatography, giving: *cis*-1-Chloro-2-methylthioethene: For  $C_3H_5ClS$  (108.6) 33.15% C, 4.64% H, 29.54% S; found: 32.85% C, 4.59% H, 28.98% S. *trans*-1-Chloro-2-methylthioethene (in mixture with the *cis*-isomer): For  $C_3H_5ClS$  (108.6) calculated: 33.15% C, 4.64% H, 29.54% S; found: 33.65% C, 4.63% H, 29.15% S. 1,1-Dichloro-2-methylthioethene: For  $C_3H_4Cl_2S$  (143.0) calculated: 22.50% S, 49.36% Cl; found: 22.22% S, 49.53% Cl.

## 1-Chloro-2-tert-butylthioethene

From 19 g tert-butyl vinyl sulfide 9 g of a mixture were obtained, b.p. 71–75°C/17 Torr, which was separated by preparative gas chromatography, giving: *cis*-1-Chloro-2-tert-butylthioethene: For  $C_6H_{11}ClS$  (150.7) calculated: 47.76% C, 7.37% H, 21.55% S; found: 48.06% C, 7.50% H, 21.05% S. 1,1-Dichloro-2-tert-butylthioethene: For  $C_6H_{10}Cl_2S$  (185.1) calculated: 17.28% S, 38.34% Cl; found: 17.19% S, 38.65% Cl.

*trans*-1-Chloro-2-tert-butylthioethene

A mixture of 3 g of *cis*-1-chloro-2-tert-butylthioethene, 5 ml of dioxan and 70 mg of iodine was heated in a sealed tube at 180°C for 30 minutes. After cooling 2 ml of dioxan were distilled off and the residue freed from iodine and the polymers formed by vacuum distillation. The product (1.5 ml of a mixture of dioxan, *cis*- and *trans*-1-chloro-2-tert-butylthioethene and three additional substances) was worked up by preparative gas chromatography. In view of the low content by the *trans*-isomer in the mixture an enriched fraction was isolated which contained 52.3% of the *trans*-isomer. For  $C_6H_{11}ClS$  (150.7) calculated: 47.76% C, 7.37% H, 21.55% S; found: 48.00% C, 7.40% H, 21.85% S.

*cis*-1-Ethoxy-2-ethylthioethene

A mixture of *cis*- and *trans*-1-bromo-2-ethylthioethene (62.5 g; 0.375 mol) was added to a solution of 53.6 g (0.865 mol) of sodium ethoxide in 250 ml of ethanol. The mixture was refluxed for 16 hours, 100 ml of ethanol were distilled off and the residue poured into 500 ml of water and the organic phase separated. The aqueous phase was extracted with two 40 ml portions of ether and the combined organic phases were dried over sodium sulfate and ether was evaporated. The residue was distilled under reduced pressure under nitrogen yielding 38 g (78%) of a mixture of three substances the main component of which (90%) was *cis*-1-ethoxy-2-ethylthioethene, b.p. 64–66°C/14 Torr. The product was purified by column distillation (a 20 cm high spiral from a glass fibre tube) in a vacuum and under nitrogen. The *cis*-isomer was obtained in a purity better than 99%, b.p. 65.4°C/14 Torr. For  $C_6H_{12}OS$  (132.2) calculated: 54.50% C, 9.17% H, 24.25% S; found: 55.00% C, 9.14% H, 24.31% S. The following compounds were prepared in an analogous manner: *cis*-1-Ethoxy-2-methylthioethene: Yield 81%, b.p. 55.0°C/14 Torr. For  $C_5H_{10}OS$  (118.2) calculated: 51.75% C, 8.55% H, 27.12% S; found: 51.53% C, 8.72% H, 26.98% S. *cis*-1-Ethoxy-2-isopropylthioethene: Yield 83%, b.p. 83.1°C/14 Torr. For  $C_7H_{14}OS$  (146.2) calculated: 57.82% C, 9.68% H, 21.92% S; found: 57.82% C, 9.73% H, 22.05% S. *cis*-1-Ethoxy-2-tert-butylthioethene: Yield 71%, b.p. 90.3°C/13 Torr. For  $C_8H_{16}OS$  (160.3) calculated: 59.89% C, 10.04% H, 17.72% S; found: 60.02% C, 10.15% H, 17.58% S.

*Identification of the intermediates:* From the mixture after the reaction of 1-bromo-2-alkylthioethene and sodium ethoxide a sample was withdrawn (one minute after the precipitation of sodium bromide) and analysed by gas chromatography. The sample contained in addition to ethanol a substance which was identified as the corresponding alkylthioethene by comparison of the retention times with an authentic sample<sup>12</sup>. For comparison two stationary phases were used: Apiezon K, 9% on Chromaton NAW-DMCS, 0.2–0.25 mm, column 2.40 m/6 mm, and dinonyl phthalate, 11% on porovina, 0.2–0.3 mm, column 2.40 m/6 mm, in all instances at 80°C.

#### *trans*-1-Ethoxy-2-ethylthioethene

The *cis*-isomer (35 g) with 3% iodine was distilled under reduced pressure and under nitrogen through a column (20 cm spiral tube of glass fibre). Fractions were not collected. Temperature in the column head was plotted against time (a thermocouple with a recorder). After 12 hours the temperature dropped by 5.6°C and the collection of fractions was started at a reflux ratio 1 : 40 to 1 : 50. A mixture was obtained (5 g) of the composition 30% *cis*- and 70% *trans*-isomer, and the whole process was repeated with the distillation residue with same result. Pure *trans*-isomer was obtained from the enriched mixture by preparative gas chromatography (5 m poly(ethylene glycol adipate), 4% on porovina, 0.2–0.3 mm, column temperature 135°C). For C<sub>6</sub>H<sub>12</sub>OS (132.2) calculated: 54.50% C, 9.17% H, 24.25% S; found: 54.79% C, 9.14% H, 24.38% S.

The following compounds were prepared in an analogous manner: *trans*-1-Ethoxy-2-methylthioethene: For C<sub>5</sub>H<sub>10</sub>OS (118.2) calculated: 51.75% C, 8.55% H, 27.12% S; found: 52.02% C, 8.48% H, 27.26% S. *trans*-1-Ethoxy-2-isopropylthioethene: For C<sub>7</sub>H<sub>14</sub>OS (146.2) calculated: 57.82% C, 9.68% H, 21.92% S; found: 57.37% C, 9.65% H, 22.07% S. *trans*-1-Ethoxy-2-tert-butylthioethene: For C<sub>8</sub>H<sub>16</sub>OS (160.3) calculated: 59.89% C, 10.04% H, 17.72% S; found: 59.15% C, 9.94% H, 17.68% S.

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