Structure-Stability Relationships in Vinyl Sulfides. II. Stabilization Energies due to Alkyl and Alkylthio Groups Attached to the β Carbon of Vinyl Sulfides and Vinyl Ethers

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On the basis of equilibration studies, it is concluded that a methyl group stabilizes the double bond of a vinyl sulfide by about 8.5 kJ mol^{-1} when the group is in the *trans* position on the β carbon of an α,β-dimethyl substituted vinyl sulfide, and by about 9.5 kJ mol^{-1} in the corresponding position of a trimethyl substituted vinyl sulfide. An ethylthio group in the *trans* position on the β carbon stabilizes the double bond by about 8 kJ mol^{-1} or 5 kJ mol^{-1} in vinyl ethers with one (at the α carbon) or two methyl groups, respectively. The corresponding stabilization energies when the ethylthio group is in the *trans* position in corresponding vinyl sulfides are about 16 kJ mol^{-1} and 5 kJ mol^{-1}. The result that the stabilization is smaller when two methyl groups are attached to the double bond is explained on the basis that the ethylthio group in these molecules has to adopt an energetically unfavourable *gauche* conformation.

The stabilization caused by various groups attached to a double bond has been widely studied, e.g. a methyl group has been reported to stabilize the olefinic double bond by 11.0–12.5 kJ mol^{-1}.[1–4] In vinyl ethers, as well as in vinyl sulfides, the double bond is not an "ordinary" double bond, since the lone-pair electrons of the oxygen or sulfur atom conjugate with the π orbital of the double bond (resonance structures **A** and **B**). Thus, the stabilization caused by various groups in vinyl sulfides and vinyl ethers may differ from the corresponding stabilization in ordinary olefins.

In this paper, the stabilization caused by alkyl and alkylthio groups attached to the β carbon of vinyl sulfides and vinyl ethers has been evaluated using the $\Delta G^{\ominus}$ and $\Delta H^{\ominus}$ values for the isomerization reactions of isomer pairs of some vinyl sulfides and vinyl ethers (Tables 1 and 2). The equilibration experiments were performed in tet-

rahydrofuran solution with *p*-toluenesulfonic acid as catalyst in the temperature range 276–424 K.

$$CH_2=CH-X-R \leftrightarrow \overset{-}{CH_2}-CH=\overset{+}{X}-R$$

$$\text{A} \qquad\qquad \text{B}$$
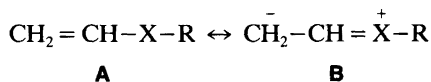
Results and discussion

The stabilization energies caused by various structural factors can be evaluated by combining the $\Delta H^{\ominus}$ or $\Delta G^{\ominus}$ values for different reactions. The reliability of this method can be tested with the aid of the reactions in eqns. (1)–(3) and the $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values involved. The same changes as those that take place in either reaction (2) or (3) are also involved in reaction (1). The $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values for these reactions are summarized in Table 1. In comparing $\Delta H^{\ominus}$ values, it must be taken into account that there is steric strain in the **b** isomer of eqn. (1), caused by the presence of three methyl groups. This is assumed to be as large as the steric strain in 2-methyl-2-butene,

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Table 1. Values of the thermodynamic functions $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the reactions in eqns. (1)–(3). The values refer to THF solution. The errors are twice the standard errors.

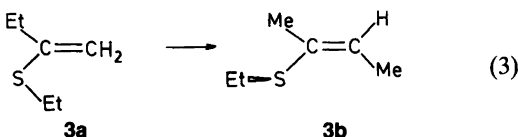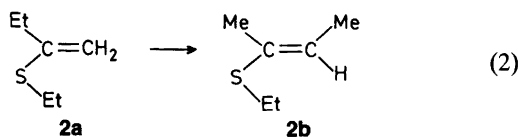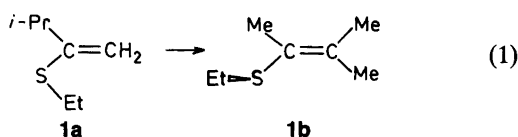| Eqn.	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J mol^{-1} K^{-1}
(1)	−7.1 (8)	7.5 (23)
(2)	−3.9 (1)	5.4 (3)
(3)	−5.4 (2)	2.3 (6)

Table 2. Values of the thermodynamic function $\Delta H^{\ominus}$ for the reactions in eqn. (4). The values for the first two reactions refer to the gas phase and for the last reaction to the THF solution. The errors are twice the standard errors.
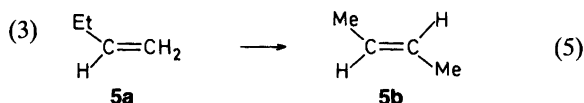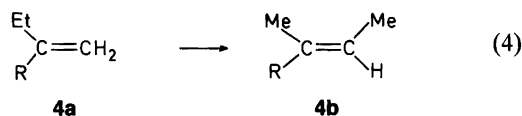
R	$\Delta H^{\ominus}$/kJ mol^{-1}	Ref.
H	−7.4 (1)	4
EtO	0.6 (4)	6
EtS	−3.9 (1)	

viz. 7.7 kJ mol^{-1}, which is the difference between the experimental and calculated (neglecting the effects of steric factors) values for the standard enthalpy of formation of 2-methyl-2-butene.[5] In the **b** isomer of eqn. (2), the two methyl groups *cis* to each other also cause steric strain (4.4 kJ mol^{-1}, which is $\Delta H^{\ominus}$ for the reaction (*E*)-2-butene → (*Z*)-2-butene).[4] Thus, the two $\Delta H^{\ominus}$ values to be compared are:

$$\Delta H_1^{\ominus} = (-7.1 - 7.7) \text{ kJ mol}^{-1} = -14.8 \text{ kJ mol}^{-1}$$

$$\Delta H_2^{\ominus} = (-3.9 - 5.4 - 4.4) \text{ kJ mol}^{-1} = -13.7 \text{ kJ mol}^{-1}.$$

The difference between these two values is 1.1 kJ mol^{-1}, whereas the possible experimental error is about 2.7 kJ mol^{-1}.[4] The $\Delta S^{\ominus}$ values to be compared are:

$$\Delta S_1^{\ominus} = 7.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_2^{\ominus} = (5.4 + 2.3) \text{ J K}^{-1} \text{ mol}^{-1} = 7.7 \text{ J K}^{-1} \text{ mol}^{-1}.$$

These values differ by only 0.2 J K^{-1} mol^{-1}, while the possible experimental error is $(2.3 + 0.3 + 0.6)$ J K^{-1} mol^{-1} = 3.2 J K^{-1} mol^{-1}. This suggests that the combination method is reliable.

With the aid of the $\Delta H^{\ominus}$ values for the reactions in eqns. (4) and (5), the stabilizing effect of a single methyl group attached to the β carbon of the double bond of an α,β-dimethyl-substituted vinyl sulfide can be evaluated. According to Table 2, $\Delta H^{\ominus}$ for the reaction in eqn. (4) is 3.5 kJ mol^{-1} more negative in the case where R = H than in the case where R = EtS, which means that the stabilizing effect of a single methyl group attached to the β carbon of vinyl sulfide is 3.5 kJ mol^{-1} smaller than the stabilizing effect in corresponding olefins. In eqn. (5), a methyl group is introduced to an olefinic double bond. The $\Delta H^{\ominus}$ for this reaction is (-11.8 ± 1.0) kJ mol^{-1},[4] and since there are no steric repulsions affecting either isomer in this reaction, the stabilization due to the methyl group attached to an olefinic double bond is 11.8 kJ mol^{-1}. Thus, the β methyl

group *trans* to the EtS group in an α,β-dimethyl-substituted vinyl sulfide stabilizes the double bond by $(11.8 - 3.5)$ kJ mol^{-1} = 8.3 kJ mol^{-1} (relative to the stabilization caused by a hydrogen atom).

The corresponding stabilization due to a methyl group in a vinyl ether molecule, evaluated by the same method, is $(11.8 - 7.4 - 0.6)$ kJ mol^{-1} = 3.8 kJ mol^{-1}, which is considerably smaller than in olefins or vinyl sulfides.

The stabilizing effect of a second methyl group on the β carbon of an α,β-dialkyl-substituted vinyl sulfide can be evaluated with the aid of the $\Delta H^{\ominus}$ values for the reactions in eqns. (1) and (3), for which $\Delta H^{\ominus}$ = (-7.1 ± 0.8) kJ mol^{-1} and (-5.4 ± 0.2) kJ mol^{-1}, respectively. In these reactions, isomer **a** can adopt the planar *s-cis* conformation (Fig. 1), whereas in the **b** isomer the EtS group must turn out of the C=C−S plane to avoid steric strain (*gauche* conformation in Fig. 1). Thus, in both reactions there is a similar change in the spatial orientation of the ethylthio group, and the effects of these rotations cancel each other when one $\Delta H^{\ominus}$ value is subtracted from the other. Moreover, in **1b** there is a second methyl group on the β carbon of a vinyl sulfide. The three methyl groups in **1b** cause steric strain, the magnitude of which is 7.7 kJ mol^{-1}, as explained earlier in this paper. The effect of the methyl group is thus $(-7.1 + 5.4 - 7.7)$ kJ mol^{-1} = -9.4 kJ mol^{-1}, i.e. the stabilization when the second methyl group is in the *trans* position on the β carbon of an α,β-dimethyl-substituted vinyl sulfide is 9.4 kJ mol^{-1} (relative to the stabilization caused by a hydrogen atom). The stabilization due to the second methyl group in the *trans* position on the β carbon of an α,β-dimethyl-substituted vinyl ether, calculated by the same method as in the case of vinyl sulfides, is $(-8.8 - 9.1 - 7.7)$ kJ mol^{-1} = 8.0 kJ mol^{-1} (the $\Delta H^{\ominus}$ values are taken from Refs. 6 and 7). Approximately the same value for this stabilization (8.3 kJ mol^{-1}) has been reported previously, although the route of evaluation was different.[8]
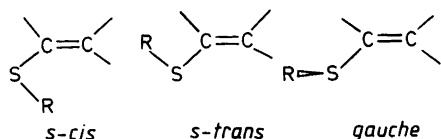

*s-cis*   *s-trans*   *gauche*

*Fig. 1.* The possible conformations of vinyl sulfides.

Thus, a single β methyl group *trans* to the alkoxy group of a vinyl ether stabilizes the double bond by 8 kJ mol^{-1} less than in ordinary olefins, whereas the stabilization caused by the second methyl group is only 3.5 kJ mol^{-1} smaller than in the olefins. The explanation for this is evidently as follows: when a single methyl group is attached to the β carbon of a vinyl ether (*trans* to the alkoxy group), the electron repelling inductive effect of the methyl group opposes the electron delocalization (resonance) in the molecule and thus the stabilization due to the introduction of the methyl group is smaller than in olefins. When the second methyl group is attached to the β carbon, the alkoxy group is predominantly in the *gauche* conformation, since the α alkyl substituent and the β alkyl substituent *cis* to the alkoxy group render the planar *s-cis* and *s-trans* conformations energetically highly unfavourable. The resonance is thus considerably decreased and the double bond behaves more like an ordinary olefinic double bond.

In vinyl sulfides, the first methyl group stabilizes the double bond by about 3.5 kJ mol^{-1} less, and the second methyl group about 2.5 kJ mol^{-1} less than in ordinary olefins. Thus, the same tendency as in vinyl ethers can be seen in vinyl sulfides, although weaker, and the same explanation is evidently valid. This means that the stabilization caused by a methyl group attached to the β carbon of a vinyl sulfide is about 8.3 kJ mol^{-1} in cases where the lone-pair electrons of the sulfur atom conjugate with the π orbital of the double bond, and about 9.4 kJ mol^{-1} in cases where this conjugation is hindered.

In **6b**, a β ethylthio group is *trans* to the alkoxy group of a vinyl ether. The $\Delta H^{\ominus}$ for reaction (6) is (-9.6 ± 0.3) kJ mol^{-1}. When the Me···S *cis* interaction in the **b** isomer $[(-1.8 \pm 0.1)$ kJ mol$^{-1}]$[9] is taken into account, the effect of the ethylthio group is $(-9.6 + 1.8)$ kJ mol^{-1} = -7.8 kJ mol^{-1}. The possible experimental error is $(0.3 + 0.1)$ kJ mol^{-1} = 0.4 kJ mol^{-1}. In other words, an ethylthio group attached to the β carbon of a vinyl ether (*trans* to the alkoxy group) stabilizes the double bond by about 8 kJ mol^{-1} relative to the stabilization caused by a hydrogen atom. The stabilization caused by a single methyl group attached at the same position is, as mentioned earlier in this paper, only 3.8 kJ mol^{-1}, and a methoxy group destabilizes the double bond of a vinyl ether by 4 kJ mol^{-1}.[10]
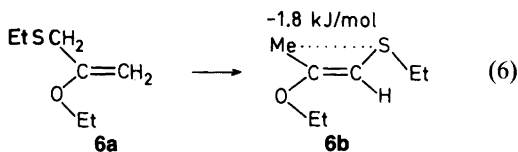
$$\text{EtSCH}_2\text{—C(OEt)}=\text{CH}_2 \quad\longrightarrow\quad \overset{-1.8\text{ kJ/mol}}{\text{Me}\cdots\cdots\text{S}} \qquad (6)$$

6a → **6b**

The stabilization caused by an ethylthio group on the β carbon of an α,β-dialkyl-substituted vinyl ether can be evaluated using the $\Delta G^{\ominus}$ values for the reactions in eqns. (7) and (8). The $\Delta G^{\ominus}$ (1,373 K) for the former reaction is (-2.1 ± 0.5) kJ mol^{-1}, where the error has been calculated from the error in K. In this case, the effect of the ethylthio group must be evaluated using the $\Delta G^{\ominus}$ for the reaction because the temperature dependence of K could not be measured accurately enough to obtain a reliable $\Delta H^{\ominus}$ value. In **7b** as well as in **8b**, a β methyl group is *cis* to the ethoxy group of a vinyl ether, so that the ethoxy group is forced to rotate out of the C=C−O plane in the reactions of eqns. (7) and (8). When the $\Delta G^{\ominus}$ values for these two reactions are compared, the energies required for these rotations cancel one another. Moreover, in **7b** there is a Me···S *cis* interaction and a Me···S *geminal* interaction, the magnitude of which is unknown. Since it is $\Delta G^{\ominus}$ that is under consideration, the asymmetric carbon atom of **7a** must be taken into account. Also, the EtS group in **7b** is in the *gauche* conformation, which makes this isomer statistically favoured by a factor of 2; however, the effects of these two factors on $\Delta G^{\ominus}$ outweigh each other. The internal symmetry number of isomer **7b** is three times as large as for isomer **7a** and the EtO group is in the *gauche* conformation; however, the same factors apply in **8b**, so that
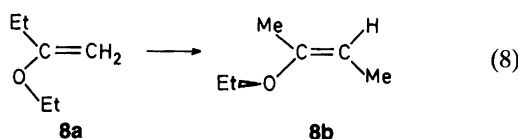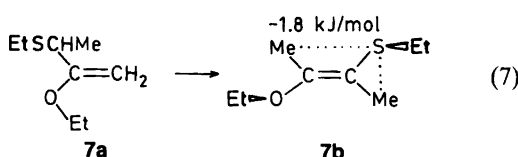
their effects outweigh each other when the $\Delta G^{\ominus}$ values for the two reactions are compared. The effect caused by the ethylthio group is thus $(-2.1 + 1.8 - 4.5)$ kJ mol^{-1} = -4.8 kJ mol^{-1} [$\Delta G^{\ominus}$(1,298 K) for the reaction in eqn. (8) is 4.5 kJ mol^{-1}].[6] Thus, the stabilization caused by an ethylthio group on the β carbon of an α,β-dimethyl-substituted vinyl ether is about 5 kJ mol^{-1}. The error of this approximation cannot be estimated, since $\Delta G^{\ominus}$ values have been used instead of $\Delta H^{\ominus}$ values. The stabilization in this case is, however, smaller than in **6b**. This is probably due to the fact that the ethylthio group is forced into a non-planar conformation in **7b**.

With the aid of the data of eqn. (9), the stabilization effect of an ethylthio group on the β carbon of a vinyl sulfide can be evaluated. The $\Delta H^{\ominus}$ for this reaction is (-17.7 ± 2.0) kJ mol^{-1} (the error is twice the standard error). When the Me···S *cis* interaction in **9b** is taken into account, the effect of the ethylthio group is $(-17.7 + 1.8)$ kJ mol^{-1} = -15.9 kJ mol^{-1}, i.e. the stabilization caused by an ethylthio group in the *trans* position on the β carbon of an α-methyl-substituted vinyl sulfide is about 16 kJ mol^{-1} (relative to the stabilization caused by a hydrogen atom). The possible experimental error is $(2.0 + 0.1)$ kJ mol^{-1} = 2.1 kJ mol^{-1}.

The corresponding stabilization in an α,β-dimethyl-substituted vinyl sulfide can be evaluated with the aid of the data for eqns. (3) and (10). The $\Delta G^{\ominus}$(1,301 K) for the former reaction is (-12.7 ± 0.3) kJ mol^{-1} (the error has been calculated from the error in K) and the $\Delta G^{\ominus}$(1,298 K) for the latter reaction is (-6.1 ± 0.1) kJ mol^{-1} (the error is twice the standard error). Using the

$$\text{EtSCHMe—C(OEt)}=\text{CH}_2 \quad\longrightarrow\quad \overset{-1.8\text{ kJ/mol}}{\text{Me}\cdots\cdots\text{S—Et}} \qquad (7)$$

7a → **7b**

$$\text{Et—C(OEt)}=\text{CH}_2 \quad\longrightarrow\quad \text{Me, H / C=C / Et—O, Me} \qquad (8)$$

8a → **8b**

$$\text{EtSCH}_2\text{—C(SEt)}=\text{CH}_2 \quad\longrightarrow\quad \overset{-1.8\text{ kJ/mol}}{\text{Me}\cdots\cdots\text{S}} \qquad (9)$$

9a → **9b**

$$\text{EtSCHMe—C(SEt)}=\text{CH}_2 \quad\longrightarrow\quad \overset{-1.8\text{ kJ/mol}}{\text{Me}\cdots\cdots\text{S—Et}} \qquad (10)$$
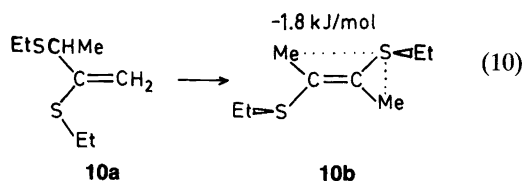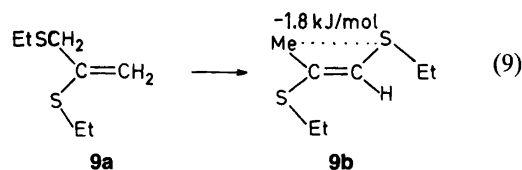
10a → **10b**

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Table 3. Chemical shifts (ppm from TMS) in the ^{1}H NMR spectra recorded (coupling constants in Hz).

Compound	Isom.	No.	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	δ(f)	J(ab)	J(cd)	J(ef)
CH₃CH₂SCH=C(CH₃)OCH₂CH₃	E	6b	1.27	2.42	4.79	1.94	3.70	1.20	7.2	0.3	6.9
a b c d e f	Z		1.25	2.50	4.73	1.83	3.86	1.25	7.2	1.0	
CH₃CH₂SC(CH₃)=C(CH₃)OCH₂CH₃	E	7b	1.16	2.51	1.84	2.05	3.74	1.22	7.2	1.5	7.1
a b c d e f	Z		1.30	2.45	1.52	2.17	3.70	1.21	~7	~0	~7
CH₃CH₂SCH=C(CH₃)SCH₂CH₃	E	9b	1.23 (1.28)	2.62	5.79	1.90	2.62	1.28 (1.23)	7.2	0.8	7.2
a b c d e f	Z		1.23 (1.28)	2.61 (2.68)	5.86	2.00	2.68 (2.61)	1.28 (1.23)	7.2	1.2	~7
CH₃CH₂SC(CH₃)=C(CH₃)SCH₂CH₃	E	10b	1.20	2.64	2.13				7.2		
a b c c b a											

same procedure as for eqns. (7) and (8), the effect of the ethylthio group can be estimated to be $(-12.7 + 1.8 + 6.1)$ kJ mol^{-1} $= -4.8$ kJ mol^{-1}. Thus, the ethylthio group on the β carbon of an α,β-dimethyl-substituted vinyl sulfide stabilizes the double bond by about 5 kJ mol^{-1}, i.e. about 11 kJ mol^{-1} less than in the α-methyl-substituted vinyl sulfide. In the reaction of eqn. (10) [as well as in that of eqn. (7)] the ethylthio group is forced into the non-planar conformation, which is probably the reason for the small stabilization.

Experimental

Materials. 2-(Ethylthio)-3-methyl-2-butene (**1b**) and 2-(ethylthio)-2-butenes (*E* isom. **2b** and *Z* isom. **3b**) were prepared by the method described in Ref. 9.

2-Ethoxy-3-(ethylthio)-2-butenes (*E* isom. **7b**). Sodium ethanethiolate was prepared from absolute ethanol, sodium and ethanethiol.[11] 3-Chloro-2-butanone was then added slowly to the solution, forming 3-(ethylthio)-2-butanone (b.p. 340–341 K at 2.7 kPa), yield 47%.[12] 2-Ethoxy-3-(ethylthio)-2-butenes were prepared from 3-(ethylthio)-2-butanone by the method of House and Kramar.[13] The product was obtained in 12% yield; b.p. 341–344 K at 1.3 kPa.

2-Ethoxy-1-(ethylthio)propenes (*E* isom. **6b**) were prepared starting from chloroacetone by the method used to prepare 2-ethoxy-3-(ethylthio)-2-butenes. The yield was 61%; b.p. 333–334 K at 1.2 kPa, lit. b.p. 345–347 K at 1.5 kPa.[14]

Bis(ethylthio)alkenes were prepared by the same

Table 4. Chemical shifts (ppm from TMS) in the ^{13}C NMR spectra recorded.

Compound	Isom.	No.	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	δ(f)	δ(g)	δ(h)
CH₃CH₂SCH=C(CH₃)OCH₂CH₃	E	6b	14.64	29.73	89.10	160.81	17.79	62.62	14.62	
a b c d e f g										
CH₃CH₂SC(CH₃)=C(CH₃)OCH₂CH₃	E	7b	15.11 (14.78) (16.73)	26.31	109.07	14.78 (15.11) (16.73)	153.99	16.73 (15.11) (14.78)	63.92	15.11 (16.73) (14.78)
a b c d e f g h	Z				104.00		163.00			
CH₃CH₂SCH=C(CH₃)SCH₂CH₃	E	9b	15.51	28.34	121.34	129.46	19.49	25.83	14.21	
a b c d e f g	Z		15.43 (15.11)	28.10	124.10	128.56	23.23 (25.26)	25.26 (23.23)	15.11 (15.43)	
CH₃CH₂SC(CH₃)=C(CH₃)SCH₂CH₃	E	10b	15.19	26.40	129.30	20.79				
a b c d c d b a										

Table 5. Equilibrium constants for the reactions in eqns. (1)–(3), (6), (7), (9) and (10).

T/K	K(1b/1a)	K(2b/2a)	K(3b/3a)	K(6b/6a)	K(7b/7a)	K(9b/9a)	K(10b/10a)
424						65	
403	21.2	6.25	6.61	12.1		92	
373	23.1	6.82	7.41	14.9	2.0±0.3[a]	128	
333				22.0		266	
323	33.8	8.36	9.81				
301							160±20[a]
299	42.9	9.38	11.53				
298				32.9			
276	55.2						

[a] Error estimated from the equilibration results.

method as described in Ref. 9 for α-alkyl-substituted vinyl sulfides, starting from an appropriate ketone. The starting materials were 3-(ethylthio)-2-butanone, 1-(ethylthio)-2-propanone, triethyl orthoformate and ethanethiol. The products were 2,3-bis(ethylthio)-2-butenes (*E* isom. **10b**) (yield 34 %; b.p. 380–282 K at 1.3 kPa, lit. b.p. 392–394 K at 2.7 kPa)[15] and 1,2-bis-(ethylthio)propenes (*E* isom. **9b**) (yield 65 %; 362–366 K at 1.2 kPa, lit. b.p. 361–370 K at 1.2 kPa).[16]

NMR spectra. The ¹H NMR spectra were recorded on a 60 MHz spectrometer in 10–20 % CCl_4 solution with TMS as internal standard. The ¹³C NMR spectra were recorded on a 15 MHz spectrometer in 10–20 % $CDCl_3$ solution with TMS as internal standard. The ¹H and ¹³C spectra of 2-(ethylthio)-3-methyl-2-butene and 2-(ethylthio)-2-butenes are reported in Ref. 9, and the ¹H spectra of other prepared compounds are summarized in Table 3 and their ¹³C spectra in Table 4.

Configurational assignments. The basis for the identification of the geometric isomers of 2-(ethylthio)-2-butene is explained in Ref. 9. The *E* and *Z* isomers of 2-ethoxy-1-(ethylthio)propene were identified on the basis of their relative stability. Taskinen has reported that the more stable isomer of 3-methoxy-4-methyl-2-pentene has the *E* configuration because the alkoxy group in this isomer can adopt an energetically favoured planar conformation.[17] Thus, the more stable isomer of 2-ethyoxy-1-(ethylthio)propene should also have the *E* configuration. Further support for the

above conclusions was provided by the order of elution of the isomers in the gas chromatograph column with XE-60 as stationary phase. It was found that all the bis(ethylthio)alkenes and ethoxy(ethylthio)alkenes which could be identified with certainty were eluted in the order *E* isomer before *Z* isomer. The geometric isomers of 2-ethoxy-3-(ethylthio)-2-butene and 2,3-bis-(ethylthio)-2-butene were identified solely on this basis.

Experimental conditions in the equilibration experiments are described in Ref. 9. The values of the equilibrium constant *K* for the reactions studied are given in Table 5.

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