Stereoselective Formation of Allylic Sulfides *via* Two Sequential [3,3]-Sigmatropic Rearrangements of Allylic Xanthates and Its Mechanistic Aspects

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O-(2-Alkenyl) S-alkyl dithiocarbonates (allylic xanthates) were pyrolyzed to give 2-alkenyl alkyl sulfides (allylic sulfides) *via* the corresponding allylically isomeric S-(2-alkenyl) S-alkyl dithiocarbonates. The reaction follows the first-order rate law with relatively low sensitivity to the ionizing power of the medium and sizeably negative entropies of activation. When a mixture of two dithiol esters having different S-(2-alkenyl) groups and different S-alkyl groups was pyrolyzed, a "cross product" was not observed. The reaction was found to be facilitated by the presence of phenolic compounds or Lewis acids.

Based on these findings together with modified neglect of diatomic overlap (MNDO) calculation data, the mechanism for the formation reaction of 2-alkenyl alkyl sulfides is discussed.

Keywords *O*-(2-alkenyl) *S*-alkyl dithiocarbonate; *S*-(2-alkenyl) *S*-alkyl dithiocarbonate; [3,3]-sigmatropy; pyrolysis; allylic sulfide; mechanism; kinetics; MNDO

Allylic sulfides (2-alkenyl or 2-cycloalkenyl alkyl sulfides) and their oxidation products, *i.e.*, sulfoxides or sulfones play an important role in organic reactions, in particular carbon skeletal construction,[1] because of the diversity of their chemical reactions. An important reaction of allylic sulfides and their oxidation products involves removal of the allylic hydrogen(s) by bases such as lithium diisopropylamide (LDA) followed by a carbon–carbon bond formation reaction.

In this connection, we have recently communicated a new and simple synthetic method of allylic sulfides.[2] The reaction involves two-step pericyclic reactions of *O*-(2-alkenyl or 2-cycloalkenyl) *S*-alkyl dithiocarbonates (I), which are commonly referred to as "allylic xanthates"; allylic xanthates undergo [3,3]-sigmatropic rearrangement[3a-c] to give allylically isomerized *S*-(2-alkenyl or 2-cycloalkenyl) *S*-alkyl dithiocarbonates (II, allylic dithiolcarbonates) which decompose, on prolonged heating or on heating under more severe reaction conditions, into the allylically rearranged sulfides (III) with extrusion of carbon oxysulfide (COS) (Chart 1).

We now discuss the reaction in detail with newly obtained data in order to clarify the overall character of the reaction.

Results and Discussion

O-(2-Alkenyl) *S*-alkyl dithiocarbonates (I) were prepared according to the previously reported method.[3b,c] Distillation of the products (I) under reduced pressure gave the [3,3]-sigmatropic rearrangement products (II) and heating these dithiol esters (II) without solvent at 170—230 °C gave the corresponding 2-alkenyl alkyl sulfides (III). Practically, distillation of the crude xanthates at atmospheric pressure or at moderately reduced pressure led to the doubly rearranged products (III) with extrusion of carbon oxysulfide (COS). The reaction conditions and yields are summarized in Table I.

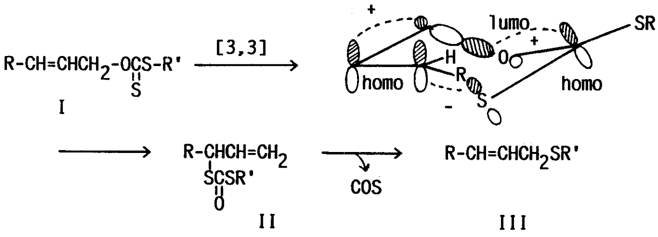


Chart 1

Inspection of the proton nuclear magnetic resonance (^{1}H-NMR) spectra of the products showed the absence of allylically isomeric sulfides. This indicates that the reaction proceeds with high regioselectivity giving rise only to the allylic isomer.

As the reaction involves an allylic shift, two geometrically isomeric products (*cis* and *trans* isomers) are possible in the pyrolysis of α-substituted allyl derivatives (Chart 2). The presence of a bulky substituent such as a phenyl group in the molecule has a marked effect on the product distribution. For example, *S*-(1-methylallyl) *S*-methyl dithiocarbonate (IId) gave a mixture of the *cis* and *trans* sulfides (IIId) in a nearly 1 : 1 ratio. In contrast, *S*-(1-methylallyl) *S*-

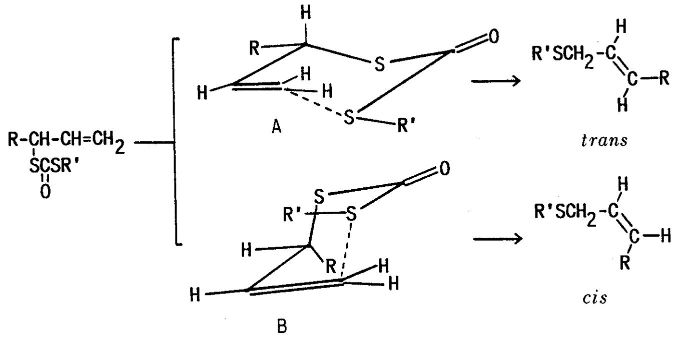


Chart 2

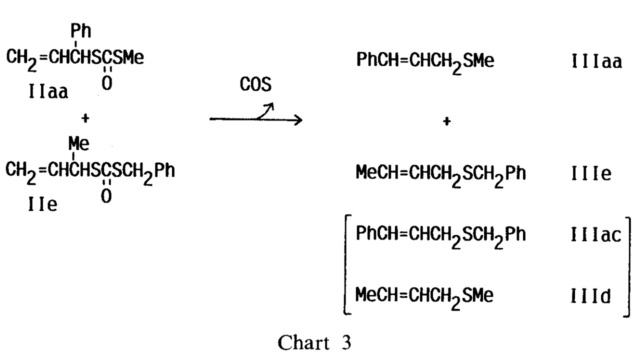
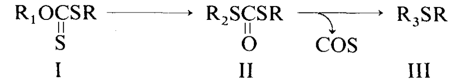
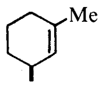
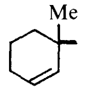
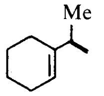
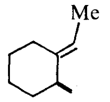
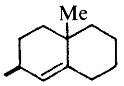
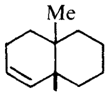


Chart 3

TABLE I. Allylic Sulfides (III) Formed from Pyrolysis of the Corresponding Xanthates (I) *via* the Dithiolcarbonates (II)



$$\underset{\text{I}}{R_1O\underset{\underset{S}{\|}}{C}SR} \longrightarrow \underset{\text{II}}{R_2S\underset{\underset{O}{\|}}{C}SR} \xrightarrow[COS]{} \underset{\text{III}}{R_3SR}$$

Compd. No.	I R₁	I R	II R₂	III R₃	Reaction temp. (°C)	Yield (%)
aa	$PhCH=CHCH_2-$	Me–	$CH_2=CH\underset{\vert}{C}HPh$	R_1	200	85
ab	$PhCH=CHCH_2-$	Et–	$CH_2=CH\underset{\vert}{C}HPh$	R_1	200	56
ac	$PhCH=CHCH_2-$	$PhCH_2-$	$CH_2=CH\underset{\vert}{C}HPh$	R_1	200	71
ad	$PhCH=CHCH_2-$	Ph_2CH-	$CH_2=CH\underset{\vert}{C}HPh$	R_1	200	69
ae	$PhCH=CHCH_2-$	$MeOCOCH_2-$	$CH_2=CH\underset{\vert}{C}HPh$	R_1	200	49
ag	$PhCH=CHCH_2-$	*p*-$BrC_6H_4CH_2-$	$CH_2=CH\underset{\vert}{C}HPh$	R_1	200	58
b	$CH_2=C(Me)CH_2-$	Me–	R_1	R_1	200	0
c	$CH_2=C(Me)CH_2-$	$PhCH_2-$	R_1	R_1	200	60
d	$MeCH=CHCH_2-$	Me–	$CH_2=CH\underset{\vert}{C}HMe$	R_1[a]	210	52
e	$MeCH=CHCH_2-$	$PhCH_2-$	$CH_2=CH\underset{\vert}{C}HMe$	R_1	200	75
f	$PhCH=CH\underset{\vert}{C}HMe$	Me–	$MeCH=CH\underset{\vert}{C}HPh$	R_1	RT[b]	67[c]
g		Me–		R_1	190	81
h		Me–		R_1	180	74
i		Me–		R_1[d]	RT[b]	45[c]

a) A mixture of the *trans* and *cis* isomers. *b*) Purified by silica gel chromatography. *c*) Calculated based on I. *d*) A mixture of the 2α- and 2β-isomers.

benzyl dithiocarbonate (IIe) gave the *trans* sulfide (IIIe) exclusively. In the case of *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (IIaa), only the *trans* sulfide (IIIaa) was produced. These facts indicate that steric factors play a leading role in determining the geometry of the products.

In order to clarify whether the reaction is intermolecular or intramolecular, a crossover reaction was carried out. An equimolar mixture of *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (IIaa) and *S*-(1-methylallyl) *S*-benzyl dithiocarbonate (IIe) was pyrolyzed without solvent and the reaction mixture was analyzed by gas chromatography (GC). The chromatogram showed the absence of a "cross product" such as benzyl cinnamyl sulfide (IIIac) or crotyl methyl sulfide (IIId), suggesting that the pyrolytic rearrangement is intramolecular.

The pyrolysis of *S*-(2-alkenyl) *S*-alkyl dithiocarbonates (II) was investigated kinetically. The rates were determined by measuring the amount of the evolved COS gas by volumetry (method A) or by weighing the decrease of II (method B). It was found that the pyrolysis followed first-order kinetics. The first-order rate constants are listed in Table II. The energies and entropies of activation were calculated from these data. The results are summarized in Tables IIIa and IIIb.

The decomposition rate is plotted against the Hammett σ- and Taft σ*-values of -SR substituents. As can be seen in Fig. 1, the conversion rate of II to III was weakly affected by the change of -SR. An electron-attracting substituent accelerates the reaction. The value of the Hammett equation can be divided into an inductive (σ*) and a resonance component ($\sigma_{\text{res.}}$). The correlation for Hammett σ-values gave an approximately straight line in comparison with the one for Taft σ*-values. This indicates that the rate of reaction depends not only on the inductive but also on the resonance effect. The weak response to change of the *S*-alkyl group is presumably due to a combination of inductive and bond-weakening effects which nearly cancel: an inductive electron-attracting effect may assist the ionization of the CO–SR bond but simultaneously may diminish the electron density on the sulfur atom of the *S*-alkyl group.

TABLE II. Rate Constants for Pyrolyses of *S*-Alkyl *S*-(1-Phenylallyl) Dithiocarbonates (IIaa—ah)

Alkyl	$k \times 10^5$[a]	σ*[b]	σ[c]
Et– (IIab)	4.72	−0.10	
Me– (IIaa)	8.79	0.00	
$PhCH_2-$ (IIac)	10.08	0.215	0.00
Ph_2CH- (IIad)	11.75	0.405	
$MeOCOCH_2-$ (IIae)	21.32	1.05	
p-$MeOC_6H_4CH_2-$ (IIaf)	7.40		−0.11
p-$BrC_6H_4CH_2-$ (IIag)	14.03		0.27
p-$NO_2C_6H_4CH_2-$ (IIah)	23.34		0.78

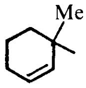
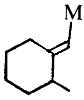
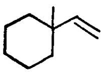
a) Values at 150 °C, s^{-1}. *b*) Taft's values. *c*) Hammett's values.

TABLE IIIa. Activation Parameters for Pyrolysis of IIaa

	Temp. (°C)	$k \times 10^4$	E_a (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
Method A[a)]	190	53.4		
	200	110	21.9	−24
	210	164		
	220	232		
Method B[a)]	120	0.118		
	150	0.749	22.1	−28
	170	2.949		

a) The rates were determined by measuring the amount of the evolved COS gas by volumetry (method A) or by weighing the decrease of IIaa (method B).

TABLE IIIb. Activation Parameters for Pyrolyses of *S*-(2-Cycloalkenyl) *S*-Methyl Dithiocarbonates

Substrate	(II)	E_a (kcal/mol)[a)]	$\Delta S^{\neq}$ (e.u.)[a)]
	(IIg)	24.8	−17
	(IIi)	25.5	−21
	(IIj)	27.2	−18

a) Measured by method B.

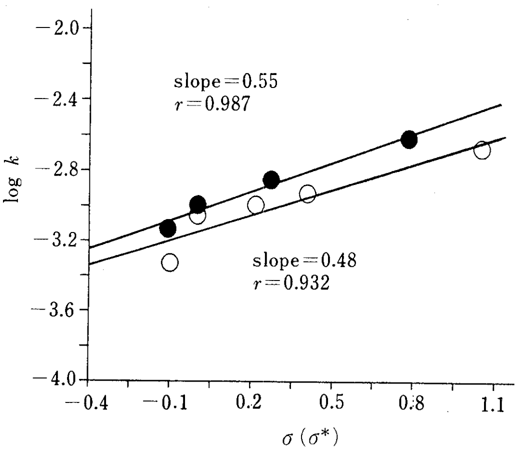
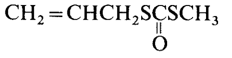
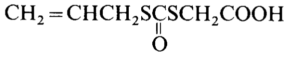
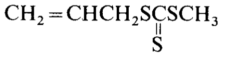


Fig. 1. Plots of log*k* *vs.* σ- and σ*-Values for Pyrolysis of IIaa—ah
●, plots *vs.* Hammett's values (σ); ○, plots *vs.* Taft's values (σ*).

The net charges (NC) of model compounds calculated by modified neglect of diatomic overlap (MNDO)[4)] method support this assumption, indicating that the concentration of negative charge (NC = −0.015) of the sulfur atom of the carboxymethylthio group in *S*-allyl *S*-carboxymethyl dithiocarbonate ($CH_2=CHCH_2SCOSCH_2COOH$) is lower than that (NC = −0.070) in *S*-allyl *S*-methyl dithiocarbonate ($CH_2=CHCH_2SCOSCH_3$) (see Table IV).

On the other hand, the effect of the *S*-(2-alkenyl) group is highly modified by the α-carbon being primary or secondary. *S*-Allyl *S*-benzyl dithiocarbonate or *S*-cinnamyl *S*-methyl dithiocarbonate[3c)] hardly decomposed under the pyrolytic condition used for *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (IIaa). In contrast, *S*-(2-cycloalkenyl) *S*-methyl dithiocarbonates split off COS during chromatography on silica gel to afford the sulfides.

TABLE IV. MNDO Calculation Data for *S*-Allyl *S*-Methyl and *S*-Carboxymethyl Dithiocarbonates and Allyl Methyl Trithiocarbonates

Compound	Bond length, Å (Bond order) $X=\underset{\vert}{C}-SR$	Net charge (NC) $>C=X$	Net charge (NC) $-S-R$
 $CH_2=CHCH_2S\underset{\underset{O}{\Vert}}{C}SCH_3$	1.712 (0.932)	0.199	−0.070
 $CH_2=CHCH_2S\underset{\underset{O}{\Vert}}{C}SCH_2COOH$	1.715 (0.929)	0.192	−0.015
 $CH_2=CHCH_2S\underset{\underset{S}{\Vert}}{C}SCH_3$	1.687 (1.049)	−0.027	−0.005

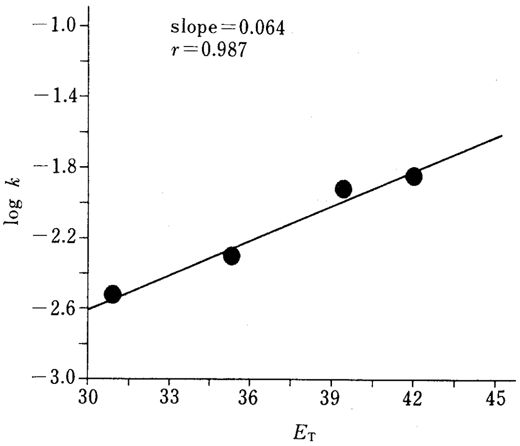


Fig. 2. Plots of log*k* *vs.* E_T Values for Thermolysis of IIaa

TABLE V. Rate Constants for Pyrolysis of IIaa in Several Solvents at 200 °C[a)]

Solvent	E_T (kcal/mol)	$k \times 10^4$
n-Hexadecane	30.9	30.2
Diphenyl ether	35.3	50.1
Quinoline	39.4	120.2
Nitrobenzene	42.0	141.3

a) IIaa (5×10^{-4} mol) was dissolved in 0.5 ml of the solvent.

Next, the solvent effects on the rate of the pyrolytic reaction were studied. The rate of reaction was found to depend slightly on the ionizing power of the solvent, increasing when the solvent was changed from nonpolar (*e.g.* *n*-hexadecane) to polar (*e.g.* nitrobenzene). The correlation of the rates with E_T values[5)] of Reichardt based on the solvatochromism of pyridinium *N*-phenol betaines is depicted in Fig. 2. The sensitivity parameter,[3b,6)] *a* (slope of the least-squares line) lies within the range reported for typical concerted [3,3]-sigmatropic reactions,[3c,5b,6)] indicating that the reaction may proceed *via* a mechanism which involves very little change in charge separation between the ground state and the transition state.

The mechanism for the pyrolytic conversion of II to III is formally similar to that for the decomposition reactions of allylic chlorosulfinates, which are intermediates in the conversion of allylic alcohols to the chlorides by reaction with thionyl chloride (S_Ni' type reaction).[7] The decomposition of allylic chloroformates[8] should resemble that of allylic chlorosulfinates in which the rate of the reaction is very sensitive to solvent polarity, being about four powers of ten faster in nitrobenzene than in decane. These reactions almost certainly involve intimate ion-pair intermediates.

Taking into consideration that the present reaction is a decomposition reaction, the value of activation entropy seems to be very low and the negative $\Delta S^{\neq}$ values suggest rearrangement *via* a highly ordered transition state rather than the ground state, *e.g.*, a concerted mechanism. The activation energy of IIaa is lower than those of the other cases, suggesting the transition state of IIaa to be stabilized by resonance with the phenyl group.

Based on these considerations, it is assumed that the reaction should not proceed through an ionic intermediate but may proceed through a concerted transition state, wherein the breakage of the C–S bond is synchronous with that of the CO–SR bond. The mechanism may be represented as in Chart 4, in which sulfur attacks the γ-carbon atom of the allylic system, with a simultaneous shift of the double bond and elimination of COS.

The transition state of the present reaction may be interpreted in terms of the reactant dissection method (three-system interaction).[9] The dissection method utilizes a dissection of the reactants into σ and π fragments and a consideration of the effect of substituents on the interaction of the frontier molecular orbitals (FMO's) of the two fragments. In the present case, the allylthio moiety and lone pair on the sulfur atom are HOMO's and the S–CO bond to be cleaved is LUMO. A cyclic (HOMO, LUMO, HOMO) interaction is depicted in Fig. 3. The carbonyl group lowers the σ LUMO, whereas the alkyl substituent(s) on the allylthio moiety raises the π HOMO. Thus, in the α or γ-alkylallylic system, the FMO interaction becomes quite favorable.

On the basis of this mechanistic consideration, we carried out MNDO calculation on possible geometries (chair and boat conformations) for the transition state of *S*-allyl *S*-methyl dithiocarbonate in which the MeS···$CH_2=C$ distance is assumed to be 2.0 Å. The geometry optimizations indicate that the chair-form transition state is about 10 kcal/mol more stable than the boat-form.

Based on the calculation data, two possible chair conformations leading to the *cis* and *trans* olefinic sulfides are depicted in Chart 2. In the conformation B leading to the *cis* isomer, the interaction between the terminal vinyl group and the -SR′ or between the carbonyl group and -R is serious, whereas, in the conformation A leading to the *trans* isomer, such an interaction is insignificant, supporting the experimental result.

In connection with the S_Ni' decomposition of allylic dithiocarbonates, we also investigated the reaction behavior of allylic trithiocarbonates toward thermal treatment. The trithiocarbonates were found to be quite stable and did not undergo extrusion of carbon disulfide (CS_2). For example, when 3-methyl-2-cyclohexenyl methyl trithiocarbonate (IV) was heated at 280 °C for 1 h, the ^{1}H-

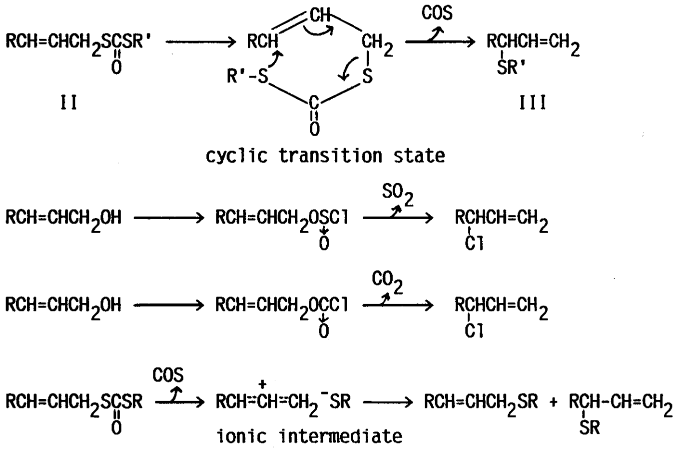


Chart 4

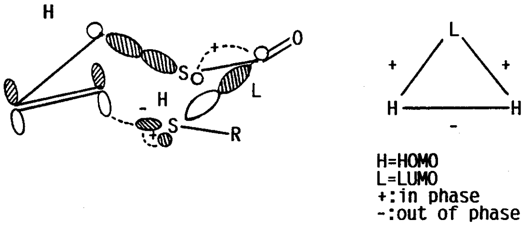
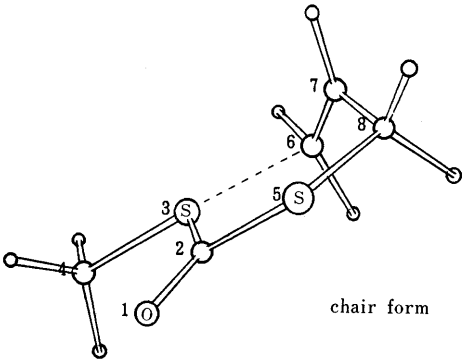
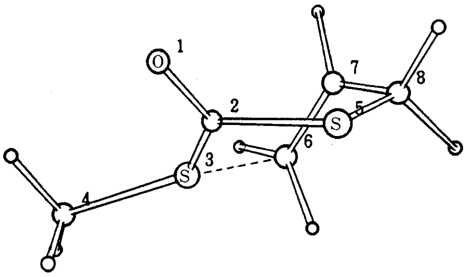


Fig. 3. Three-System Interaction in the Transition State



chair form



boat form

Fig. 4. MNDO-Optimized Structures of the Transition States for the Chair and Boat Forms

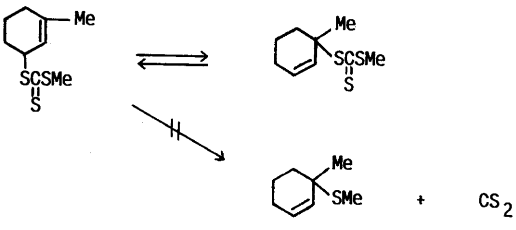


Chart 5

NMR spectrum of this sample showed two sharp singlets in the methylthio region, indicating that equilibration of the two possible isomeric allylic structures occurred rapidly at the given temperature (Chart 5). The stability of allylic trithiocarbonates may be, at least in part, due to a high degree of delocalization energy of the –S–CS–S– moiety.[10] The MNDO calculations support this assumption. The MeS–CS bond (bond order 1.049) of allyl methyl trithiocarbonate is 0.035 Å shorter than the MeS–CO bond (bond order 0.932) of *S*-allyl *S*-methyl dithiocarbonate (see Table IV).

The present reaction is particularly valuable for conversion of allylic alcohols to the corresponding sulfides without rearrangement of the carbon skeleton.[11] As far as we know, the preparative methods of allylic sulfides by replacement reactions of allylic halides usually produce isomeric sulfides with regard to the double bond and moreover offer poor yields due to side reactions on prolonged operation. In this sense, this pericyclic procedure is superior to the known methods in terms of yield and simplicity of operation. The procedure developed here can be carried out in a single operation. It is practically important that use of phenols or Lewis acids lowers the reaction temperature by about 50—100 °C. For example, the dithiolester, IIaa, easily decomposed in the presence of *p*-chlorophenol or $AlCl_3$ on heating at 80 °C.[12] The details of the catalytic reaction will be reported in a forth-coming paper.

Experimental

The infrared (IR) spectra were taken with a Hitachi 270-30 spectrophotometer. The ^{1}H-NMR spectra were taken with Hitachi R-600 (60 MHz), JEOL PS-100 (100 MHz) and JEOL GX-400 (400 MHz) spectrometers using tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. High resolution mass spectra (HRMS) were taken with a JEOL JMS-DX303HF spectrometer. Gas chromatographic analyses were performed with a Yanagimoto G-80 gas chromatograph with a thermal conductivity detector using a column of 10% SE-30 on Chamelite CK (60—80 mesh 3 mm × 3 m).

Molecular orbital calculations were performed on a FACOM M-360 computer in the Computer Center of Kumamoto University. Graphic analysis of the MO calculation data and least-squares calculations were performed on Fujitsu FM-16β FDII, FM R-50LT and FM R-60HD personal computers.

***S*-(2-Alkenyl or 2-Cycloalkenyl) *S*-Methyl Dithiocarbonates (II)** *S*-(1-Phenylallyl) *S*-alkyl dithiocarbonates (Iaa—ah) were prepared according to a procedure developed in this laboratory.[3b] In the case of IIa, *O*-cinnamyl *S*-methyl dithiocarbonate (Iaa) was isolated in crystalline form. Heating Ia at 80 °C for 1 h gave IIaa quantitatively.

O-(1-Phenylallyl) *S*-ethyl (Iab), *S*-benzyl (Iac), *S*-diphenylmethyl (Iad), *S*-methoxycarbonylmethyl (Iae), *S*-(*p*-methoxybenzyl) (Iaf), *S*-(*p*-bromobenzyl) (Iag) and *S*-(*p*-nitrobenzyl) (Iah) dithiocarbonates were prepared according to the procedure used for Iaa and underwent allylic rearrangement to give the corresponding dithiol esters (IIaa—ah) during purification by column chromatography on silica gel. Yield 30—70%.

The ^{1}H-NMR spectral data for *S*-alkyl *S*-cinnamyl dithiocarbonates (IIab—ah) are as follows:

Compound IIab (R = Et) was obtained as an oil: IR (liquid film) cm^{-1}: 1650, 870 (–SCOS–), 1610 (C = C). ^{1}H-NMR ($CDCl_3$) δ: 1.28 (3H, t, J = 7.3 Hz, –SMe), 2.98 (2H, q, J = 7.3 Hz, $-SCH_2-$), 5.23 (2H, dd, J = 10.3, 16.9 Hz, $>C=CH_2$), 5.40 (1H, d, J = 7.0 Hz, >CH–Ph), 6.10 (1H, m, J = 7.0, 10.3, 16.9 Hz, $-CH=C<$), 7.31 (5H, m, Ph). HRMS, M$^+$ for $C_{12}H_{14}OS_2$ *m/z* 238.0486, Found: 238.0488.

Compound IIac ($R = CH_2Ph$) was obtained as an oil: IR (liquid film) cm^{-1}: 1640, 880 (–SCOS–), 1600 (C = C). ^{1}H-NMR ($CDCl_3$) δ: 4.19 (2H, s, $-S-CH_2-Ph$), 5.22 (2H, dd, J = 9.9, 16.9 Hz, $>C=CH_2$), 5.42 (1H, d, J = 7.0 Hz, >CH–Ph), 6.09 (1H, m, J = 7.0, 9.9, 16.9 Hz, $-CH=C<$), 7.25 (10H, m, 2Ph). HRMS, M$^+$ for $C_{17}H_{20}OS_2$ *m/z* 300.0642, Found: 300.0625.

Compound IIad ($R = CHPh_2$) was obtained as an oil: IR (liquid film) cm^{-1}: 1640, 870 (–SCOS–), 1600 (C = C). ^{1}H-NMR ($CDCl_3$) δ: 5.18 (2H, dd, J = 9.9, 16.9 Hz, $>C=CH_2$), 5.37 (1H, d, J = 7.0 Hz, >CH–Ph), 6.05 (1H, s, $-S-CHPh_2$), 6.05 (1H, m, J = 7.0, 9.9, 16.9 Hz, $-CH=C<$), 7.26 (15H, m, 2Ph). HRMS, M$^+$ for $C_{17}H_{20}OS_2$ *m/z* 300.0642, Found: 300.0625.

Compound IIae ($R = CH_2COOMe$) was obtained as an oil: IR (liquid film) cm^{-1}: 1745 (–COO–), 1645, 870 (–SCOS–), 1600 (C = C). ^{1}H-NMR ($CDCl_3$) δ: 3.73 (3H, s, –OMe), 3.76 (2H, s, $-S-CH_2-COO-$), 5.24 (2H, dd, J = 10.2, 16.9 Hz, $>C=CH_2$), 5.42 (1H, d, J = 7.0 Hz, >CH–Ph), 6.09 (1H, m, J = 7.0, 10.3, 16.9 Hz, $-CH=C<$), 7.31 (5H, m, Ph). HRMS, M$^+$ for $C_{13}H_{14}O_3S_2$ *m/z* 282.0385, Found: 282.0355.

Compound IIaf ($R = CH_2C_6H_4$-*p*-OMe) was obtained as an oil: IR (liquid film) cm^{-1}: 1640, 880 (–SCOS–), 1615 (C = C). ^{1}H-NMR ($CDCl_3$) δ: 3.78 (3H, s, –OMe), 4.17 (2H, s, $-S-CH_2-Ar$), 5.09 (2H, dd, J = 10.3, 16.9 Hz, $>C=CH_2$), 5.42 (1H, d, J = 7.0 Hz, >CH–Ph), 5.87—6.13 (1H, m, J = 7.0, 10.3, 16.9 Hz, $-CH=C<$), 6.74—6.86 (4H, d, *p*-MeO–C_6H_4–), 7.31 (5H, m, Ph). HRMS, M$^+$ for $C_{19}H_{18}O_2S_2$ *m/z* 330.0748, Found: 330.0748.

Compound IIag ($R = CH_2C_6H_4$-*p*-Br) was obtained as an oil: IR (liquid film) cm^{-1}: 1640, 890 (–SCOS–), 1600 (C = C). ^{1}H-NMR ($CDCl_3$) δ: 4.14 (2H, s, $S-CH_2-Ar$), 5.14 (2H, dd, J = 10.3, 16.9 Hz, $>C=CH_2$), 5.42 (1H, d, J = 7.0 Hz, >CH–Ph), 5.86—6.13 (1H, m, J = 7.0, 10.3, 16.9 Hz, $-CH=C<$), 7.22—7.36 (9H, m, Ar). HRMS, M$^+$ for $C_{17}H_{15}BrOS_2$ *m/z* 377.9748, Found: 377.9744.

Compound IIah ($R = CH_2C_6H_4$-*p*-NO_2) was obtained as an oil: IR (liquid film) cm^{-1}: 1640, 860 (–SCOS–), 1415, 1345 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 4.23 (2H, s, $-S-CH_2-Ar$), 5.24 (2H, dd, J = 10.3, 16.9 Hz, $>C=CH_2$), 5.42 (1H, d, J = 7.0 Hz, >CH–Ph), 6.09 (1H, m, J = 7.0, 10.3, 16.9 Hz, $-CH=C<$), 7.35 (5H, m, Ph), 7.13, 7.43 (4H, d, *p*-NO_2–C_6H_4–). MS, *m/z*: 345 (M$^+$).

O-(2-Methylallyl) and *O*-crotyl *S*-benzyl dithiocarbonates (Ic and Ie) were prepared according to the reported method.[3a] The products purified by silica-gel chromatography were the corresponding dithiolcarbonates (IIc and IIe). ^{1}H-NMR spectral data are as follows: *S*-Benzyl *S*-(2-methylallyl) dithiocarbonate (IIc), ^{1}H-NMR ($CDCl_3$, 60 MHz) δ: 1.78 (3H, s, =C–Me), 3.66 (2H, s, $=C-CH_2-$), 4.23 (2H, s, $-CH_2Ph$), 4.91 (2H, br q, J = 27 Hz, terminal vinyl protons), 7.28 (5H, s, Ph). *S*-Benzyl *S*-(1-methylallyl) dithiocarbonate (IIe), ^{1}H-NMR ($CDCl_3$, 60 MHz) δ: 1.43 (3H, d, J = 6 Hz, =C–Me), 4.21 (2H, s, $-CH_2Ph$), 4.36 (1H, m, >CH–S–), 5.07 (1H, dd, J = 2, 11 Hz, terminal vinyl proton), 5.23 (1H, dd, J = 2, 18 Hz, terminal vinyl proton), 5.92 (1H, ddd, J = 6, 11, 18 Hz, –S–C–CH = C), 7.38 (5H, s, Ph).

O-(2-Methylallyl) (Ib), *O*-crotyl (Id), *O*-(3-methyl-2-cyclohexenyl) (Ig), *O*-(1-(1-cyclohexenyl) ethyl) (Ih), *S*-methyl dithiocarbonates were also prepared according to the established method.[3a] Distillation of the crude xanthates under reduced pressure gave the [3,3]-sigmatropic rearrangement products.

O-(1-Methyl-3-phenyl-2-propenyl) (If) and *O*-(10-methyl-$\Delta^{1,9}$-octalin-2-yl) (Ii) *S*-methyl dithiocarbonates were extremely unstable and the corresponding dithiol esters were recognized by IR spectroscopy. The products isolated were the corresponding sulfides (see below).

Pyrolysis of II. Formation of 2-Alkenyl Alkyl Sulfides (General Procedure) A dithiol ester (II, 5 mmol) was placed in a distillation flask and heated at 150—200 °C until evolution of COS gas ceased. The distillate was collected and purified by redistillation or chromatography on silica gel. In the case of sulfides having higher boiling points, the distillations were performed under a moderately reduced pressure.

Alkyl Cinnamyl Sulfides (IIIaa, ab, ac, ad, ae, ag) Heating *S*-alkyl *S*-(1-phenylallyl) dithiocarbonates at 150—200 °C gave the corresponding sulfides. The physical data are as follows.

Cinnamyl Methyl Sulfide (IIIaa) Isolated as an oil. ^{1}H-NMR ($CDCl_3$, 100 MHz) δ: 2.03 (3H, s, –SMe), 3.24 (2H, d, J = 6.0 Hz, $-CH_2-S-$), 6.21 (1H, dt, J = 6.0, 16.5 Hz, >C = CH–), 6.46 (1H, d, J = 16.5 Hz, Ph–CH = C<), 7.32 (5H, m, Ph). The spectral data were identical with those of an authentic sample.[13]

Cinnamyl Ethyl Sulfide (IIIab) Isolated as an oil. IR (liquid film) cm^{-1}: 3100—3000 (Ph and CH =), 1600 (C = C), 960 (*trans* CH = CH), 750, 700 (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.24 (3H, t, J = 7.3 Hz, Me), 2.50 (2H, q, J = 7.3 Hz, $>CH_2$), 3.30 (2H, d, J = 7.3 Hz, $-CH_2-S-$), 6.18 (1H, dt, J = 7.3, 15.8 Hz, >C = CH–), 6.42 (1H, d, J = 15.8 Hz, Ph–CH = C<), 7.30 (5H, m, Ph). HRMS, M$^+$ for $C_{11}H_{14}S$ *m/z* 178.0816, Found: 178.0817.

Benzyl Cinnamyl Sulfide (IIIac) Isolated as an oil. IR (liquid film) cm^{-1}: 960 (*trans* CH = CH). ^{1}H-NMR ($CDCl_3$) δ: 3.18 (2H, d, J = 7.3 Hz, $=C-CH_2-S-$), 3.68 (2H, s, $-CH_2-Ph$), 6.15 (1H, dt, J = 7.3, 15.8 Hz, >C = CH–), 6.37 (1H, d, J = 15.8 Hz, PhCH = C<), 7.30 (10H, m, 2Ph). *Anal.* Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71. Found: C, 80.11; H, 6.85.

Cinnamyl Diphenylmethyl Sulfide (IIIad) Isolated as an oil. IR (liquid film) cm^{-1}: 3100—3000 (Ph and CH=), 1600 (C=C), 970 (*trans* CH=CH), 750, 700 (Ph). ^{1}H-NMR ($CDCl_3$) δ: 3.15 (3H, d, =C–CH_2–S–), 5.15 (1H, s, –S–$CHPh_2$), 6.21 (2H, m, Ph–CH=CH–), 7.35 (15H, m, 3Ph). The product contained a small amount of by-product but the formation of IIIad was confirmed by the spectral data.

Cinnamyl Methoxycarbonylmethyl Sulfide (IIIae) Isolated as an oil. IR (liquid film) cm^{-1}: 3100—300 (Ph and CH=), 1740, 1135 (–COO–), 1600 (C=C), 970 (*trans* CH=CH), 755, 700 (Ph). ^{1}H-NMR ($CDCl_3$) δ: 3.18 (3H, s, Me), 3.39 (2H, d, J=7.3 Hz, –CH_2–S–), 6.12 (1H, dt, J=7.3, 15.8 Hz, >C=CH–), 6.47 (1H, d, J=15.8 Hz, PhCH=C<), 7.30 (5H, m, Ph). HRMS, M^+ for $C_{12}H_{14}O_2S$ m/z 222.0715, Found: 222.0716.

***p*-Bromobenzyl Cinnamyl Sulfide (IIIag)** Isolated as an oil. IR (liquid film) cm^{-1}: 3100—3000 (Ph and CH=), 1600 (C=C), 980 (*trans* CH=CH), 760, 700 (Ph). ^{1}H-NMR ($CDCl_3$) δ: 3.20 (3H, d, =C–CH_2–S–), 3.65 (2H, d, J=7.3 Hz, –S–CH_2–C_6H_4–Br), 6.15 (1H, dt, J=7.3, 15.8 Hz, >C=CH–), 6.26 (1H, d, J=15.8 Hz, Ph–CH=C<), 7.14—7.53 (9H, m, Ph). HRMS, M^+ for $C_{16}H_{15}BrS$ m/z 318.0078, Found: 318.0048.

Benzyl 2-Methylallyl Sulfide (IIIc) Colorless oil. bp 99 °C/4 mmHg. ^{1}H-NMR ($CDCl_3$) δ: 1.85 (3H, s, =C–Me), 3.05 (2H, s, –SCH_2), 3.65 (2H, s, –CH_2–Ph), 4.86 (2H, br q, olefinic protons), 7.32 (5H, s, –Ph). *Anal.* Calcd for $C_{11}H_{14}S$: C, 74.13; H, 7.92. Found: C, 74.27; H, 8.02.

Crotyl Methyl Sulfide (IIId) Isolated as a mixture of the *cis* and *trans* isomers. Colorless oil. bp 86—87 °C. IR (liquid film) cm^{-1}: 900—1000 (*cis*, *trans* CH=CH). ^{1}H-NMR ($CDCl_3$) δ: 2.02 (1.5 H × 2, split s, –SMe), 2.98 (2H, m, –CH_2–), 5.42 (2H, complex m, olefinic protons). The gas chromatogram showed that the pyrolytic product contained a small amount of low boiling by-products and the formation ratio of the *cis* and *trans* isomers was 1 : 1. MS m/z: 102 (M^+).

Benzyl Crotyl Sulfide (IIIe) Colorless oil. bp 109 °C/5 mmHg. ^{1}H-NMR ($CDCl_3$, 60 MHz) δ: 1.62 (3H, m, J=5.1 Hz, C–Me), 2.96 (2H, d, J=6 Hz, –CH_2–S–), 3.62 (2H, s, –S–CH_2–Ph), 5.46 (2H, m, J=15 Hz, *trans* –CH=CH–), 7.38 (5H, s, –Ph). *Anal.* Calcd for $C_{11}H_{14}S$: C, 74.13; H, 7.92. Found: C, 74.45; H, 7.89.

1-Methyl-3-phenylallyl Methyl Sulfide (IIIf) The crude dithiol ester [IR (liquid film) cm^{-1}: 1645, 875 (–SCOS–)] was subjected to column chromatography on silica gel to give the sulfide. Colorless oil. bp 100 °C/2 mmHg. IR (liquid film) cm^{-1}: 1602 (C=C), 964 (*trans* CH=CH). ^{1}H-NMR ($CDCl_3$, 60 MHz) δ: 1.39 (3H, d, J=6.9 Hz, C–Me), 1.96 (3H, s, –SMe), 3.28 (1H, m, J=6.9, 7.5 Hz, –S–CH<), 5.67 (1H, dd, J=7.5, 16.8 Hz, >C=CH–C), 6.30 (1H, d, J=16.8 Hz, Ph–CH=C<), 6.9—7.55 (5H, m, Ph). *Anal.* Calcd for $C_{11}H_{14}S$: C, 74.13; H, 7.92. Found: C, 73.90; H, 7.80.

3-Methyl-2-cyclohexenyl Methyl Sulfide (IIIg) Colorless oil. bp 100 °C/55 mmHg. ^{1}H-NMR ($CDCl_3$, 100 MHz) δ: 1.66 (3H, s, =C–Me), 1.73—2.68 (6H, m, ring CH_2), 1.95 (3H, s, –SMe), 2.95—3.30 (1H, m, >CH–S–), 5.68 (1H, m, =CH–). *Anal.* Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92. Found: C, 67.32; H, 9.98.

1-(1-Cyclohexenyl)ethyl Methyl Sulfide (IIIh) Colorless oil. bp 121 °C/60 mmHg. ^{1}H-NMR ($CDCl_3$, 100 MHz) δ: 1.19 (3H, d, J=7.2 Hz, Me), 1.4—1.8 (4H, m, ring CH_2), 1.8—2.4 (4H, m, ring –CH_2C=), 1.8 (3H, s, –SMe), 3.13 (1H, q, J=7.2 Hz, >CH–S–), 5.43 (1H, m, –CH=). *Anal.* Calcd for $C_9H_{16}S$: C, 69.17; H, 10.32. Found: C, 70.10; H, 10.46.

10-Methyl-$\Delta^{1,9}$-octalin-2-yl Methyl Sulfide (IIIi) Colorless oil. bp 60 °C (oil bath)/0.27 mmHg. IR (liquid film) cm^{-1}: 1651 (C=C). ^{1}H-NMR ($CDCl_3$, 100 MHz) δ: 1.04, 1.08 (1.5 H × 2, s, >C–Me of the 2α- and 2β-isomers), 0.9—2.5 (12H, m, ring CH_2), 1.97, 2.03 (1.5 H × 2, s, –SMe of the 2α- and 2β-isomers), 3.03—3.30 (1H, m, >CH–S–), 5.15—5.31 (1H, m, –CH=). *Anal.* Calcd for $C_{12}H_{20}S$: C, 73.43; H, 10.27. Found: C, 73.10; H, 10.44.

Crossover Reaction An equimolar mixture of *S*-cinnamyl *S*-methyl dithiocarbonate (IIaa) and *S*-(1-methylallyl) *S*-benzyl dithiocarbonate (IIe) was heated without solvent at 200 °C for 2 h. The reaction mixture was analyzed by gas chromatography. The chromatogram showed the absence of benzyl cinnamyl (IIIac) and crotyl methyl sulfides (IIId).

Kinetics The rearrangement rate was followed at a given temperature by measuring the amount of evolved carbon oxysulfide gas by volumetry (method A) using a gas burette apparatus filled with a solution of concentrated H_2SO_4–NaCl or by following the weight loss of a tared sample due to loss of volatile reaction products (method B)[14] using a Shimadzu AEL-200 electronic balance (readability 0.1 mg). The data were treated by means of a nonweighted least-squares program written in F-BASIC86 V3.1. The results are listed in Tables II, III and V.

Pyrolysis of IIaa in the Presence of $AlCl_3$ A mixture of IIaa (5 mmol) and $AlCl_3$ (0.16 mmol) was heated at 80 °C until disappearance of IIaa as judged by thin layer chromatography (TLC). After cooling, the reaction mixture was treated with water. The sulfide was extracted with *n*-hexane. The *n*-hexane was evaporated *in vacuo* to give a residue, which was purified by chromatography on silica gel to give IIIaa, yield 55%.

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