Phenol-Catalyzed Thione–Thiol Rearrangement of Xanthates and Modified Intermediate Neglect of Differential Overlap (MINDO/3) Analysis of the Reaction Mechanism

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***S*-Alkyl dithiocarbonates (xanthates) of alkanols containing strained σ bonds underwent rearrangement to *S,S*-dialkyl dithiocarbonates, catalyzed by phenolic compounds. The reaction followed first-order kinetics and the rates were affected by the acidity of the phenols. The rate constants are proportional to the square of the concentration of phenol.**

The modified intermediate neglect of differential overlap (MINDO/3) geometry optimization indicates that *S,S*-dialkyl dithiocarbonate is *ca.* 9 kcal/mol more stable than *O,S*-dialkyl xanthate. The thione–thiol rearrangement and sulfide formation reactions were analyzed by MO simulations. The experimental results can be well reproduced by the MINDO/3 method rather than the modified neglect of diatomic overlap (MNDO) method. Based on these data, the reaction mechanism is discussed.

Keywords *O,S*-dialkyl dithiocarbonate; *S,S*-dialkyl dithiocarbonate; catalytic rearrangement; phenol; mechanism; modified intermediate neglect of differential overlap

In the previous paper,[1a] it was reported that phenolysis of homoallylic xanthates (*O,S*-dialkyl dithiocarbonates) resulted in thione–thiol rearrangement to give the dithiol esters. In the valence-isomeric system,[1b] *O*-(1-cyclopropylethyl) *S*-methyl dithiocarbonate (Ia) also underwent thione–thiol rearrangement under solvolytic conditions in various solvents to give the corresponding dithiol ester, *S*-(1-cyclopropylethyl) *S*-methyl dithiocarbonate (IIa) and plots of the rate constants *vs.* Grunwald–Winstein *Y* values[2] for protic solvent system showed a good linear relationship.

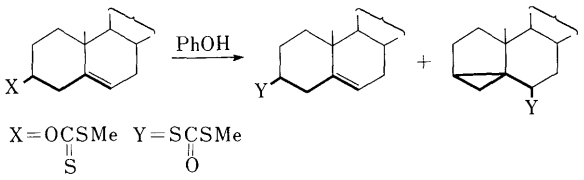

Chart 1

In this paper, we wish to discuss kinetic and molecular orbital (MO) calculation data of the rearrangement reaction of several xanthates to clarify the catalytic behavior of phenolic compounds in the thione–thiol rearrangement of xanthates.

Results

Xanthates of Cyclopropylalkanols To obtain some information about the effect of structure on reactivity, phenolyses of *O*-(1-cyclopropylethyl) (Ia), *O*-cyclopropylmethyl (Ib) and *O*-(1-methylcyclopropylmethyl) (Ic) *S*-methyl xanthates were studied.

When Ia was dissolved in phenol at room temperature, Ia was immediately phenolyzed to give the thione–thiol rearrangement product (IIa) and a small amount of 1-(cyclopropylethyl) phenyl ether.[1b] In contrast, the reaction rates of Ib and Ic in phenol were very small. Therefore, the reactions were carried out using *p*-

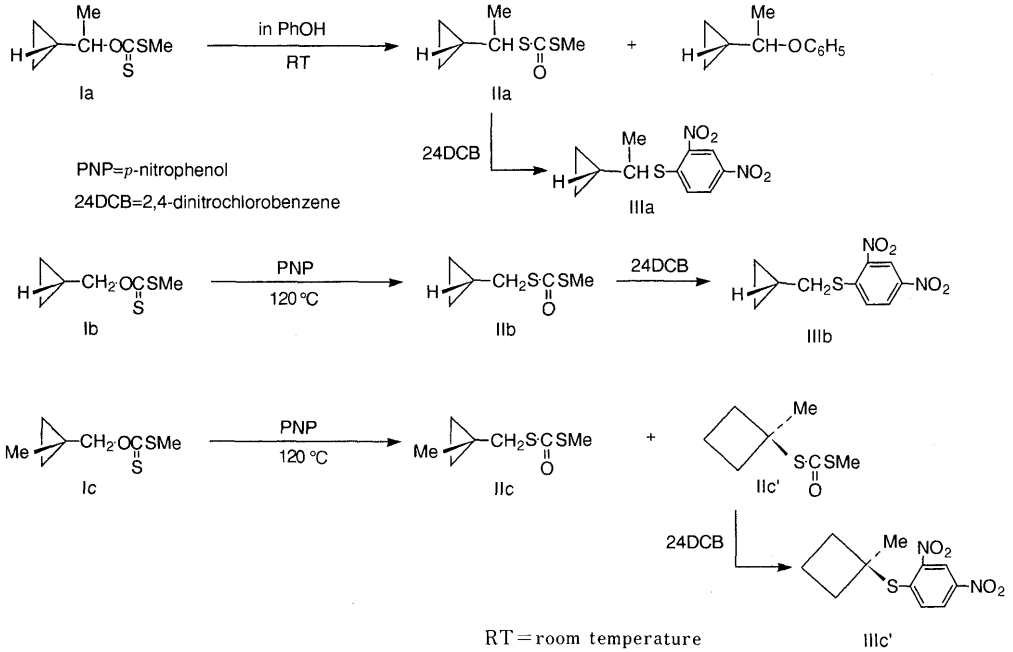

Chart 2

nitrophenol as a catalyst. Heating Ib with *p*-nitrophenol at 120 °C in the absence of solvent gave the corresponding dithiol ester (IIb) in 76% yield. The structure of IIb was determined by inspection of the infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectral data. The IR spectrum of IIb shows characteristic absorption bands at 1644 and 872 cm^{-1} due to the –S(C=O)S– moiety. In the ^{1}H-NMR spectrum of IIb, five protons resonate at considerably high field (0.27—1.04 ppm) as multiplets, reflecting the highly shielded nature[3] of the cyclopropane ring protons. The 2,4-dinitrophenyl sulfide (IIIb) was prepared by warming IIb with ethanolamine[4] followed by treatment with 2,4-dinitrochlorobenzene. Similarly, Ic was heated with *p*-nitrophenol to give two kinds of the dithiol esters (IIc and IIc′) in 62% total yield. The formation ratio of IIc and IIc′ was determined by inspection of –SMe signals in the ^{1}H-NMR spectrum of the crude product. The yields of IIc and IIc′ were 10% and 52%, respectively. The structure of IIc was easily deduced from the presence of the cyclopropane ring protons in the high-field region. In the ^{1}H-NMR spectrum of IIc′, the cyclopropane ring signals could not be recognized. The methyl protons resonate at 1.69 ppm, which could not be assignable to the methyl of an –S–C–C–Me system. The presence of –S(C=O)SMe at the α-carbon of the methyl group (–S–C–Me) accounts for its downfield shift. These observations indicate that the structure of IIc′ has a cyclobutane ring moiety, and the skeletal rearrangement (ring expansion reaction) occurred during the thione–thiol rearrangement. The ^{1}H-NMR spectrum of the 2,4-dinitrophenyl sulfide also supports this conclusion.

Next, we examined the effect of the acidity of phenols on the product ratio of IIc and IIc′. Compound Ic was heated in several phenols and the product ratios were evaluated from the ^{1}H-NMR spectral data (Table I). As can be seen in Table I, the amount of IIc′ increase with increasing acidity of phenols, indicating that the rearrangement proceeds *via* an ionic intermediate.

The phenolytic reactions of Ia—c were investigated kinetically. The rates were determined by measuring the amount of the remaining reactants by ultraviolet (UV) spectrometry. The reaction rates were appreciably affected by substrate structure, *O*-alkyl being primary or secondary. Compound Ia was phenolyzed *ca.* two hundred times faster than Ib. The activation parameters were calculated for the phenolytic reactions of Ia—c in *p*-chlorophenol (Table II).

The activation entropy of Ia is highly negative in comparison with those of Ib and Ic. The low entropy of activation may reflect the highly ordered structure of the activated complex.

The phenolysis rates in some phenols were measured using Ic as a substrate. A plot of the reaction rate against the Pocker's values[5] (k_2) for the catalytic coefficients of phenols is roughly linear, suggesting that hydrogen-bonding capacity plays an important role in the dissociation step of the reaction (Fig. 1).

To elucidate the role of the phenols in detail, we have studied the dependence of the reaction rate on the amount of phenols. The reaction rates of Ia were measured for

Table I. Product Ratios of IIc and IIc′ in Phenolysis of Ic in Several Phenols[a]

Phenols	IIc′/IIc
p-Cresol	1.3
Phenol	2.0
p-Chlorophenol	2.0
p-Bromophenol	2.3
p-Nitrophenol	5.0

a) At 130 °C.

Table II. Relative Rate and Activation Parameters for Phenolysis of Ia—c in *p*-Chlorophenol

Compd.	$k \times 10^4$ (s^{-1})[a]	ΔE (kcal/mol)[b]	$\Delta S^{\neq}$ (e.u.)
Ia	306	8.55	−42
Ib	1.53	22.6	−9
Ic	2.91	16.8	−26

a) Rate constant at 55 °C. *b*) Correlation coefficients of the Arrhenius plots for Ia—c are 0.999, 0.995 and 0.992, respectively.

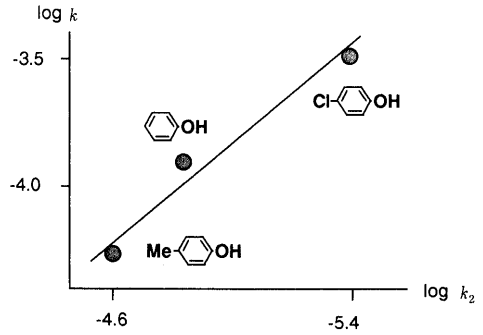

Fig. 1. Plots of the Reaction Rates of Ic (log k) *vs.* Catalytic Coefficients[5] (k_2) of Some Phenols

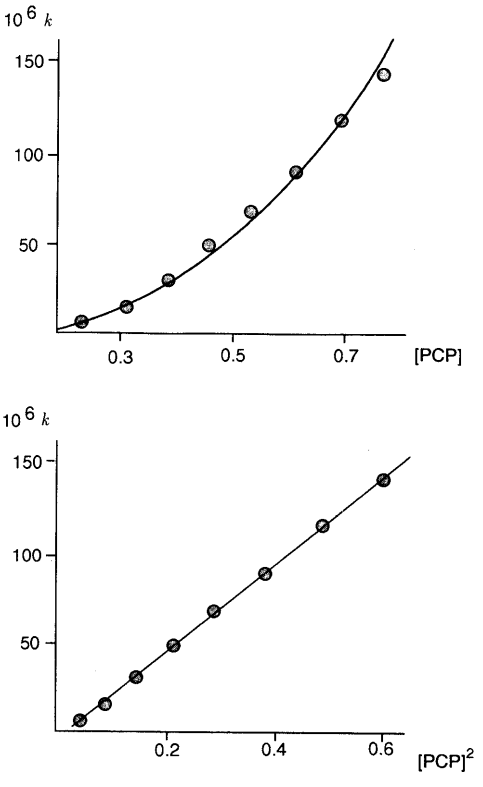

Fig. 2. Plots of the Reaction Rates of Ia (log k) *vs.* Amount of *p*-Chlorophenol (PCP)

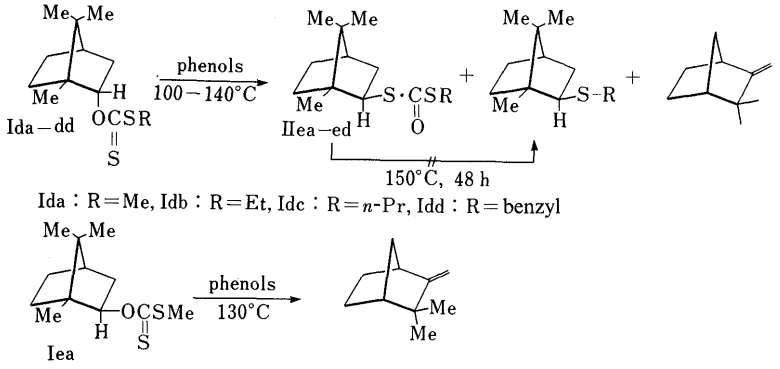

Chart 3

TABLE III. Rate Constants for Phenolysis of Ia in Various Concentrations of *p*-Chlorophenol at 60 °C

[Catalyst] (mol/l)	$k \times 10^6$ (s^{-1})	$r^{a)}$
0.7778	145.8	0.999
0.7001	119.8	0.999
0.6223	89.7	0.999
0.5445	67.7	0.999
0.4667	47.7	0.999
0.3889	26.9	0.994
0.3111	11.7	0.999
0.2334	2.69	0.992

a) Correlation coefficient.

TABLE IV. Catalytic Rearrangement of Ida to IIea in Various Phenols[a] at 140 °C

Phenols	Temp (°C)	Time (h)	Yield (%)
p-Chlorophenol	140	20	18
	100	140	38[b]
p-Bromophenol	140	16	40
p-Nitrophenol	140	20	41
o-Nitrophenol	140	80	0[c]
2,4-Dinitrophenol	140	26	19
2,4,6-Trinitrophenol	140	6	44

a) Ida: phenols = 1 : 1. *b*) Ida: *p*-chlorophenol = 1 : 3. Camphene was produced in 6% yield. *c*) No reaction occurred.

TABLE V. Effects of *S*-Alkyl Group on the Rearrangement of Ida—dd to IIea—ed in the Presence of *p*-Nitrophenol[a]

R	Temp. (°C)	Time (h)	Yield (%)
Me	140	20	41
Et	140	20	42
n-Pr	140	26	59
Bz	120	16	78
	140	4	67

a) I: *p*-nitrophenol = 1 : 1.

binary mixtures of 1—10% *p*-chlorophenol and benzene, in which the association degree of phenols is considered to be very low.[6] The results are presented in Table III. A plot of the rate constants for Ia against the various concentrations of *p*-chlorophenol is shown in Fig. 2. As shown in Fig. 2, the pseudo first-order rate constant is not proportional to the catalyst concentration. Interestingly, the rate is proportional to the square of the catalyst concentration.

TABLE VI. Rate Constants and Activation Parameters for the Catalytic Reaction of Ida in the Presence of *p*-Nitrophenol[a]

Temp. (°C)	$k \times 10^3$ (s^{-1})	$r^{b)}$	ΔE (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
150.2	20.7	0.994		
139.9	11.2	0.999	23.3[c]	−23
130.9	4.87	0.997		
120.0	2.60	0.997		

a) Ida: *p*-nitrophenol = 1 : 1. *b*) Correlation coefficient. *c*) Correlation coefficient of the Arrhenius plot is 0.995.

Xanthates of Bicyclo[2.2.1]heptane Derivatives We also examined moderately strained xanthates having a bicyclo-[2.2.1]heptane skeleton. Heating of *O*-bornyl *S*-methyl xanthate (Ida) in *p*-chlorophenol gave the isobornyl-type dithiol ester (IIea), together with small amounts of isobornyl methyl sulfide and camphene, whereas *O*-isobornyl *S*-methyl xanthate (Iea) readily underwent elimination reaction to give camphene *via* the Wagner–Meerwein rearrangement.[7] The dithiol ester (IIea) was stable on heating at 150 °C for 48 h, indicating that IIea is not a precursor of isobornyl methyl sulfide.

Similar reactions were carried out in the presence of various phenolic compounds. Phenols bearing electron-attracting substituents showed catalytic activity. However, *o*-nitrophenol did not show any reactivity (Table IV).

The change of *S*-alkyl group from *S*-methyl to *S*-benzyl shortened the reaction time (Table V).

The configuration of the –S(C=O)SR groups was determined by comparison of the ^{1}H-NMR spectral patterns of the methine protons [>CH–S(C=O)SR] with those of related compounds whose configurations had been firmly established.[8]

The reactions of Ida—dd in the presence of *p*-nitrophenol (1 eq) obeyed a first-order rate law. The activation enthalpy and entropy are 23.3 kcal/mol and −23 e.u., respectively. The values are comparable to those observed in phenolysis of *O*-cholesteryl *S*-methyl xanthate in *p*-chlorophenol (ΔH = 22.4 kcal/mol, $\Delta S^{\neq}$ = −14 e.u.).[1a)]

Next, we studied the reaction behavior of *S*-methyl xanthate (If) of *endo*-5-norbornen-2-ol, which has a strained homoallylic system. Heating the xanthate (If) at 130 °C for 26 h in the presence of *p*-nitrophenol gave two kinds of dithiol esters (IIg and IIh) (Chart 4).

Taking into consideration the stereoelectronic requirement of homoallylic participation, the configurations of S(C=O)SMe groups of the two compounds are assumed to be *exo*. The *exo* isomer underwent the elimination reaction.

Xanthates of Common Primary Alkanols As hitherto mentioned, phenolic compounds show catalytic activity for thione–thiol rearrangement of xanthates. Next, we studied the reaction behavior of xanthates of common alkanols which do not have any anchimeric assistance of the neighboring group or special orbital interaction. For example, when *O*-(*n*-butyl) *S*-methyl xanthate (Ii) was heated in electron-deficient phenols or in mixtures of different phenols at 180 °C, the corresponding dithiol ester was obtained in moderate yield. However, the reaction is not applicable to *O*-(secondary alkyl) xanthates because the heating causes *cis*-elimination reaction (Chugaev reaction).[9]

MO (Molecular Orbital) Simulation To understand the observed reaction behaviors, we performed MO calculations on the ground-state structures of *O*,*S*-dimethyl dithiocarbonate (Ij) and the rearranged product (*S*,*S*-dimethyl dithiocarbonate) (IIj) using modified intermediate neglect of differential overlap (MINDO/3)[10a] and modified neglect of diatomic overlap (MNDO)[10b] methods. However, MNDO calculation could not sufficiently reproduce the X-ray structural features of xanthates.[11] Therefore, we used MINDO/3 methodology for MO analysis of the xanthate reactions.[12] The MINDO/3 structures (bond lengths) and net charges for Ij and IIj are included in Fig 3.

The rearrangement of I to II is formally analogous to the previously reported Lewis-acid catalyzed rearrangement.[13] In order to confirm that this is so, the MINDO/3 simulation

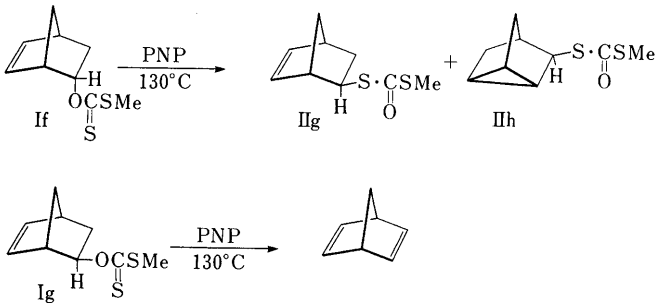

Chart 4

TABLE VII. Rearrangement of *O*,*S*-Dialkyl Xanthates [RO(C=S)SR'] (I) to *S*,*S*-Dialkyl Dithiocarbonates [RS(C=O)SR'] (II) Catalyzed by Phenols

I		Phenols[a]	Temp. (°C)	Time (h)	Yield of II (%)
R	R'				
Me	Et	PNP	180	3	41
Et	Me	PNP	160	6	35
n-Pr	Me	PNP	160	8	50
n-Bu	Me	PNP	180	8.5	24
		PNP[b]+PBP[b]	180	9	65
		PNP[b]+PCP[b]	180	7	82
			180	30	54

a) PNP: *p*-nitrophenol, PBP: *p*-bromophenol, PCP: *p*-chlorophenol. One molar eq of catalyst was used. *b*) 0.5 molar eq.

TABLE VIII. MINDO/3 Stabilization Energy of Hydrogen Bond Formation between *O*,*S*-Dimethyl Xanthate (Ij) and Phenol

Distance (Å)[a] PhOH···S=C<	ΔH_f (kcal/mol)	Calculated distance (Å) S=C<
10.0	−89.663	1.610
5.0	−89.847	1.611
3.5	−90.130	1.611
3.0	−90.509	1.611
2.5	−91.723	1.612
2.0	−94.028	1.621
1.9	−94.480	1.623
1.8	−94.350	1.628
1.824 (relaxed)[b] (IVa)	−94.884	1.625
1.6	−92.652	1.638
1.5	−89.807	1.643

a) Reaction coordinate. *b*) All structural parameters were optimized.

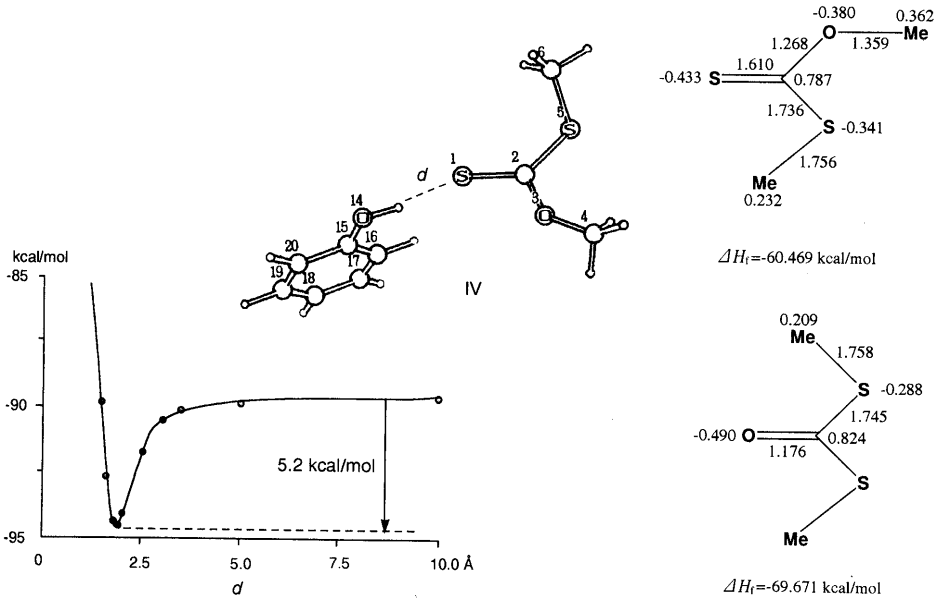

Fig. 3. Stabilization of the Reaction System by Hydrogen Bonding between *O*,*S*-Dimethyl Xanthate (Ij) and Phenol, and Bond Lengths and Net Charges of Ij and IIj Calculated by the MINDO/3 Method

was carried out. To reduce the computation time, the simplest reaction, *i.e.*, the reaction of *O*, *S*-dimethyl xanthate (Ij) with phenol, was used as a model reaction system.

In the early stage of the reaction, the phenolic proton was considered to approach the sulfur atom of C=S along the axis through the C=S bond, for which the all structure parameters except the interacting distance (*d*) were optimized. Inspection of the optimized structure at the distance of 10 Å indicates that the angle of PhOH$\cdots$S=C$<$ is 151.9° ($\Delta H_f = -89.663$ kcal/mol).

The ΔH_f for the interaction of the phenolic proton with the thiocarbonyl sulfur of Ij decreases with decrease of the interacting distance, and reaches the minimum value ($\Delta H_f = -94.884$ kcal/mol) at 1.824 Å, having the H$\cdots$S=C$<$ angle of 158.7°. The stabilization energy due to the formation of the hydrogen bond is *ca.* 5.2 kcal. The value is considered to reproduce well the observed value (3.35 kcal/mol) which is derived from the blue shift[14] of the UV absorption band of the >C=S group [$\lambda_{(\text{in phenol})}$ 338.55 nm ($E_T = 84.44$ kcal/mol) $-$ $\lambda_{(\text{in } n\text{-hexane})}$ 352.55 nm ($E_T = 81.09$ kcal/mol)]. Fig. 4 shows the minimum energy structure (IVa) of the complex derived from full MINDO/3 optimization. The MNDO simulation could not reproduce the energy profile observed in the MINDO/3 simulation.

Next, we performed computer simulation of the phenol-catalyzed reaction of *O*,*S*-dimethyl xanthate (Ij). The calculations were performed along the reaction coordinate, taking the length of the dissociating $H_3C\cdots O$

Table IX. Change in Heat of Formation (ΔH_f) of Phenol-Coordinated *O*,*S*-Dimethyl Xanthate (Ij) along Dissociation of the Me–O Bond *via* Conformational Isomer IVa (Formation of Sulfide)

Distance (Å)[a] PhOH·S=C(SMe)O$\cdots$Me	ΔH_f (kcal/mol)	Calculated distance (Å) PhOH·S=C$\cdots$SMe
1.359[b]	−94.884	1.735
1.5	−86.341	1.738
1.6	−74.563	1.740
1.7	−61.037	1.742
1.8	−47.427	1.743
2.0	−23.492[c]	1.749
2.1	−54.748	1.944
2.2	−58.885	1.952
2.3	−64.211	2.003
2.4	−76.482	2.134
2.6	−86.153	2.287
3.0	−91.586	2.450
4.0	−94.532	2.964
5.0	−94.658	3.475
7.0	−95.564	5.003
8.0	−96.133	5.921

a) Reaction coordinate. *b*) All structural parameters were optimized. *c*) Dimethyl sulfide and O=C=S$\cdots$PhOH.

Table X. Change in Heat of Formation (ΔH_f) of Phenol-Coordinated *O*,*S*-Dimethyl Xanthate (Ij) along Dissociation of the Me–O Bond *via* Conformational Isomer IVb (Formation of Dithiol Ester)

Distance (Å)[a] PhOH·S=C(SMe)O$\cdots$Me	ΔH_f (kcal/mol)	Calculated distance (Å) PhOH$\cdots$S=C<
1.360 (relaxed)[b]	−94.038	1.826
1.5	−86.226	1.813
1.6	−75.034	1.822
1.7	−61.699	1.823
1.8	−48.534	1.825
1.9	−35.723	1.812
2.0	−24.120	1.813
2.1	−14.126	1.816
2.2	−6.105	1.814
2.3	0.762	1.821
2.4	6.106	1.805
2.5	10.562	1.797
2.6	13.872	1.787
2.7	16.305	1.783
2.8	18.244	1.783
2.9	−79.662[c]	2.655
3.0	−82.768	2.432
3.613 (relaxed)[b]	−98.271	4.892

a) Reaction coordinate. *b*) All structural parameters were optimized. *c*) *S*,*S*-Dimethyl dithiocarbonate (IIj) and PhOH.

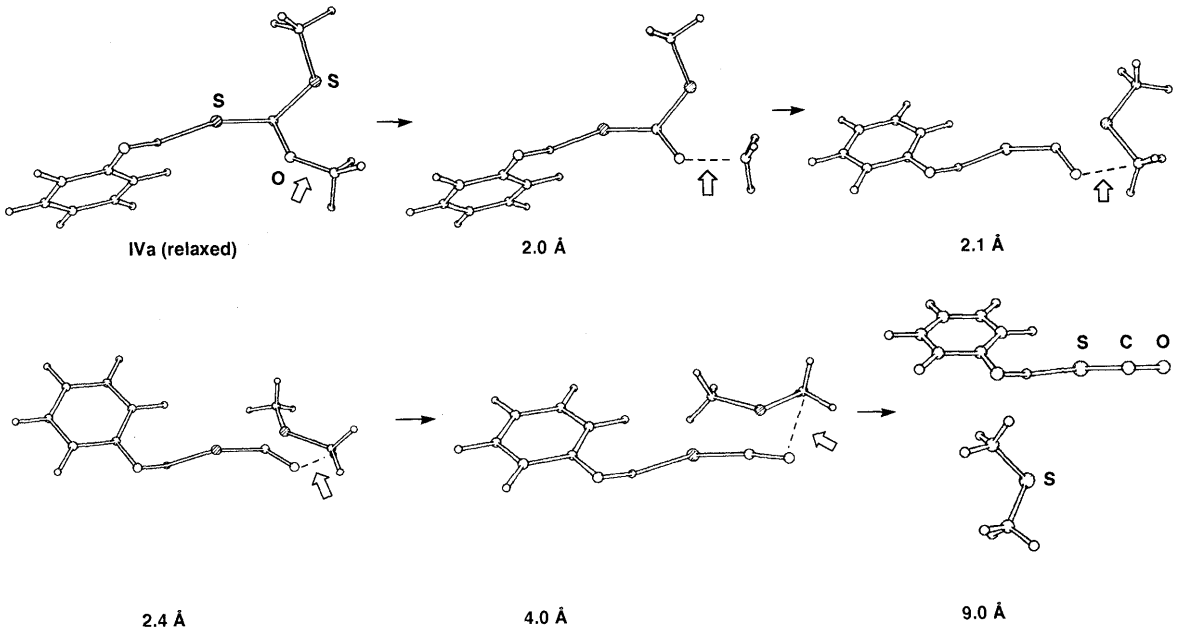

Fig. 4. Optimized Structures for the Sulfide Formation Reaction of *O*,*S*-Dimethyl Xanthate (Ij) Catalyzed by Phenol

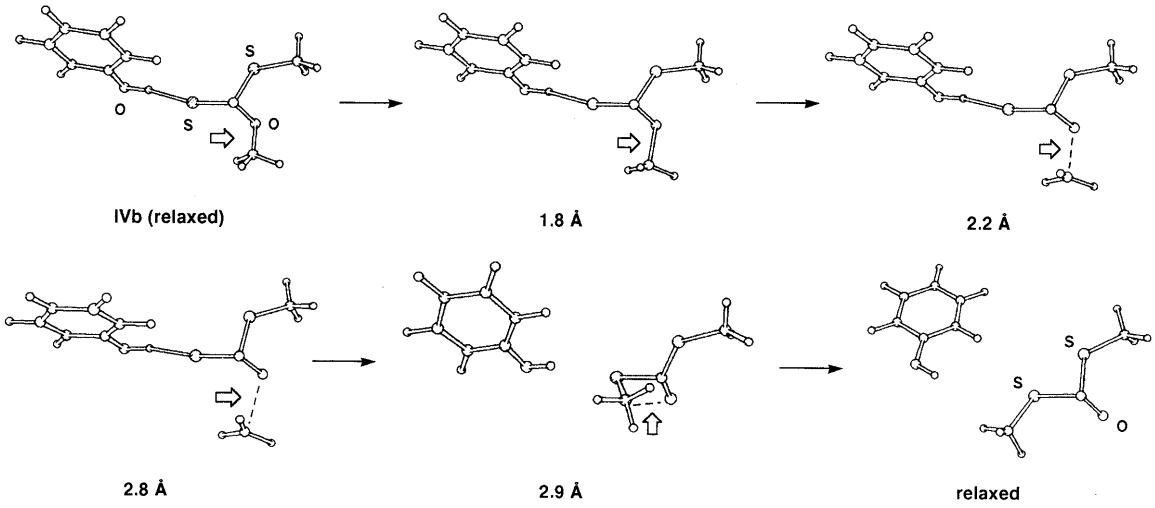

Fig. 5. Optimized Structures for the Thione–Thiol Rearrangement Reaction of *O*,*S*-Dimethyl Xanthate (Ij) Catalyzed by Phenol

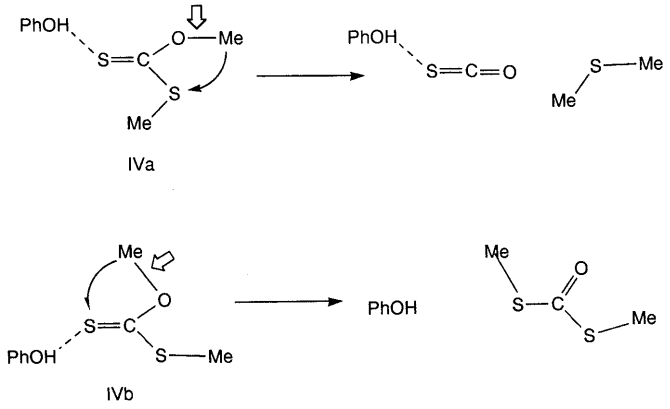

Chart 5

bond of IVa as the reaction coordinate. Several optimized structures along the coordinates are depicted in Fig. 4. The heat of formation of the complex increases with increase of the distance to reach the maximum value at *ca.* 2.0 Å. As the distance exceeds 2.0 Å, the reaction system undergoes sudden relaxation to give dimethyl sulfide and bent O=C=S, which coordinates with PhOH by hydrogen-bonding. Further increase of the distance gradually decreases the heat of formation with increase of the linearity of the COS molecule and reaches the stationary state at *ca.* 9 Å.

The MINDO/3 simulation was also performed for the conformational isomer (IVb) represented by Fig. 5. In the simulation, heat of formation increases with increase of the O–C distance to reach the maximum value at *ca.* 2.8 Å. The methyl group migrates to the sulfur atom, expelling a phenol molecule from the thiocarbonyl sulfur. With further increase of the C–O bond length, PhOH gradually falls away from *S*,*S*-dimethyl dithiocarbonate (IIj).

The calculated activation energies are considerably greater than the actual values because solvent effects were entirely ignored in the calculations.

Interestingly, the calculations suggest that the phenol-catalyzed thione–thiol rearrangement and sulfide formation reactions depend upon the conformation of the hydrogen-bonded xanthate (Chart 5).

Discussion

In the previous study[1a] on phenolysis of homoallylic xanthates such as *O*-cholesteryl *S*-methyl xanthate, we assumed that the catalytic activity of phenols is probably a consequence of the formation of a complex of the type RO(RS′)C=S···H–OAr between the catalyst and substrate. The rearrangement may proceed by specific solvation of phenols at the thiocarbonyl sulfur atom.

The reaction sequence based on the MINDO/3 simulation is as follows; phenol coordinates to the thione sulfur and pulls the O(C=S)SR′ group to promote scission of the C–O bond, during which the alkyl group migrates from the oxygen to the sulfur atom to give the dithiol ester and phenol, which again coordinates to xanthate. The resultant dithiol ester is thermodynamically more stable than the starting xanthate.[15]

The MO simulation is assumed to be a gas phase reaction wherein solvation or intermolecular interaction of reactants is not operative. Therefore, the MO prediction is considered to be somewhat different from the actual situation. In phenolytic conditions such as the case of Ia, the reaction is considered to proceed *via* a more ionic pathway. At low concentrations of the catalyst (phenols), the catalytic reaction is second-order with respect to catalyst concentration and first-order with respect to substrate concentration. The reaction may be pictured as resulting from the combination of a "pushing" and "pulling" action.[16a] The "pull" may be exerted by phenol and the "push" is exerted by the lone pair of the oxygen. The resulting carbonium ion may be stabilized by solvation with two or more solvent molecules. The presence of a solvated carbonium ion in the reaction medium is supported by the isolation of a small amount of 1-cyclopropylethyl phenyl ether in the reaction of Ia with phenol.[1a] However, the exact role of the second molecule of phenol is still obscure.

The MINDO/3 heats of formation of 1-cyclopropylethyl (A), 1-methylcyclopropylmethyl (B), 1-methylcyclobutyl (C) and 3-buten-1-yl (D) cations were calculated to be 185.6, 206.8, 186.1 and 223.9 kcal/mol, respectively.[17] The secondary cation, A is more stable than B. The bent σ bonds of the cyclopropane ring and methyl group act as donors and stabilize the methylium cation of A.[18] The ring

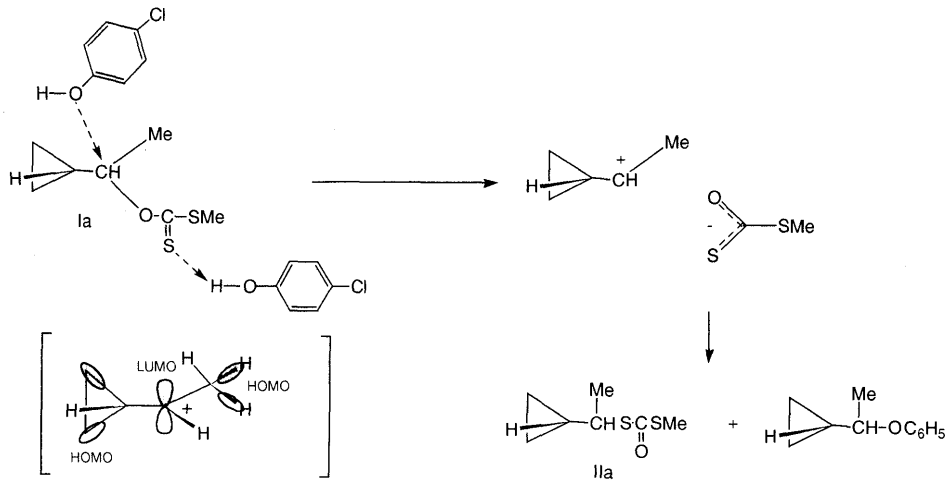

Chart 6

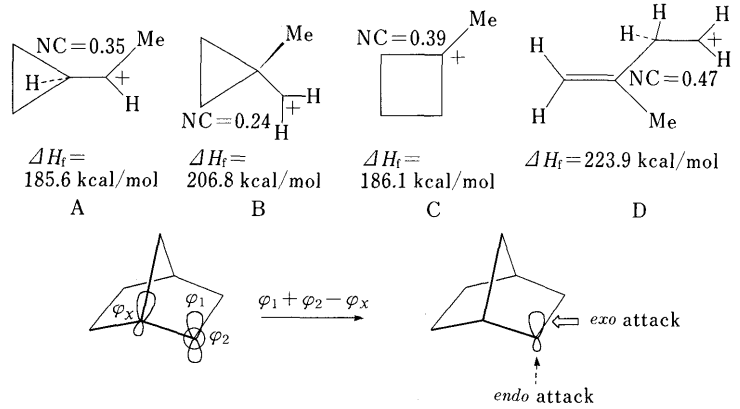

Fig. 6. MINDO/3 Heats of Formation of Homoallylic Cations and Predominant *Exo*-Attack in Bicyclo[2.2.1]heptene System

expansion from A to C can be rationalized by taking their relative stability into consideration; the ΔH_f of A is comparable to that of C and the positive net charge (0.393) of C is larger than the value (0.350) of A, supporting the formation of the cyclobutyl derivative (IIc') in the reaction of Ic.

With regard to the catalytic reaction, the MO calculations indicate that the frontier molecular orbital (FMO) interaction is very small and the coulombic interaction is operative.[19] However, in the case of bornyl system, the *exo* attack is probably due to an unsymmetrical *p*-orbital in which the *exo*-oriented *p* lobe is larger than the *endo* one owing to a $\sigma-\pi$ interaction between the adjacent strained σ bond and the growing *p*-orbital.[18] The formation of isobornyl methyl sulfide may be explained by the mechanism derived from the computer simulation stated above.

Experimental

All melting points are uncorrected. ^{1}H-NMR spectra were taken with Hitachi R-600 and JEOL GX-400 spectrometers for *ca.* 10% (w/v) solution with tetramethylsilane (TMS) as an internal standard; chemical shifts are expressed in δ values. IR spectra were recorded on a Hitachi 270-30 IR spectrophotometer equipped with a grating. UV spectra were recorded on a Hitachi 150-20 spectrophotometer.

MO calculations were performed on a FACOM M-780 computer in the Computer Center of Kumamoto University and on a Fujitsu S4/2 engineering workstation. Graphic analyses of MO calculation data and least-squares calculations were performed on a Fujitsu FM-16β or a FMR-60 personal computer.

***O*-(1-Cyclopropylethyl) (Ia), *O*-(Cyclopropylmethyl) (Ib) and *O*-(1-Methylcyclopropylmethyl) (Ic) *S*-Methyl Xanthates** The xanthates were prepared according to the reported method.[1b,9] Compound Ib was purified by column chromatography on silica gel and obtained as a yellow oil. IR (liquid film) cm^{-1}: 1220, 1070 [–O(C=S)S–]. ^{1}H-NMR (in $CDCl_3$): 0.5—1.2 (4H, m, CH_2 of cyclopropane ring), 4.8—4.9 (2H, d, J=6 Hz, $-CH_2-O-$), 2.99 (3H, s, SMe). The structures were confirmed by transformation to the corresponding 2,4-dinitrophenyl sulfide of the rearranged product (see below).

***O*-Bornyl and *O*-Isobornyl *S*-Alkyl Xanthates (Ida—dd)** The xanthates were prepared according to the reported method.[9] *O*-Bornyl *S*-ethyl (Idb), *S*-(*n*-propyl) (Idc) and *S*-benzyl (Idd) xanthates and *O*-(5-norbornen-2-yl) *S*-methyl xanthate (If) were prepared in a similar manner to that used for Ida.

Compound Idb (S-Et): Yield 56%. mp 54 °C. IR (liquid film) cm^{-1}: 1218, 1070 [–O(C=S)S–]. ^{1}H-NMR (in $CDCl_3$) ppm: 0.90 (6H, s, Me), 0.92 (3H, s, Me), 1.36 (3H, t, Me), 1.0—2.0 (7H, m, aliphatic ring protons), 3.11 (2H, q, SMe), 5.50 (1H, m, >CH–O). *Anal.* Calcd for $C_{13}H_{22}OS_2$: C, 60.42; H, 8.58. Found: C, 60.70; H, 8.80.

Compound Idc (S-*n*-Pr): Yield 82%. Oil. IR (liquid film) cm^{-1}: 1218, 1064 [–O(C=S)S–]. ^{1}H-NMR (in $CDCl_3$) ppm: 0.91 (12H, s, 4Me), 1.0—2.0 (9H, m, aliphatic ring protons and CH_2), 3.09 (2H, t, SCH_2), 5.52 (1H, m, >CH–O). HRMS, Calcd for $C_{14}H_{24}OS_2$ (M^+) m/z: 272.1269. Found: 272.1274.

Compound Idd (S-CH_2Ph): Yield 31%. Oil. IR (liquid film) cm^{-1}: 1220, 1062 [–O(C=S)S–]. ^{1}H-NMR (in $CDCl_3$) ppm: 0.89 (6H, s, Me), 0.94 (3H, s, Me), 1.0—2.0 (7H, m, aliphatic ring protons), 4.36 (2H, s, SCH_2), 5.48 (1H, m, >CH–O), 7.28 (5H, s, aromatic protons). HRMS, Calcd for $C_{18}H_{24}OS_2$ (M^+) m/z: 320.1269. Found: 320.1270.

***endo*- and *exo*-*O*-(5-Norbornen-2-yl) *S*-Methyl Xanthate (If)** A mixture

of the corresponding *endo* and *exo* alcohols was xanthated in a similar method to that used for Ida (yield 93%). The mixture of the xanthates (*endo* : *exo* = 3 : 1) was purified by chromatography on silica gel to give pure samples.

Endo Form: Yield 70%. Oil. IR (liquid film) cm^{-1}: 3064 (C=C), 1224, 1064 [–O(C=S)S–], 722 (*cis* olefin). 400 MHz ^{1}H-NMR (in $CDCl_3$) ppm: 1.11 (1H, sextet, *endo* H_3, J = 12.8, 2.9 Hz), 1.37 (1H, d, *anti* H_7, J = 9.2 Hz), 1.52 (1H, nonet, *syn* H_7), 2.25 (1H, heptet, *exo* H_3, J = 12.8, 8.1, 3.7 Hz), 2.49 (3H, s, SMe), 2.89 (1H, br, H_4), 3.33 (1H, br, H_1), 5.97 (1H, sextet, H_2, J = 8.1, 3.7, 2.9 Hz), 6.02 (1H, dd, H_6, J = 5.9, 2.9 Hz), 6.38 (1H, dd, H_5, J = 5.9, 3.0 Hz). HRMS, Calcd for $C_9H_{12}OS_2$ (M^+) m/z: 200.0330. Found: 200.0334.

Exo Form: Yield 23%. Oil. IR (liquid film) cm^{-1}: 3068 (C=C), 1218, 1062 [–O(C=S)S–], 722 (*cis* olefin). 60 MHz ^{1}H-NMR (in $CDCl_3$) ppm: 1.5—2.0 (4H, m, CH_2), 2.45 (3H, s, SMe), 2.92 (1H, m, H_4), 3.02 (1H, m, H_1), 5.40 (1H, m, >CH–O–), 6.20 (2H, m, olefin). MS m/z: 200.

S-Alkyl Xanthates of Primary Alcohols The xanthates were prepared by the method developed in our laboratory: a mixture of alcohol and KOH in acetone was stirred until all the KOH had dissolved. The solution was diluted with ether to give precipitates. The precipitates were collected by filtration, washed with ether and dried. The resultant xanthogenate was allowed to react with alkyl halide to give the xanthate.

This method could not be applied to secondary alcohols because of side reactions (mainly aldol condensation of acetone).

Catalytic Rearrangement of *O*-Cyclopropylmethyl (Ib) and *O*-(1-Methylcyclopropyl) (Ic) *S*-Methyl Xanthates to the Corresponding Dithiol Esters (IIb and IIc) in the Presence of *p*-Nitrophenol A mixture of Ib and *p*-nitrophenol (0.25 eq) was heated at 120 °C on an oil bath until Ib was no longer detectable by thin-layer chromatography (TLC). The product was passed through a short column of silica gel to remove *p*-nitrophenol. The *n*-hexane eluent was evaporated to leave IIb as a colorless oil in 76% yield. IR (liquid film) cm^{-1}: 3080 (cyclopropane ring), 1644, 872 [–S(C=O)S–]. ^{1}H-NMR (in $CDCl_3$): 0.27—0.59 (4H, m, CH_2 of cyclopropane ring), 1.04 (1H, m, >CH–), 2.43 (3H, s, SMe), 2.97 (2H, d, J = 7.3 Hz, SCH_2–).

Compound Ic was heated with *p*-nitrophenol (0.25 eq) to give a mixture of IIc (10%) and IIc′ (52%). The structures of IIc and IIc′ were determined by examination of the 400 MHz ^{1}H-NMR spectrum. IIc: ^{1}H-NMR (in $CDCl_3$): 0.58 (4H, m, cyclopropane ring), 1.10 (3H, s, Me), 2.41 (3H, s, SMe), 3.02 (2H, s, CH_2). IIc′: ^{1}H-NMR (in $CDCl_3$): 1.69 (3H, s, Me), 2.23 (6H, m, cyclobutane ring), 2.36 (3H, s, SMe).

The structures of the rearranged products were confirmed by formation of the 2,4-dinitrophenyl sulfides.

Transformation of IIb and IIc′ to the 2,4-Dinitrophenyl Sulfide (IIIb, c, c′) A solution of IIb (683 mg) and ethanolamine (1 ml) in ethanol (2 ml) was heated at 70 °C on a water bath until the evolution of methanethiol ceased, then allowed to cool. A solution of 2,4-dinitrochlorobenzene (851 mg) in ethanol (2 ml) was added to the reaction mixture and the whole was allowed to stand overnight at room temperature. A small amount of water was added to the solution, and precipitates that appeared were collected and washed with water. Recrystallization from ethanol gave yellow crystals (IIIb), mp 81—82 °C, 150 mg. *Anal.* Calcd for $C_{10}H_{10}N_2O_4S$: C, 47.24; H, 3.96; N, 11.02. Found: C, 47.75; H, 4.16; N, 11.36. ^{1}H-NMR (in $CDCl_3$): 0.5—1.0 (5H, m, cyclopropane ring), 3.00 (2H, d, J = 6 Hz, $–CH_2S$), 7.48—9.09 (3H, m, Ar).

The dithiol ester IIc′ (1196 mg) containing a small amount of IIc was transformed into a mixture of the 2,4-dinitrophenyl sulfides (IIIc′ and IIIc) in a similar manner to that used for IIb. mp 105—110 °C, 787 mg. *Anal.* Calcd for $C_{11}H_{12}N_2O_4S$: C, 49.25; H, 4.51; N, 10.44. Found: C, 49.10; H, 4.29; N, 10.19.

Compound IIIc′, ^{1}H-NMR (in $CDCl_3$): 1.76 (3H, m, cyclobutane ring), 2.19—2.6 (6H, m, cyclobutane ring), 7.42—9.08 (3H, m, Ar).

Compound IIIc, ^{1}H-NMR (in $CDCl_3$): 0.5—0.7 (4H, m, cyclopropane ring), 1.28 (3H, s, Me), 3.03 (2H, s, $–CH_2–$), 7.42—9.08 (3H, m, Ar).

Phenolysis of *O*-Bornyl and *O*-Isobornyl *S*-Methyl Xanthates A solution of Ida (0.02 mol) in *p*-chlorophenol (0.06 mol) was heated at 100° for 140 h. After cooling, the product was extracted with *n*-hexane. The *n*-hexane was evaporated, and the residue was purified by chromatography on silica gel to give the dithiol ester (IIda) and camphene[9] in 38 and 6% yields, respectively. The products were identified by comparison of the ^{1}H-NMR spectral data with those of the samples which were prepared by the Lewis-acid catalyzed reaction.[13c] The ^{1}H-NMR spectrum and gas chromatogram of the crude product showed the presence of a small amount of isobornyl methyl sulfide.[13c]

Compound IIda: Colorless oil. IR (liquid film) cm^{-1}: 1644 (C=O), 868 (C–S). ^{1}H-NMR (in $CDCl_3$) ppm: 0.92 (6H, s, Me), 0.97 (3H, s, Me), 1.0—2.0 (7H, m, aliphatic ring protons), 2.45 (3H, s, SMe), 3.84 (1H, dd, J = 5.7, 9.5 Hz, >CHS–). *Anal.* Calcd for $C_{12}H_{20}OS_2$: C, 58.97; H, 8.25. Found: C, 59.14; H, 8.08. HRMS, Calcd for $C_{12}H_{20}OS_2$ (M^+) m/z: 244.0956. Found: 244.0952. The configuration of the S(C=O)SMe group was determined to be *exo* from the splitting pattern of the methine proton attached to the carbon bearing the dithiocarbonyl group.

Heating of *O*-isobornyl *S*-methyl xanthate in *p*-chlorophenol gave camphene as a sole product.

Catalytic Rearrangement of *O*-Bornyl *S*-Alkyl Xanthates (Ida—dd) to *S*-Isobornyl *S*-Alkyl Dithiocarbonates (IIda—dd) in the Presence of *p*-Nitrophenol A mixture of Ida—dd and an equimolar amount of *p*-nitrophenol was heated until the starting material was no longer detectable by TLC. After cooling, the product was extracted with *n*-hexane and purified by chromatography on silica gel. The reaction conditions are listed in Table V. The spectral data are as follows.

Compound IIda (S-Me): Yield 41%. The spectral data are described above.

Compound IIdb (S-Et): Yield 42%. Oil. IR (liquid film) cm^{-1}: 1644, 862 [–S(C=O)S–]. ^{1}H-NMR (in $CDCl_3$) ppm: 0.84 (6H, s, 2Me), 0.91 (3H, s, Me), 1.1—2.1 (10H, m, aliphatic ring protons and Me), 2.97 (2H, q, SCH_2), 3.78 (1H, dd, J = 6.1, 9.4 Hz, >SCH). HRMS, Calcd for $C_{13}H_{22}OS_2$ (M^+) m/z: 258.1112. Found: 258.1112.

Compound IIdc (S-*n*-Pr): Yield 59%. Oil. IR (liquid film) cm^{-1}: 1644, 866 [–S(C=O)S–]. ^{1}H-NMR (in $CDCl_3$) ppm: 0.84 (6H, s, 2Me), 0.91 (3H, s, Me), 1.0—2.1 (12H, m, aliphatic ring protons and CH_2), 2.97 (2H, t, SCH_2), 3.80 (1H, dd, J = 5.6, 9.5 Hz, >SCH). The rearrangement products were treated with $LiAlH_4$ (1 mol) followed by oxidation with I_2 to give isobornyl disulfide, mp 227—229 °C.

Compound IIdd (S-CH_2Ph): Yield 78%. Oil. IR (liquid film) cm^{-1}: 1642, 872 [–S(C=O)S–]. ^{1}H-NMR (in $CDCl_3$) ppm: 0.83 (6H, s, 2Me), 0.91 (3H, s, Me), 1.0—2.0 (7H, m, aliphatic ring protons), 3.67 (1H, dd, J = 5.4, 8.8 Hz), 4.17 (2H, s, $–SCH_2$), 7.24 (5H, s, aromatic protons). HRMS, Calcd for $C_{18}H_{24}OS_2$ (M^+) m/z: 320.1269. Found: 320.1268.

Catalytic Rearrangement of *O*-(5-Norbornen-2-yl) *S*-Methyl Xanthate (If) in the Presence of *p*-Nitrophenol The xanthate (If) was heated at 130 °C for 26 h in the presence of *p*-nitrophenol (1.0 eq). The reaction mixture was purified by chromatography on silica gel to give IIg (yield 29.4%) and a small amount of IIh (yield 5.4%).

Compound IIg: Oil. IR (liquid film) cm^{-1}: 3068 (cyclopropane ring), 1648, 864 [–S(C=O)S–], 812 (nortricyclene ring). ^{1}H-NMR (in $CDCl_3$) ppm: 1.18—1.26 (3H, m, H_1, H_2, H_6), 1.27 (1H, d, J = 9.5 Hz, H_5 or H_7), 1.38 (1H, dd, J = 10.6, 1.5 Hz, H_5 or H_7), 1.48 (1H, dd, J = 10.6, 1.1, H_5, H_7), 1.57 (1H, d, J = 9.5, H_5 or H_7), 2.09 (1H, s, H_4), 2.41 (3H, s, SMe), 3.58 (1H, s, >CH-S). ^{13}C-NMR (in $CDCl_3$) ppm: 10.668 (C_1 or C_2 or C_6), 12.246 (C_1 or C_2 or C_6), 14.584 (C_1 or C_2 or C_6), 12.884 (SMe, q), 30.734 (C_5 or C_7, t), 32.799 (C_5 or C_7, t), 34.954 (C_4, d), 50.346 (C_3, d), 189.902 (C=O, s). HRMS Calcd for $C_9H_{12}OS_2$ (M^+) m/z: 200.0330. Found 200.0325.

Thione–Thiol Rearrangement of Xanthates in the Presence of Phenols A mixture of xanthate (I) and a phenol was heated at 180 °C until I was no longer detectable by TLC. The mixture was diluted with *n*-hexane. The *n*-hexane solution of the product was passed through a short column of silica gel. The eluate was evaporated *in vacuo* to give an oil. The product (II) was identified by comparison of the spectral data with those of an authentic sample.[13] The composition of the product was analyzed by gas chromatography (GLC) and ^{1}H-NMR spectroscopy. The results are summarized in Table VII.

Kinetics a) The reaction rates for Ia—c were followed at a given temperature by measuring the decrease of the thiocarbonyl absorption at *ca.* 350 nm, using a ground glass stoppered 10 × 10 mm quartz cell which was thermostated with flowing water at constant temperature. The absorption data were collected automatically. The first-order rate constants were calculated from a plot of $\ln(A_t - A_\infty)$ *vs.* time by a least-squares method, where A_t is the absorbance at time t and A_∞ is the absorbance after about 10 half-lives. All spectra were calculated by means of a nonweighted least-squares program coded by F-BASIC86HG (V1.2).

b) A mixture of Ida—dd (0.8 mmol) and *p*-nitrophenol (0.8 mmol) was heated at a given temperature in a thermostated oil bath (Advantec Toyo Ltd., LHB-20) controlled to ±0.05 °C. The reaction was followed at a given temperature by measuring the decrease of the peak of Ida—dd at 288 nm by HPLC using *p*-nitrophenol as an internal standard.

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