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Solvolytic Behavior of *O*-(1-Cyclopropylethyl) *S*-Methyl Dithiocarbonate and Related Compounds

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O-(1-Cyclopropylethyl) *S*-methyl dithiocarbonate (Ib) was solvolyzed in various solvents to give *S*-(1-cyclopropylethyl) *S*-methyl dithiocarbonate (IIb) quantitatively. The reaction obeyed the first-order rate law and the rates were considerably affected by the polarity of the solvent used. Phenolysis of Ib with *p*-chlorophenol gave IIb and a small amount of the phenol ether. Plots of the logarithm of the reaction rates against *Y* values gave a linear relationship. The reaction was found to be markedly accelerated by phenolic solvents. The rate in *p*-chlorophenol is 509 times faster than that in ethanol. The role of hydrogen-bonding to the thione sulfur in the rearrangement reaction is discussed.

Keywords—1-cyclopropylethanol; thione–thiol rearrangement; solvolysis; phenolysis; kinetics; solvent effect; hydrogen-bonding; homoallylic participation; *O,S*-dialkyl dithiocarbonate; *S,S*-dialkyl dithiocarbonate

Introduction

Pyrolysis of *O,S*-dialkyl dithiocarbonates (xanthates) (I) has been used for the structure determinations of natural products because of the stereoselective formation of olefins by *cis*-elimination (Chugaev reaction) and has also been used as an olefin-forming reaction, which is particularly valuable for the conversion of sensitive alcohols to the corresponding olefins without rearrangement of the carbon skeleton.¹⁾ However, during the past twenty years, the progress in spectroscopic methods has made the former principal role of the Chugaev reaction redundant, and consequently it has become unfamiliar to organic chemists.

On the other hand, xanthates (I) are of interest because of their synthetic utility as precursors of thiols. In this connection, Taguchi and one of the authors have carried out systematic studies²⁾ on thermal and catalytic rearrangements of xanthates (I) to *S,S*-dialkyl

dithiocarbonates (II) and have clarified both the usefulness of the reaction from a synthetic standpoint and the reaction mechanism from a theoretical viewpoint. The rearrangement reactions have been used for synthesis of thiosugars³⁾ and other synthetic intermediates.⁴⁾

In the previous paper,⁵⁾ we reported that phenolysis of *O*-cholesteryl *S*-alkyl dithiocarbonates (Ia) having a homoallylic electron system (A) caused the thiono (-OCSS-)thiol (-SCOS-) rearrangement to give the corresponding *S*-alkyl *S*-cholesteryl dithiocarbonates (IIa) in high yield. In the reaction, we observed the skeletal rearrangement of cholesteryl (Ia) to *i*-cholesteryl (IIa') with thione-thiol rearrangement, in which the intermolecular hydrogen-bonding to the thione sulfur plays a leading role in the dissociation step. We have anticipated that the cyclopropylmethyl system (B) would show similar reaction behavior.

This paper describes the solvolytic and phenolytic behavior of *O*-(1-cyclopropylethyl) *S*-methyl dithiocarbonate (Ib) and related compounds in comparison with the previous results and with further additional data that we have obtained.

Results and Discussion

Warming Ib in dipolar aprotic solvents gave the corresponding dithiol ester (IIb) quantitatively.⁶⁾ When Ib was dissolved in a phenolic solvent at room temperature, Ib was immediately phenolyzed to the dithiol ester (IIb) and 1-(cyclopropylethyl) phenyl ether (III), whereas, in *n*-hexane, it remains unchanged for several months.

The structure of IIb was determined by inspection of the infrared (IR) and proton nuclear magnetic resonance (¹H-NMR) spectra and by conversion to the corresponding 2,4-dinitrophenylsulfide (IV). The IR spectrum of IIb shows characteristic bands at 1645 and 870 cm⁻¹ due to the -SCOS- moiety. In the ¹H-NMR spectrum of the rearranged product (IIb), five protons resonate at considerably high field (0.5–0.9 ppm) as complicated multiplets,⁷⁾ reflecting the highly shielded nature of the cyclopropane protons. The spectral pattern is essentially the same as that of the starting material with the exception of the chemical shift of the methine proton adjacent to the -SCOSMe group.

The ¹H-NMR spectrum of the crude product showed the absence of the multiplet at 4.0–5.0 ppm which is attributable to olefinic protons, ruling out the formation of an open chain compound, such as *S*-methyl *S*-(3-pentenyl) dithiocarbonate (IIb'). This suggests that skeletal rearrangement of the cyclopropyl system to the homoallylic system did not occur.

The thermal behavior of *O*-(1-cyclopropylethyl) *S*-methyl dithiocarbonate (Ib) was first studied by Overberger and Borchert.⁸⁾ They reported yields of 45% of olefins (cyclopropylethylene (V) in the main) and 35% of dithiol esters (IIb and IIb'), of which the major

r.t. = room temperature

Chart 2

TABLE I. First-Order Rate Constants for Solvolysis of *O*-(1-Cyclopropylethyl) *S*-Methyl Dithiocarbonate (Ib) in Various Solvents at $47.8 \pm 0.1^\circ\text{C}$

Solvent	$E_T^{a)}$ ($E_T^{N})^{b)}$	$Z^{a)}$	$Y^{a)}$	$\delta^c)$	$k \times 10^6 \text{ (s}^{-1}\text{)}$
HCONH ₂	56.6 (0.799)		0.604	19.2	11200
Glycol	56.3 (0.790)	81.88		17.05	2890
MeOH	55.5 (0.765)	81.46	-1.09	14.50	454
HCONHMe	54.1 (0.722)			16.1	606
80% EtOH	53.6 (0.767)	84.8	0.0	0.0	1620
EtOH	51.9 (0.654)	78.6	-2.033	12.78	78.4
AcOH	51.9 (0.654)	79.2	-1.639	13.0	114
<i>n</i> -PrOH	50.7 (0.617)	78.3		12.18	38.4
<i>n</i> -BuOH	50.2 (0.602)	77.7		11.6	77.8
iso-PrOH	48.6 (0.552)	76.3		11.44	21.6
iso-AmOH	47.0 (0.503)			11.09	28.0
DMSO	45.0 (0.441)	71.1		13.0	1045
Sulfolane	44.0 (0.410)			12.5	298.6
<i>tert</i> -BuOH	43.9 (0.407)	71.3	-3.26	10.5	5.68
DMF	43.8 (0.404)	68.5		11.79	205
TMU ^{d)}	41.0 (0.318)				24.5
Anisole	37.2 (0.201)			9.0	1.80
<i>p</i> -ClC ₆ H ₅ OH					39900
<i>o</i> -ClC ₆ H ₅ OH					1460
2,6-Xylenol	47.6				175

a) See ref. 11c. b) $E_T = [E_T(\text{solvent}) - E_T(\text{TMS})]/[E_T(\text{water}) - E_T(\text{TMS})]$. c) See ref. 14.
d) Tetramethylurea.

TABLE II. Activation Parameters for Solvolysis of *O*-(1-Cyclopropylethyl) *S*-Methyl Dithiocarbonate (Ib)

Solvent	E_a (kcal/mol)	$\Delta S^\ddagger$ (e.u.)
HCONHMe	25.2	3.3
EtOH	28.1	8.1
DMSO	22.2	-4.4
DMF	22.8	-6.4
<i>p</i> -ClC ₆ H ₄ OH	19.6	-6.0
<i>o</i> -ClC ₆ H ₄ OH	16.0	-24

component was identified as *S*-(1-cyclopropylethyl) *S*-methyl dithiocarbonate (IIb). Subsequently, pyrolysis of *O*-(1-cyclopropylethyl) *S*-methyl dithiocarbonate (Ib) has been cited by several researchers as a typical example of a compound which undergoes thermal rearrangement to the corresponding dithiol ester (IIb), although it has four hydrogen atoms at the adjoining carbons.^{1,9)}

In order to get some information about the nature of the transition state of the rearrangement reaction, we have studied solvent effects on the rate of the solvolytic reaction. The rates of reaction were determined in various solvents by measuring the decrease of the thione chromophore. In all cases, excellent first-order rate plots were obtained to over 70% reaction. The rate constants obtained are given in Table I. The enthalpy and entropy of activation were calculated from these data by using the least-squares method. The values obtained are given in Table II.

The rate of reaction was found to depend significantly on the ionizing power of the solvent, increasing greatly when the solvent was changed from aprotic to protic. As can be

seen in Table I, the rates for the phenolic solvents are larger than those observed for other protic solvents. The largest rate was found in *p*-chlorophenol among all the solvents used. The xanthate solvolyzed about 509 times faster in *p*-chlorophenol than in ethanol. In contrast, the rate acceleration of *o*-chlorophenol is far less than of *p*-chlorophenol, being comparable to that for 80% ethanol. The intermolecular hydrogen-bonding power of *o*-chlorophenol may be reduced by its intramolecular hydrogen-bonding.¹⁰⁾

When the xanthate (Ib) was treated with *p*-chlorophenol, a considerable amount of phenolysis product (III) was found in the reaction mixture indicating that the reaction

Chart 3

Fig. 1. Plots of k vs. E_T Values for the Solvolysis of IbTABLE III. Sensitivity of Thione-Thiol Isomerization Reactions to Solvent Ionizing Power (E_T Value)

Substrate ^{a)}	Solvent sensitivity parameter, $a^b \times 10^2$	Reaction type
<i>O</i> -(2-Diethylaminoethyl) <i>S</i> -methyl dithiocarbonate (If)	40.4	c)
<i>O</i> -(1-Cyclopropylethyl) <i>S</i> -methyl dithiocarbonate ^{e)} (Ib)	34.1 (aprotic) 23.3 (protic)	c)
<i>O</i> -(2-Methylthioethyl) <i>S</i> -methyl dithiocarbonate ^{e)} (Ig)	22.4	c)
<i>O</i> -Cinnamyl <i>S</i> -methyl dithiocarbonate (Ie)	12.6	d)
<i>O</i> -Allyl <i>S</i> -methyl dithiocarbonate (Ic)	6.31	d)
<i>O</i> -Methallyl <i>S</i> -methyl dithiocarbonate ^{e)} (Id)	5.54	d)
<i>O</i> -Allyl thiobenzoate (VI)	4.24	d)

a) See ref. 12 and references cited therein. b) $\log k = aE_T + b$. c) Solvolysis. d) [3,3]-Sigmatropy. e) This study.

proceeds through, at least in part, a solvent-separated ion-pair intermediate (D and D'). This is in sharp contrast to the result in the case of *O*-cholesteryl *S*-alkyl dithiocarbonates (Ia) which underwent rearrangement *via* a tight ion-pair intermediate (C and C').⁵⁾

For an estimate of solvent effects on chemical reactions, a large variety of empirical parameters of solvent polarity^{11c,d)} have been proposed. In this study, the E_T values of Reichardt,¹¹⁾ based on the bands of solvatochromism of pyridinium *N*-phenoxide betaine dye were used as a scale of solvent ionizing power in studying the effect of solvents on the rate of reaction.^{11e)}

As illustrated in Fig. 1, plots of $\log k$ vs. E_T values for aprotic and protic solvent systems show roughly linear relationships with slopes $a=0.341$ and 0.233 , respectively. The magnitude of the slope a has been successfully used as a measure of the sensitivity of a reaction to the ionizing power of the medium.^{2c,12)} Values of the least-squares slope a for thione-thiol isomerization reaction are summarized in Table III.

As shown in Table III, the values of a are 6.31×10^{-2} for *O*-allyl *S*-methyl dithiocarbonate (Ic), 5.5×10^{-2} for *O*-(2-methylallyl) *S*-ethyl dithiocarbonate (Id) and 4.24×10^{-2} for *O*-allyl thionbenzoate (VI). These values are very small, indicating that these thione esters may rearrange by a mechanism which involves very little change in charge separation between the ground state and the transition state ([3, 3]-sigmatropy). On the other hand, a in the case of Ib is very large and comparable to the value in the case of the allylic rearrangement of *cis*-5-methyl-2-cyclohexenyl acid phthalate (VII) ($a=29.1 \times 10^{-2}$),¹²⁾ the pyrolysis of benzhydryl *S*-phenylthiocarbonate (VIII) to the sulfide (31.2×10^{-2})¹²⁾ and the thione-thiol rearrangements of *O*-(2-dimethylaminoethyl) (If) (40.4×10^{-2}) and *O*-(2-methylthioethyl) *S*-methyl (Ig) (22.4×10^{-2}) dithiocarbonates. These values are very large, suggesting that the rearrangement reactions occur through highly polarized transition states, such as an ion-pair.

A plot of the logarithm of the rate constants for Ib vs. the Grunwald-Winstein Y values¹³⁾ is shown in Fig. 2. It is well known that the classical $SN1$ and $SN2$ mechanisms are only the extremes in a continuous spectrum of mechanisms, and reactions at the $SN2$ end have m -values in the neighborhood of 0.4, while those at the $SN1$ end have m -values of about 1.0. Reactions having intermediate or borderline mechanisms have m -values between these extremes. As can be seen in Fig. 2, m in the case of the concerted reaction for the allylic rearrangement of *O*-allyl *S*-methyl dithiocarbonate (Ic) is only 0.14. On the other hand, m for the present case (Ib) is 0.68. The results are in agreement with the conclusion arrived at from the E_T values, as described above.

For further evaluation of the Fainberg-Winstein Y values^{13b)} for binary mixtures of 10,

Fig. 2. Plots of k vs. Grunwald-Winstein Y Values for the Solvolysis of Ib

Fig. 3. Plots of k vs. Fainberg-Winstein Y Values for the Phenolysis of Ib,e in Phenol-Benzene Solvent

20, 30, 40 and 50% phenol with benzene, the phenolysis rates of Ia and *O*-cinnamyl *S*-methyl dithiocarbonate (Ie) in these solvent systems were also determined at 33.9 °C. The results are presented in Table IV. A plot of the logarithm of the rate constants for Ib, e against the Fainberg–Winstein *Y* values is shown in Fig. 3.

It is noteworthy that plots of *k* for protic solvents vs. δ values¹⁴⁾ (solubility parameters) show a linear relationship, and there is a rough correlation with hydrogen-bonding abilities.

The activation energy for ethanol (protic) is 5 kcal/mol larger than that for dimethylformamide (DMF) (dipolar aprotic), suggesting that the xanthate is stabilized in the ground state by hydrogen-bonding between the thione sulfur and solvent. The activation energies for the phenolic solvents are considerably smaller than that for ethanol (see Table II).

The values of activation entropy vary considerably from –6.0 to 8.1 e. u. on going from DMF to ethanol. The large entropy effect in ethanol is due in part to the highly ordered

TABLE IV. First-Order Rate Constants for Phenolyses of *O*-(1-Cyclopropylethyl) (Ib) and *O*-Cinnamyl (Ie) *S*-Methyl Dithiocarbonates in Phenol–Benzene Solvents at 33.9 °C

PhOH ^{a)} (%)	<i>Y</i> ^{b)}	$k \times 10^5$ (s ^{–1})	
		Ib	Ie
90	1.427	557	276
70	1.101	245	126
50	0.425	85.8	51.5
30	–0.192	21.2	16.8
20	–0.711	7.43	7.78

a) First-order constants ($k \times 10^6$) for phenolyses of Ib in *p*-chlorophenol–benzene solvents are as follows: 10%, 33.5; 20%, 170; 30%, 415; 40%, 1002; 50%, 1704. b) See ref. 13b.

structure of the reactants in the ground state. When a phenolic solvent was used, a low entropy of activation was observed, which may be due to its high hydrogen-bonding ability to the leaving group, as well as the steric crowding in solvation. A large negative entropy of activation for *o*-chlorophenol may reflect a crowded transition state in which freedom of motion of the substituents is hindered by the presence of the *o*-chloro group.

O-(1-Methylcyclopropylmethyl) *S*-methyl dithiocarbonate (Ih) reacts about 300 times more slowly than Ib in *p*-chlorophenol at 60 °C. The interaction between the methylium carbon and the cyclopropyl ring can be rationalized by means of the dissection method¹⁵⁾ as illustrated in Chart 4, wherein the cyclopropane ring acts as a donor (HOMO) and the methylium carbon acts as an acceptor (LUMO), resulting in effective anchimeric assistance for ionization of the C–O bond.

In connection with the rearrangement reaction, mention should be made of the alteration of the mechanism of the thione–thiol rearrangement of *S*-(2-alkenyl) *S*-alkyl dithiocarbonates in phenolic solvents. In the phenolysis of *O*-cinnamyl *S*-methyl dithiocarbonate (Ie) in *p*-chlorophenol, the mechanism of the rearrangement reaction changes dramatically from the concerted reaction^{2c)} to the ionic one. In usual protic solvents such as ethanol, the [3,3]-sigmatropic reaction takes place to give IIe. However, when the same reaction is carried out in a phenolic solvent such as *p*-chlorophenol, a pair of allylic isomers (IIe and IIe') was obtained as the result of an ionic nucleophilic replacement reaction *via* an intermediate, F.¹⁶⁾ In the reaction, the carbonium ions may be stabilized by the specific solvation¹⁷⁾ of phenols to the extent that the solvent stabilizing energy exceeds the resonance energy of the styrene moiety.

Chart 6

It is concluded that the hydroxyl group is distinctly the center of the reaction in hydroxylic solvents such as alcohols or phenols and they play a role not only as a general solvent but also as a kind of reactant molecule in the ionization process of the *S*_N1-type solvolysis.¹⁸⁾ The reaction constants in hydroxylic solvents can be used as a measure of the hydrogen-bonding capacity of the solvent with a sulfur atom.

Experimental

The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. The ultraviolet (UV) spectra were determined by Hitachi EPS-3T and JASCO UVIDECD-220B digital spectrophotometers. The ¹H-NMR spectra were taken with Hitachi R-600 or JEOL PS-100 and GX-400 spectrophotometers using tetramethylsilane as an internal standard, and the chemical shifts are expressed in δ values. The IR spectra were taken with JASCO IRA-1 and DS-301 grating spectrophotometers.

All the calculations were performed on FACOM M-200 and 382 computers in the computer center of Kyushu University.

Solvents—Solvents were purified by distillation or by recrystallization before use.

O, S-Dialkyl Dithiocarbonates—*O*-(1-Cyclopropylethyl) (Ib) and *O*-(1-methylcyclopropylmethyl) (Ih) *S*-methyl dithiocarbonates were prepared according to the reported method.⁸⁾ *O*-Allyl (Ic), *O*-(2-methylallyl) (Id), *O*-(3-phenylallyl) (Ie), *O*-(2-diethylaminoethyl) (If) and *O*-(2-methylthioethyl) (Ig) *S*-methyl dithiocarbonates were prepared according to procedures developed in this laboratory.^{2c)}

The ¹H-NMR spectral data for Ib are as follows; ¹H-NMR (in CCl₄) of Ib: 0.47, 0.62 (4H, m, >CH₂ of cyclopropane ring), 0.90 (1H, m, >CH- of cyclopropane ring), 1.41 (3H, d, *J* = 6 Hz, -Me), 2.53 (3H, s, SMe), 5.18 (1H, dt, *J* = 5.3 Hz, >CH-O).

Compound Ih¹⁹⁾ was obtained as a yellow oil: bp 111 °C (23 mmHg). IR (liquid film) cm⁻¹: 3084 (cyclopropane ring), 1222, 1066 (-OC=SS-). ¹H-NMR (in CDCl₃, 400 MHz): 0.453 (2H, t, CH₂ of cyclopropane ring), 0.562 (2H, t, CH₂ of cyclopropane ring), 1.198 (3H, s, SMe), 4.377 (2H, s, CH₂-O). *Anal.* Calcd for C₇H₁₂OS₂: C, 47.69; H, 6.86. Found: C, 47.80; H, 7.1.

Phenolysis of Ib with *p*-Chlorophenol—Compound I was dissolved in *p*-chlorophenol at room temperature to give immediately the corresponding dithioester (IIb) and *p*-chlorophenyl 1-cyclopropylethyl ether (III) in 77% and 14% yields, respectively. The products were purified by column chromatography on silica gel with *n*-hexane–benzene. The structure of IIb was determined on the basis of its ¹H-NMR spectrum (100 MHz). The data obtained in a double-resonance experiment are as follows; ¹H-NMR (in CDCl₃): 0.24–0.7 (4H, m, >CH₂ of cyclopropane ring), 0.7–1.13 (1H, m, >CH- of cyclopropane ring), 1.45 (3H, d, *J* = 6.9 Hz, Me), 2.41 (3H, s, MeS-), 3.07 (1H, dt, *J* = 7.5 Hz, >CH-S).

The IR spectrum of III was identical with that of an authentic sample (see below).

Rearrangement of Ib to IIb—A solution of Ib (3 g) in an aprotic solvent (5 ml) such as dimethyl sulfoxide (DMSO) was heated at 50 °C for 1 h. After cooling, 10 ml of water was added. The rearranged product (IIb) was extracted with *n*-hexane and distilled under reduced pressure to give IIb, bp 234–236 °C, quantitative yield. Water-soluble solvents such as ethanol gave a similar result.

1-Cyclopropylethyl 3,5-Dinitrobenzoate (IX)—Prepared by the reported method.²⁰⁾ The ¹H-NMR spectral data (400 MHz) are as follows; ¹H-NMR (in CDCl₃): 0.375 (1H, sextet, >CH₂ of cyclopropane ring), 0.495 (1H, sextet, >CH₂ of cyclopropane ring), 0.573–0.712 (2H, m, >CH₂ of cyclopropane ring), 1.209 (1H, nonet, >CH- of cyclopropane ring), 1.515 (3H, d, *J* = 6.35 Hz, Me), 4.655 (1H, m, octet, >CH-O), 9.174 (2H, d, *J* = 2.4 Hz, H₄), 9.224 (1H, d, *J* = 2.4 Hz, H₂ and H₆). The signals appear as complex multiplets, presumably due to restricted rotation about the bond connecting the cyclopropane ring and C₁ carbon.

***p*-Chlorophenyl 1-Cyclopropylethyl Ether (III)**—1-Cyclopropylethyl 3,5-dinitrobenzoate (IX) was added to a solution of *p*-chlorophenol (6 ml) containing 0.5 g of sodium *p*-chlorophenolate, and the mixture was heated on a water bath for 3 h. The reaction mixture was diluted with 20 ml of benzene and treated with 10% NaOH solution. The benzene layer was separated, washed once with water, dried over anhydrous MgSO₄, and evaporated. The residue was chromatographed on silica gel to give a colorless oil, 487 mg. *Anal.* Calcd for C₁₁H₁₃ClO₂: C, 67.18; H, 6.66. Found: C, 67.23; H, 6.66. ¹H-NMR (in CDCl₃): 0.16–1.23 (5H, m, cyclopropane ring), 1.31 (3H, d, *J* = 6 Hz, -Me), 3.83 (1H, sextet, *J* = 6 Hz, >CH-O), 6.75 (4H, AB quartet, *J* = 9 Hz, *p*-ClC₆H₄O-).

Transformation of IIb to 1-Cyclopropylethyl 2,4-Dinitrophenyl Sulfide (IV)—A solution of IIb (176 mg) and ethanolamine (200 mg) in ethanol (2 ml) was heated on a water bath until the evolution of methanethiol ceased. After cooling, a solution of 2,4-dinitrochlorobenzene (203 mg) in ethanol (2 ml) was added to the reaction mixture and the whole was allowed to stand overnight at room temperature. The precipitates were recrystallized from ethanol to give yellow crystals, mp 71–73.5 °C, identical with the reported sample.⁸⁾

Kinetics—The phenolysis rates were followed at a given temperature by measuring the decrease of the thione absorption at 350 nm, using a 10 × 10 mm quartz cell which was thermostated with flowing water at constant temperature. The first-order rate constants were calculated from a plot of ln(*A_t* – *A_∞*) 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. The absorption data were collected automatically. The results are listed in Tables I–III. All spectra were calculated by means of a nonweighted least-squares program written in FORTRAN.

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