Chem. Pharm. Bull.
26(12)3807—3814(1978)

UDC 546.264'547.26.04 : 546.273.13.04

# Catalytic Rearrangement of O,S-Dialkyl Dithiocarbonates to S,S-Dialkyl Dithiocarbonates. IV.[1] Use of Boron Trifluoride Etherate as Catalyst[1c]

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(Received June 26, 1978)

Migration of alkyl group from O to S in the reaction of O,S-dialkyl dithiocarbonates with boron trifluoride etherate was studied to elucidate the reaction mechanism on the basis of results from kinetics, crossover reaction, and products formed.

It was worthy of note that dialkyl methyl sulfonium fluoroborates were formed in a fairly good yield in reactions with O-alkyl S-methyl dithiocarbonates (alkyl=benzyl and cholesteryl) with boron trifluoride etherate. Formation mechanism of these by-products was investigated and discussed.

**Keywords**——O,S-dialkyl dithiocarbonate; S,S-dialkyl dithiocarbonate; Lewis acid-catalyzed rearrangement; kinetics of rearrangement; trialkyl sulfonium fluoroborate

The first paper of this series[3] reported that O,S-dialkyl dithiocarbonates (xanthates) (I) underwent rearrangement to S,S-dialkyl dithiocarbonates (II) by the catalysis of aluminum chloride in carbon disulfide. Subsequently, it has been shown that the rearrangement is caused also by other Lewis acids such as boron trifluoride etherate and stannic chloride.[1b]

Reaction mechanisms have been proposed for catalytic rearrangements of other thionic esters by boron trifluoride etherate.[4,5] However, our preliminary study suggested that the proposed reaction mechanisms seemed to be inapplicable to the case where O,S-dialkyl dithiocarbonate was employed as a substrate. The present study was undertaken to solve this problem by examining the catalytic rearrangement of O,S-dialkyl dithiocarbonates with boron trifluoride etherate in detail.

## Results

### Syntheses of O,S-Dialkyl Dithiocarbonates (ROCSSR') (I)

The compounds (I) in which R is primary alkyl were synthesized according to the improved procedure[6] developed in this laboratory by treatment of a mixture of alcohol and $CS_2$ with KOH in $(CH_3)_2SO$ followed by alkylation. On the other hand, I in which R is secondary alkyl were synthesized by the usual method depending upon treatment of sodium or potassium alkoxide with $CS_2$ and alkyl halide in benzene.

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[1] *a*) Part III: T. Kawata, K. Harano, and T. Taguchi, *Yakugaku Zasshi*, **98**, 600 (1978); *b*) *Idem*, *ibid*., **96**, 832 (1976); *c*) Presented in part at the 24th Symposium on Organic Reaction Mechanism, Fukuoka, Japan, October 12, 1973.

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[3] T. Kawata, K. Harano, and T. Taguchi, *Chem. Pharm. Bull.* (Tokyo), **21**, 604 (1973).

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[6] K. Harano and T. Taguchi, *Yakugaku Zasshi*, **94**, 1495 (1974).

**Catalytic Rearrangement**——O,S-Dialkyl dithiocarbonates (I) were dissolved in a large excess of $BF_3 \cdot Et_2O$ and the mixture was heated without a solvent until the characteristic bands of the thion–ester disappeared in the ultraviolet (UV) spectrum. Products were analyzed by gas chromatographic method (GLC). The data are summarized in Table I.

As can be seen in Table I, O-primary alkyl S-methyl dithiocarbonates underwent rearrangement to the corresponding thiol esters (II) in a moderate yield (50—80%) and variation

TABLE I. S,S-Dialkyl Dithiocarbonates (RSCOSR′) (II) derived from Reaction of O,S-Dialkyl Dithiocarbonates (ROCSSR′) (I) with Excess $BF_3 \cdot Et_2O$

| R | R′ | Reaction conditions | | Yield (%) | bp (°C/Torr) or mp (°C) | Identification method |
|---|---|---|---|---|---|---|
| | | Time (hr) | Temp. (°C) | | | |
| $CH_3$ | $CH_3$ | 8.0 | 100 | 60 | 167—168/760 | A |
| $CH_3$ | $CH_3CH_2$ | 17.0 | 75 | 69 | 83—85/30 | A |
| $CH_3CH_2$ | $CH_3$ | 7.0 | 80 | 70 | | |
| $CH_3$ | $p$-$ClC_6H_4CH_2$ | 6.0 | 80 | 71 | 106—107.5/0.7 | B |
| $CH_3CH_2$ | $CH_3CH_2$ | 11.0 | 90 | 79 | 83—86/14 | A |
| $CH_3(CH_2)_2$ | $CH_3$ | 8.0 | Reflux | 60 | 92—94/22 | A |
| $(CH_3)_2CH$ | $CH_3$ | 2.0 | 90 | 27 | 79—82/19 | A |
| $CH_3$ | $(CH_3)_2CH$ | 10.0 | 80 | 53 | | |
| $(CH_3)_2CH$ | $C_6H_5CH_2$ | 3.5 | Reflux | 25[a] | 70—75/0.7[b] | B |
| $CH_3(CH_2)_3$ | $CH_3$ | 11.0 | 100 | 55 | 96—97/2 | A |
| $CH_3(CH_2)_4$ | $CH_3$ | 8.5 | 100 | 56 | 62—64/0.8 | B |
| $(CH_3)_2CH(CH_2)_2$ | $CH_3$ | 10.0 | 100 | 55 | 60—63/0.8 | B |
| $C_6H_5CH_2$ | $CH_3$ | 2.0 | 50 | 31[c] | 110—111/1.0 | A |
| $CH_3$ | $C_6H_5CH_2$ | 10.0 | 80 | 70 | | |
| $C_6H_5CH_2CH_2$ | $CH_3$ | 6.0 | 75 | 58 | 109—109.5/0.7 | B |
| $CH_3$ | $C_6H_5CH_2CH_2$ | 13.0 | 75 | 60 | | |
| Cyclohexyl | $CH_3$ | 2.0 | Reflux | 15[d] | 145—147/17 | A |
| Isobornyl | $CH_3$ | 1.0 | 40 | 71[e] | Oil | B |
| Cholesteryl | $CH_3$ | 2.0 | rt[f] | 40[g] | 130—134[h] | A |

a) By-products: Isopropyl methyl sulfide (23%) and phenylmethanethiol (40%).
b) Bath temperature.
c) By-products: Benzyl methyl sulfide (3%) and dibenzyl methyl sulfonium fluoroborate (35%).
d) By-products: Cyclohexyl methyl sulfide (18%) and cyclohexene (50%).
e) Prepared from O-bornyl S-methyl dithiocarbonate. By-product: Isobornyl methyl sulfide (2%).
f) Room temperature.
g) By-product: Dicholesteryl methyl sulfonium fluoroborate (40%).
h) From ethyl acetate.

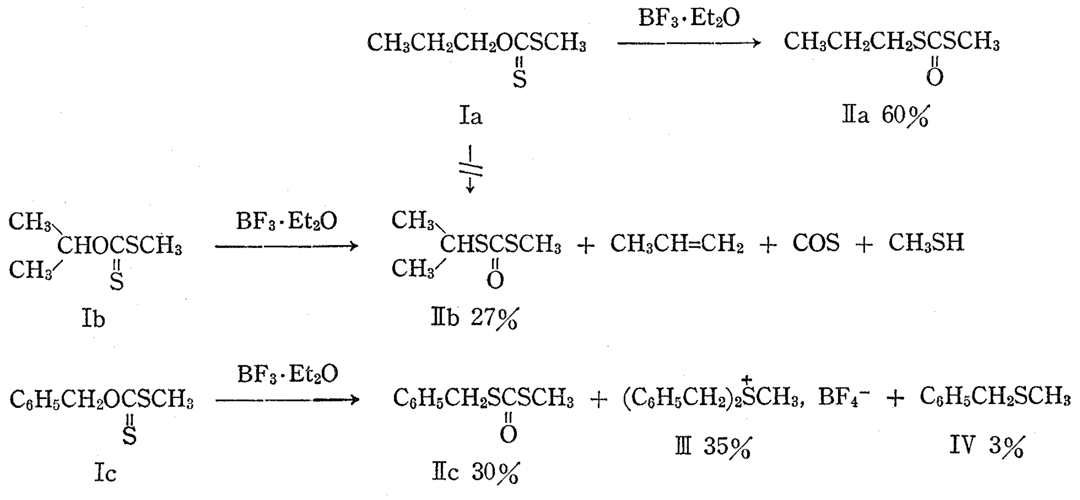
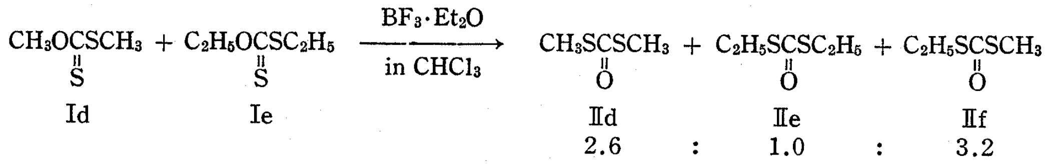


Chart 1

of S-alkyl group of I did not affect the essential feature of the rearrangement. Isomerization of propyl to isopropyl in the rearrangement process from O to S was not observed in this treatment, although it has often been observed in the Friedel–Crafts reaction[7] (Chart 1). On the contrary, when the substrate was O-secondary alkyl S-methyl dithiocarbonates, yields were much lower because side reactions (elimination reaction in the main) were competing (Chart 1).

When O-benzyl S-methyl dithiocarbonate (Ic) was subjected to the rearrangement reaction, the rearrangement product (IIc) was obtained in 30% yield, together with dibenzyl methyl sulfonium fluoroborate (III) and benzyl methyl sulfide (IV) in 35% and 3% yield, respectively (Chart 1).

**Crossover Reaction**——In order to clarify whether the rearrangement is intermolecular or intramolecular, an equimolar mixture of O,S-dimethyl dithiocarbonate (Id) and O,S-diethyl dithiocarbonate (Ie) was treated with $BF_3 \cdot Et_2O$ in $CHCl_3$. The reaction mixture was analyzed by GLC. The chromatogram showed the presence of S-ethyl S-methyl dithiocarbonate (IIf) which should be formed by a crossover reaction, besides S,S-dimethyl and S,S-diethyl dithiocarbonate (IId and IIe). This observation suggests that the rearrangement may be ionic and intermolecular (Chart 2).



$$\underset{\text{Id}}{CH_3O\underset{\underset{S}{\|}}{C}SCH_3} + \underset{\text{Ie}}{C_2H_5O\underset{\underset{S}{\|}}{C}SC_2H_5} \xrightarrow[\text{in } CHCl_3]{BF_3 \cdot Et_2O} \underset{\text{IId}}{CH_3S\underset{\underset{O}{\|}}{C}SCH_3} + \underset{\text{IIe}}{C_2H_5S\underset{\underset{O}{\|}}{C}SC_2H_5} + \underset{\text{IIf}}{C_2H_5S\underset{\underset{O}{\|}}{C}SCH_3}$$

$$2.6 : 1.0 : 3.2$$

Chart 2

**Kinetics of the Rearrangement**——The reaction of O,S-dialkyl dithiocarbonates with $BF_3 \cdot Et_2O$ in $CHCl_3$ was investigated kinetically. The rates were determined by measuring

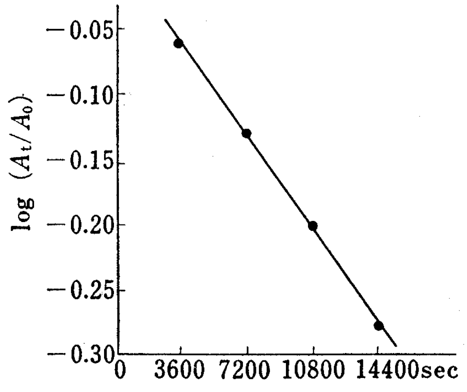


Fig. 1. Plots of Rate for the Rearrangement of O-Methyl S-Benzyl Dithiocarbonate (Ig) at 45.2 ±0.1° in $CHCl_3$

Ig: $2.49 \times 10^{-2}$ mol·l$^{-1}$
$BF_3 \cdot Et_2O$: $62.82 \times 10^{-2}$ mol·l$^{-1}$
$k_1 = 4.75 \times 10^{-5}$ sec$^{-1}$

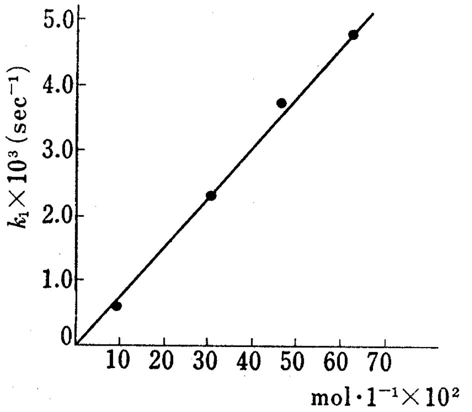


Fig. 2. Plots of $k_1$ against Concentration of $BF_3 \cdot Et_2O$ for the Rearrangement of O-Methyl S-Benzyl Dithiocarbonate (Ig) at 45.2±0.1° in $CHCl_3$

| $BF_3 \cdot Et_2O$ mol·l$^{-1}$ × $10^2$ | $k_1$(sec$^{-1}$) × $10^5$ |
|---|---|
| 10.59 | 0.53 |
| 30.92 | 2.29 |
| 46.73 | 3.70 |
| 62.82 | 4.75 |

Ig: $2.49 \times 10^{-2}$ mol·l$^{-1}$
$k_2 = 7.61 \times 10^{-5}$ l·mol$^{-1}$·sec$^{-1}$

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[7] C.C. Price, *Org. Reactions*, 3, 1 (1964).

Table II. Rate Constants for the Rearrangement of O,S-Dialkyl Dithiocarbonate (ROCSSR′) at 45.2±0.05° in Chloroform[a)]

| ROCSSR′ | | $k_1(\mathrm{sec}^{-1}) \times 10^3$ |
|---|---|---|
| R | R′ | |
| $CH_3$ | $CH_3$ | 5.00 |
| | $C_2H_5$ | 1.05 |
| | $C_6H_5CH_2$ (Ig) | 4.75 |
| | $p$-$ClC_6H_4CH_2$ | 3.20 |
| $C_2H_5$ | $CH_3$ | 1.07 |
| $CH_3(CH_2)_2$ | $CH_3$ (Ia) | 0.78 |
| $(CH_3)_2CH$ | $CH_3$ (Ib) | *ca.* 30[b)] |
| $CH_3(CH_2)_3$ | $CH_3$ | 1.11 |

a) O,S-Dialkyl dithiocarbonate: $2.49 \times 10^{-2}$ mol·l⁻¹. $BF_3 \cdot Et_2O$: $62.82 \times 10^{-2}$ mol·l⁻¹.
b) The rate constant was calculated from data obtained by tracing the decrease of Ib and the increase of IIb because this reaction is accompanied by elimination reaction to produce propylene as a by-product.

the amount of the remaining reactants (I) by UV spectrometry. It was found that the rearrangement followed first-order kinetics. A typical run is shown in Fig. 1. The first-order rate constants were determined from the slopes of the straight lines obtained by plotting $ln\ A_t/A_0$ against time, where $A_0$ and $A_t$ are the absorbances of I at time 0 and time $t$, respectively. These data are summarized in Table II. The rearrangement rate of I to II was not appreciably affected by the change of S-alkyl group, as can be seen in Table II. On the other hand, the effect of O-alkyl is highly affected by the alkyl being primary or secondary. For example, the rearrangement rate of O-propyl S-methyl dithiocarbonate (Ia) was much slower than that of the sec-propyl derivative (Ib) under analogous reaction conditions. Then, the effect of concentration of $BF_3 \cdot Et_2O$ on the rearrangement of O-methyl S-benzyl dithiocarbonate (Ig) was examined. As shown in Fig. 2, the pseudo-first-order rate constants are roughly proportional to the concentration of $BF_3 \cdot Et_2O$. Thus, the rearrangement is first-order for the catalyst and for the substrate. A second-order rate constant ($k_2$) was obtained from the slope of the line by means of the method of least squares (Fig. 2).

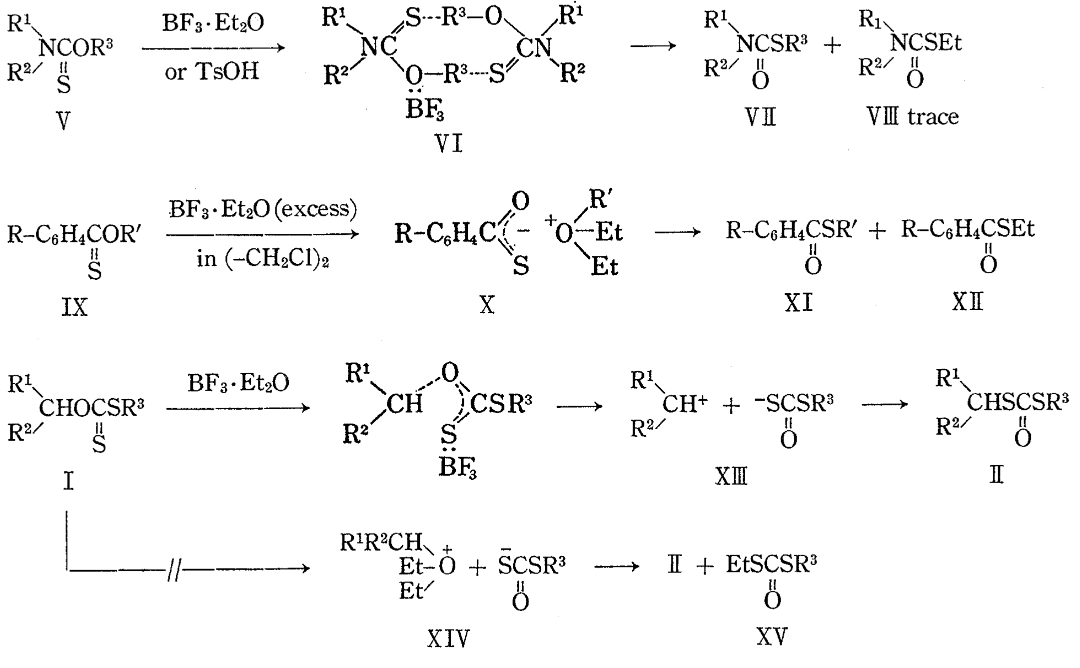

Chart 3

## Discussion

With respect to the rearrangement of thioesters to thiol esters by the catalysis of boron trifluoride etherate, studies on O-alkyl N,N-dialkyl thiocarbamates4) (V) and O-alkyl thiobenzoates5) (IX) have already been made.

In the reactions of O-alkyl thiobenzoate (IX) with boron trifluoride etherate in dichloroethane, a large amount of S-ethyl benzoate (XII) was found in the reaction mixture, in addition to normal rearrangement product (XI). On the basis of this finding and kinetic data, Oishi *et al.*5) concluded that the rearrangement took place through an alkyl diethyloxonium ion intermediate (X) which was derived from ether of boron trifluoride etherate as shown in Chart 3. On the other hand, in the reaction of O-alkyl N,N-dialkyl thiocarbamate with boron trifluoride etherate, only a very small amount of S-ethyl N,N-dimethyl thiocarbamate (VIII) was detected in the products by GLC. On this basis, Kinoshita *et al.*4) presumed that alkyl diethyloxonium ion intermediate similar to X might not play a leading role in the rearrangement, proposing the speculative reaction pathway as shown in Chart 3. As an additional remark, they suggested that the mechanistic difference between the reactions might be due to the difference in nucleophilicity of the thiocarbonyl (C=S) in both kinds of substrates. In the present studies on rearrangement of O,S-dialkyl dithiocarbonates (I), the rate of the rearrangement was found to be proportional to the concentration of both O,S-dialkyl dithiocarbonates (I) and boron trifluoride etherate. Moreover, S-alkyl S-ethyl dithiocarbonate (XV), which might be derived *via* an alkyl diethyl oxonium ion intermediate (XIV), was not detected by either nuclear magnetic resonance (NMR) spectrometry or GLC. These observations suggest that the rearrangement proceeds not through an alkyl diethyloxonium ion intermediate (XIV), similar to that proposed in the case of alkyl thiobenzoate (IX), but through carbonium ion intermediate (XIII), as shown in Chart 3.

The reason why the oxonium intermediate cannot be formed may be attributed to the fact that $^-$SCOSR is a stronger nucleophile than oxygen of ether toward the carbonium cation, because the electron density of C=S is increased by the *I*-effect of the alkylthio group in this case.

Considering the result from the crossover reaction in addition to the ionic character of the reaction mentioned above, it is concluded that the reaction proceeds through an intermolecular ionic mechanism as shown in Chart 3. This feature is quite analogous to the mechanism of rearrangement of O,S-dialkyl dithiocarbonate by catalysis of aluminum chloride.3)

Among by-products found in the present catalytic reaction, trialkylsulfonium fluoroborate was an unexpected product. Therefore, the course of reaction for the formation of sulfonium fluoroborates was considered. For example, the reaction of O-benzyl S-methyl dithiocarbonate (Ic) with boron trifluoride etherate (unpurified) produced dibenzyl methyl

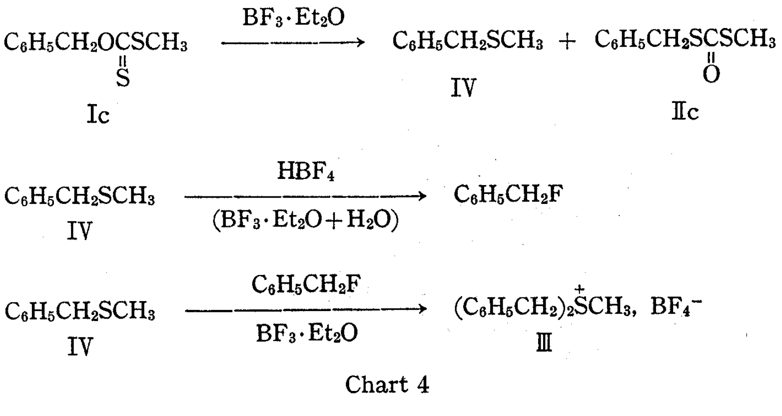

Chart 4

sulfonium fluoroborate (III) (35%) and dibenzyl sulfide (3%), besides the rearrangement product (IIc). For the formation mechanism of the sulfonium salt (III), schemes shown in Chart 4 were proposed on the basis of following reasons.

When purified boron trifluoride etherate was used for this reaction, the sulfonium salt (III) was never produced. However, the formation of III was observed by using purified boron trifluoride etherate to which a few drops of water was added. Thus, the presence of water seemed essential for this reaction. It is already known that boron trifluoride reacts with water to produce fluoroboric acid,[8] and benzyl halides are formed from benzyl alkyl sulfides on treatment with Lewis acids or hydrogen halides.[9] In the same way, fluoroboric acid is formed and reacts with benzyl methyl sulfide to produce benzyl fluoride. Benzyl fluoride, in turn, reacts with benzyl methyl sulfide (IV) in the presence of boron trifluoride etherate to form the end product (III). Actually, the sulfonium salt (III) was produced in 25% yield when benzyl methyl sulfide (IV) was treated with boron trifluoride etherate which contained a few drops of water. These considerations and observations support the proposed formation mechanism.

## Experimental

All melting and boiling points are uncorrected. Infrared (IR) spectra were recorded with a JASCO DS-701G spectrophotometer. NMR spectra were obtained with a Nihon Denshi C-60H spectrophotometer at 60 MHz, using tetramethylsilane (TMS) as an internal standard. UV spectra were obtained with a Hitachi EPS-3T automatic recording spectrophotometer. Gas chromatographic analyses were performed with a Yanagimoto G-800T gas chromatograph with a thermal conductivity detector using 30% SE-30 on Chamelite CK (60—80 mesh, 3 mm × 4 m) column.

Chloroform was dried over phosphorous pentoxide and redistilled. Boron trifluoride etherate was purified by distillation.

**Preparation of O,S-Dialkyl Dithiocarbonates (I)**——The following compounds (I) in which R is primary alkyl were prepared by a procedure similar to that described in the previous paper:[6] O-methyl,[10] O-ethyl,[11] O-propyl,[12] O-butyl,[13] O-pentyl,[14] O-benzyl,[15] and O-(2-phenylethyl) S-methyl dithiocarbonates; O-methyl[11] and O-ethyl[16] S-ethyl dithiocarbonates; O-methyl S-benzyl dithiocarbonate;[17] O-methyl S-isopropyl dithiocarbonate and O-methyl S-(2-phenylethyl) dithiocarbonate.

TABLE III. O,S-Dialkyl Dithiocarbonates (ROCSSR′)

| R | R′ | Yield (%) | IR cm$^{-1\,a)}$ | | bp (°C/Torr) | Formula | Analysis (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $\nu_{C-O}$ | $\nu_{C=S}$ | | | Calcd. | | Found | |
| | | | | | | | C | H | C | H |
| $C_6H_5CH_2CH_2$ | $CH_3$ | 45 | 1222 | 1065 | 105—109/1 | $C_{10}H_{12}OS_2$ | 56.57 | 5.70 | 56.36 | 5.57 |
| $CH_3$ | $C_6H_5CH_2CH_2$ | 75 | 1231 | 1062 | 103—107/0.9 | $C_{10}H_{12}OS_2$ | 56.57 | 5.70 | 56.81 | 5.75 |
| $CH_3$ | $(CH_3)_2CH$ | 25 | 1220 | 1083 | 66—67/13 | $C_5H_{10}OS_2$ | 39.97 | 6.71 | 40.15 | 6.87 |

a) In liquid film.

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[8] F. Sowa, J. Kroeger, and J. Nieuwland, *J. Am. Chem. Soc.*, **57**, 454 (1935); K. Kuratani and K. Harai, "Muki Kagaku Zensho," (Inorganic Chemistry) X2, ed. by K. Saito, Maruzen, Tokyo, 1965, p. 145.

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[14] F. Whitmore and C. Simpson, *J. Am. Chem. Soc.*, **55**, 3809 (1933).

[15] S.S. Nametkin and D. Kurssanow, *J. Prakt. Chem.*, **112**, 164 (1926).

[16] F. Salomon, *J. Prakt. Chem.* [2], **6**, 445 (1872).

[17] H. Yoshida and S. Inokawa, *Nippon Kagaku Zasshi*, **86**, 950 (1965).

The others (I) in which R is secondary alkyl were prepared by the usual synthetic method of O,S-dialkyl dithiocarbonates: O-isopropyl,[18)] O-isopentyl,[19)] O-cyclohexyl,[20)] O-bornyl,[21)] and O-cholesteryl[22)] S-methyl dithiocarbonates and O-isopropyl S-benzyl dithiocarbonate.[23)] The known compounds were identified by comparison of spectral data with those of authentic samples. For new compounds, yield and physical properties are listed in Table III.

**Catalytic Rearrangement of O,S-Dialkyl Dithiocarbonates with $BF_3 \cdot Et_2O$**——General Method: A mixture of O,S-dialkyl dithiocarbonate (2 g) and $BF_3 \cdot Et_2O$ (6—10 ml) was heated at 70—125° until the completion of reaction was observed by UV spectrometry or by thin-layer chromatography (TLC). When cooled, ice water (20—30 ml) was cautiously poured into the flask with shaking and the mixture was extracted with $Et_2O$. The $Et_2O$ layer was washed with $H_2O$, dried over anhydrous $MgSO_4$ and freed of solvent by evaporation under reduced pressure. The residue (S,S-dialkyl dithiocarbonates) was purified by column chromatography on silica gel followed by distillation or recrystallization. The data are summarized in Table I. The known compounds were identified by comparison of their physical properties (IR and NMR spectra and retention time in GLC) with those of authentic samples[1,3)] (Method A). The new compounds were identified by elemental analysis, IR and NMR spectrometry (Method B).

TABLE IV. S,S-Dialkyl Dithiocarbonates (RSCOSR′)

| R | R′ | IR cm$^{-1}$ [a)] |  | bp (°C/Torr) | Formula | Analysis (%) |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Calcd. |  | Found |  |
|  |  | $\nu_{C=O}$ | $\nu_{C-S}$ |  |  | C | H | C | H |
| $CH_3(CH_2)_4$ | $CH_3$ | 1644 | 870 | 96—97/2 | $C_7H_{14}OS_2$ | 47.15 | 7.91 | 47.09 | 7.95 |
| $(CH_3)_2CH(CH_2)_2$ | $CH_3$ | 1644 | 868 | 60—63/0.8 | $C_7H_{14}OS_2$ | 47.15 | 7.91 | 47.42 | 7.85 |
| $C_6H_5CH_2CH_2$ | $CH_3$ | 1643 | 869 | 109—109.5/0.7 | $C_{10}H_{12}OS_2$ | 56.57 | 5.70 | 56.84 | 5.29 |
| $p$-$ClC_6H_4CH_2$ | $CH_3$ | 1644 | 883 | 106—107.5/0.7 | $C_9H_9ClOS_2$ | 46.44 | 3.90 | 46.45 | 4.11 |
| $C_6H_5CH_2$ | $(CH_3)_2CH$ | 1641 | 870 | 70—75/0.7[b)] | $C_{11}H_{14}OS_2$ | 58.37 | 6.23 | 58.06 | 6.20 |
| Isobornyl | $CH_3$ | 1644 | 868 | oil | $C_{12}H_{20}OS_2$ | 58.97 | 8.25 | 59.42 | 8.44 |

a) In liquid film. b) bp by bath temperature.

**Crossover Reaction**——An equimolar mixture of O,S-dimethyl dithiocarbonate (Id) and O,S-diethyl dithiocarbonate (Ie) was refluxed with 3 mol equivalents of $BF_3 \cdot Et_2O$ in $CHCl_3$ for 18 hr. After the reaction mixture was treated as above, the resulting products were analyzed by GLC, using diethyl trithiocarbonate as an internal standard. The chromatogram showed the presence of S-ethyl S-methyl dithiocarbonate (IIf) and S,S-diethyl and S,S-dimethyl dithiocarbonate (IIe and IId) in a formation ratio 3.2: 1.0: 2.6.

**Dibenzyl Methyl Sulfonium Fluoroborate (III)**——a) From O-Benzyl S-Methyl Dithiocarbonate (Ic): A mixture of unpurified $BF_3 \cdot Et_2O$ (3.0 g) and Ic (1.0 g) was heated at 50° for 2 hr. When cooled, the reaction mixture was poured into ice water (20 ml). The precipitate was collected, washed with $Et_2O$, and recrystallized from EtOH to colorless leaflets, mp 111—113°, yield 280 mg (35%). *Anal.* Calcd. for $C_{15}H_{17}BF_4S$: C, 56.98; H, 5.42; S, 10.14. Found: C, 56.76; H. 5.31; S, 10.09. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1035—1080 ($BF_4^-$).

The $Et_2O$ solution was dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue (oil) was purified by chromatography on silica gel to give benzyl methyl sulfide (IV) (3%) and S-benzyl S-methyl dithiocarbonate (IIc) (31%).

In this operation, when purified $BF_3 \cdot Et_2O$ was used, III was not produced. When 5 drops of water were added to the reaction mixture before heating, III was produced in 31% yield.

b) From Benzyl Methyl Sulfide (IV): A mixture of unpurified $BF_3 \cdot Et_2O$ (3.0 g) and IV (1.0 g) was heated at 70° for 3 hr. Working up as in a) produced III in 25% yield.

**Dicholesteryl Methyl Sulfonium Fluoroborate**——O-Cholesteryl S-methyl dithiocarbonate (1.0 g) was dissolved in a solution of $BF_3 \cdot Et_2O$ (3.0 g) in $CHCl_3$ (5 ml). After allowing to stand at room temperature for 2 hr, the reaction mixture was poured into ice water. The precipitate was collected and washed repeatedly with $CHCl_3$. The precipitate was insoluble in organic solvents; mp 244—246°, yield 366 mg. *Anal.* Calcd. for $C_{35}H_{93}BF_4S$: C, 75.65; H, 10.73. Found: C, 75.56; H, 10.74. The IR spectrum of this compound showed

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the characteristic band due to sulfonium fluoroborate group in the vicinity of 1050 $cm^{-1}$. The parent peak of the compound in the mass spectrum appeared at *m/e* 770 which is ascribable to dicholesteryl sulfide.

The $CHCl_3$ solution was dried over anhydrous $MgSO_4$ and evaporated. The residue was recrystallized from EtOH to give S-cholesteryl S-methyl dithiocarbonate as colorless needles, mp 130—134°; yield 400 mg; identical with an authentic sample.[24]

**Kinetic Run**——A $CHCl_3$ solution (25 ml) containing I ($6.23 \times 10^{-4}$ M) and $BF_3 \cdot Et_2O$ (2.0 ml, $1.57 \times 10^{-2}$ M) was prepared. The flask was sealed with a silicone gum stopper and immersed in a constant bath kept at $45.0 \pm 0.05°$. At appropriate intervals, samples were withdrawn, quenched in *ca.* 20 ml of EtOH and examined for absorption at 355 nm with a Hitachi EPS-3T spectrophotometer equipped with a photomultiplier.

**Acknowledgement** This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, for which the authors gratefully acknowledge.

Thanks are also due to the Analytical Section of this Faculty for the determination of IR, mass, and NMR spectra and for microanalyses.

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