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Catalytic Rearrangement of *O*,*S*-Dialkyl Dithiocarbonates to *S*,*S*-Dialkyl Dithiocarbonates by Pyridine *N*-Oxides. The Reaction Mechanism

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The reaction of *O*-alkyl *S*-methyl dithiocarbonates (xanthates) (I) with pyridine *N*-oxides (II) gave the corresponding *S*-alkyl *S*-methyl dithiocarbonates (dithiolcarbonate) (III) together with the symmetric *S*,*S*-dialkyl and *S*,*S*-dimethyl dithiocarbonates in good yields. Pyridine *N*-oxides bearing electron-donating substituents are efficient catalysts for rearrangement of I to III. The reaction is pseudo-first-order and the apparent first-order rate constant is proportional to the concentration of II. The role of pyridine *N*-oxides and the reaction behavior of *O*,*S*-dialkyl dithiocarbonates are discussed on the basis of kinetic and molecular orbital calculation data. The rearrangement may proceed by nucleophilic attack of $^{-}$SCOSR derived from a complex of I and II on the *O*-alkyl group of xanthates. The reaction provides a useful preparation method for alkanethiols by aminolysis of the products with ethanolamine.

Keywords *O*,*S*-dialkyl dithiocarbonate; *S*,*S*-dialkyl dithiocarbonate; pyridine *N*-oxide, thiol; charge transfer; catalytic rearrangement; kinetics; ethanolamine; frontier molecular orbital

Introduction

Rearrangements of the *O*-thioacyl system (R–O–C=S) to the *S*-acyl system (R–S–C=O)[1a,b] have been utilized for the conversion of alkanols to alkanethiols by hydrolysis of the rearranged products.[1c] For this purpose, thermal and Lewis acid-catalyzed rearrangements of *O*-alkyl thiobenzoates, *O*,*S*-dialkyl thiocarbonates or *O*-alkyl thiocarbamates have been investigated. However, these methods require thiophosgene or chlorine gas in the synthesis of acylating reagents and also involve the isolation of the intermediate and its treatment under strongly acidic or basic conditions to induce hydrolysis.

In this connection, we have proposed the usefulness of Lewis acid-catalyzed rearrangement of *O*,*S*-dialkyl dithiocarbonates (xanthates) (I), which can be readily synthesized by xanthation of alcohols, to *S*,*S*-dialkyl dithiocarbonates (III).[2] However, the catalytic reaction has limited value because by-products such as sulfides or olefins are produced from the *O*-secondary alkyl substrates.

Recently we found that *O*,*S*-dialkyl dithiocarbonates (I) underwent rearrangement to *S*,*S*-dialkyl dithiocarbonates (III) by the catalysis of pyridine *N*-oxides (II),[3] and combination of this reaction and aminolysis of III with ethanolamine[4a] serves as an efficient method for the generation of thiols under neutral non-aqueous conditions.[4b] This paper deals with the role of pyridine *N*-oxides (II) in catalytic rearrangement of I to III.

Results and Discussion

A mixture of *O*-propyl *S*-methyl dithiocarbonate (Ica) (10 mmol) and pyridine *N*-oxide (IIa) (5 mmol) was heated at 110 °C for 1 h to afford a mixture of the dithiol esters, *S*,*S*-dimethyl (IIIaa), *S*-methyl *S*-propyl (IIIac) and *S*,*S*-dipropyl (IIIcc) dithiocarbonates, in 92% yield (total yield). Similarly, heating of *O*-alkyl *S*-methyl dithiocarbonates (Iaa—ea) with IIa at 60—110 °C gave the mixtures of dithiol esters in good yields. The main products were the corresponding dithiol esters (IIIaa—ea).

The product ratios were determined by ^{1}H-nuclear magnetic resonance (^{1}H-NMR) and gas liquid phase chromatographic (GLPC) analyses. The structures of the products were determined by comparison of their spectral data with those of authentic samples obtained from catalytic rearrangement of the corresponding xanthates by $AlCl_3$.[2]

The dithiol esters (III) commonly exhibited characteristic infrared (IR) absorption bands at *ca.* 1640 and 870 cm^{-1}

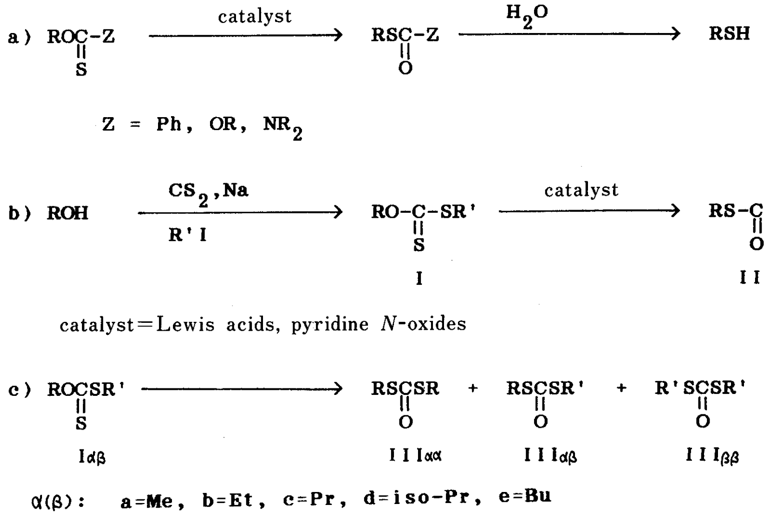


Chart 1

which can be ascribed to the –SCOS– moiety.[2]

Some important features of the reaction are as follows. (a) In general, high yields are obtained when the ratio of I to II is 2.0. (b) Skeletal rearrangement of the alkyl moiety, *e.g.* propyl to isopropyl, was not observed under the conditions used. (c) The order of reactivity of xanthates (Me > Et > Pr > iso-Pr) is consistent with the relative rates of S_N2-type reactions. (d) Of the pyridine *N*-oxides (II) tested as catalysts, IIa, 3-methylpyridine (3-picoline) *N*-oxide (IIc), 3,5-dimethylpyridine (3,5-lutidine) *N*-oxide (IIb) and 4-dimethylaminopyridine *N*-oxide (IIg) are effective catalysts, whereas pyridine *N*-oxides bearing electron-attracting substituents (IIf) or a substituent at the 2-position (IIe) are far less active than IIa (Table II).

TABLE I. Rearrangement of *O*-Alkyl *S*-Methyl Dithiocarbonates (Iaa—Iea) to *S*,*S*-Dialkyl Dithiocarbonates (III) Catalyzed by Pyridine *N*-Oxide (IIa)

Compd. No.	Alkyl	Reaction conditions[a] Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
Iaa	Me	No solvent	65	5	96 (IIIaa)
Iba	Et	No solvent	90	7	93 (IIIaa + IIIab + IIIbb)
Ica	Pr	No solvent	110	9	92 (IIIaa + IIIac + IIIcc)
Ica	Pr	DMSO-d_6	110	2	98 (IIIaa + IIIac + IIIcc)
Ida	iso-Pr	No solvent	110	15	63 (IIIaa + IIIad + IIIdd)
Ida	iso-Pr	DMSO-d_6	110	6	93 (IIIaa + IIIad + IIIdd)
Iea	Bu	No solvent	115	4	92 (IIIaa + IIIae + IIIee)

a) The molar ratio (I/IIa) was 2.0. *b*) Total yield.

TABLE II. Effect of Pyridine *N*-Oxides (IIa—g) upon the Rearrangement of *O*-Ethyl *S*-Methyl Dithiocarbonate (Iba)

IIa—g[a]	Substituent	Reaction time (h)[b]	Yield (%)
a	H	2.5	99
b	3,5-Me_2	1.0	92
c	3-Me	1.5	83
d	4-Ph	4.0	57
e	2-Ph	18.5	20
f	3,5-Br_2	18.5	32
g	4-NMe_2	3.0	83[c]

a) The molar ratio (Iba/IIa—f) was 2.0. *b*) All reactions at 110 °C. *c*) The reaction was carried out in the presence of 0.1 mol eq of IIg at 80 °C.

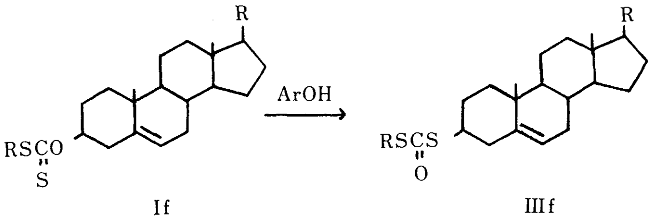


Chart 2

In the previous paper,[5] we reported that some homoallylic xanthates such as *O*-cholesteryl *S*-alkyl dithiocarbonates (If) underwent thione–thiol rearrangement to the corresponding dithiol esters (IIIf) by catalysis of phenolic compounds and the catalytic activity arises from the hydrogen bonding between thione sulfur and phenolic hydrogen atoms.

Based on these findings, we anticipated that pyridine *N*-oxide bearing an OH group such as 3-hydroxypyridine *N*-oxide (IIh) would show an enhanced catalytic activity towards the rearrangement of xanthates. However, the rearrangement rate for IIh was found to be smaller than that of IIa (see experimental section). When *O*-ethyl *S*-carbamoylmethyl xanthate (Ibj) was subjected to the rearrangement, IIh showed an interesting catalytic behavior. When IIa was used as a catalyst, a considerable amount of carbamoylmethyl ethyl sulfide (IV) was produced, which might have arisen from loss of COS from the intermediate (V). In contrast, IIh suppressed the sulfide formation. A possible explanation for this discrepancy is that the phenolic OH group of IIh may stabilize the $^{-}S{-}CO{-}S{-}CH_2{-}CONH_2$ anion by hydrogen bonding.

In order to examine whether the rearrangement proceeds through intermolecular or intramolecular alkylation process, a crossover reaction was carried out. A mixture of *O*-ethyl *S*-methyl and *O*-methyl *S*-ethyl dithiocarbonates (Iba and Iab) was heated with IIa at 110 °C. The reaction mixture was analyzed by GLPC. The chromatogram showed the presence of *S*,*S*-dimethyl and *S*,*S*-diethyl dithiocarbonates (IIIaa and IIIbb) which should be formed by a crossover reaction, besides *S*-ethyl *S*-methyl dithiocarbonate (IIIba).

From the above investigation, we believed that the rearrangement proceeds intermolecularly. However, we found that the rearranged products react again with $^{-}SCOSMe$ and produce the equilibration products (the symmetric dithiol esters), indicating that the result of the crossover experiment does not represent definitive evidence of intermolecular reaction. The symmetric *S*,*S*-dialkyl and *S*-alkyl *S*-methyl dithiocarbonates were clearly formed from an equilibrium reaction[6] of *S*-alkyl *S*-methyl dithiocarbonate with $^{-}SCOSMe$ derived from the intermediate. The ^1H-NMR monitoring of a reaction mixture revealed that the symmetric dithiol esters were produced at an early stage of the reaction and the product ratios were uniform all over the reaction course. Consequently, the product distributions were statistically controlled to give a 1 : 2 : 1 mixture of MeSCOSMe : RSCOSMe : RSCOSR. This fact indicates that the equilibration rate is significantly faster than the rearrangement rate.

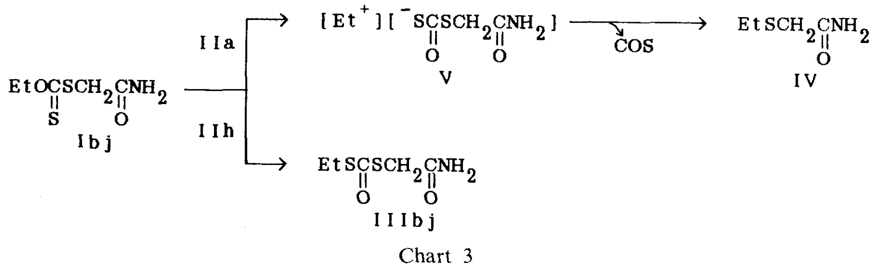


Chart 3

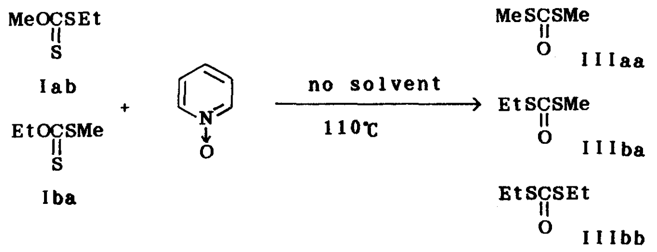


Chart 4

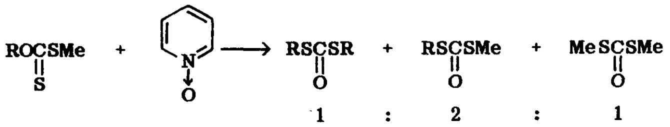


Chart 5

To clarify the reaction mechanism, we performed kinetic studies. The reaction of *O*,*S*-dimethyl dithiocarbonate (Iaa) with IIa obeyed pseudo first-order kinetics and the apparent first-order rate constant is proportional to the concentration of IIa. The rate is affected by whether the *O*-alkyl group being primary or secondary. The rearrangement rate of *O*-propyl *S*-methyl dithiocarbonate (Ica) is five times larger than that of the isopropyl derivative (Ida) under the same reaction conditions. The use of a dipolar aprotic solvent such as dimethylformamide (DMF) enhances the rearrangement rate, suggesting that the rearrangement proceeds *via* an ionic intermediate. The activation energy (E_a) and entropy ($\Delta S^{\neq}$) for the rearrangement reaction of Iaa are 24.1 kcal/mol and −7 e.u. (at 65 °C), respectively. These values are slightly higher than those observed in typical thione–thiol rearrangements, *e.g.* Lewis acid-catalyzed rearrangement of *O*-alkylthiobenzoates.[7]

In order to get some information about the reaction mechanism, molecular orbital (MO) calculations were carried out using semiempirical self-consistent field molecular orbital (SCF) MO methods.[8] Inspection of the frontier orbital interaction calculated by modified neglect of diatomic overlap (MNDO) between Iaa and IIa reveals that the dominant interaction occurs between the highest occupied molecular orbital (HOMO) of IIa, which acts as a donor, and the lowest unoccupied molecular orbital (LUMO) of Iaa, which behaves as an acceptor (Fig. 1).

As shown in Fig. 1, both the reactants have abnormally large frontier molecular orbital (FMO) coefficients at the O atom of $>N\rightarrow O$ and C atom of $>C=S$ moieties. Application of the "hard and soft" concept[9] allows us to predict that the first bond would link the softest centers, *i.e.*, O atom of $>N\rightarrow O$ and C atom of $>C=S$. In this situation, the

Table III. Effect of the Catalyst Amount on the Rearrangement Rate of Iaa at 65 °C[a)]

Molar ratio Iaa : IIa	$k_1 \times 10^4$ [b)]	Correlation coefficient
3.0 : 2.0	4.592	0.996
3.0 : 1.5	3.430	0.999
3.0 : 1.0	2.627	0.995
3.0 : 0.3	0.973	0.991

a) The rate equation for the reaction of Iaa with IIa is expressed as follows: $-d[\text{Iaa}]/dt = k'_2[\text{Iaa}]\cdot[\text{IIa}] + k_2''[\text{Iaa}]\cdot[\text{ArN}^+\text{OMe}\ ^-\text{SCOSMe}]$.

$\text{MeOCS}_2\text{Me} + \text{ArN}\rightarrow\text{O} \xrightarrow{k_2'} \text{ArN}^+\text{O–Me}\ ^-\text{SCOSMe}$

$\text{MeOCS}_2\text{Me} + \text{ArN}^+\text{O–Me}\ ^-\text{SCOSMe} \xrightarrow{k_2''} \text{MeSCOSMe} + \text{ArN}^+\text{O–Me}\ ^-\text{SCOSMe}$

A plot of the apparent first-order rate constant (k_1) against the amount of IIa was roughly linear (correlation coefficient = 0.998). A second-order rate constant (k_2) was obtained from the slope of the line by means of the least-squares method ($k_2 = 4.179 \times 10^{-5}$ l/mol·s). *b)* In the rate measurement, diphenyl ether was used as an internal standard.

Table IV. Solvent Effect on the Rearrangement of Iaa at 65 °C[a)]

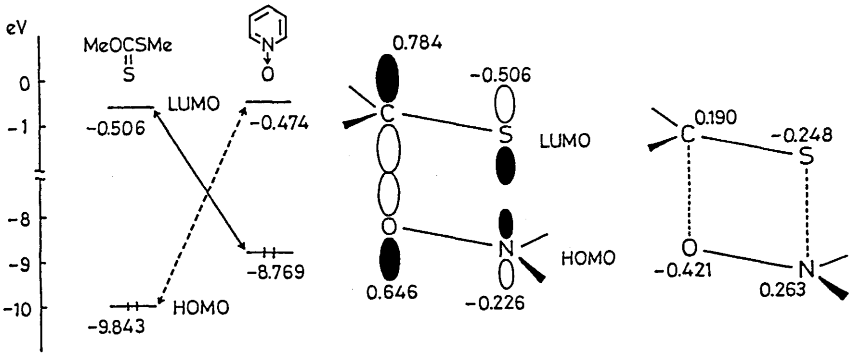
Solvent	E_T value[b)]	$k_1 \times 10^4$
DMSO-d_6	(45.0)[c)]	3.573
DMF	43.8	3.727
Nitrobenzene	42.0	3.026
Diphenyl ether	35.3	3.074
Benzene	34.5	1.332

a) A solution (0.7 ml) of Iaa (3 mmol) and IIa (1.5 mmol) in the indicated solvent was used. *b)* Solvent ionizing power based on the solvatochromism of pyridinium-*N*-phenoxide betaines, see ref. 16. *c)* Value of DMSO.

Table V. Effect of the Reaction Temperature on the Rearrangement Rate[a)] of Iaa and the Activation Parameters

Temp. (°C)	$k_1 \times 10^4$	E_a (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
60	1.841		
65	3.573	24.1	−7
70	5.075		
75	9.477		

a) The molar ratio (Iaa/IIa) was 2.0.



a) FMO energies b) FMO interaction c) coulomb–coulomb interaction

Fig. 1. FMO Energies, Coefficients and Net Charges Calculated by the MNDO Method

electronic force (coulombic interaction) is also operative because the polar centers of the reactant molecules are identical with those having the largest FMO coefficients (see the net charges in Fig. 1).

To confirm this assumption, complete neglect of differential overlap (CNDO/2)[10] calculations on intermediates were carried out. In the calculation, the N$\rightarrow$O moiety was considered to approach the C$=$S moiety in such a way as to keep the dipoles lined up in an antiparallel manner. The interacting distance was varied from 3.6 to 1.4 Å. The net charges on the interacting four atoms increase with decreasing molecular distance, resulting in polarization of the $>$N$\rightarrow$O and C$=$S double bonds. Total energy (E_{total}) for the interaction of the two reactants decreases with decrease of the distance to stabilize the reaction system and has the minimum value at *ca.* 1.65 Å, which is more stable by *ca.* 6 eV than that at 3.6 Å.

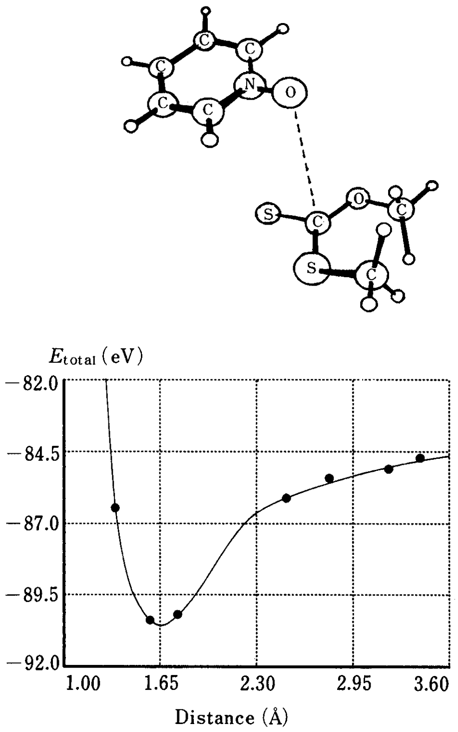


Fig. 2. Total Energy Change in the Transition State Calculated by the CNDO/2 Method

The possibility of the formation of a complex based on the MO calculation is supported by the spectral evidence. In the reaction[11] of an electron-rich pyridine *N*-oxide such as IIg, a coloration of the reaction mixture was recognized, which gradually faded away with the progress of the reaction. The visible absorption spectra showed absorption maxima at *ca.* 450 and 620 nm, characteristic for charge-transfer complexation.

The catalytic activity of pyridine *N*-oxides is probably a consequence of the formation of a complex of the orthocarbonic ester type (A) between the catalyst and substrate as shown in Chart 6. In such a complex, the alkyl cation should dissociate much more readily than from the thione ester itself. The alkyl group cleaved from the complex was attacked by the O atom of pyridine *N*-oxide accompanied with the generation of $^{-}$SCOSR$_2$.

^{1}H-NMR monitoring of the reaction mixture of IIg and Iba in dimethylsulfoxide (DMSO)-d_6 revealed that

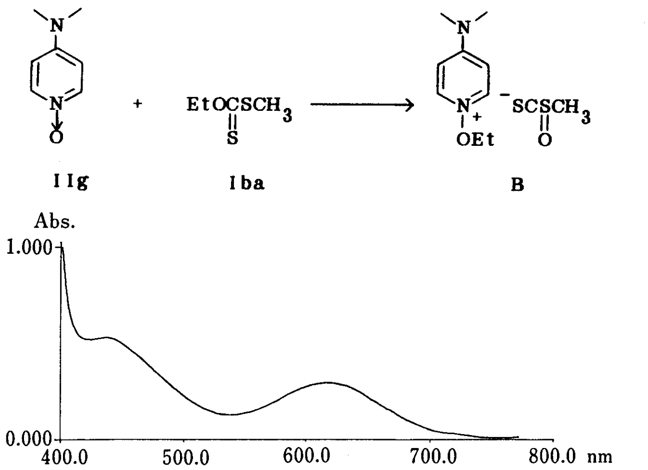


Fig. 3. Visible Absorption Spectrum of the Reaction Mixture of IIg and Iba in DMSO Solution

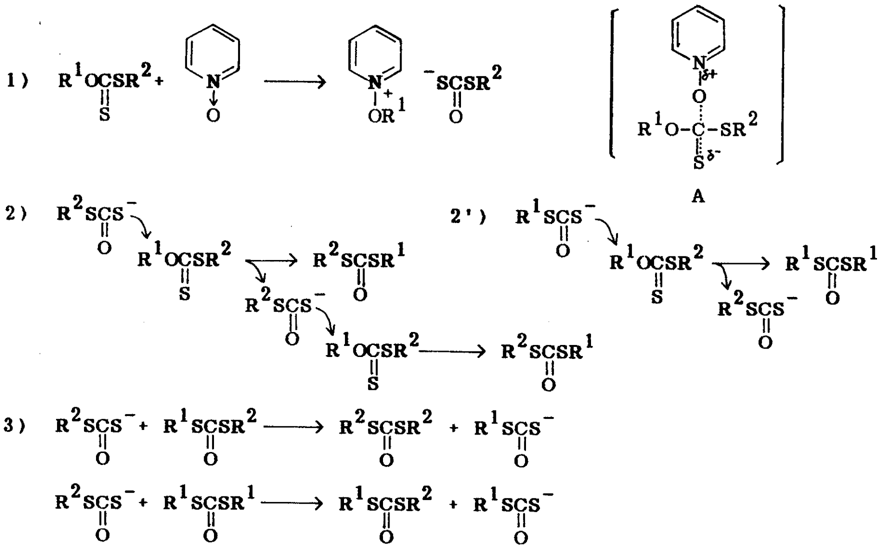


Chart 6

the intermediate [1-ethoxy-4-dimethylaminopyridinium S-methyldithiocarbonate, (B)] was formed in a short time and the aromatic protons (C_2-H and C_6-H) of B showed a pattern nearly identical with that of 1-ethoxy-4-dimethylaminopyridinium iodide. The downfield shift of the aromatic protons from δ 7.86 (C_2) in IIg to δ 8.71 (C_2) in B indicates a large electron withdrawal from the vicinity of the aromatic protons. The formation of $^{-}$SCOSMe was also confirmed by the NMR spectrum, which showed the highfield shift of the –SMe proton signal (2.40 ppm) by +0.17 ppm as compared with those of O-alkyl S-methyl xanthates. Analysis of the ^{1}H-NMR signals of the SMe groups of Iba at δ 2.57 and IIIab at δ 2.43 revealed that the concentration of B increased rapidly and then Iba decreased gradually with the increase of IIIab.

These facts together with the kinetic data indicate that the rate-determining step of this reaction is not formation of B but reaction of $^{-}SCOSR_2$ with xanthates.

The resultant dithiolcarbonate anion ($^{-}SCOSR_2$) is alkylated by the xanthate (I) to produce the rearranged product (III) and $^{-}SCOSR_2$.[6)] This process will be repeated until all of the xanthate is consumed. The dithiol ester is then converted into the equilibrium mixture of dithiol esters by the action of $^{-}SCOSR_2$ *via* the mechanism proposed by Yoshida.[6d)] (Chart 6).

An alternative pathway (Chart 7) may be possible: the alkylated pyridine N-oxide is attacked by the electron-rich thiocarbonyl sulfur atom to produce the alkoxydialkylthiocarbonium ion intermediate (C) accompanied with regeneration of pyridine N-oxide. The intermediate is considered to be a more effective alkylating agent[1b)] than the xanthate. However, this pathway was ruled out because the N-methoxypyridinium iodide showed low catalytic reactivity for the rearrangement.[12)]

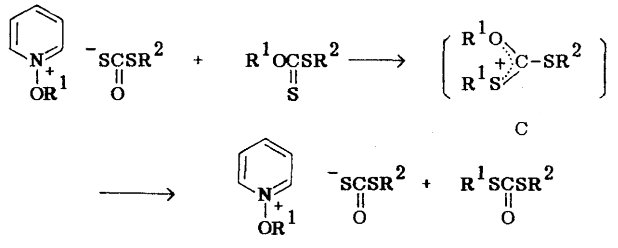


Chart 7

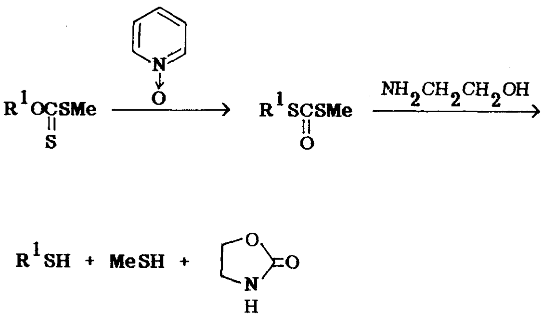


Chart 8

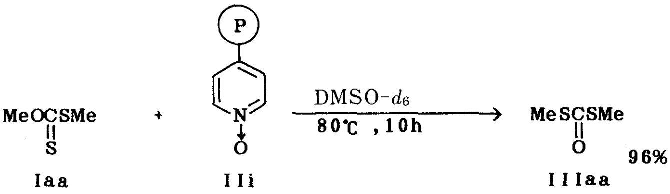


Chart 9

The reaction products are of synthetic value because of the simplicity of operation. The starting materials are readily available from xanthation of the corresponding alkanols. The products are distilled from the mixture of the rearranged products and catalyst, usually without a solvent. An excellent procedure for the preparation of volatile thiols involves their distillation from a reacting mixture consisting of higher-boiling ethanolamine and oxazolidine-2-one.[4b)]

The procedure developed here can be carried out in only a distilling flask. After completion of the rearrangement, the reaction mixture is heated with 2-aminoethanol (1 mol) to afford alkanethiol.

During the course of this work, we discovered that a solid-phase copolymer of 4-vinylpyridine N-oxide (IIi)[13)] is a useful catalyst for the rearrangement of I to III. Use of a solid-phase copolymer of pyridine N-oxide as a catalyst for the rearrangement reaction has the important advantage that the resins are insoluble in water and in common organic solvents and can be removed by filtration without leaving any unwanted catalyst in the solution. A catalyst can be used repeatedly after washing with organic solvents.

Experimental

All melting points are uncorrected. The IR spectra were taken with a Hitachi 270-30 grating spectrophotometer. The ultraviolet (UV) spectra were determined by using a Hitachi 150-20 or a JASCO UVIDEC-220B digital spectrophotometer. The ^{1}H-NMR spectra were taken with a Hitachi R-600 (60 MHz) or a JEOL GX-400 (400 MHz) spectrometer using tetramethylsilane as an internal standard, and the chemical shifts are expressed in δ values. The progress of the reactions was monitored by Fourier-transform (FT) pulse NMR spectroscopy (Hitachi R-600). Gas chromatographic analyses were performed with a Yanagimoto G-80 gas chromatograph with a thermal conductivity detector using 10% SE-30 on a Chamelite CK (60—80 mesh 3 mm × 3 m) column.

Molecular orbital calculations were performed on the FACOM M-360 computer in the Computer Center of Kumamoto University.

Least-squares calculations were performed on a Fujitsu FM-16β microcomputer.

Pyridine *N*-Oxides Pyridine N-oxide (IIa), 3,5-dimethylpyridine N-oxide (IIb), 3-methylpyridine N-oxide (IIc), 4-phenylpyridine N-oxide (IId), 2-phenylpyridine N-oxide (IIe) and 3,5-dibromopyridine N-oxide (IIf) were prepared according to the established method.[14)]

4-Dimethylaminopyridine N-oxide[15)] (IIg) was prepared by heating of 4-chloropyridine N-oxide[14)] with 30% dimethylamine in an autoclave at 140 °C for 18 h, mp 223—225 °C, yield 81%.

The solid-phase copolymer of 4-vinylpyridine N-oxide was prepared by oxidizing the corresponding 4-vinylpyridine polymer[13)] with 30% hydrogen peroxide in glacial acetic acid.[15)]

***O,S*-Dialkyl Dithiocarbonates** O-Methyl (Iaa), O-ethyl (Iba), O-propyl (Ica), O-isopropyl (Ida) and O-butyl (Iea) S-methyl dithiocarbonates were prepared according to the previously described method.[3)]

O-Ethyl S-Carbamoylmethyl Dithiocarbonate (Ibj): mp 114—115 °C, yield 44%. *Anal.* Calcd for $C_5H_9NO_2S_2$: C, 33.50; H, 5.06; N, 7.81. Found: C, 33.72; H, 4.96; N, 7.61.

Rearrangement of I to III (General Procedure) A mixture of I (10 mmol) and II (5 mmol) was heated at 100 °C until disappearance of I as judged by thin layer chromatography (TLC). After cooling, the reaction mixture was treated with n-hexane and washed with water to remove the catalyst. The organic layer was separated, dried over anhydrous $MgSO_4$, concentrated *in vacuo* by rotary evaporation, and distilled under reduced pressure to give III. The products were identified by comparison of the spectral data with those of authentic samples.[2,6)]

The catalyst can be easily removed by passing the extract through a short column of silica gel.

Crossover Reaction An equimolar mixture of Iba and Iab was heated with 0.5 mol eq of IIa at 110 °C for 4 h. The reaction mixture was analyzed by gas chromatography. The chromatogram showed the presence of *S*-ethyl *S*-methyl dithiocarbonate (IIIba) and *S,S*-dimethyl and *S,S*-diethyl dithiocarbonates (IIIaa and IIIbb) in a formation ratio of 1 : 2 : 1.

Measurement of Visible Absorption Spectra A solution of IIg (1 mmol) and Iba (10 mmol) in DMSO (3 ml) was used for the measurement. The visible absorption spectrum is shown in Fig. 3.

NMR Tube Experiment (Formation of 1-Ethoxy-4-dimethylaminopyridinium *S*-Methyldithiocarbonate, B) A solution of Iba (1 mmol) and IIg (0.1 mmol) in DMSO-d_6 (0.4 ml) was prepared. The sample was placed in an NMR tube and warmed in an oil bath at 80 °C until IIg had dissolved. The solution acquired a green color which slowly faded during 15 min. The ^{1}H-NMR spectrum of the green-colored solution showed new peaks due to formation of the intermediate (B). ^{1}H-NMR (in DMSO-d_6) δ: 2.40 (3H, s, Me-S), 3.25 (6H, s, 2Me-N), 7.08 (2H, dd, $J=8.1$ Hz, $J<1$ Hz, H_3 and H_5), 8.71 (2H, dd, $J=8.1$ Hz, $J<1$ Hz, H_2 and H_6).

Kinetics Mixtures of solvent, Iaa and IIa were prepared. Samples were placed in NMR tubes and heated in a constant-temperature silicone oil bath controlled to ± 0.1 °C. The rearrangement rate was followed at a given temperature by analyzing the NMR signals of the *S*-methyl group of Ia using *p*-nitroanisole or diphenyl ether as an internal standard. The relative amounts of Iaa left unreacted at each interval were estimated by ^{1}H-NMR digital integration. The output data were treated by means of a nonweighted least-squares program written in F-BASIC86 V2.0 (MS-DOS). The maximum error in integration was estimated to be about 2.5%.

The results are listed in Tables III (effect of the catalyst amount), IV (solvent effect) and V (activation parameters).

The rearrangement rates of Iaa (1 mmol) catalyzed by IIa (0.5 mmol) and IIh (0.5 mmol) in DMSO-d_6 at 70 °C were 2.89×10^{-4} and $0.649 \times 10^{-4}\,\mathrm{s}^{-1}$ respectively.

Rearrangement of Iaa to IIIaa Catalyzed by Polymeric Pyridine *N*-Oxide (IIi) A mixture of Iaa (122 mg) and IIi (30 mg) in DMSO-d_6 was placed in an NMR tube and heated at 80 °C for 10 h. The composition of the product mixture was estimated by integration of the ^{1}H-NMR spectra of the isolated materials. Yield 96%.

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