Simple synthesis of furfuryl sulfides *via* extrusion of COS from the xanthates and its mechanistic aspects

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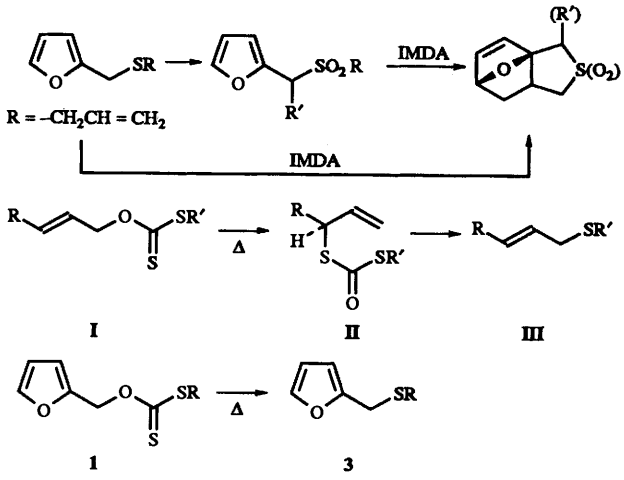
Heating of *O*-furfuryl *S*-alkyl dithiocarbonates (xanthates) gave furfuryl alkyl sulfides together with *S*-furfuryl *S*-alkyl dithiocarbonates. The crossover reaction using differently substituted furfuryl xanthates in polar solvents indicates that the reaction proceeds intermolecularly, whereas the reaction in non-polar solvents showed intramolecular reaction behaviour. The reaction is first-order and the rates are considerably affected by a change in the solvent polarity. The activation enthalpy and entropy for the extrusion of *O*-furfuryl *S*-methyl xanthate in xylene are 28.0 ± 1.3 kcal mol^{-1} † and −2 ± 4 cal K^{-1} mol^{-1}, respectively. Based on these findings together with the MO calculation data, the mechanism for the conversion reaction of furfuryl xanthates to furfuryl alkyl sulfides is discussed.

Fulfuryl sulfides and their oxidation products are very important synthones for carbon skeleton construction *via* intramolecular Diels–Alder (IMDA) cycloaddition.[1] In previous papers,[2] we reported that thermolysis of *O*-(alk-2-enyl) *S*-alkyl dithiocarbonates [allylic xanthates (**I**)] caused two sequential [3,3]-sigmatropic rearrangements to give alk-2-enyl alkyl sulfides [allylic sulfides (**III**)] with extrusion of carbon oxysulfide (COS) *via* allylically isomeric *S*-(alk-2-enyl) *S*-alkyl dithiocarbonates (**II**). Coupling of this reaction with intramolecular [4 + 2]π cycloaddition provides a one-pot synthetic method of isobenzothiophene derivatives *via* three-step sequential pericyclic reactions of *O*-(alka-2,4-dienyl) *S*-(alk-2-enyl) dithiocarbonates.[3] During the course of the study, we found that *O*-furfuryl *S*-methyl xanthate (**1a**) also showed similar behaviour towards thermal treatment.

This paper describes a simple synthesis of furfuryl sulfides (**3**) from **1** and clarification of its formation mechanism.



Scheme 1

Results

Preparation of xanthates (1)

The xanthates (**1**) were prepared by alkylation of potassium *O*-furfuryl dithiocarbonates (xanthogenates) which were prepared using acetone as a solvent and KOH as a base. In this reaction, the use of DMSO as a solvent caused ionic thione-to-thiol isomerization to give *S*-furfuryl *S*-alkyl dithiocarbonates (**2**), whose formation mechanism is assumed to be identical to that proposed for *O*-benzyl *S*-alkyl xanthates.[4]

Thermal treatment of the xanthates (1)

O-Furfuryl *S*-methyl xanthate (**1a**) was refluxed with benzene to give furfuryl methyl sulfide (**3a**) and *S*-furfuryl *S*-methyl dithiocarbonate (**2a**) in 68% and 6% yields, respectively. The product ratio (**3a**:**2a**) was found to vary with a change of solvent. However, there is no correlation between the solvent polarity and the product ratio.‡ Note that the yield of **3a** increased when ethereal solvents such as dioxane or anisole were used.

The effect of the reaction temperature on the product ratio is interesting. For example, in the reaction of **1a** in xylene, the yield of the sulfide (**3a**) increases with a rise in the reaction temperature (Fig. 1).

The effects of the *S*-alkyl group and the furan moiety on the product ratio in refluxing benzene have been studied. Introduction of the methyl substituent at the 5-position of the furan ring decreased the formation of the sulfide (**3**) with an increase in the rearranged product (**2**). The change of the *S*-alkyl group did not show a marked alteration in the product ratio.

The dithioesters did not transform to the corresponding sulfides on heating, indicating that the dithioesters are thermally stable and not precursors of the sulfides.

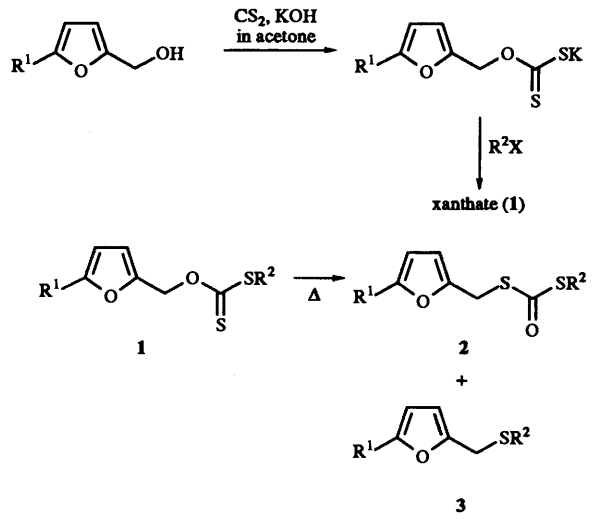
Crossover reaction

In order to clarify whether the reaction proceeds *via* an intramolecular or intermolecular pathway, crossover reaction experiments were carried out. A mixture of *O*-furfuryl *S*-methyl (**1a**) and *O*-(2-methyl-3-furylmethyl) *S*-ethyl xanthates (**1i**) was heated at 80 °C without solvent. Inspection of the chromatogram of the reaction mixture showed the presence of the crossover products of ethyl furfuryl (**3b**) and 2-methyl-3-furylmethyl methyl sulfides (**3h**), suggesting that the reaction proceeds *via* an intermolecular reaction pathway at least in the reaction without solvent.

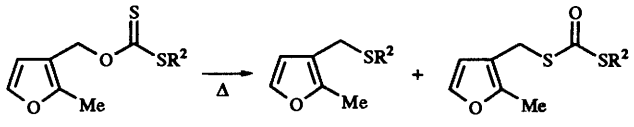
In the crossover reaction, the yields of the intramolecular reaction products (furfuryl methyl sulfide and 2-methyl-3-furyl methyl sulfide) are high compared with the intermolecular reaction products. The presence of *S*-ethyl *S*-furfuryl and *S*-(2-methyl-3-furylmethyl) *S*-methyl dithiocarbonates (**2b** and

† 1 kcal = 4.184 kJ.

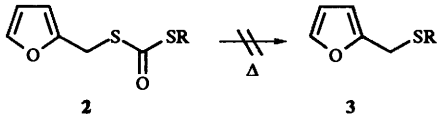
‡ A referee pointed out that the solvent viscosity might be operative.



R^1 = H, **1a**: R^2 = Me, **1b**: R^2 = Et, **1c**: R^2 = Bz, **1d**: R^2 = CH_2CO_2Me
R^1 = Me, **1e**: R^2 = Me, **1f**: R^2 = Et
R^1 = Br, **1g**: R^2 = Me



1h: R^2 = Me, **1i**: R^2 = Et



Scheme 2

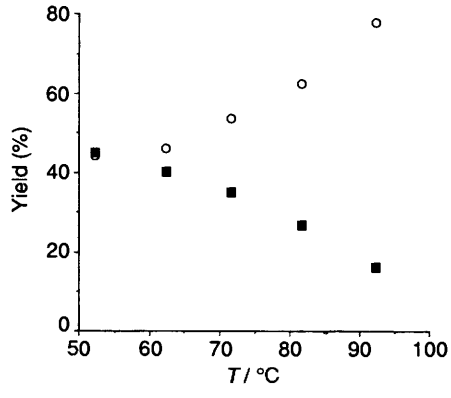


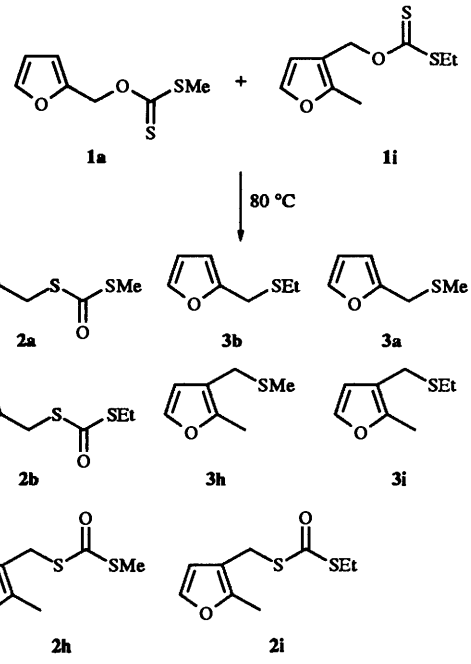
Fig. 1 Temperature dependence on the product ratio for the reaction of **1a**; (○) furfuryl methyl sulfide and (■) *S*-furfuryl *S*-methyl dithiocarbonate

2h) suggests that the thione-to-thiol isomerization also takes place intermolecularly.

In a non-polar solvent, *e.g.* xylene, the formation of the crossover products was hardly observed. On the other hand, in a polar solvent, *e.g.* DMF, the yield of the crossover products increased. In an ethereal solvent such as anisole, the amount of intermolecular reaction products was very small and the yield of the sulfides was found to be increased.

Kinetics

The rate constants (k) for the disappearance of the xanthate (**1a**) in some solvents were determined from the first-order rate equation, in which the remaining xanthates were measured by following the decrease in the visible absorption band (n–π^*) of



Scheme 3

Table 1 Rate constants for thione-to-thiol rearrangement and COS extrusion reactions of **1a** in xylene

	$k/10^{-5}$ s^{-1}		
T/°C	Total $k = k_r + k_d$	Rearrangement[a] k_r	Extrusion[b] k_d
61.6	0.76	0.311	0.353
65.9	1.25	0.481	0.610
69.7	2.06	0.746	1.06
75.0	3.93	1.27	2.20
79.8	4.69	1.34	2.86
85.2	8.60	2.03	5.82

[a] E_a = 18.7 ± 1.8 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −30 ± 5 cal K^{-1} mol^{-1}. [b] E_a = 28.0 ± 1.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −2 ± 4 cal K^{-1} mol^{-1}.

the >C=S group of **1**. In each case, a good first-order reaction behaviour was observed.

The rate constants for the thione-to-thiol rearrangement (k_r) and decomposition (k_d) in xylene were evaluated assuming that a reaction occurs by two competing first-order processes ($k = k_r + k_d$). The first-order rate constants (k) are listed in Table 1. The activation parameters (E_a and $\Delta S^{\ddagger}$) were evaluated on the basis of the rate constants measured at several temperatures. The E_a and $\Delta S^{\ddagger}$ values for the rearrangement are 18.7 ± 1.8 kcal mol^{-1} and −30 ± 5 cal K^{-1} mol^{-1}, respectively, whereas the E_a and $\Delta S^{\ddagger}$ values for the decomposition are 28.0 ± 1.3 kcal mol^{-1} and −2 ± 4 cal K^{-1} mol^{-1}, respectively.

The activation parameters based on the decrease of **1a** in anisole and DMF were also measured. The observed data are found to be reflected by the dominant reaction.

Next, we studied substituent effects on the rates for the decrease of *O*-furfuryl *S*-alkyl xanthates in xylene at 80.4 °C. The rates were measured for the ethyl, methyl, benzyl and methoxycarbonylmethyl derivatives. The ρ^* value for Taft's σ^* constants[5] was calculated to be 1.03, smaller than the one for benzhydryl thiocarbonates (ρ^* = 1.47§) which has been proposed to proceed *via* an ion-pair intermediate.[6]

§ The original paper reported that the ρ^* value *vs.* six of Taft's σ^* constants was 1.54. The ρ^* value *vs.* four constants used in this paper is 1.4651.

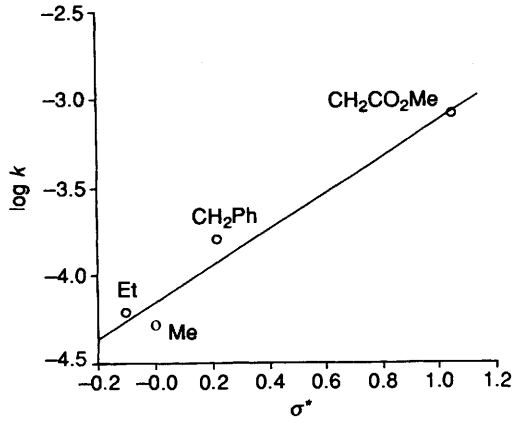


Fig. 2 Plot of log k *vs.* σ^*-values for the thermolysis of **1a–d** in benzene

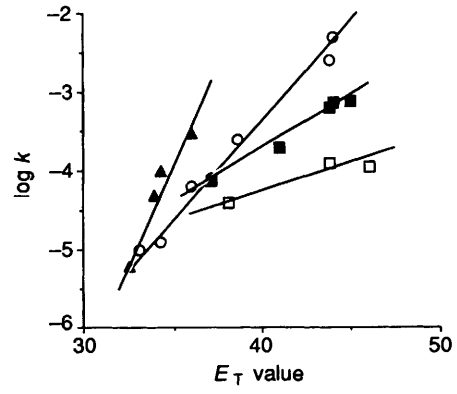


Fig. 3 Plots of log k *vs.* E_T values for the thermolysis of **1a** in various solvents. (□) *O*-Allyl *S*-methyl xanthate, a = 3.9; (■) *O*-(3-phenylallyl) *S*-methyl xanthate, a = 12.6; (○) *O*-furfuryl *S*-methyl xanthate, a = 24; (▲) *O*-(2-diethylaminoethyl) *S*-methyl xanthate, a = 40.3.

Correlation with E_T and Y values

The effects of solvent upon the first-order rate constants (k) for the reaction of **1a** at 62.4 °C are depicted in Fig. 3. To examine the correlation between the reaction rates and empirical parameters of the solvent polarity, the logarithms of the rate constants were plotted against Reichardt's E_T values,[7] based on the transition energy for the longest wavelength solvatochromic absorption band of pyridinium *N*-phenoxide betaine dye. As can be seen in Fig. 3, a plot of log k *vs.* E_T for aprotic solvents showed a nearly linear relationship with a slope of 24.1 × 10^{-2}.

In connection with the correlation with the E_T values, correlation between the thermolysis rates and Y values was investigated using alcoholic and PhOH–benzene binary solvent systems.[8] The least-square slopes (m) of the lines for both the solvent systems are depicted in Fig. 4(*a*) and (*b*).

Molecular orbital calculations

The MNDO-PM3 method[9] was used for the semiempirical MO calculations using the modified version for a Fujitsu S4/2 engineering workstation.

The ground-state geometries were obtained from the corresponding molecular models and fully optimized by the PM3 method.

The transition states for the [3,3]-sigmatropic rearrangement (TS1), the S_{Ni}-type sulfide formation reaction (TS2) and S_{Ni}-type thione-to-thiol rearrangement reaction (TS3) in the gas phase were located using the SADDLE routine[10] implemented in MOPAC[11] and refined with the NLLSQ method[12] or TS routine.[13]

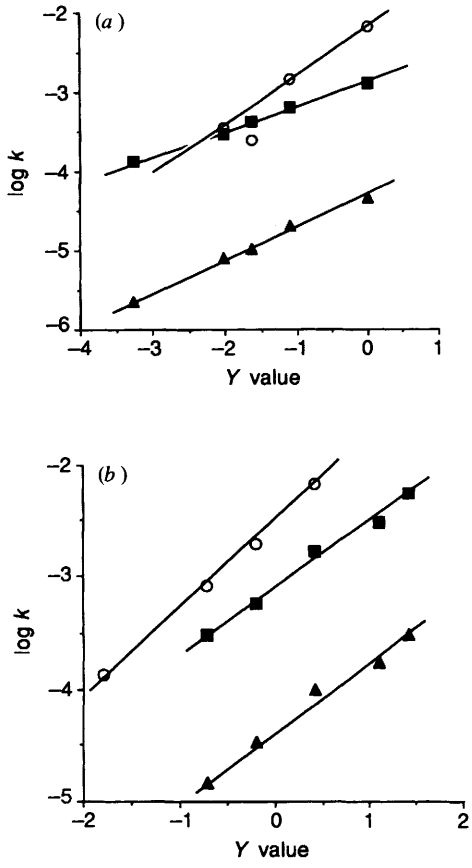


Fig. 4 (*a*) Plots of log k *vs.* Y values for the thermolysis of **1a** in alcohols and related reactions. (▲) *O*-(2-methylsulfanylethyl) *S*-methyl xanthate, m = 0.402; (■) *O*-(3-phenylallyl) *S*-methyl xanthate, m = 0.310; (○) *O*-furfuryl *S*-methyl xanthate, m = 0.619. (*b*) Plots of log k *vs.* Y values for the thermolysis of **1a** in phenol–benzene solvent and related reactions. (▲) *O*-(2-methylsulfanylethyl) *S*-methyl xanthate, m = 0.597; (■) *O*-(3-phenylallyl) *S*-methyl xanthate, m = 0.583; (○) *O*-furfuryl *S*-methyl xanthate, m = 0.760.

The heats of formation of **1a**, **2a**, TS1, TS2 and TS3 in the gas phase are −0.012, −31.9, 26.2, 62.3 (62.0 in UHF) and 46.4 kcal mol^{-1}, respectively.

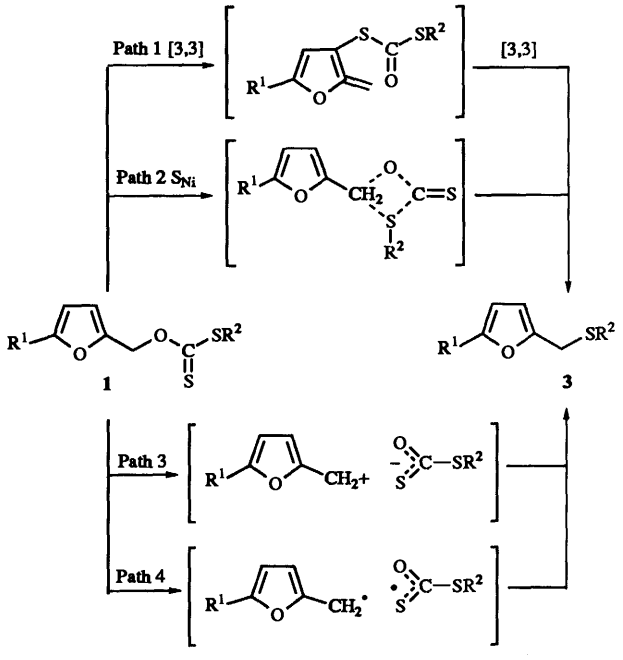
Discussion

Possible pathways for the extrusion reaction of **1** are shown in Scheme 4. As previously reported,[2] allylic xanthates (**I**) undergo two sequential [3,3]-sigmatropic rearrangements to give allylic sulfides (**III**) with extrusion of COS *via* dithiocarbonate intermediates (**II**). At first glance, we supposed that the sulfide formation reaction of furfuryl xanthates (**1**) proceeds through a mechanism similar to that of allylic xanthates, because the aromaticity of the furan ring is lower than those of thiophene and pyrrole.[14] As shown in Scheme 5, the PM3-calculated activation enthalpy ($\Delta\Delta_fH$) of path 1 is *ca.* 26 kcal mol^{-1}, which is *ca.* 8 kcal mol^{-1} higher than the value of *O*-allyl *S*-methyl xanthate (**Ia**) ($\Delta\Delta_fH$ = 18.2 kcal mol^{-1}).[15] This discrepancy is considered to be due to an additional energy required for destruction of aromaticity of the furan ring.¶ Taking into account that the experimental $\Delta H^{\ddagger}$ of [3,3]-sigmatropic rearrangement of **Ia** is *ca.* 26 kcal mol^{-1},[16] the $\Delta H^{\ddagger}$ of the furfuryl xanthate (**1a**) is estimated to be *ca.* 34 kcal mol^{-1}. These suggest

¶ The PM3 calculation seems to underestimate the resonance energies in furan: Δ_fH = −8.3 kcal mol^{-1} (obs.); Δ_fH = 4.0 kcal mol^{-1} (calcd.).[9]

that the [3,3]-sigmatropic rearrangement involving the furan ring is energetically unfavourable.

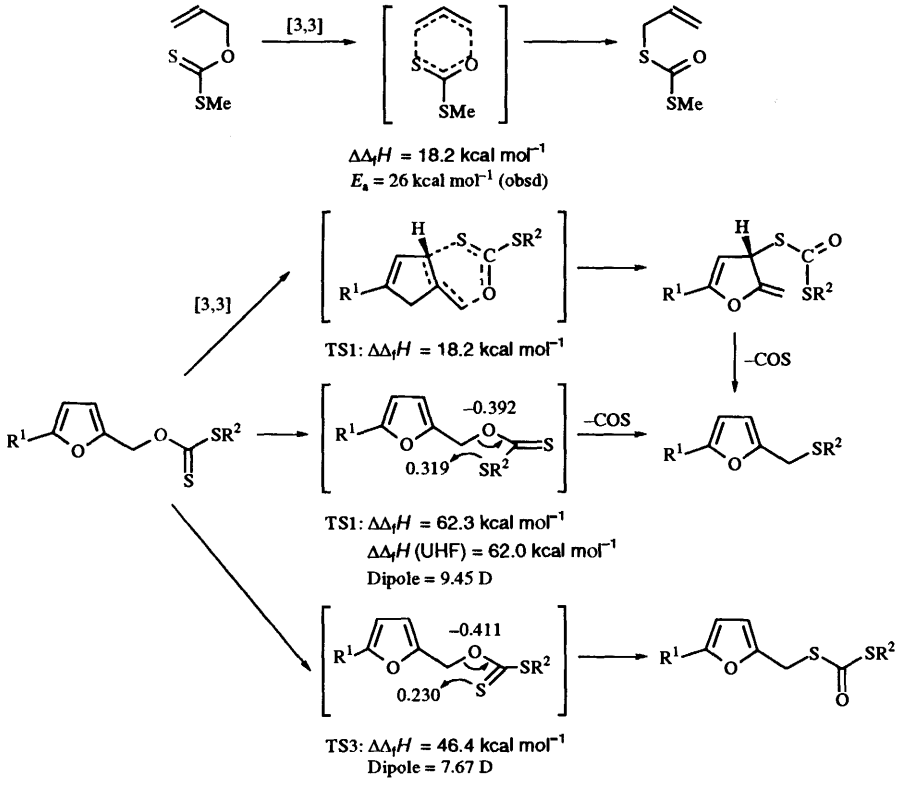
An alternative mechanism of S_{Ni} type for the extrusion reaction is possible (path 2). When the dissociation of the >C–O(C=S)–bond occurs, the methylsulfanyl group simultaneously would attack the α-carbon atom from the front side to give furfuryl methyl sulfide (**3a**) plus COS. The PM3 calculated TS energy for the S_{Ni} extrusion in the gas phase (TS2) is very high ($\Delta\Delta_fH$ = 62.3 kcal mol^{-1}). The S_{Ni}-type thione-to-thiol rearrangement derived from a conformational isomer of the TS2 structure requires a large activation energy (TS2: $\Delta\Delta_fH$ = 46.4 kcal mol^{-1}). Although the calculations are in the gas phase, considerable charge separations and large dipole moments were observed (see Scheme 5). These results suggest that these two S_{Ni}-type reactions can occur with the aid of solvents.



Scheme 4

In polar solvents, the crossover products were detected, ruling out an intramolecular S_{Ni}-type mechanism. For assessment of the reaction mechanism, the solvent effect on the rate of the extrusion reaction was studied. The rate of the reaction for **1a** was found to depend greatly on the ionizing power of the solvent, increasing when the solvent was changed from non-polar to polar. The correlation of the rates with Reichardt's E_T values,[7,16] is depicted in Fig. 3. The solvent sensitivity parameter (a = slope of the least-squares line × 10^2) was compared with those of the known reactions. As shown in Table 2, values of a for non-ionic reactions are small: a = 6.40 for [3,3]-sigmatropic extrusion of *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (**IIb**), a = 6.46 for non-ionic [3,3]-sigmatropic rearrangement of *O*-allyl *S*-methyl xanthate (**Ia**), a = 12.6 for the [3,3]-sigmatropic rearrangement of *O*-cinnamyl *S*-methyl xanthate (**Ib**) which proceeds through a slightly dipolar mechanism.[16a] On the other hand, a = 31.2 for extrusion of benzhydryl *S*-phenyl thiocarbonate, a = 40.3 for the thione-to-thiol rearrangement of *O*-(2-diethylaminoethyl) *S*-methyl xanthate (**Ic**).[16a] These values are very large, indicating that the reactions occur through highly polarized transition states such as ion-pair. The value of a for **1a** is 24.1, considerably greater than those observed in the concerted reactions. These facts indicate that **1a** may undergo extrusion by a mechanism which involves considerable change in charge separation between the ground state and the transition state.

The protic solvents promote the thione-to-thiol rearrangement reaction. When the furfuryl xanthate (**1a**) was treated with water, the thione-to-thiol rearrangement took place preferentially (**2a**:**3a** 5:1). As previously reported, the thermolysis rate of the cinnamyl xanthate (**Ib**)[17] is markedly affected by a change in solvent polarity, in which the mechanism alters from non-

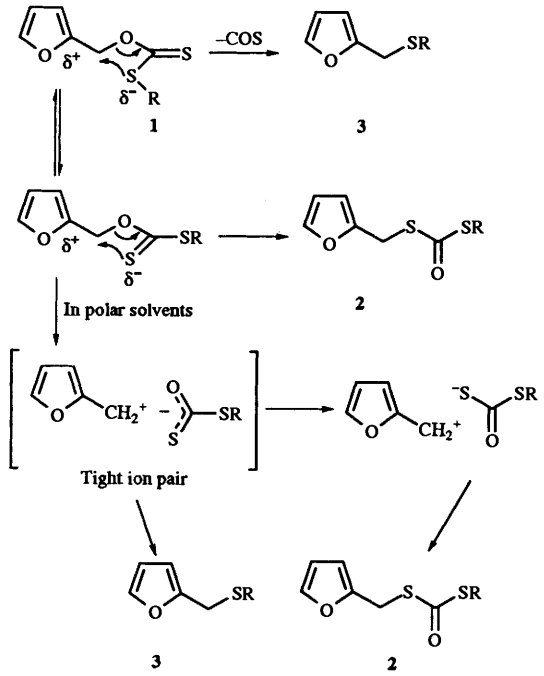


Scheme 5

Table 2 Sensitivity of various reactions to solvent ionizing power

Substrate	Reaction	Solvent sensitivity parameter,[a] a
O-(2-Diethylaminoethyl) *S*-methyl xanthate[b]	Thione-to-thiol rearrangement	40.3
Benzhydryl *S*-phenyl thiocarbonate[b]	Extrusion	31.2
O-Furfuryl *S*-methyl xanthate	Extrusion	24.1
p-Methoxyneophyl toluene-*p*-sulfonate[b]	Solvolysis	17.9
1-Methylallyl chloroformate[b]	[3,3]-Extrusion	17.6
O-Cinnamyl *S*-methyl xanthate[b]	[3,3]-Rearrangement	12.6
1-Trifluoromethylallyl chlorosulfinate[b]	[3,3]-Extrusion	7.60
O-Allyl *S*-methyl xanthate[b]	[3,3]-Rearrangement	6.46
S-1-Phenylallyl *S*-methyl dithiocarbonate[b]	[3,3]-Extrusion	6.40
Allyl *p*-cresyl ether[b]	[3,3]-Rearrangement	4.34

[a] $\log k = a\ 10^{-2}E_T + b$. [b] See ref. 16*b*.



Scheme 6

ionic to ionic in going from aprotic to protic solvent. The slope (m) for the thermolysis of **1a** in alcohols is 0.619, which is larger than those for allylic rearrangement of **Ib** (m = 0.310) and thione-to-thiol rearrangement of *O*-(2-methylsulfanylethyl) *S*-methyl xanthate (**Id**) (m = 0.402).[17] As can be seen in Fig. 4, the m value for the thermolysis of **1a** in phenol–benzene is 0.760, larger than those for **Ib** (m = 0.583) and **Id** (m = 0.597).[17] These facts suggest that the reaction of **1a** in protic solvents proceeds through a loosely united ion-pair intermediate. However, the reaction of **1a** in phenol did not give any phenolysis product as observed in the reaction of *O*-(1-cyclopropylethyl) *S*-methyl xanthate (m = 0.797 for alcoholic solvents and m = 0.861 for the benzene–PhOH binary solvent system).[18]

The activation parameters for **1a** are different from those of a typical concerted extrusion reaction, *i.e.* conversion of *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (**IIb**) to cinnamyl methyl sulfide (**IIIb**). The $\Delta H^{\ddagger}$ for the extrusion of **1a** in xylene (28.0 kcal mol^{-1}) is higher than that for the extrusion of **IIb** (22.1 kcal mol^{-1}). The $\Delta S^{\ddagger}$ (−2 cal K^{-1} mol^{-1}) for **1a** is greater than that for **IIb** (−28 cal K^{-1} mol^{-1}), indicating that the TS structure for the decomposition of **1a** is less ordered than that for **IIb**.

These observations and considerations suggest that the degree of the dissociation of the intermediate continuously increases with the increase in the solvent polarity. In fact, the crossover reaction in non-ionic solvent such as benzene did not give any crossover products. The plausible reaction mechanism is shown in Scheme 6. In non-polar solvents, whether the thione-to-thiol rearrangement occurs predominantly over the COS extrusion reaction seems to depend upon the conformational mobility of the TS structure. In ethers, the cationic part may be effectively solvated by the ether oxygen. The ion pair may split off COS to give the alkylsulfide anion which in turn combines with the allylic cation to give the sulfide. As described above, in the reaction of **1a**, water enhanced the thione-to-thiol rearrangement reaction (**2a**:**3a** 5:1). In contrast, the presence of β-CD (2 equiv.) promoted the formation of the sulfide (**2a**:**3a** 1:1). β-Cyclodextrin (β-CD) has two interaction sites, *i.e.* hydroxylic groups of the opening site and the ether linkages of the cavity of β-CD. With β-CD, the furan ring of the guest molecule is entirely included within the cavity of β-CD and the >C=S group makes a hydrogen bond with the hydroxy groups of β-CD. In such a conformation, the sulfide formation must be effectively accelerated by a mechanism worked in ethereal solvents.

Furfuryl alkyl sulfides can be prepared from the corresponding xanthates by a single step. The yield of the sulfides is improved by use of ethereal solvents at an elevated temperature (*i.e.* 90 °C). Based on these findings, further studies on the synthetic applications are in progress.

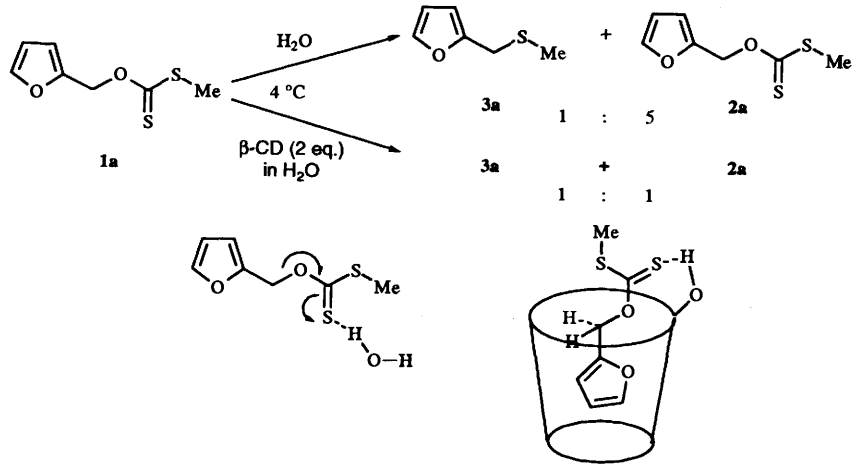
Experimental

The IR spectra were taken with a Hitachi 270–30 spectrophotometer. The ^{1}H NMR spectra were taken with Hitachi R-600 (60 MHz), JNM-EX 270 (270 MHz) and JEOL GX-400 (400 MHz) spectrometers using tetramethylsilane as an internal standard; the chemical shifts are expressed in δ values. The coupling constants (J) are presented in Hz. High resolution mass spectra (HRMS) were taken with a JEOL JMS-DX303HF spectrometer. GLC analyses were performed with a Shimadzu GC-8A gas chromatograph with a frame ionization detector using 30% SE-30 on a Uniport B (60–80 mesh 3 mm × 3 m) column.

Molecular orbital calculations were performed on a FACOM M-780 computer in the Computer Center of Kumamoto University and on a Fujitsu S4/2 and S4/10 engineering workstations. Least-squares calculations were performed on a FMR-60HX personal and a Macintosh 520 computers.

Potassium *O*-furfuryl dithiocarbonate

A mixture of furfuryl alcohol (0.1 mol) and an equimolar amount of solid KOH in acetone was stirred until the KOH had disappeared. The resulting yellow solution was diluted with diethyl ether to give crystals. The crystals were collected by filtration and recrystallized from acetone–diethyl ether to give colourless crystals. Yield 14.2 g (67%). The product was pure for the preparation of the xanthates.



Scheme 7

Potassium salts of substituted furylmethyl xanthates were prepared in a similar manner.

Synthesis of xanthates (general procedure)
Potassium *O*-furfuryl dithiocarbonate (0.01 mol) was dissolved in acetone (30 cm^3). Alkyl halide (0.01 mol) was added to the acetone solution cooled in an ice bath. After 20 min stirring, water was added to the solution. The separated oil was extracted with hexane. The hexane extract was dried ($MgSO_4$). Evaporation of hexane at room temperature gave a yellow oil. Inspection of the ^1H NMR spectrum revealed that the product was pure enough for further use. Similarly, furfuryl alkyl (or alkenyl) xanthates were prepared from the corresponding xanthates.

Sulfides from thermolysis of xanthates (general procedure)
A solution of **1** (0.0085 mol) in benzene (20 cm^3) was refluxed for 2 h. Evaporation of benzene gave a colourless oil. The residue was purified by column chromatography on silica gel using a hexane–benzene eluent to give the dithioester (**2**) and sulfide (**3**). The sulfide was easily separated from the dithioester. Similarly, furfuryl alkyl (or alkenyl) sulfides were prepared from the corresponding xanthates.

The physical properties, yields and spectral data of the products are as follows.

***O*-Furfuryl *S*-methyl xanthate (1a)**
1a was prepared following the standard procedure by using methyl iodide. Evaporation of the solvent gave **1a** as a pale yellow oil (85%); ν_{max}/cm^{-1} 1232 and 1056 [–O(C=S)S–]; δ_H 2.55 (3 H, s, SCH_3), 5.59 (2 H, s, Ar–CH_2–O), 6.45 (2 H, m, 3- and 4-H) and 7.44 (1 H, m, 5-H). The crude product was used for thermolysis without purification. The structure was confirmed by isolation of the corresponding dithioester.

***S*-Furfuryl *S*-methyl dithiocarbonate (2a)**
According to the general procedure, thermolysis of **1a** gave **2a** as a colourless oil (6%); ν_{max}/cm^{-1} 1646 [–S(C=O)S–]; δ_H 2.43 (3 H, s, SCH_3), 4.24 (2 H, s, Ar–CH_2–S–), 6.27 (2 H, m, 3- and 4-H) and 7.33 (1 H, m, 5-H); *m/z* 188 (M^+). The structure was identified by conversion to 2,4-dinitrophenyl sulfide.[19]

Furfuryl methyl sulfide (3a)
According to the general procedure, thermolysis of **1a** gave **3a** as a colourless oil (68%); ν_H/cm^{-1} 1504, 1152, 1012 and 736 (furan); δ_H 2.07 (3 H, s, SCH_3), 3.67 (2 H, s, Ar–CH_2S–), 6.26 (2 H, m, 3- and 4-H) and 7.37 (1 H, m, 5-H); *m/z* 128 (M^+). The ^1H NMR spectral data are identical to those of the authentic sample.

***O*-Furfuryl *S*-ethyl xanthate (1b)**
1b was prepared following the standard procedure by using ethyl iodide. Evaporation of the solvent gave **1b** as a pale yellow oil (92%); ν_{max}/cm^{-1} 1232 and 1062 (C=S); δ_H 1.31 (3 H, t, *J* 7.2, CH_2–CH_3), 3.11 (2 H, q, *J* 7.2, CH_2–CH_3), 5.57 (2 H, s, Ar–CH_2–O), 6.45 (2 H, m, 3- and 4-H) and 7.46 (1 H, m, 5-H). The crude product was used for thermolysis without purification. The structure was confirmed by isolation of the corresponding dithioester.

***S*-Furfuryl *S*-ethyl dithiocarbonate (2b)**
According to the general procedure, thermolysis of **1b** gave **2b** as a colourless oil (26%) (Found: M^+, 202.0102. $C_8H_{10}O_2S_2$ requires *M*, 202.0122); ν_{max}/cm^{-1} 1646 [–S(C=O)S–]; δ_H 1.31 (3 H, t, *J* 7.3, CH_2–CH_3), 3.02 (2 H, q, *J* 7.3, CH_2–CH_3), 4.25 (2 H, s, Ar–CH_2–S), 6.24 (1 H, dd, *J* 1.0, 3.3, 3-H), 6.30 (1 H, dd, *J* 2.0, 3.3, 4-H) and 7.33 (1 H, dd, *J* 1.0, 2.0, 5-H); *m/z* 202 (M^+).

Furfuryl ethyl sulfide (3b)
According to the general procedure, thermolysis of **1b** gave **3b** as a colourless oil (44%) (Found: M^+, 142.0459. $C_7H_{10}OS$ requires *M*, 142.0452); ν_H/cm^{-1} 1502, 1152, 1014 and 738 (furan); δ_H 1.22 (3 H, t, *J* 6.6, CH_2–CH_3), 2.50 (2 H, q, *J* 6.6, CH_2–CH_3), 3.73 (2 H, s, Ar–CH_2–S), 6.26 (2 H, m, 3- and 4-H) and 7.36 (1 H, m, 5-H).

***O*-Furfuryl *S*-benzyl xanthate (1c)**
1c was prepared following the standard procedure by using benzyl chloride. Evaporation of the solvent gave **1c** as a pale yellow oil (88%); ν_{max}/cm^{-1} 1234 and 1056 (C=S); δ_H 4.58 (2 H, s, –CH_2–Ph), 5.56 (2 H, s, Ar–CH_2–O), 6.37 (2 H, m, 3- and 4-H) and 7.34 (6 H, m, 2-H and Ph). The crude product was used for thermolysis without purification. The structure was confirmed by isolation of the corresponding dithioester.

***S*-Furfuryl *S*-benzyl dithiocarbonate (2c)**
According to the general procedure, thermolysis of **1c** gave **2c** as a colourless oil (18%) (Found: M^+, 264.0293. $C_{13}H_{12}O_2S_2$ requires *M*, 264.0279); ν_{max}/cm^{-1} 1646 [–S(C=O)S–]; δ_H 4.24 (2 H, d, *J* 1.7, Ar–CH_2–S), 4.27 (2 H, ABq, *J* 1.7, –SCH_2–Ph), 6.24 (1 H, d, *J* 3.3, 3-H), 6.30 (1 H, dd, *J* 3.3, 2.0, 4-H), 7.33 (1 H, d, *J* 2.0, 5-H) and 7.24–7.35 (5 H, m, Ph); *m/z* 264 (M^+).

Furfuryl benzyl sulfide (3c)
According to the general procedure, thermolysis of **1c** gave a colourless oil (48%) (Found: M^+, 204.0592. $C_{12}H_{12}O_2S_2$ requires *M*, 204.0609); ν_{max}/cm^{-1} 1496, 1150, 1012 and 738 (furan); δ_H 3.58 (2 H, s, –CH_2–Ph), 3.69 (2 H, s, Ar–CH_2–O), 6.24 (2 H, m, 3- and 4-H) and 7.34 (6 H, m, 2-H and Ph).

O-Furfuryl S-methoxycarbonylmethyl xanthate (1d)
1d was prepared following the standard procedure by using methyl bromoacetate. Evaporation of the solvent gave **1d** as a pale yellow oil (83%); ν_{max}/cm^{-1} 1238 and 1056 (C=S); δ_H 3.72 (3 H, s, $-OCH_3$), 3.92 (2 H, s, $S-CH_2CO_2-$), 5.56 (2 H, s, $Ar-CH_2-O$), 6.43 (2 H, m, 3- and 4-H) and 7.39 (1 H, m, 2-H). The crude product was used for thermolysis without purification. The structure was confirmed by isolation of the corresponding dithioester.

S-Furfuryl S-methoxycarbonylmethyl dithiocarbonate (2d)
According to the general procedure, thermolysis of **1d** gave **2d** as a colourless oil (23%); (Found: M^+, 245.9955. $C_9H_{10}O_4S_2$ requires *M*, 246.0021); ν_{max}/cm^{-1} 1742 (CO) and 1646 [-S-(C=O)S-]; δ_H 3.75 (3 H, s, $-OCH_3$), 3.80 (2 H, s, $S-CH_2CO_2-$), 4.28 (2 H, s, $Ar-CH_2-O$), 6.24 (1 H, dd, *J* 1.0, 3.3, 3-H), 6.30 (1 H, dd, *J* 2.0, 3.3, 4-H) and 7.33 (1 H, dd, *J* 1.0, 2.0, 5-H); *m/z* 245 (M^+).

Furfuryl methoxycarbonylmethyl sulfide (3d)
According to the general procedure, thermolysis of **1d** gave **3d** as a colourless oil (73%); (Found: M^+, 186.0345. $C_8H_{10}O_3S$ requires *M*, 186.0351); ν_{max}/cm^{-1} 1740 (CO_2Me), 1504, 1152, 1012 and 742 (furan); δ_H 3.20 (3 H, s, $-OCH_3$), 3.73 (2 H, s, $S-CH_2CO_2-$), 3.86 (2 H, s, $Ar-CH_2-O$), 6.28 (2 H, m, 3- and 4-H) and 7.37 (1 H, m, 2-H).

O-(5-Methylfurfuryl) S-methyl and S-ethyl xanthates (1e, f)
1e, f were prepared following the standard procedure by using methyl iodide. Concentration gave the title product. The xanthate undergoes thione-to-thiol rearrangement to give the corresponding dithioester even at room temperature. The crude product was used for thermolysis without purification. The structure was confirmed by isolation of the corresponding dithioester.

S-(5-Methylfurfuryl) S-methyl dithiocarbonate (2e)
According to the general procedure, thermolysis of **1e** gave **2e** as a colourless oil (68%) (Found: M^+, 202.0087. $C_8H_8O_2S_2$ requires *M*, 202.0122); ν_{max}/cm^{-1} 1648 [-S(C=O)S-]; δ_H 2.24 (3 H, s, CH_3), 2.42 (3 H, s, $5-CH_3$), 4.21 (2 H, s, $Ar-CH_2-O$), 5.87 (1 H, d, *J* 3.1, 4-H) and 6.11 (1 H, d, *J* 3.1, 3-H); *m/z* 202 (M^+).

5-Methylfurfuryl methyl sulfide (3e)
According to the general procedure, thermolysis of **1e** gave **3e** as a colourless oil (11%) (Found: M^+, 142.0408. $C_8H_{10}S$ requires *M*, 142.0452); ν_{max}/cm^{-1} 1012 and 786 (furan); δ_H 2.08 (3 H, s, $-SCH_3$), 2.27 (3 H, d, *J* 1.1, $5-CH_3$), 3.63 (2 H, s, $Ar-CH_2-O$), 5.87 (1 H, dd, *J* 1.1, 2.9, 4-H) and 6.04 (1 H, d, *J* 2.9, 3-H); *m/z* 142 (M^+).

S-(5-Methylfurfuryl) S-ethyl dithiocarbonate (2f)
According to the general procedure, thermolysis of **1f** gave **2f** as a colourless oil (32%) (Found: M^+, 216.0261. $C_9H_{12}O_2S_2$ requires *M*, 216.0279); ν_{max}/cm^{-1} 1646 [-S(C=O)S-]; δ_H 1.30 (3 H, t, *J* 7.5, $-CH_2CH_3$), 2.26 (3 H, s, $5-CH_3$), 3.02 (2 H, q, *J* 7.5, $-CH_2CH_3$), 4.21 (2 H, s, $Ar-CH_2-O$), 5.88 (1 H, d, *J* 2.7, 4-H) and 6.11 (1 H, d, *J* 2.7, 3-H); *m/z* 216 (M^+).

5-Methylfurfuryl ethyl sulfide (3f)
According to the general procedure, thermolysis of **1f** gave **3f** as a colourless oil (7%) (Found: M^+, 156.1642. $C_9H_{12}S$ requires *M*, 156.0609); ν_{max}/cm^{-1} 1022 and 786 (furan); δ_H 1.29 (3 H, t, *J* 7.4, CH_2CH_3), 2.26 (3 H, s, $5-CH_3$), 3.00 (2 H, q, *J* 7.4, $-CH_2CH_3$), 3.67 (2 H, s, $Ar-CH_2-O$), 5.88 (1 H, dd, *J* 2.3, 4-H) and 6.04 (1 H, d, *J* 2.3, 3-H); *m/z* 156 (M^+).

O-(5-Bromofurfuryl) S-methyl xanthate (1g)
1g was prepared following the standard procedure by using methyl iodide. Evaporation of the solvent gave **1g** as a pale yellow oil (90%); ν_{max}/cm^{-1} 1224 and 1078 [-O(C=S)S-]; δ_H 2.56 (3 H, s, SCH_3), 5.53 (2 H, s, $ArCH_2O$), 6.31 (2 H, d, *J* 3.5, 3-H), 6.48 (1 H, d, *J* 3.5, 4-H). The crude product was used for thermolysis without purification. As the bromo derivatives (**1g**, **2g** and **3g**) are unstable, the ^1H NMR spectral data are given.

S-(5-Bromofurfuryl) S-methyl dithiocarbonate (2g)
According to the general procedure, thermolysis of **1g** gave a colourless oil (12%); ν_{max}/cm^{-1} 1644 [-S(C=O)S-]; δ_H 2.44 (3 H, s, SCH_3), 4.21 (2 H, s, $ArCH_2O$) and 6.22 (2 H, s, 3- and 4-H).

5-Bromofurfuryl methyl sulfide (3g)
According to the general procedure, thermolysis of **1g** gave **3g** as a colourless oil (62%); δ_H 2.08 (3 H, s, SCH_3), 3.36 (2 H, s, $ArCH_2O$) and 6.19 (2 H, s, 3- and 4-H).

O-(2-Methyl-3-furylmethyl) S-methyl xanthate (1h)
1h was prepared following the standard procedure by using methyl iodide. Evaporation of the solvent gave **1h** as a pale yellow oil (93%); ν_{max}/cm^{-1} 1210 and 1062 [-O(C=S)S-]; δ_H 2.31 (3 H, s, $2-CH_3$), 2.54 (3 H, s, $-SCH_3$), 5.44 (2 H, s, $ArCH_2O-$), 6.39 (1 H, d, *J* 1.1, 4-H) and 7.24 (1 H, d, *J* 1.1, 5-H). The crude product was used for thermolysis without purification. The structure was confirmed by isolation of the corresponding dithioester.

S-(2-Methyl-3-furylmethyl) S-methyl dithiocarbonate (2h)
According to the general procedure, thermolysis of **1h** gave **2h** as a colourless oil (6%) (Found: M^+, 202.0090. $C_8H_{10}O_2S_2$ requires *M*, 202.1222); ν_{max}/cm^{-1} 1646 [-S(C=O)S-]; δ_H 2.27 (3 H, s, $2-CH_3$), 2.42 (3 H, s, SCH_3), 4.01 (2 H, s, $ArCH_2O-$), 6.25 (1 H, d, *J* 1.5, 4-H) and 7.21 (1 H, d, *J* 1.5, 5-H); *m/z* 202 (M^+).

2-Methyl-3-furylmethyl methyl sulfide (3h)
According to the general procedure, thermolysis of **1h** gave **3h** as a colourless oil (39%); ν_{max}/cm^{-1} 1516, 1136 and 738 (furan); δ_H 2.11 (3 H, s, $S-CH_3$), 2.24 (3 H, s, $2-CH_3$), 3.46 (2 H, s, $ArCH_2S-$), 6.30 (1 H, d, *J* 1.9, 4-H) and 7.24 (1 H, d, *J* 1.9, 5-H); *m/z* 142 (M^+).

O-(2-Methyl-3-furylmethyl) S-ethyl xanthate (1i)
1i was prepared following the standard procedure by using ethyl iodide. Evaporation of the solvent gave **1i** as a pale yellow oil (96%); ν_{max}/cm^{-1} 1200 and 1062 [-O(C=S)S-]; δ_H 1.33 (3 H, t, *J* 7.3, $-CH_2CH_3$), 2.33 (3 H, s, $2-CH_3$), 3.11 (2 H, q, *J* 7.3, $-SCH_2-$), 5.44 (2 H, s, $ArCH_2O-$), 6.38 (1 H, d, *J* 2.0, 4-H) and 7.27 (1 H, d, *J* 2.0, 5-H). The crude product was used for thermolysis without purification. The structure was confirmed by isolation of the corresponding dithioester.

S-(2-Methyl-3-furylmethyl) S-ethyl dithiocarbonate (2i)
According to the general procedure, thermolysis of **1i** gave **2i** as a colourless oil (5%) (Found: M^+, 216.0233. $C_9H_{12}O_2S_2$ requires *M*, 216.0279); ν_{max}/cm^{-1} 1646 [-S(C=O)S-]; δ_H 1.31 (3 H, t, *J* 7.3, $-CH_2CH_3$), 2.27 (3 H, s, $2-CH_3$), 3.01 (2 H, q, *J* 7.3, SCH_2-), 4.01 (2 H, s, $ArCH_2O-$), 6.25 (1 H, d, *J* 2.0, 4-H) and 7.21 (1 H, d, *J* 2.0, 5-H); *m/z* 216 (M^+).

2-Methyl-3-furylmethyl ethyl sulfide (3i)
According to the general procedure, thermolysis of **1i** gave **3i** as a colourless oil (38%) (Found: M^+, 156.0169. $C_8H_{12}OS$ requires *M*, 156.0609); ν_{max}/cm^{-1} 1514, 1136 and 736 (furan); δ_H 1.24 (3 H, t, *J* 7.3, $-CH_2CH_3$), 2.25 (3 H, s, $2-CH_3$), 2.46 (2 H, q, *J* 7.3, $-SCH_2-$), 3.50 (2 H, s, $ArCH_2O-$), 6.31 (1 H, d, *J* 2.0, 4-H) and 7.27 (1 H, d, *J* 2.0, 5-H); *m/z* 156 (M^+).

Preparation of inclusion complex

The xanthate **1a** (360 mg, 0.0016 mol) was added to an aqueous solution (100 cm^3) of β-cyclodextrin (2.0 g). After stirring for 7 days in an ice–water bath (0–4 °C), the resulting precipitates were filtered and washed with diethyl ether to remove any guest molecule not included and dried (P_2O_5) *in vacuo* at room temperature for 1 day. Thus, the white crystalline powders (1.97 g) were obtained as a 1:1 molar complex of **1a** with β-cyclodextrin in 90% yield.

Extraction of the product from the inclusion complex

After the inclusion complex (2.19 g) was allowed to stand at room temperature for several days, the complex was dissolved in Me_2SO (4 cm^3). To the Me_2SO solution was added benzene (30 cm^3) and stirred until the completion of precipitation. The resulting precipitates were filtered off. The filtrate was washed with water (5 times) and dried ($MgSO_4$). Evaporation of benzene gave an oily product (0.162 mg). The formation ratio was analysed by ^1H NMR spectroscopy, showing **1a**:**2a**:**3a** 1:9:9.

Crossover reaction

A mixture of **1a** (0.188 g, 1.0 mmol) and **1i** (0.216 g, 1.0 mmol) was heated at 80 °C for 0.5 h. After cooling, the reaction mixture was analysed by GLC. In the absence of solvent and in *N*,*N*-dimethylformamide (DMF), the chromatogram showed the presence of the crossover products. In xylene, the crossover products were not detected.

Product ratio (2:3) in various solvents

A solution of **1a** (0.188 g, 1.0 mmol) in a given solvent (20 cm^3) was heated on a water bath (62.4 °C) for 5 h. The product ratio was analysed by GLC using 4-methoxyacetophenone as an internal standard. The product ratio (**2a**:**3a**) in various solvents are as follows: xylene, 40:46; benzene, 36:50; dioxane, 19:67; anisole, 20:74; diethylene glycol dimethyl ether, 27:42; DMF, 49:40; sulfolane (tetramethylenesulfone), 43:33; ethanol, 76:24; methanol, 72:28.

Rate measurement

A solution of **1** in a given solvent (0.188 g in 20 cm^3) was heated at a given temperature in a constant water bath which was controlled to ± 0.1 °C. At an appropriate time, a settled amount of the reaction mixture was taken out and diluted with the solvent to a fixed volume. The remaining amount of **1** was measured by following the n–π^* visible absorption band (350 nm) of the >C=S chromophore. The first-order rate constants were calculated from the plot of $\ln(A_t - A_\infty)$ *vs.* time having correlation coefficients better than 0.998 by non-weighted least-squares method.

The rate constants ($k/10^{-5}$ s^{-1}) for the thermolyses of **1a** are as follows: in aprotic solvent at 62.4 °C, *p*-xylene, 1.00; benzene, 1.30; dioxane, 6.60; anisole, 7.10; diethylene glycol dimethyl ether, 23.0; DMF, 264; sulfolane, 494; in the PhOH–benzene system at 45 °C, 10% PhOH, 0.135; 20% PhOH, 0.826; 30% PhOH, 1.93; 50% PhOH, 6.84; in protic solvents at 45 °C, 80% EtOH, 6.59; MeOH, 1.46; AcOH, 0.250; EtOH, 0.363.

The activation parameters for thermolysis of **1a** are as follows: in xylene, E_a = 24.1 ± 1.5 kcal mol^{-1}, $\Delta S^\ddagger$ = −12 ± 4 cal K^{-1} mol^{-1}; in anisole, E_a = 24.5 ± 0.3 kcal mol^{-1}, $\Delta S^\ddagger$ = −6 ± 1 cal K^{-1} mol^{-1}; in DMF, E_a = 18.0 ± 0.5 kcal mol^{-1}, $\Delta S^\ddagger$ = −18 ± 2 cal K^{-1} mol^{-1}.

The rate constants ($k/10^{-5}$ s^{-1}) for thermolyses of *O*-furfuryl *S*-alkyl xanthates in xylene at 80.4 °C are as follows: methyl, 5.20; ethyl, 6.20; benzyl, 15.9; methoxycarbonylmethyl, 82.6.

Acknowledgements

We thank Miss S. Yorifuji, Miss N. Shimizu and Mr O. Tajiri for experimental assistance.

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Paper 4/05987E
Received 30*th September* 1994
Accepted 11*th January* 1995