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Formation Mechanism of Furfuryl Sulfides from *O*-Furfuryl Dithiocarbonates: Density Functional Theory Study for Aromatic [3,3]-Sigmatropic Rearrangement

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Density functional theory (DFT) calculations at the B3LYP/6-31G(d) and B3LYP/6-31G+(d) levels demonstrated that *O*-furfuryl *S*-alkyl dithiocarbonate (1) undergoes aromatic [3,3]-sigmatropic rearrangement to the energetically unfavorable *S*-(2-methylene-2,3-dihydrofuran-3-yl) *S*-alkyl dithiocarbonate (2′), which then rearranges to furfuryl alkyl sulfide (3) with COS extrusion to regain the aromaticity lost in the first step.

Key words furfuryl alkyl sulfide; dithiocarbonate; thione-to-thiol rearrangement; aromatic [3,3]-sigmatropic rearrangement; density functional theory calculation

Recently, we proposed a new reaction mechanism for the formation of allylic trithiocarbonate from sodium *O*-(2-alkenyl) dithiocarbonate,[1] in which a suspension of sodium hydride in benzene, containing 2-alkenol and an excess of carbon disulfide is heated to obtain the corresponding di(2-alkenyl)trithiocarbonates in good yields.[2,3] The trithiocarbonates are convenient precursors of the thermodynamically stable allylic thiols (Chart 1).

Based on data obtained from density functional theory (DFT) calculations at the B3LYP/6-31G(d) level, we demonstrated that sodium *O*-(3-phenylallyl) dithiocarbonate undergoes [3,3]-sigmatropic rearrangement to form sodium *S*-(1-phenylallyl) dithiocarbonate, which then allylically isomerizes to the more thermodynamically stable sodium *S*-(3-phenylallyl) dithiocarbonate.

Furfuryl and benzyl alcohols were subjected to xanthation in dimethyl sulfoxide (DMSO) containing excess CS_2 in the presence of NaOH followed by alkylation to give the mixtures of trithiocarbonates.[3]

On the other hand, it was observed that heating of *O*-furfuryl *S*-alkyl dithiocarbonates (xanthates) (**1**) afforded furfuryl alkyl sulfides (**3**) together with *S*-furfuryl *S*-alkyl dithiocarbonates (**2**). It was initially assumed that the sulfide (**3**) had formed *via* an intramolecular S_Ni-type fragmentation reaction mechanisms (Chart 2).[4]

These considerations prompted us to reinvestigate the key step of the conversion of the furfuryloxy ($ArCH_2O$–) moiety to the furfurylthio ($ArCH_2S$–) moiety in the formation of the trithiocarbonate from sodium *O*-furfuryl dithiocarbonates as well as in the formation of *S*-furfuryl *S*-alkyl dithiocarbonates (**2**) and furfuryl alkyl sulfides (**3**) from *O*-furfuryl *S*-alkyl xanthates (**1**) with the assumption that aromatic [3,3]-sigmatropic rearrangement was operative.

This paper presents a detailed discussion of the reaction mechanisms in the formation of *O*-furfuryl dithiocarbonates on the basis of the DFT calculations[5] at the B3LYP/6-31G(d) and B3LYP/6-31G+(d) levels.

Results and Discussion

Rearrangement of *O*-Furfuryl Dithiocarbonate Anion (1-Anion) On the basis of the reaction behavior of the *O*-allyl dithiocarbonate anion,[1] two possible reaction pathways were proposed for the formation of the *S*-furfuryl dithiocar-

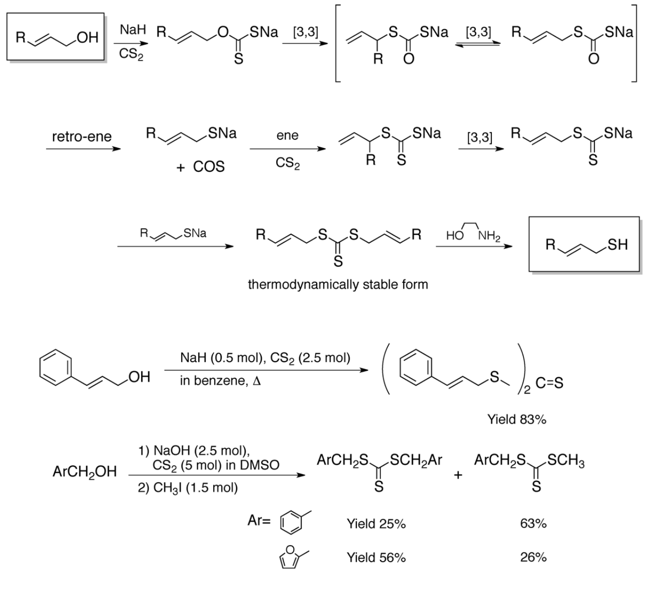

Chart 1

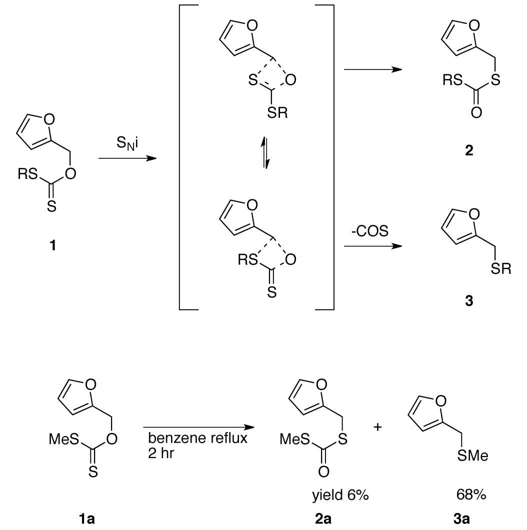

Chart 2

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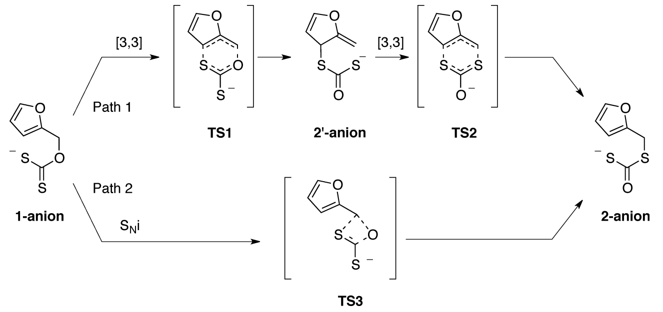


Chart 3

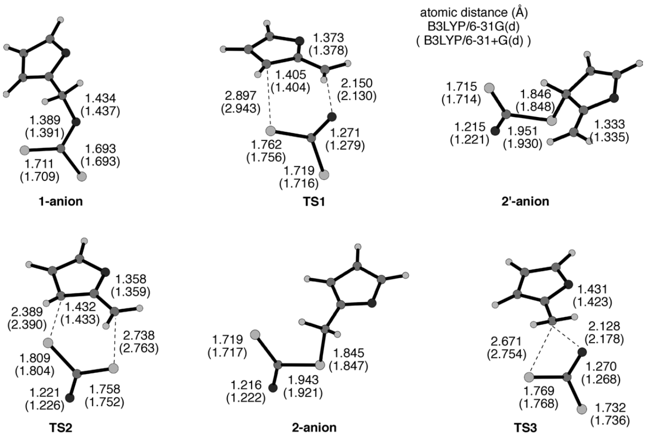
bonate anion (**2-anion**) from *O*-furfuryl dithiocarbonate anion (**1-anion**), *i.e.*, two-step [3,3]-sigmatropic rearrangement (path 1) and *SNi*-type thione-to-thiol rearrangement (path 2) (Chart 3).

In order to elucidate the reaction behavior of **1-anion**, the energy profile from DFT calculations at the B3LYP/6-31G(d) and B3LYP/6-31G+(d) levels were examined along each pathway. The energy profile and the transition state (**TS**) structures are depicted in Fig. 1.

As shown in Fig. 1, the reaction barrier (ΔE) for the aromatic [3,3]-sigmatropic rearrangement (initial step of path 1) from B3LYP/6-31G(d) calculations is 34.8 kcal/mol. This value is 7.5 kcal/mol higher than that of the allylic rearrangement of the *O*-allyl dithiocarbonate anion (27.3 kcal/mol).[1] This energy difference might be attributable to the additional energy required for disruption of the resonance of the furan ring.[6] However, in spite of loss of aromatic energy of the furan ring, the reaction barrier is 8.7 kcal/mol lower than that of the *SNi*-type rearrangement of **1-anion** (path 2). The values obtained at the higher levels with the B3LYP/6-31G+(d) and B3LYP/6-31G++(d,p) basis sets were 31.8 and 30.4 kcal/mol, respectively. Taking into account the results of gas-phase calculations, these barriers might be lowered with increasing solvent polarity.

The secondary transition-state energy (**TS2**) of the second-step of the [3,3]-sigmatropic rearrangements is considerably lower (10.8 kcal/mol) than that of the initial rearrangement (**TS1**). These results indicate that **1-anion** undergoes sequential [3,3]-sigmatropic rearrangements to yield **2-anion** *via* the thermodynamically unfavorable *S*-(2-methylene-2,3-dihydrofuran-3-yl) dithiocarbonate anion (**2′-anion**). However, in the light of the reaction conditions used, the isomerization of **1-anion** into **2′-anion** is not very likely.

Sulfide Formation from *O*-Furfuryl *S*-Alkyl Dithiocarbonate (1) The mechanism of formation of furfuryl methyl sulfide (**3a**) derived from *O*-furfuryl *S*-methyl xanthate (**1a**) was investigated. *O*-Furfuryl *S*-methyl xanthate (**1a**) was refluxed in benzene to afford furfuryl methyl sulfide (**3a**) and *S*-furfuryl *S*-methyl dithiocarbonate (**2a**) in 68% and 6% yields, respectively.[4] The yield of the sulfide was affected by the reaction temperature and the solvent polarity. Two possible reaction pathways for the formation of the sulfide (**3a**) are shown in Chart 4. The first pathway involves sequential two-step pericyclic reactions; *O*-furfuryl methyl xanthate (**1a**) undergoes [3,3]-sigmatropic rearrangement to obtain the energetically unfavorable dithiocarbonate (**2′a**), which extrudes COS to yield the allylically rearranged sulfides (**3a**). The second pathway proceeds *via* the *SNi* mechanism for the extrusion reaction, in which the MeS-group attacks the α-carbon atom from the front side.



	B3LYP/6-31G(d)		B3LYP/6-31+G(d)	
	E[a]	ΔE_{rel}[b]	E[a]	ΔE_{rel}[b]
1-anion	-1178.49830	0.0	-1178.52560	0.0
	(-1178.39028)	(0.0)	(-1178.41791)	(0.0)
TS1	-1178.43914	37.12	-1178.47138	34.02
	(-1178.33485)	(34.78)	(-1178.36724)	(31.80)
2'-anion	-1178.49382	2.81	-1178.52598	-0.24
	(-1178.38803)	(1.41)	(-1178.42052)	(-1.64)
TS2	-1178.45652	26.22	-1178.49034	22.13
	(-1178.35202)	(24.01)	(-1178.38608)	(19.97)
2-anion	-1178.51966	-13.40	-1178.55089	-15.87
	(-1178.41269)	(-14.06)	(-1178.44424)	(-16.52)
TS3	-1178.42583	45.48	-1178.45634	43.46
	(-1178.32097)	(43.49)	(-1178.35202)	(41.35)

a) hartree. ZPE is shown in paretheses. b) Potential energy barriers relative to **1-anion**. kcal/mol

Fig. 1. DFT-Calculated Potential Energy Profile at B3LYP/6-31G(d) and B3LYP/6-31G+(d) Level for the Formation Reaction of *S*-Furfuryl Dithiocarbonate Anion (**2-Anion**)

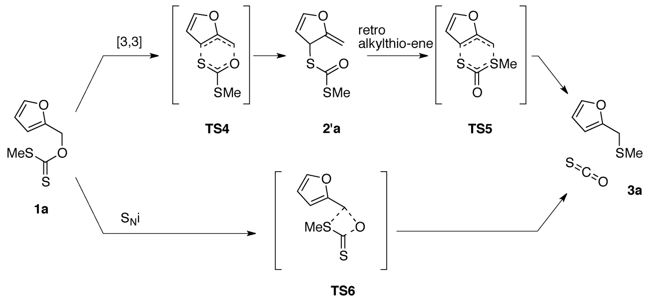
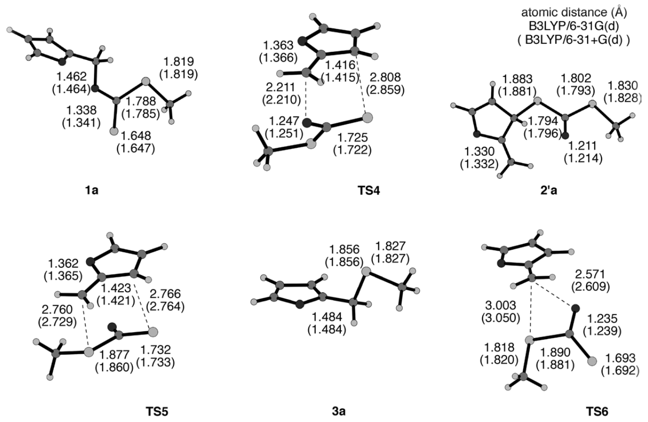


Chart 4

The energy profile along the rearrangements and **TS** structures calculated at the B3LYP/6-31G(d) and B3LYP/6-31G+(d) levels of approximation are shown in Fig. 2.

The energy barriers for the aromatic [3,3]-rearrangement and the *SNi*-type rearrangement at the B3LYP/6-31G(d) level are estimated to be 20.8 and 34.1 kcal/mol, respectively. These values are much lower than those obtained for the *O*-furfuryl dithiocarbonate anion (**1-anion**) (see Fig. 1). The difference in the energies obtained for the [3,3]-sigmatropic rearrangement **1a** and **1-anion** may be interpreted qualitatively by the three-system interaction[7] in the transition state. A favorable orbital phase relation among two highest occupied molecular orbitals (HOMOs) (π-bonds of C=C and C=S) and the lowest unoccupied molecular orbital (LUMO)



	B3LYP/6-31G(d)		B3LYP/6-31+G(d)	
	$E^{a)}$	$\Delta E_{rel}^{b)}$	$E^{a)}$	$\Delta E_{rel}^{b)}$
1a	-1218.34282	0.0	-1218.36043	0.0
	(-1218.19434)	(0.0)	(-1218.21230)	(0.0)
TS4	-1218.30658	22.74	-1218.32561	21.85
	(-1218.16118)	(20.81)	(-1218.18053)	(19.94)
2'a	-1218.34230	0.33	-1218.36151	-0.68
	(-1218.19649)	(-1.35)	(-1218.21520)	(-1.82)
TS5	-1218.30719	22.36	-1218.32718	20.87
	(-1218.16196)	(20.32)	(-1218.18232)	(18.81)
3a + COS	-1218.37499	-19.87	-1218.39343	-20.71
	(-1218.22928)	(-21.93)	(-1218.24859)	(-22.77)
TS6	-1218.28462	36.52	-1218.30477	34.93
	(-1218.14005)	(34.07)	(-1218.16048)	(32.52)

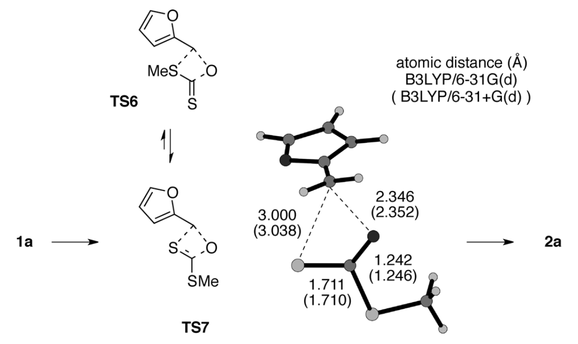
a) hartree. ZPE is shown in parentheses. b) Potential energy barriers relative to **1a**. kcal/mol

Fig. 2. DFT-Calculated Potential Energy Profile and Geometries at B3LYP/6-31G(d) and B3LYP/6-31G+(d) Level for the Formation Reaction of Furfuryl Methyl Sulfide (**3a**)

of the cleaved C–O σ bond stabilizes the transition state. In this situation, the replacement of the dithiol anion (OCSS$^-$) by the *S*-alkyl dithiol ester (OCSSR) lowers the energy of the high-lying σ-LUMO of the C–O bond, resulting in the rate enhancement. In fact, the reaction rate constants for the thermolysis of *O*-furfuryl *S*-alkyl xanthates depends on the electronegativity of the substituents. For instance, the thermolysis of the *S*-methoxycarbonylmethyl derivative proceeds at a rate approximately 16 times faster than that of the *S*-methyl derivative.[4]

The energy barriers for the [3,3]-rearrangement and *SNi*-type rearrangement of **1a** calculated at the B3LYP/6-31G+(d) level are 19.9 and 32.5 kcal/mol, respectively. These values suggest that the formation of the sulfide (**3a**) from *O*-furfuryl xanthate (**1a**) *via* aromatic [3,3]-rearrangements is energetically more favorable than the *SNi*-pathway. The initial step of the sequential pericyclic reactions requires loss of resonance stabilization, and the energetically unfavorable *S*-(2-methylene-2,3-dihydrofuran-3-yl) *S*-methyl dithiocarbonate (**2′a**) is considered to be formed as an intermediate. The succeeding COS extrusion from the intermediate (**2′a**) proceeds through a six-membered cyclic **TS5** which arises from the intermediate (**2′a**) (retro alkylthio-ene reaction[8]). The regain of the aromaticity of the furan ring plays an important role in the progress of the cascade reactions.

In comparison with the COS extrusion reaction, another *SNi*-type thione-to-thiol rearrangement derived from a conformational isomer of **TS6**, with a relatively low reaction barrier, is also possible (Fig. 3).



	B3LYP/6-31G(d)		B3LYP/6-31+G(d)	
	$E^{a)}$	$\Delta E_{rel}^{b)}$	$E^{a)}$	$\Delta E_{rel}^{b)}$
TS7	-1218.30149	25.94	-1218.32022	25.23
	(-1218.15622)	(23.92)	(-1218.17533)	(23.20)

a) hartree. ZPE is shown in parentheses.
b) Potential energy barriers relative to **1a**. kcal/mol

Fig. 3. Reaction Barriers for Formation Reactions of *S*-Furfuryl Dithiolcarbonate (**2a**) Calculated by B3LYP/6-31G(d) and B3LYP/6-31+G(d) Method

The difference between the reaction barriers of **TS7** and **TS4** is 3.1 kcal/mol. The energy difference at the B3LYP/6-31G+(d) level is 3.3 kcal/mol. As shown in Fig. 3, the degree of dissociation for the **TS7** structure is considerably large in comparison with **TS4**. The interacting C$\alpha\cdots$S= and C$\alpha\cdots$O< bond distances are 3.000 and 2.346 Å, respectively. Taking into the consideration that the calculations are performed for the gas-phase, the energy difference is expected to be smaller in solution. In fact, this reaction was affected by the solvent polarity. When the compound **1a** was treated with polar solvents such as DMF or MeOH, the formation of **2a** *via SNi*-type rearrangement reaction occurs rather than the formation reaction of the sulfide **3a**.[4]

Thermal Treatment of *O*-Furfuryl *S*-(Alkenyl or Alkynyl) Xanthate (1b—f) Coupling the sequential reactions (aromatic [3,3]→retro alkylthio-ene) with intramolecular Diels–Alder (IMDA) reaction provides a useful method for the construction of complex fused heterocyclic systems containing the sulfur atom.[9—11] The synthetic utility of the sequential reaction was examined by the thermal treatment of *O*-furfuryl *S*-allyl xanthate (**1b**). Heating of **1b** in refluxing toluene afforded furfuryl allyl sulfide (**3b**) and *S*-furfuryl *S*-allyl dithiocarbonate (**2b**) in 80% and 6% yields, respectively. Similar reaction conditions were applied to *O*-furfuryl *S*-propargyl xanthate (**1c**), *O*-furfuryl *S*-cinnamyl xanthate (**1d**), *O*-furfuryl *S*-(3-ethoxycarbonylallyl) xanthate (**1e**), *O*-furfuryl *S*-(3-butenyl) xanthate (**1f**) to afford the corresponding sulfides (**3c—f**) in 83%, 35%, 52% and 61% yields, respectively.

The sulfide (**3b**) was further refluxed in toluene to afford a colorless oily product in 20% yields, with the recovery of the reactant. The ^{1}H-NMR spectrum of the product showed the absence of the olefinic protons assignable to the furan ring, indicating that the intramolecular cycloaddition reaction had taken place to obtain *cis*-FUSED cycloadduct (***cis*-4b**) (Chart 5). The stereochemistry of **4b** was assigned using ^{1}H-NMR and the literature data.[12] Similar treatment of furfuryl propargyl sulfide (**3c**) derived from *O*-furfuryl *S*-propargyl

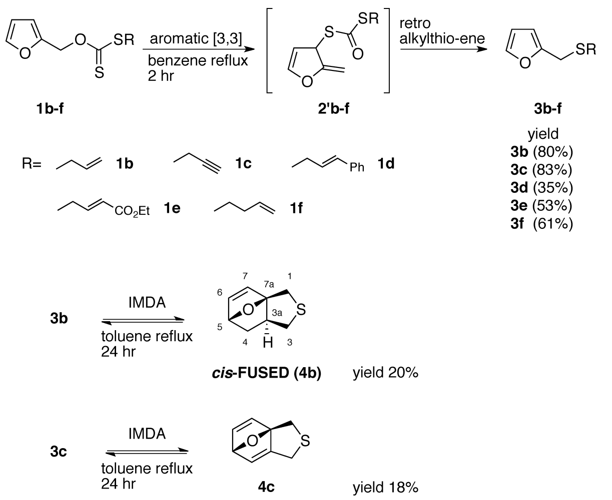


Chart 5

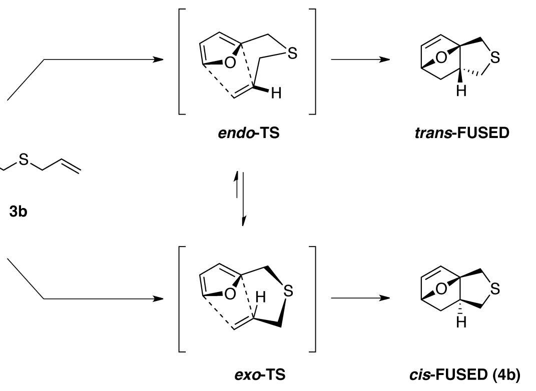


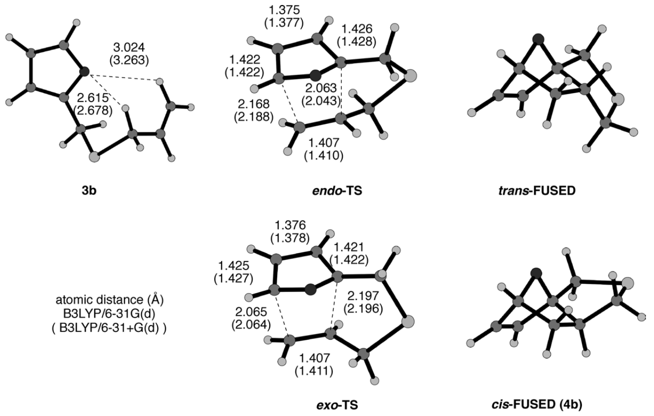
Chart 6

xanthate (**1c**) afforded the corresponding FUSED cycloadduct (**4c**) in 18% yields.

Generally, Diels–Alder reaction of the furan diene is reported to have an equilibrium that proceeds towards the starting materials (*i.e.*, retro Diels–Alder reaction).[12] Due to this unfavorable equilibrium, the yield of the isolated cycloadduct (**4**) under refluxing toluene is limited. DFT calculations were performed in order to elucidate the formation mechanism of the IMDA product. The two possible transition state conformations (***exo*-TS** and ***endo*-TS**) for furfuryl allyl sulfide (**3b**), leading to the ***cis*-FUSED** and ***trans*-FUSED** adducts are shown in Chart 6.

The energy difference at the B3LYP/6-31G(d) level between ***exo*-TS** and ***endo*-TS** was calculated to be 6.4 kcal/mol, indicating that ***exo*-TS** leading to the ***cis*-FUSED** adduct is considerably stable compared with the ***endo*-TS**. This result is in accordance with the observed predominant formation of the ***cis*-FUSED** adduct (**4b**).

The heat of reaction of the ***cis*-FUSED** adduct at B3LYP/6-31G(d) level is estimated to be 1.3 kcal/mol, indicating that furfuryl allyl sulfide (**3b**) is slightly more stable than ***cis*-FUSED** (**4b**). The energy difference is reflected in the yield of the IMDA product. As shown in Fig. 4, the fully optimized structure of the sulfide has intramolecular CH/O type hydrogen bonds[13—16] between the furan oxygen atom and the hydrogen atoms of the allyl moiety. This conformation is *ca.* 1.8 kcal/mol more stable than a non-hydrogen-bonded model, affecting the subtle equilibrium between the sulfide (**3b**) and the IMDA product (**4b**).



	B3LYP/6-31G(d)		B3LYP/6-31+G(d)	
	E[a)]	ΔE_{rel}[b)]	E[a)]	ΔE_{rel}[b)]
3b	-784.23399	0.0	-784.24999	0.0
	(-784.06546)	(0.0)	(-784.08193)	(0.0)
***endo*-TS**	-784.17751	35.44	-784.19202	36.38
	(-784.01022)	(34.66)	(-784.02514)	(35.64)
***trans*-FUSED**	-784.22216	7.42	-784.23644	8.50
	(-784.05153)	(8.74)	(-784.06617)	(9.89)
***exo*-TS**	-784.18773	29.03	-784.20235	29.90
	(-784.02043)	(28.26)	(-784.03546)	(29.16)
***cis*-FUSED**	-784.23382	0.11	-784.24793	1.29
	(-784.06333)	(1.34)	(-784.07780)	(2.59)

a) hartree. ZPE is shown in paretheses. b) Potential energy barriers relative to **3b**. kcal/mol

Fig. 4. B3LYP/6-31G(d) and B3LYP/6-31G+(d) Calculated Energies and Geometries for the IMDA Reaction of Furfuryl Allyl Sulfide

Conclusion

In this work, we have theoretically dealt with aromatic [3,3]-sigmatropic rearrangement and *S*N*i*-type thione-to-thiol rearrangement of *O*-furfuryl dithiocarbonates. Furfuryl sulfides derived from *O*-furfuryl *S*-alkyl xanthates and their oxidation products are very important synthones in the synthesis of carbon skeleton construction. A synthetic design using IMDA reaction of furfuryl allyl sulfides, which can be easily derived from sequential pericyclic reactions (aromatic [3,3]→retro alkylthio-ene) of *O*-furfuryl xanthates, affords an efficient and stereoselective method for the construction of heterocyclic ring systems. Difurfuryl trithiocarbonates derived from sodium *O*-furfuryl dithiocarbonates and *S*-furfuryl *S*-alkyl dithiocarbonates are convenient precursor of unstable and unpleasantly odorous furfuryl thiols.

Experimental

The IR spectra were obtained with a Hitachi 270-30 spectrophotometer. The ^{1}H-NMR spectra were obtained with Hitachi R-600 (60 MHz) and JEOL GX-400 (400 MHz) spectrometers using tetramethylsilane (TMS) as an internal standard. High resolution mass spectra (HR-MS) were taken with a JEOL JMS-DX303HF spectrometer.

Materials *O*-Furfuryl *S*-allyl xanthate (**1b**), *O*-furfuryl *S*-propargyl xanthate (**1c**), furfuryl allyl sulfide (**3b**) and furfuryl propargyl sulfide (**3c**) were prepared by the previously reported method.[4)] The xanthates were unstable and the structures were identified by ^{1}H-NMR and IR spectroscopy. The crude xanthates were used for thermolysis without purification. Furfuryl allyl sulfide (**3b**), furfuryl propargyl sulfide (**3c**) and IMDA adduct (**4b**) were identified by comparison of their spectral properties with literature reports.[12,17)]

O-Furfuryl *S*-Allyl Xanthate (**1b**): Pale yellow oil. Yield 84%. ^{1}H-NMR

(60 MHz, $CDCl_3$) δ: 3.76 (2H, d, J=6.6 Hz, SCH_2), 5.18—5.28 (2H, m, $CH{=}C\underline{H}_2$), 5.57 (2H, s, CH_2O), 5.80—5.90 (1H, m, $-C\underline{H}{=}CH_2$), 6.38—6.48 (2H, m, furyl C3-H, C4-H), 7.40—7.50 (1H, m, furyl C5-H). IR (KBr) cm^{-1}: 1238, 1054 [$-O(C{=}S)S-$].

O-Furfuryl S-Propargyl Xanthate (**1c**): Pale yellow oil. Yield 86%. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 2.22 (1H, t, J=2.4 Hz, CCH), 3.87 (2H, d, J=2.4 Hz, SCH_2), 5.59 (2H, s, OCH_2), 6.38—6.48 (2H, m, furyl C3-H, C4-H), 7.40—7.50 (1H, m, furyl C5-H). IR (KBr) cm^{-1}: 1234, 1058 [$-O(C{=}S)S-$].

O-Furfuryl S-Cinnamyl Xanthate (**1d**): Pale yellow oil. Yield 90%. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 3.91 (2H, d, J=6 Hz, SCH_2), 5.56 (2H, s, CH_2O), 6.18—7.73 (4H, m, $C\underline{H}{=}C\underline{H}$, 3-H, 4-H), 7.29—7.44 (6H, m, furyl C5-H, Ph). IR (KBr) cm^{-1}: 1238, 1054 [$-O(C{=}S)S-$].

O-Furfuryl S-(3-Ethoxycarbonylallyl) Xanthate (**1e**): Pale yellow oil. Yield 91%. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.28 (3H, t, J=7.2 Hz, CH_3), 3.86 (2H, d, J=7 Hz, SCH_2), 4.20 (2H, q, J=7.2 Hz, $C\underline{H}_2CH_3$), 5.57 (2H, s, CH_2O), 6.08—6.60 (4H, m, $C\underline{H}{=}C\underline{H}$, furyl C3-H, 4-H), 7.43—7.53 (1H, m, furyl C5-H). IR (KBr) cm^{-1}: 1238, 1054 [$-O(C{=}S)S-$].

O-Furfuryl S-(3-Butenyl) Xanthate (**1f**): Pale yellow oil. Yield 72%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.43 (2H, ddd, J=1.32, 6.93, 7.59 Hz, $SCH_2-C\underline{H}_2$), 3.18 (2H, t, J=7.59 Hz, SCH_2), 5.03—5.13 (2H, m, $CH{=}C\underline{H}_2$), 5.56 (2H, s, CH_2O), 5.80 (1H, ddd, J=6.93, 10.2, 13.5 Hz, $-C\underline{H}{=}CH_2$), 6.39 (1H, dd, J=1.65, 3.3 Hz, furyl 4-H), 6.50 (1H, dd, J=0.66, 3.3 Hz, furyl C3-H), 7.46 (1H, dd, J=0.66, 1.65 Hz, furyl C5-H). IR (KBr) cm^{-1}: 1210, 1060 [$-O(C{=}S)S-$].

Furfuryl Cinnamyl Sulfide (**3d**): Colorless oil. Yield 35%. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 3.27 (2H, d, J=6 Hz, $SC\underline{H}_2-CH{=}$), 3.67 (2H, s, SCH_2), 6.12—6.36 (4H, m, $C\underline{H}{=}C\underline{H}$, furyl C3-H, C4-H), 7.29—7.44 (6H, m, furyl C5-H, Ph). HR-MS m/z: 230.0768 (Calcd for $C_{14}H_{14}OS$: 230.0766). MS m/z: 230 (M^+).

Furfuryl 3-Ethoxycarbonylallyl Sulfide (**3e**): Colorless oil. Yield 53%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.30 (3H, t, J=7.0 Hz, CH_3), 3.20 (2H, d, J=7.3 Hz, $S-C\underline{H}_2-CH{=}$), 3.66 (2H, s, CH_2S), 4.20 (2H, q, J=7.0 Hz, $C\underline{H}_2CH_3$), 5.88 (1H, d, J=15.4 Hz, $=C\underline{H}-COO$), 6.17 (1H, d, J=3.3 Hz, furyl C3-H), 6.31 (1H, dd, J=1.8, 3.3 Hz, furyl C4-H), 6.86 (1H, dt, J=7.3, 15.4 Hz, $SCH_2-C\underline{H}{=}$), 7.36 (1H, d, J=1.8 Hz, furyl C5-H). HR-MS m/z: 226.0660 (Calcd for $C_{11}H_{14}O_3S$: 226.0664). MS m/z: 226 (M^+).

Furfuryl 3-Butenyl Sulfide (**3f**): Colorless oil. Yield 61%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.31 (2H, ddd, J=1.32, 6.6, 7.59 Hz, $SCH_2-C\underline{H}_2-$), 2.57 (2H, t, J=7.59 Hz, $SC\underline{H}_2-CH_2$), 3.73 (2H, s, CH_2S), 5.02 (1H, dd, J=1.32, 10.2 Hz, $CH{=}C\underline{H}_2$), 5.07 (1H, dd, J=1.32, 13.9 Hz, $CH{=}C\underline{H}_2$), 6.17 (1H, dd, J=0.99, 3.3 Hz, furyl C3-H), 6.30 (1H, dd, J=1.98, 3.3 Hz, furyl C4-H), 7.36 (1H, dd, J=0.99, 1.98 Hz, furyl C5-H). HR-MS m/z: 168.0620 (Calcd for $C_9H_{12}OS$: 168.0609). MS m/z: 168 (M^+).

IMDA Adducts from Sulfides The sulfide (1 mmol) in toluene (10 ml) was refluxed for 24 h. Evaporation of the solvent gave the crude adduct, which was purified by chromatography on silica-gel using n-hexane–benzene as an eluent to give the corresponding IMDA adduct as a colorless oil.

IMDA Adduct (**4c**): Colorless oil. Yield 18%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.11—3.24 (2H, m, C1-H_2), 3.37—3.60 (2H, m, C3-H_2), 5.51 (1H, s, furyl C5-H), 6.40 (1H, d, J=1.83 Hz, furyl C4-H), 7.00 (1H, d, J=5.0 Hz, C7-H), 7.09 (1H, d, J=5.0 Hz, furyl C6-H). HR-MS m/z: 152.0296 (Calcd for C_8H_8OS: 152.0273). MS m/z: 152 (M^+).

Molecular Orbital (MO) Calculation The MO calculations were performed by density functional theory (DFT) based *ab initio* method at the B3LYP/6-31G(d) and B3LYP/6-31G+(d) level using the Linda-Gaussian03 program package.[5)] The input geometries of the ground states (GS) and the transition states (TS) were obtained by semi-empirical MO calculations.[18—20)] Vibrational frequencies were used to characterize the nature of the stationary points. Zero point energy (ZPE) corrections were scaled by 0.9804.[21)] All of the calculations were performed on an HIT PC cluster of 4—16 processors (Pentium 4, 3.0 MHz) or an HIT Linux cluster server (4 CPU) made up of dual 1.6 GHz Itanium 2 processors.

References and Notes

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6) Similar calculations were performed on the possible formation pathways of S-benzyl dithiocarbonate anion from O-benzyl dithiocarbonate anion. The DE for the aromatic [3,3]-sigmatropic rearrangement is estimated to be 40.9 kcal/mol. Reflecting the high aromaticity of the benzene ring, the value is *ca.* 6 and 14 kcal/mol higher than that of O-furfuryl dithiocarbonate anion (**1-anion**) and O-allyl dithiocarbonate anion, respectively.
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