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Review

Unsaturated cyclic compounds possessing disulfide linkage

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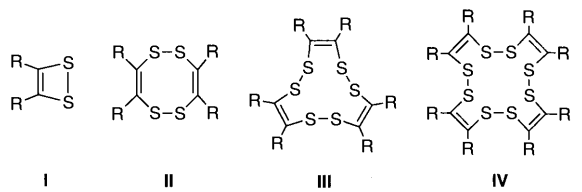
Abstract

Unsaturated cyclic compounds possessing disulfide linkage, such as 1,2-dithiete, 1,2,5,6-tetrathiocin, 1,2,5,6,9,10-hexathiacyclododeca-3,7,11-triene and 1,2,5,6,9,10,13,14-octathiacyclohexadeca-3,7,11,15-tetraene, can be synthesized and isolated. Crystal structures of 1,2-dithietes show planar geometry for the dithiete rings. The structures of 1,2,5,6-tetrathiocins show chair or twist conformation in their crystalline states due to fused or non-fused structure of the tetrathiocin rings, and the 16-membered cyclic compound shows cage structure having cavity in the molecule. Ring conversion reaction takes place among the cyclic compounds under various conditions. The ring-size selectivity of the ring conversion reactions is found to be due to ring strains of the compounds on the basis of ab initio MO calculations. Reactions of 1,2-dithietes with alkenes yield the cycloadducts stereospecifically, and it is found to be reverse electron demand hetero Diels–Alder reaction between ethane-1,2-dithiones, valence isomers of the 1,2-dithietes, and the alkenes by experimental and theoretical studies.

Keywords: 1,2-Dithiete; 1,2,5,6-Tetrathiocin; Disulfide; Unsaturated cyclic compound; Ring conversion reaction; Hetero Diels–Alder reaction

1. Introduction

In the organosulfur chemistry, unsaturated cyclic compounds possessing disulfide linkage, such as 1,2-dithiete (**I**) and 1,2,5,6-tetrathiocin (**II**), have been the subject of considerable interest. Among those, ever since 1,2-dithiete, 3,4-bis(trifluoromethyl)-1,2-dithiete, was isolated for the first time by Krespan and co-workers in 1960 [1], the chemistry of 1,2-dithiete has been extensively studied [2–4]. There are number of reports concerning 1,2-dithiete as reactive intermediates [5–8]. In which, the relation with the valence isomer, ethane-1,2-dithione, has been especially focused on. Some reports on isolation of 1,2-dithietes are also appeared [1,9–18]. The dimeric compound of 1,2-dithiete, 1,2,5,6-tetrathiocin, is also of great interest in respect of their conformations and reactivities [1,8,9,18–26]. Larger cyclic systems of this type were unknown compounds until recently. Recently, we succeeded in isolating this type of compounds **III** [27] and **IV** [18,25]. In this short account, synthesis and structure of isolable unsaturated cyclic compounds possessing disulfide linkage will be described including our recent results. Ring conversion reaction among those compounds and reaction with unsaturated compounds will also be focused on.



I II III IV

2. Synthesis

2.1. Synthesis of 1,2-dithiete

It is well known that equilibrium exists between 1,2-dithiete and its valence isomer, ethane-1,2-dithione (see Eq.(1)), and electron withdrawing substituents stabilize the dithiete structure and electron donating

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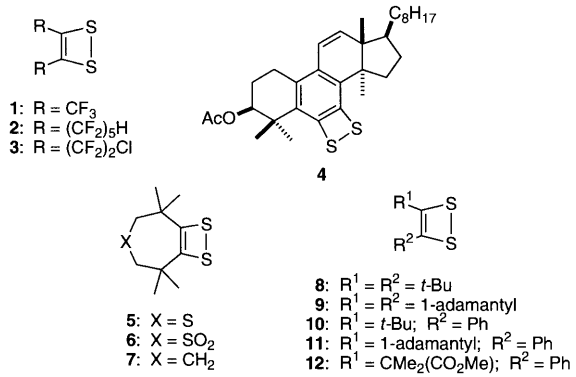
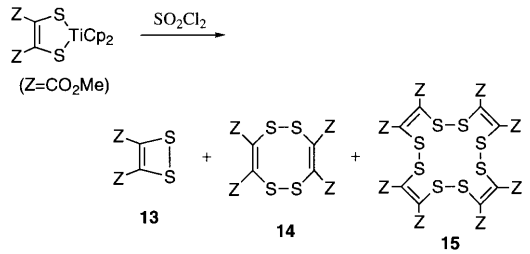
groups stabilize the dithione structure [7,28]. In this section, synthesis of isolable 1,2-dithietes is focused on. Very recently, Nakayama and Ishii presented excellent review including generation of 1,2-dithietes as reactive intermediates [2].

(1)

In 1960, Krespan and co-workers isolated 1,2-dithiete **1**, stabilized by electron withdrawing groups, as yellow liquid for the first time by passing the hexafluoro-2-butyne through vapors of boiling sulfur in 80% yield [1]. This procedure can be utilized for preparing 3,4-bis(-polyfluoroalkyl)-1,2-dithietes, and dithietes **2** and **3** were synthesized from corresponding acetylenes in 41 and 82% yields, respectively [9]. Benzodithiete **4** was synthesized as stable yellow crystals in 91% yield by photolysis of corresponding 2,3-dihydro-1,4-benzodithiin, and the crystal structure has been determined by X-ray crystallographic analysis by Boar et al. [10,11]. Dialkyl 1,2-dithietes **5** and **6**, which are not stabilized by electron withdrawing groups, have been obtained by Krebs et al. from elemental sulfur and the corresponding seven-membered cycloalkynes in refluxing dimethylformamide in 77 and 51% yields, respectively [12]. 1,2-Dithiete **5** was also synthesized by Nicolaou et al. from corresponding acetylene using dithiatopazine as a source of sulfur in 65% yield [13]. 1,2-Dithietes **5** and **6** are stabilized by bulky substituents which prevent cleavage of sulfur–sulfur bond to form corresponding dithiones by repulsion of the bulky groups. 1,2-Dithiete **7** can also be obtained by photolysis of corresponding dithiocarbamate [3,14]. 3,4-Di-*t*-butyl-1,2-dithiete (**8**) was obtained in 45% yield from 2,2,5,5-tetramethyl-4-thioxohexan-3-one by using Lawesson's reagent by Köpke and Voss [15]. 1,2-Dithietes **8**–**12** stabilized by bulky substituents, were also synthesized by Nakayama and co-workers, by the reactions of corresponding acetylenes with elemental sulfur in aromatic solvents at high temperature in 58, 65, 56, 46 and 21% yields, respectively [16]. 1,2-Dithietes **5** and **8** have also been synthesized from corresponding acetylenes by treatment with zirconocene then sulfur dichloride [2,17], and dithiete **5** also formed from corresponding hydrazone by treatment with sulfur chloride [2,14,17]. Similarly, reaction of bis-1-adamantyl acetylene with sulfur chloride also yielded 1,2-dithiete **9** [2].



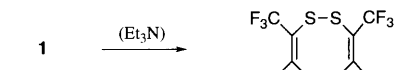
Recently, we isolated 3,4-bis(methoxycarbonyl)-1,2-dithiete (**13**), which has been suggested to be generated as an intermediate by the reaction of dimethyl acetylenedicarboxylate (DMAD) with elemental sulfur by Nakayama et al. [6], in 66% yield by oxidation of corresponding titanocene dithiolene complex with sulfuryl chloride under dilution conditions [18] (see Eq. (2)).



(2)

2.2. Synthesis of 1,2,5,6-tetrathiocin

In the preparation of 1,2-dithiete **13**, small amounts of 1,2,5,6-tetrathiocin **14** (1.6%) and octathiacyclohexadecatetraene **15** (2.0%) were also obtained [18]. 1,2,5,6-Tetrathiocin has also been the subject of considerable interest, especially its conformational behavior in view of contrast with carbon analogue, cycloocta-1,5-diene, and some 1,2,5,6-tetrathiocins have been synthesized. Trifluoromethylated tetrathiocin **16** has been obtained from 1,2-dithiete **1** [1,9]. A sample of **1** crystallized as 1,2,5,6-tetrathiocin **16** in 87% yield on standing two months at 25°C, and addition of a trace amount of triethylamine accelerates the dimerization (see Eq. (3)). Dibenzo derivative of tetrathiocin **17** was obtained by iodine oxidation of *o*-benzenedithiol by Field and co-workers [19] (see Eq. (4)). Tetrathiocin **17** can also be obtained by pyrolysis of sulfoxide in 14% yield [20] (see Eq. (5)). Tetraamino-substituted benzotetrathiocin **18** was obtained from corresponding dipotassium dithiosulfonate, and the structure has been determined by X-ray analysis [21] (see Eq. (6)). Dibenzotetrathiocins **19** and **20** have also been synthesized by Ogawa and Sato from corresponding dichlorobenzodithiatellurole by treatment of aqueous tetrahydrofuran in total yield of 84% [22] (see Eq. (7)), and tetrathiocin **21** was also obtained from dithiastannole in 66% yield [23] (see Eq. (8)). Fused tetrathiocin **22** was synthesized by oxidation of zinc reagent with sulfuryl chloride in 46% yield by Yang and co-workers [24] (see Eq. (9)).



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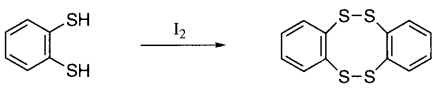

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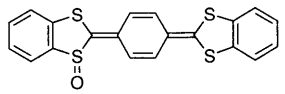

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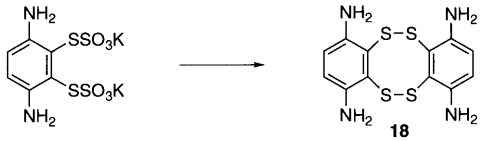

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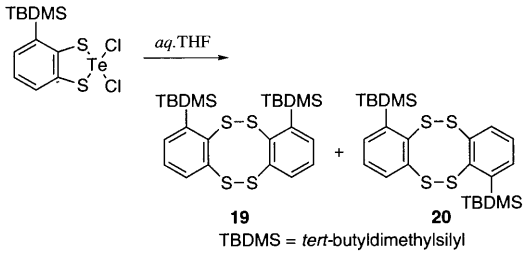

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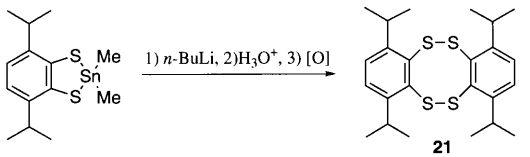

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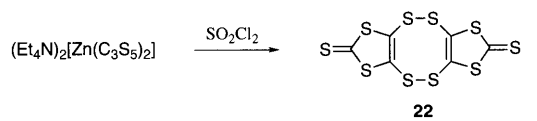
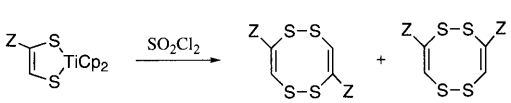


(9)

We also synthesized some 1,2,5,6-tetrathiocins beside tetra(methoxycarbonyl)-substituted tetrathiocin **14**. Oxidation of a titanocene dithiolene complex possessing one methoxycarbonyl group with sulfuryl chloride afforded tetrathiocin derivatives **23** and **24** in yields of 22 and 17%, respectively, and the structure of **23** could be confirmed by X-ray analysis [18] (see Eq. (10)). In this reaction, corresponding 1,2-dithiete was not obtained maybe due to instability of the structure. Under similar conditions, most simple 1,2,5,6-tetrathiocin **25** (substituents on carbon atoms are hydrogen) was obtained by oxidation of corresponding titanocene dithiolene complex in 21% yield together with 10% of 16-membered cyclic compound **26** [27] (see Eq. (11)). 1,2,5,6-Tetrathiocin **25** and 16-membered cyclic compound **26** was also obtained in 14 and 1.6% yields by oxidation of *cis*-disodium ethene-1,2-dithiolate with iodine–potassium iodide at −10°C in a heterogeneous solution (ether–water) [25] (see Eq. (12)). 1,2,5,6-Tetrathiocin **14** can also be obtained by ring conversion reaction of 1,2-dithiete **13** or 16-membered cyclic compound **15**, as described later.



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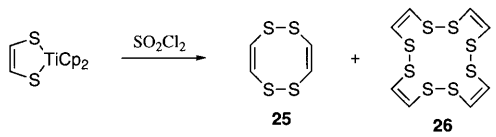

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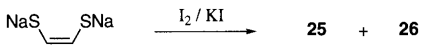
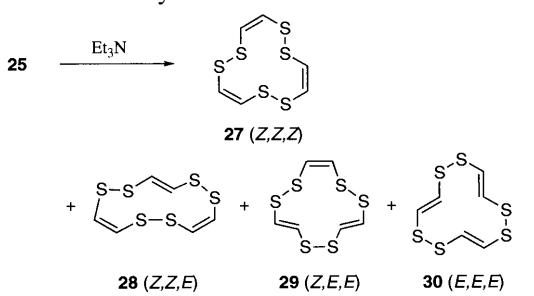


(12)

2.3. Synthesis of 1,2,5,6,9,10-hexathiacyclododeca-3,7,11-triene

Twelve-membered cyclic compound of this type has not yet been isolated until recently. Very recently, 12-membered cyclic compound **27** could be obtained from tetrathiocin **25** in a presence of triethylamine, although the yield was low, together with small amounts of three isomers **28**, **29** and **30** [27] (see Eq. (13)). Krespan reported 1,2-dithiete **1** dimerized in the presence of triethylamine to give tetrathiocin **16**, as described before, and the result indicates tetrathiocin **16** is stable in the presence of triethylamine. Therefore, tetrathiocin **25** is more reactive than trifluoromethylated tetrathiocin **16** in the presence of triethylamine. Formation of the 12-membered cyclic compounds having *trans*-olefin moiety in the molecules **28**, **29** and **30** may be explained based on existence of corresponding 1,2-dithione for the *Z*–*E* isomerization although the dithione is presumed to be very reactive.



(13)

2.4. Synthesis of 1,2,5,6,9,10,13,14-octathiacyclohexadeca-3,7,11,15-tetraene

Compounds **15** and **26** are only known 16-membered cyclic compounds of this series [18,25]. Efficient synthetic method for compounds **15** and **26** is ring conversion reaction from corresponding smaller ring systems, as described later.

3. Structure

3.1. Structure of 1,2-dithiete

Molecular structures of 1,2-dithietes **4** [10], **9** [29,30] and **13** [18] have been determined by X-ray crystallo-

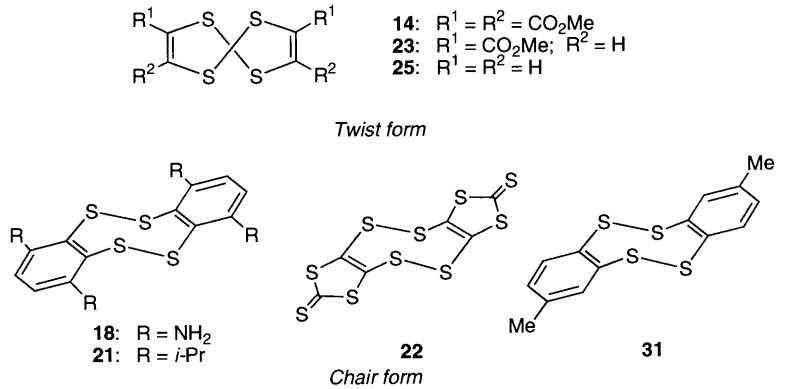


Fig. 1. Conformational figures of 1,2,5,6-tetrathiocins based on their X-ray crystallographic analysis.

graphic analysis, and **1** [31] was by electron diffraction. Geometries of these compounds including the bond lengths and angles are summarized in recent review [2]. The lengths of their carbon–carbon double bond are 1.36–1.40 Å and are slightly greater than those of the corresponding strain-free bonds in eight-membered cyclic compounds **14** (1.34 Å, average), **23** (1.33 Å, average) and **25** (1.33 Å). The lengths of the sulfur–sulfur bond (2.05–2.12 Å) are almost normal. The bond angles around the 1,2-dithiete skeleton are of course strained. The most interesting point of the structure of the 1,2-dithietes is the planarity of the four-membered ring. The crystal structures of these compounds show almost planar geometry; for example, the dihedral angle around the sulfur–sulfur bond of dithiete **13** is 0.1°. The dihedral angle around the sulfur–sulfur bond (0°) is strained (ca. 11.5 kcal mol^{-1}) compared to those calculated for disulfides with strain-free geometries (ca. 90°) [32,33].

3.2. Structure of 1,2,5,6-tetrathiocin

The molecular structures of 1,2,5,6-tetrathiocins **14** [18], **23** [18], **25** [25], **18** [21], **21** [23], **22** [24] and **31** [26] have been determined by X-ray analysis. Crystal structures of tetrathiocins **14**, **23** and **25** show twisted geometry for the eight-membered ring systems, and those of **18**, **21**, **22** and **31** show chair conformation, as shown in Fig. 1. This difference of conformations is considered to be due to the fused or non-fused structure of the olefin moieties. The dihedral angles around the sulfur–sulfur bonds of **14** and **25** are 111.8 and 108.8°, respectively, and are slightly extended compared with those in strain-free geometry of disulfides.

Conformational study of tetrathiocin **25** based on ab initio MO calculations has been carried out [32]. Three local minima **25**–T, **25**–C and **25**–HC were found for tetrathiocin **25** (Fig. 2), and the twist conformer **25**–T was calculated to be at global minimum (Fig. 3), in contrast to the corresponding twist conformer of carbon analogue, cycloocta-1,5-diene [34,35], which frequency analysis shows one imaginary number indicating the transition state. Furthermore, twistboat form of **25** could not be optimized at a stationary point, though the structure was optimized at global minimum for cycloocta-1,5-diene. The calculated structure of **25**–T shows good agreement with the X-ray structures of tetrathiocins **14**, **23** and **25**. Torsional strains around the sulfur–sulfur bonds of the conformers **25**–T, **25**–C and **25**–HC have been also estimated by calculations of dimethyl disulfide as a model molecule. The torsional strains of the disulfide units for the conformers **25**–T, **25**–C and **25**–HC were in order of 1.4, 1.2 and 3.4 kcal mol^{-1}, respectively. The bond angles of S4–C5–C6 and C5–C6–S7 for **25**–HC are strongly extended (143.6°), and the bond angle strain on the olefin sp^2 carbons of **25**–HC was estimated to be 13.7 kcal mol^{-1}. This value is 9.9 kcal mol^{-1} larger than twofold of corresponding

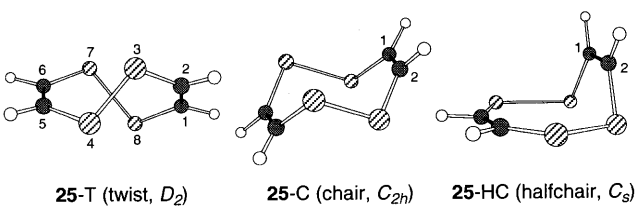


Fig. 2. Optimized geometries of 25 at the local minima calculated by using the Hartree–Fock (HF) method with the double-zeta plus polarization basis set.

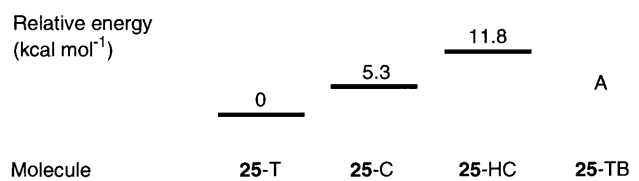


Fig. 3. Relative energies for optimized geometries of **25**. Energies were calculated by using the second order Møller–Plesset perturbation (MP2) method with the double-zeta plus polarization basis set for the HF-optimized geometries. A: Twistboat form could not be optimized as a stationary point.

bond angle strains of **25**–T. The remaining energy for **25**–C is considered to be attributable to repulsion between lone pair electrons on the sulfur atoms.

3.3. Structure of 1,2,5,6,9,10-hexathiacyclododeca-3,7,11-triene

Molecular structure of 12-membered cyclic compound of this series has not been clarified although compound **27** has been recently obtained only a very small amount, as described before. Conformation of 12-membered cyclic system with all-*cis* geometry of olefins **27** has been estimated by using ab initio MO calculations [18]. Structural optimization of **27** from several initial guesses gave the structure, as shown in Fig. 4, having C_2 symmetry as the global minimum.

3.4. Structure of 1,2,5,6,9,10,13,14-octathiacyclohexadeca-3,7,11,15-tetraene

Crystal structure of 16-membered cyclic compound **26** has been determined by X-ray analysis, and was found to have cage structure (nearly D_{2d} symmetry) possessing a cavity in the molecule [25] (Fig. 5). Distances between the center of the molecule and the sulfur atoms are 3.41 Å (average) and those between the center and the carbon atoms are 2.53 Å (average). Torsional angles around the disulfide moieties (74°, average) are slightly contracted from the stable vertical geometry of disulfides. The cage structure of **26** indicates that the compound **26** is expected to become a new inclusion compound with two types of coordination site (π-electrons of the olefins and lone pairs on the sulfur atoms).

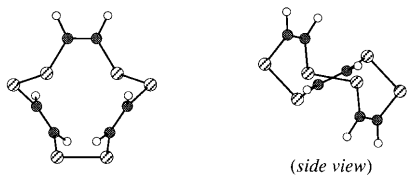


Fig. 4. Optimized geometry of **27** as the global minimum calculated by using the Hartree–Fock (HF) method with the 6–31G* basis set.

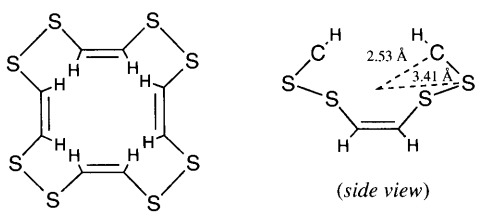


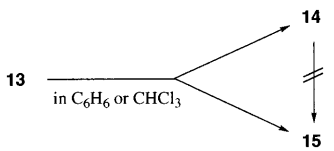
Fig. 5. Conformational figure of **26** based on X-ray crystallographic analysis.

4. Reactions

Some types of reactions, such as oxidation, photochemical reaction, ring-opening reaction and complexation, of 1,2-dithietes have been examined [2–4]. In this account, ring conversion reaction and reaction with unsaturated compounds will be focused on.

4.1. Ring conversion reaction

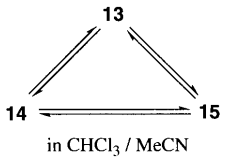
Ring conversion reaction occurs among the cyclic compounds possessing disulfide units under various conditions due to high reactivity of the sulfur–sulfur bonds. Although 1,2-dithiete **13** is stable in crystalline state, when dithiete **13** was dissolved in benzene, ring conversion reaction took place to give 16-membered cyclic compound **15** in 74% yield, together with a small amount of tetrathiocin **14** after 4 h [18] (see Eq. (14)). This reaction is useful to synthesize the 16-membered cyclic compound **15**. Similar reaction also occurs in a chloroform solution to yield **15** in 71% from **13** along with small amount of **14**. This reactivity of **13** is different from that of dithiete **1**, which dimerized to give tetrathiocin **16** selectively on standing, as described before. However, tetrathiocin **14** and 16-membered cyclic compound **15** are stable in chloroform solution even after 4 h. Furthermore, when a mixture of the same amounts of **13** and **14** by weight was stirred in chloroform for 4 h, almost the same amount of **14** was recovered, and **13** and **15** were formed in a weight ratio of 1:1.1. This result indicates that the 16-membered cyclic compound **15** is not a secondary product from **14**, and **14** does not react with **13** under the conditions. This reaction may be caused by the high reactivity of dithiete **13** due to the ring strains.



(14)

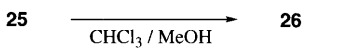
A chloroform–acetonitrile solution (1:4) of dithiete **13** also yielded tetrathiocin **14** and tetramer **15** in yields of 19 and 41%, respectively [18] (see Eq. (15)). Under this condition, tetrathiocin **14** also reacted to give dithiete **13** and ring-expansion product **15** in yields of 13 and 44%, respectively, and 16-membered cyclic compound **15** afforded dithiete **13** and tetrathiocin **14** in yields of 5.8 and 12%. Similarly, ring-expansion product **26** was obtained in 76% yield from tetrathiocin **25** in chloroform–acetonitrile solution, whereas no change is observed in chloroform solution [25] (see Eq. (16)). Sixteen-membered cyclic compound **26** was also obtained from a chloroform–methanol solution (1:4) of **25**, although the yield was low (15%) (see Eq. (17)). 1,2,5,6-Tetrathiocin **14** was transformed in a chloro-

form–ethanol solution (1:4) into **15** in 74% yield together with a trace amount of dithiete **13** (see Eq. (18)). This result is contrast to the reaction of tetrathiocin **16**, which reacts in ethanol solution to form dithiinodithiin **32** [9] (see Eq. (19)). The reactions in the polar solvents are considered to proceed via ionic pathway by nucleophilic attack on the cyclic compounds by the solvents.

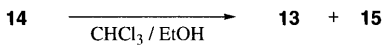


(15)

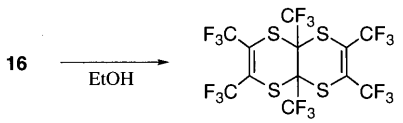
(16)



(17)



(18)



32

(19)

Unsaturated cyclic compounds with disulfide units **13**, **14** and **15** also react on silica-gel [18]. A chloroform solution of dithiete **13** yielded tetrathiocin **14** as a main product (45%) in the presence of silica-gel together with 16-membered cyclic compound **15** (24%) (see Eq. (20)). 1,2,5,6-Tetrathiocin **14** and 16-membered heterocycle **15** also reacted in chloroform solution in the presence of silica-gel: compounds **13** (5.3%) and **15** (42%) were formed from **14**, and **13** (10%) and **14** (40%) from **15**, respectively. Although the mechanism of these reactions on the surface of silica-gel has not yet been clarified, the products ratio is different from the reaction of **13** without silica-gel. The long reaction time led to the formation of bicyclic product **33**. A time-course study on the reaction of dithiete **13** showed that tetrathiocin **14** and then tetramer **15** were formed, as shown in Fig. 6. This result indicates that tetramer **15** was formed stepwise via tetrathiocin **14** in the presence of silica-gel although the reaction is reversible.

33

(20)

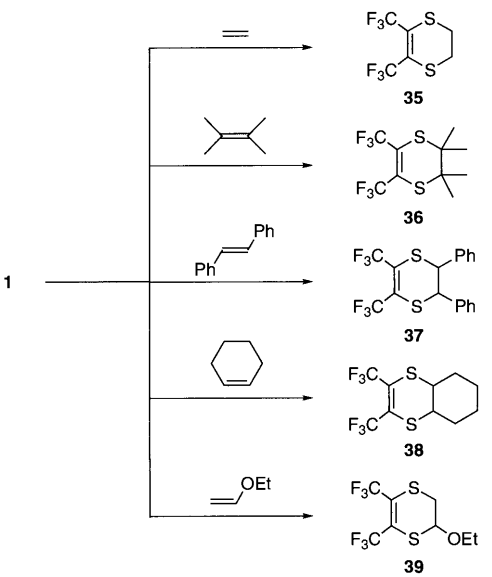
4.2. Theoretical study of ring-size selectivity

A 12-membered cyclic compound of this series has not been obtained until recently, and has hardly been obtained in any ring conversion reactions. This lack of formation of the 12-membered cyclic compound may be due to the unfavorable configuration in the ring closure reaction. To clarify the ring-size selectivity, the relative energies of 12-membered cyclic molecule **27** were compared with those of corresponding four-, eight-, and 16-membered cyclic molecules **34**, **25** and **26** based on ab initio MO calculations, since the configuration in the ring closure reaction is considered to be strongly influenced by the conformation and strain of the products [18]. The four optimized geometries for **34**, **25**, **27** and **26**, as shown in Fig. 7, have C_{2v}, D_2, C_2 and D_{2d} symmetries, respectively. The relative energy for one $C_2H_2S_2$ unit in these molecules, as shown in Fig. 8, may reflect the strain energy for one $C_2H_2S_2$ unit, since all of these molecules have similar bonding characteristics. The relative energy of 16-membered heterocycle **26** is lower than that of other cyclic molecules, while that of dithiete **34** is highest. However, the dithiete can be formed under dilution conditions. The relative energy of 12-membered molecule **27** is slightly higher than or even almost equal to that of tetrathiocin **25**. Since the configuration in the ring closure reaction is not influenced by the geometry of one $C_2H_2S_2$ unit, but rather by those of corresponding molecule chains, and this effect is believed to be greater in longer chains. Therefore, it is reasonable that the lack of formation of a 12-membered cyclic compound is due to a configurational disadvantage.

34

4.3. Reaction with alkenes and alkynes

Some reactions of 1,2-dithietes with unsaturated cyclic compounds have been examined. 1,2-Dithiete **1** reacted with ethylene and tetramethylethylene by heat



(21)

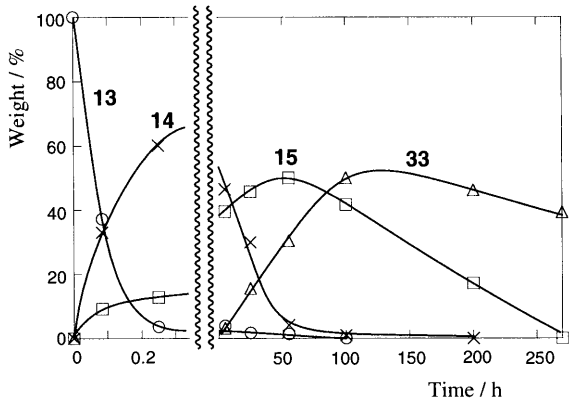


Fig. 6. Time course diagram of the reaction of **13** in chloroform in the presence of silica-gel.

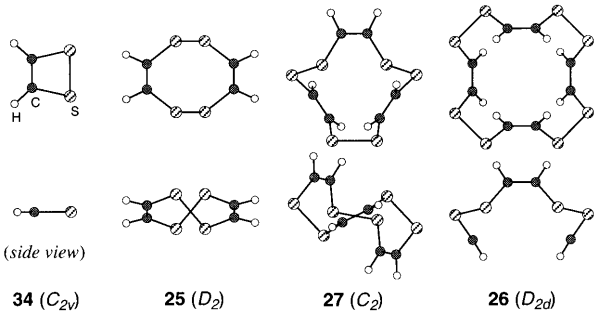
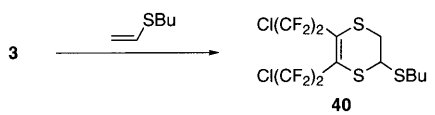


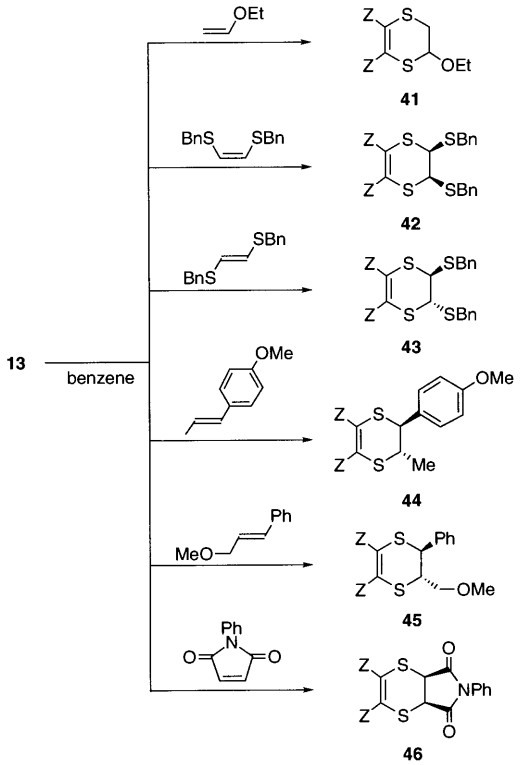
Fig. 7. Optimized geometries of **34**, **25**, **27** and **26** calculated by using the Hartree–Fock (HF) method with the 6–31G* basis set.

ing to give corresponding dihydrodithiins **35** and **36** in 24 and 47% yields, respectively [1,36] (see Eq. (21)). Similarly, reactions of dithiete **1** with various alkenes yielded cycloadducts **37**, **38** and **39** in yields of 36, 36 and 50%, respectively. 1,2-Dithiete **3** also gave cycloadduct **40** in 31% yield by the reaction with butyl vinyl sulfide (see Eq. (22)).



(22)

Similar cycloaddition has been observed in the case of dithiete **13** [37]. 1,2-Dithiete **13** reacted with ethyl vinyl ether to give 2,3-dihydro-1,4-dithiin **41** in 65% yield at room temperature (r.t.) (see Eq. (23)). Although the reactions of **13** with *Z*- and *E*-bis(benzylthio)ethenes were very slow at r.t., the reactions proceeded smoothly and stereospecifically in refluxing benzene to give *cis*- and *trans*-cycloadducts **42** and **43** in 72 and 60% yields, respectively. Similarly, reactions of **13** with *E*-anethole and *E*-cinnamyl methyl ether also afforded only one stereoisomers **44** and **45** in 59 and 22% yields, respectively, though the reactions were slow even in refluxing benzene. The reaction of **13** with *N*-phenylmaleimide also formed cycloadduct **46** although the yield was low (11%) together with tetrakis(methoxycarbonyl) thiophene in 38% yield, which may be formed by thermal reaction of **13** due to long reaction time (45 h). However, 1,2-dithiete **13** did not react with maleic anhydride even in refluxing benzene.



(23)

Some plausible mechanisms are considered for the reactions of 1,2-dithietes with the alkenes including ionic pathway. However, the reactions of dithiete **13** with alkenes are stereospecific, indicating the reactions are proceeding via a concerted path. The FMO energy levels of the ethane-1,2-dithione **47** as a *cisoid*-form and the alkenes used for the reaction have been calculated [37]. Differences of energy levels between LUMO of dithione **47** and HOMO of the alkenes are smaller than those of the π orbital of **47** and LUMO of the alkenes (Fig. 9). These results indicate the reaction is reverse electron demand hetero Diels–Alder reaction due to

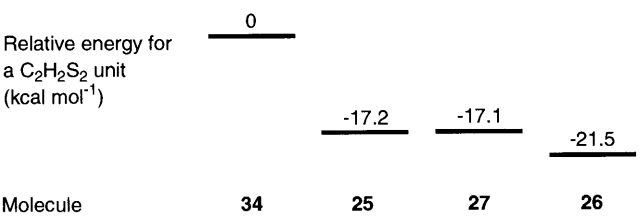
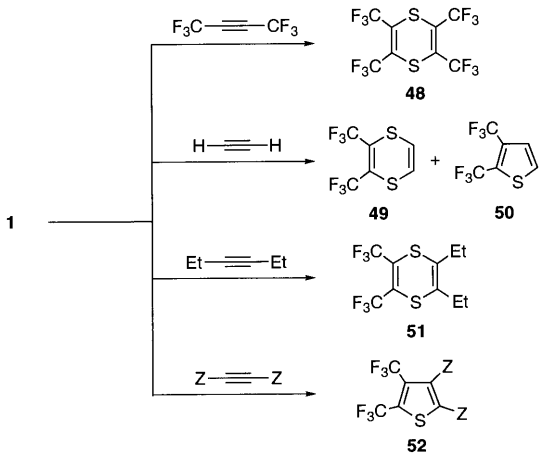


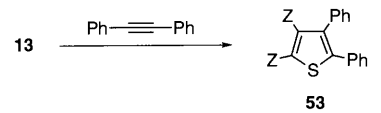
Fig. 8. Relative energies for a $C_2H_2S_2$ unit of **34**, **25**, **27** and **26** calculated by using the second order Møller–Plesset perturbation (MP2) method with the 6–31G* basis set for the HF-optimized geometries.

the low energy level of LUMO (π*) for ethane-1,2-dithione **47**, and it can also explain the inert reactivity of maleic anhydride toward the dithione **47**, in which the energy level of HOMO of maleic anhydride is lower than those of the other alkenes. Under this situation, possibility of formation of ethane-1,2-dithione **47** from dithiete **13** arises to be a problem. ^{1}H- and ^{13}C-NMR spectra of **13** only show the dithiete structure, and no signal assigned to the dithione can be detected even at high temperature (80°C in toluene-d_8). The activation energy of the interconversion for 1,2-dithiete **13** to 1,2-dithione **47** has been estimated by MO calculations [37]. The calculation (MP2/6–31G(d)) shows dithiete **13** is 5.8 kcal mol^{-1} more stable than ethane-1,2-dithione **47**, and the tautomerization energy is 28.5 kcal mol^{-1} from the dithiete **13**. This value of the activation energy supports the possibility of the tautomerization between 1,2-dithiete **13** and ethane-1,2-dithione **47** at least at high temperature.

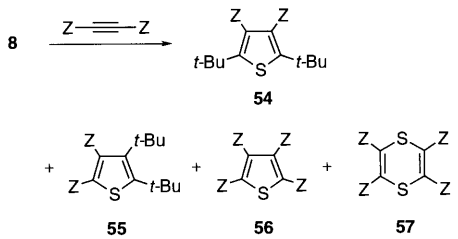
1,2-Dithiete also reacts with acetylenes. 1,2-Dithiete **1** reacted with hexafluoro-2-butyne at 100°C to give 1,4-dithiin derivative **48** in 33% yield [9] (see Eq. (24)). 1,2-Dithiete **1** also reacted with acetylene to yield 1,4-dithiin **49** and thiophene **50** [36]. Ratio of the products is due to the reaction temperature, and 1,4-dithiin **49** can be obtained mainly at 70°C and the reaction at higher temperature yielded thiophene **50**. Similar results have also been obtained; reaction of dithiete **1** with 3-hexyne yielded 1,4-dithiin **51** at 25°C, and the reaction with DMAD afforded thiophene derivative **52** in refluxing methanol. 1,2-Dithiete **13** also reacted with diphenylacetylene in refluxing *p*-xylene yielded thiophene derivative **53** in 44% yield [37] (see Eq. (25)). Formation of thiophenes **50**, **52** and **53** is considered to be from corresponding 1,4-dithiins formed initially [38,39]. The FMO calculations of ethane-1,2-dithione **47** and diphenylacetylene also indicates the reaction of the 1,2-dithietes with acetylenes is the reverse electron demand hetero Diels–Alder reaction between ethane-1,2-dithiones and acetylenes [37]. Interesting results have been obtained by Nakayama and co-workers [38]. 1,2-Dithiete **8** reacted with DMAD in refluxing *o*-dichlorobenzene to yield thiophene **54**, **55** and **56** and 1,4-dithiin **57** in 44, 5, 43 and 4% yields, respectively (see Eq. (26)).



(24)

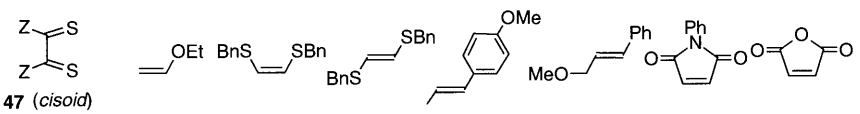


(25)



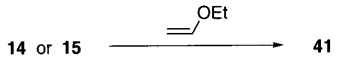
(26)

1,2,5,6-Tetrathiocin **14** and 16-membered cyclic compound **15** also reacted with ethyl vinyl ether at r.t. to give dihydrodithiin derivative **41** in 64 and 63% yields, respectively [37] (see Eq. (27)). In these reactions, 1,2-dithiete **13** or ethane-1,2-dithione **47** is considered to be formed initially by ring conversion reaction by ethyl vinyl ether [18], then 1,2-dithione **47** reacted with the ether. The reactions of **14** and **15** with diphenylacetylene in refluxing *p*-xylene also yielded thiophene derivative **53** in 49 and 41% yields, respectively (see Eq. (28)).

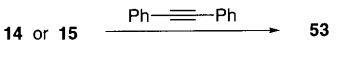


Difference of energy level (eV)							
π (**47**) and LUMO (alkene)	16.3	14.3	14.2	14.1	14.0	12.2	11.7
LUMO (**47**) and HOMO (alkene)	8.3	7.3	7.7	7.1	7.2	8.2	11.3

Fig. 9. FMO energy levels of **47** as a *cisoid*-form and alkenes calculated by using the Hartree–Fock (HF) method with the 6–31G(d) basis set.



(27)



(28)

5. Conclusion

Afer first isolation of 1,2-dithiete in 1960, some 1,2-dithietes and 1,2,5,6-tetrathiocins have been isolated. Recently, larger cyclic compounds of this series, 12- and 16-membered cyclic compounds, were also synthesized. Structures and conformations of these cyclic compounds were clarified by X-ray analysis, electron diffraction or MO calculations. Among the cyclic compounds, it was found that ring conversion reaction took place under various conditions. 1,2-dithietes were found to react with alkenes and alkynes to give the cycloadducts, and the reaction proceeded via ethane-1,2-dithiones. The reaction was also found to be reverse electron demand hetero Diels–Alder reaction by experimental and theoretical studies. Reactions of 1,2,5,6-tetrathiocin and 16-membered cyclic compound with alkenes and alkynes proceeded via corresponding 1,2-dithione formed by ring conversion reaction.

References

[1] C.G. Krespan, B.C. McKusick, T.L. Cairns, J. Am. Chem. Soc. 82 (1960) 1515.
[2] Review: J. Nakayama, A. Ishii, Adv. Heterocycl. Chem. 77 (2000) 221.
[3] S.B. Nielsen, A. Senning, Sulfur Rep. 16 (1995) 371 review.
[4] J. Nakayama, K. Akimoto, M. Hoshino, Rev. Heteroat. Chem. 3 (1990) 146 review.
[5] For examples: (a) H.E. Simmons, D.C. Blomstrom, R.D. Vest, J. Am. Chem. Soc. 84 (1962) 4772. (b) E. Fanghänel, R. Ebisch, B. Adler, Z. Chem. 13 (1973) 431. (c) P. de Mayo, A.C. Weedon, G.S.K. Wong, J. Org. Chem. 44 (1979) 1977. (d) M. Breitenstein, R. Schulz, A. Schweig, J. Org. Chem. 44 (1979) 47 (1982) 1979. (e) D. Sülzle, N. Beye, E. Fanghänel, H. Schwarz, Chem. Ber. 122 (1989) 2411. (f) G. Maier, J. Schrot, H.P. Reisenauer, G. Frenking, V. Jonas, J. Org. Chem. 125 (1992) 265. (g) W. Küsters, P. de Mayo, J. Am. Chem. Soc. 95 (1973) 2383. (h) W. Küsters, P. de Mayo, J. Am. Chem. Soc. 96 (1974) 3502. (i) S. Wawzonek and S.M. Heilmann, J. Org. Chem. 39 (1974) 511. (j) A. Orahovatz, M.I. Levinson, P.J. Carroll, M.V. Lakshmikantham, M.P. Cava, J. Org. Chem. 50 (1985) 1550. (k) N. Tokitoh, H. Ishizuka, A. Yabe, W. Ando, Tetrahedron Lett. 30 (1989) 2955.
[6] (a) J. Nakayama, R. Yomoda M. Hoshino, Heterocycles 26 (1987) 2215. (b) J. Nakayama, M. Kashiwagi, R. Yomoda, M. Hoshino, Nippon Kagaku Kaishi (1987) 1424.
[7] H.E. Simmons, D.C.B. Blomstrom, R.D. Vest, J. Am. Chem. Soc. 84 (1962) 4782.
[8] N. Jacobsen, P. de Mayo, A.C. Weedon, Nouv. J. Chim. 2 (1978) 331.
[9] C.G. Krespan, J. Am. Chem. Soc. 83 (1961) 3434.
[10] R.B. Boar, D.W. Hawkins, J.F. McGhie, S.C. Misra, D.H.R. Barton, M.F.C. Ladd, D.C. Povey, J. Chem. Soc. Chem. Commun. (1975) 756.
[11] R.B. Boar, D.W. Hawkins, J.F. McGhie, D.H.R. Barton, J. Chem. Soc. Perkin Trans. 1 (1977) 515.
[12] A. Krebs, H. Colberg, U. Höpfner, H. Kimling, J. Odenthal, Heterocycles 12 (1979) 1153.
[13] (a) K.C. Nicolaou, C.K. Hwang, S. DeFrees, N.A. Stylianides, J. Am. Chem. Soc. 110 (1988) 4868. (b) K.C. Nicolaou, S.A. DeFrees, C.K. Hwang, N. Stylianides, P.J. Carroll, J.P. Snyder, J. Am. Chem. Soc. 112 (1990) 3029.
[14] K. Schütz, Dissertation, University of Hamburg, 1983.
[15] B. Köpke, J. Voss, J. Chem. Res. (S) (1982) 314.
[16] (a) J. Nakayama, K.S. Choi, I. Akiyama, M. Hoshino, Tetrahedron Lett. 34 (1993) 115. (b) K.S. Choi, I. Akiyama, M. Hoshino, J. Nakayama, Bull. Chem. Soc. Jpn. 66 (1993) 623.
[17] J. Wilken, Dissertation, University of Hamburg, 1992.
[18] T. Shimizu, H. Murakami, Y. Kobayashi, K. Iwata, N. Kamigata, J. Org. Chem. 63 (1998) 8192.
[19] L. Field, W.D. Stephens, E.L. Lippert, Jr., J. Org. Chem. 26 (1961) 4782.
[20] M. Sato, M.V. Lakshmikantham, M.P. Cava, A.F. Garito, J. Org. Chem. 43 (1978) 2084.
[21] M.V. Lakshmikantham, M.S. Raasch, M.P. Cava, S.G. Bott, J.L. Atwood, J. Org. Chem. 52 (1987) 1874.
[22] S. Ogawa, M. Yamashita, R. Sato, Tetrahedron Lett. 36 (1995) 587.
[23] S. Ogawa, M. Sugawara, Y. Kawai, S. Niizuma, T. Kimura, R. Sato, Tetrahedron Lett. 40 (1999) 9101.
[24] X. Yang, T.B. Rauchfuss, S. Wilson, J. Chem. Soc. Chem. Commun. (1990) 34.
[25] (a) T. Shimizu, K. Iwata, N. Kamigata, Angew. Chem. 108 (1996) 2505. (b) T. Shimizu, K. Iwata, N. Kamigata, Angew. Chem. Int. Ed. Engl. 35 (1996) 2357.
[26] J. Kopf, K. von Deuten, B. Nakhdjavan, G. Klar, Z. Naturforsch. 34B (1979) 48.
[27] T. Shimizu, Y. Kobayashi, N. Kamigata, unpublished results.
[28] For examples: (a) G. Bergson, Arkiv. Kemi. 19 (1962) 181. (b) G. Bergson, Arkiv. Kemi. 19 (1962) 265. (c) G. Calzaferri, R. Gleiter, J. Chem. Soc. Perkin Trans. 2 (1975) 559.
[29] J.P. Donahue, R.H. Holm, Acta Crystallogr. C54 (1998) 1175.
[30] Y. Yokomori, J. Nakayama, personal communication.
[31] J.L. Hencher, Q. Shen, D.G. Tuck, J. Am. Chem. Soc. 98 (1976) 899.
[32] (a) T. Shimizu, K. Iwata, N. Kamigata, S. Ikuta, J. Chem. Res. (S), (1997) 38. (b) T. Shimizu, K. Iwata, N. Kamigata, S. Ikuta, J. Chem. Res. (M) (1997) 344.
[33] (a) A. Veillard, J. Demuynck, Chem. Phys. Lett. 4 (1970) 476. (b) A. Rauk, J. Am. Chem. Soc. 106 (1984) 6517. (c) R. Block, L. Jansen, J. Chem. Phys. 82 (1985) 3322. (d) D.A. Dixon, D. Zeroka, J.J. Wendoloski, Z.R. Wasserman, J. Phys. Chem. 89 (1985) 5334.
[34] (a) R. Pauncz and D. Ginsburg, Tetrahedron 9 (1960) 40. (b) N.L. Allinger, J.T. Sprague, J. Am. Chem. Soc. 94 (1972) 5734. (c) N.L. Allinger, J.T. Sprague, Tetrahedron 31 (1975) 21. (d) O. Ermer, J. Am. Chem. Soc. 98 (1976) 3964. (e) D.N.J. White, M.J. Bovill, J. Chem. Soc. Perkin Trans. 1 (1977) 1610. (f) W.R. Roth, O. Adamczak, R. Breuckmann, H.W. Lennartz, R. Boese, Chem. Ber. 124 (1991) 2499.
[35] T. Shimizu, K. Iwata, N. Kamigata, S. Ikuta, J. Chem. Res. (S) (1994) 436.
[36] C.G. Krespan, B.C. McKusick, J. Am. Chem. Soc. 83 (1961) 3438.

[37] T. Shimizu, H. Murakami, N. Kamigata, J. Org. Chem. 64 (1999) 8489.
[38] J. Nakayama, K.S. Choi, A. Ishii, M. Hoshino, Bull. Chem. Soc. Jpn. 63 (1990) 1026.
[39] (a) W.E. Parham, V.J. Traynelis, J. Am. Chem. Soc. 76 (1954) 4960. (b) R. Grigg, R. Hayes, J.L. Jackson, J. Chem. Soc. Chem. Commun. (1969) 1167. (c) K. Kobayashi, K. Mutai, H. Kobayashi, Tetrahedron Lett. (1979) 5003. (d) J. Nakayama, M. Shimomura, M. Iwamoto, M. Hoshino, Heterocycles 23 (1985) 1907.