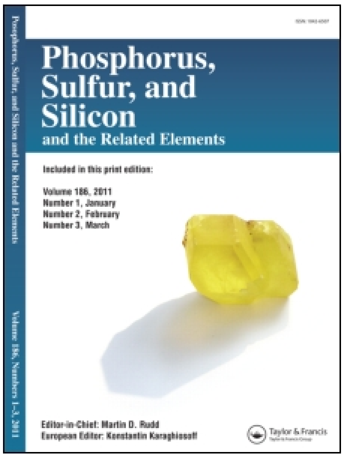

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Reaction of Novel Sulfur Containing Heterocyclic Systems

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To cite this Article Ando, Wataru , Tokitoh, Norihiro and Kabe, Yoshio(1991) 'Synthesis and Reaction of Novel Sulfur Containing Heterocyclic Systems', Phosphorus, Sulfur, and Silicon and the Related Elements, 58: 1, 179 — 205

To link to this Article: DOI: 10.1080/10426509108040631

URL: http://dx.doi.org/10.1080/10426509108040631

Phosphorus, Sulfur, and Silicon, 1991, Vol. 58, pp. 179–205
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SYNTHESIS AND REACTION OF NOVEL SULFUR CONTAINING HETEROCYCLIC SYSTEMS

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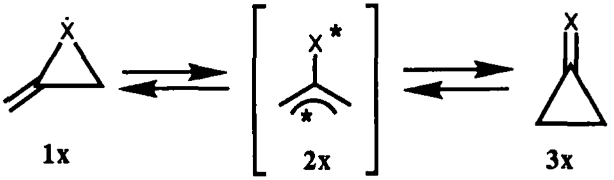
Abstract: The strained alkylidene episulfides were synthesized by carbene and alkylidene carbene additions to thiocarbonyl compounds.Thermal, photochemical, and acid catalyzed reactions have been extensively investigated, and and the transition metal-promoted reaction results in the first isolation of thioallyl iron tricarbonyl complex. Germylene and zirconocene also reacted with thioketene to give metallic analogue of alkylidene episulfides, which are excellent synthetic source of a variety of cyclogermanes and stable enethiolizable thioaldehyde. Thermal sulfurization of some 1,2,3-butatriene derivatives and 1,2,3-selenadiazoles with elemental sulfur has been examined to give a variety of novel cyclic polysulfides having an unique structure. Reactive silicon and germanium species also reacted with elemental sulfur and selenium to afford cyclic metallachalcogenides.

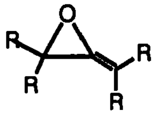
1. STRAINED AND ITS IMPLICATION IN ALKYLIDENE EPISULFIDE

Considerable interest has long been focused on the synthesis of three-membered ring bearing exocyclic double bonds. Among these are methylenecyclopropane ($\mathbf{1}_{\mathrm{CH_2}}$), allene oxides (1o) and allene episulfide (1s). These systems undergo interconversion

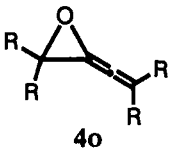


X = CH$_2$, O, S

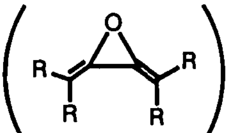
* = radical or ions



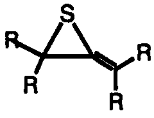
1o



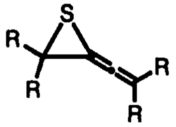
4o



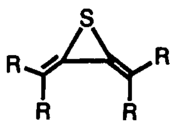
5o



1s

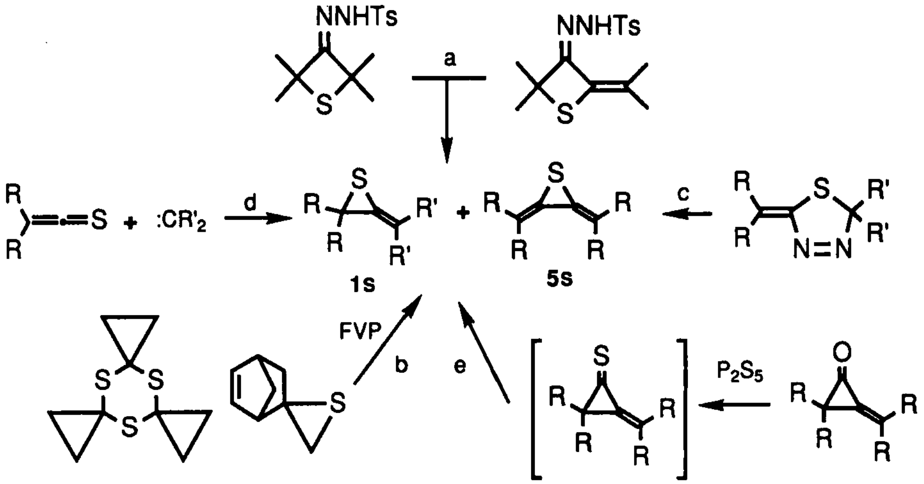


4s



5s

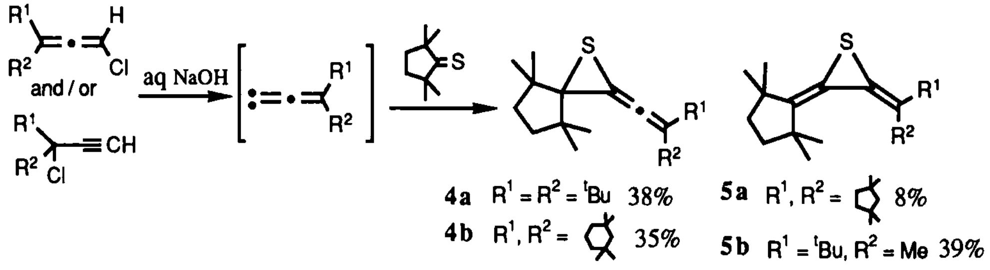
(1)-(2)-(3), and always intrigued chemist from both a theoretical and synthetic point of view. Trimethylenemethane (2CH_2), oxyallyl (2o) and thioallyl (2s) are still elusive intermediate. Interestingly, the theoretical studies suggest 1o is less stable than 3o by about 23 kcal mol^{-1}, while 1s is 7 kcal mol^{-1} more stable than 3s. However the chemistry of the sulfur-containing tautomeric system[1] has been far behind the other systems due to the lack of the convenient synthetic route for allene episulfide after the pioneer works of Hortmann and Block[2], where intramolecular carbene rearrangement (route a) and thermal fragmentation of trithiane and spirothiirane (route b) were examined. Middleton and Schaumann[3] reported the formation of episulfides by decomposition of thiadiazoles and the direct carbene addition reaction to stable thioketene (route c and d).

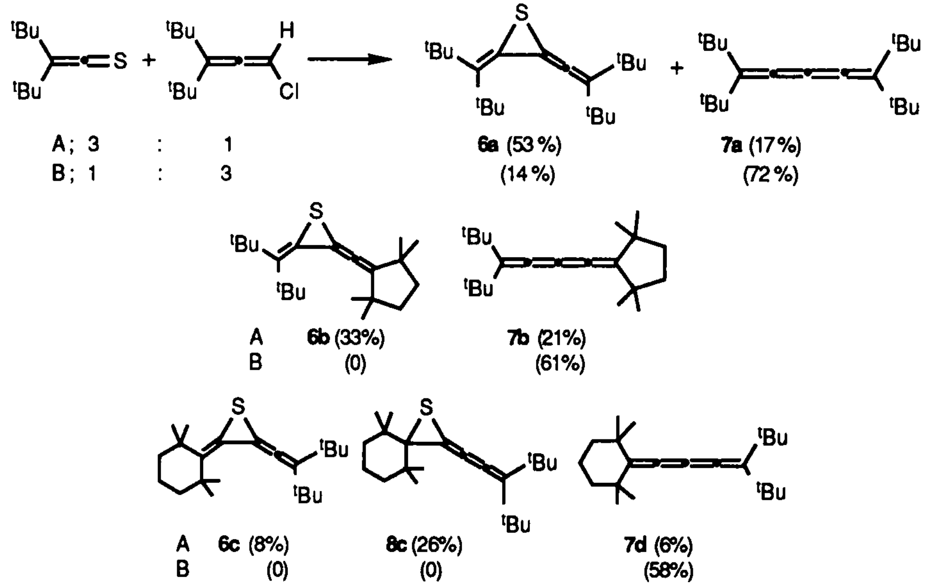


The discovery of this carbene route laid our foundation for the project aimed at developing the chemistry of strained alkylidene episulfide, which involves not only 1s but also 4s and 5s. In contrast to 4s and 5s, oxygen analogue 4o is only observed by NMR at -50°C and 5o is so far unknown. Meanwhile there have been no attempts on the direct sulfurization of cumulene and cyclopropanone which is expected to provide a new synthetic route for alkylidene episulfides. Although thionation of cyclopropanone (route e) yielded alkylidene episulfide, the direct sulfurization of 1,2,3-butatrienes resulted in a novel formation of 6,7-bisalkylidene-1,2,3,4,5-pentathiepanes. This unexpected result made us pursue the second project aimed at developing the chemistry of novel cyclic polysulfides. Up to now, both projects have been widely expanded covering the main group and transition metal chemistry.

FACILE FORMATION OF ALKYLIDENE EPISULFIDES BY ALKYLIDENE CARBENE ADDITION TO THIOKETONE AND THIOKETENE

In a similar way to the carbene addition reaction to stable thioketene, we have already synthesized 1,2,3-butatriene 1- and 2-episulfides, (**4a,b**) and (**5a, b**) by alkenylidene carbene addition to thioketones using several kinds of chloroallenes and/or chloroalkynes as the carbene source under phase transfer catalytic reaction conditions.^{4} However, we cannot neglect the sterically repulsive influence of bulky substituents on these labile systems and their intrinsic reactivity has not been fully investigated. We have found here a new and convenient method for the synthesis of novel pentatetraene episulfide (**6a-c** and **8c**) by the addition of alkenylidene carbene to thioketene, which can be useful in turn as a route to 1,2,3,4-pentatetraene (**7a-c**).^{5} When thioketenes were treated with several kinds of haloalkenes under phase transfer reaction conditions, the corresponding 1,2,3,4-pentatetraene 2-episulfide (**6a-c**) were obtained in moderate yields based on the

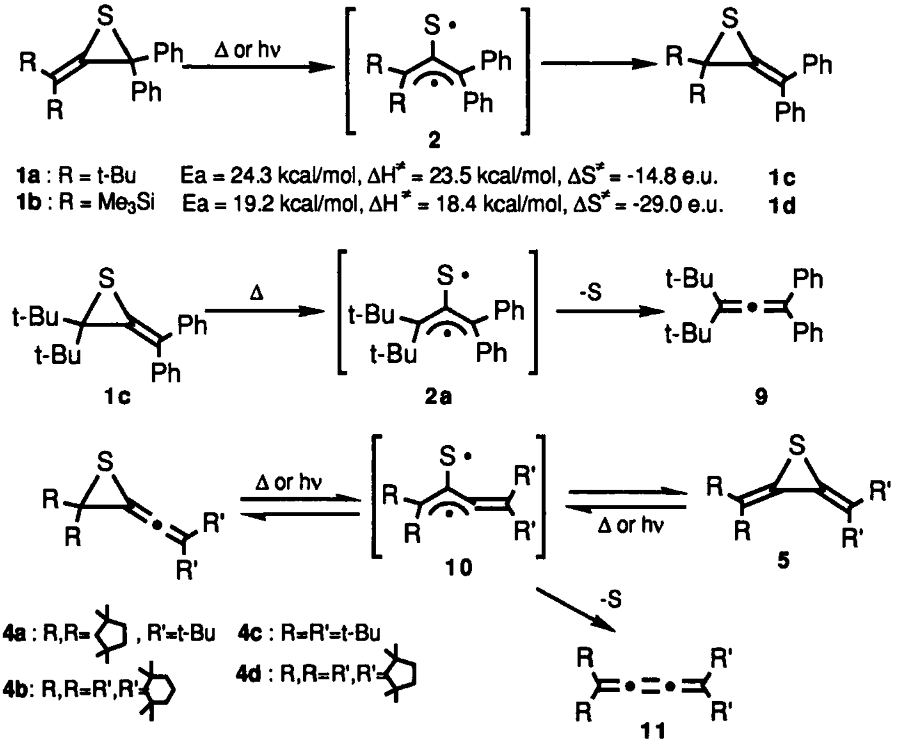




carbene sources along with a small amount of desulfurized 1,2,3,4-pentatetraene (**7a-c**). (Method A). Using an excess amount of carbene sources (3 equivalent to thioketene) resulted in an almost exclusive formation of **7a-c** in good yields. (Method B). In the last case, isomerized 1-episulfide (**8c**) was formed together with **6c** and **7c**. Method B is of particular note as a useful synthetic method for a variety of substituted 1,2,3,4-pentatetraenes, which are difficult to construct by the common carbene coupling reactions.

THERMOLYSIS AND PHOTOLYSIS OF ALKYLIDENE EPISULFIDES

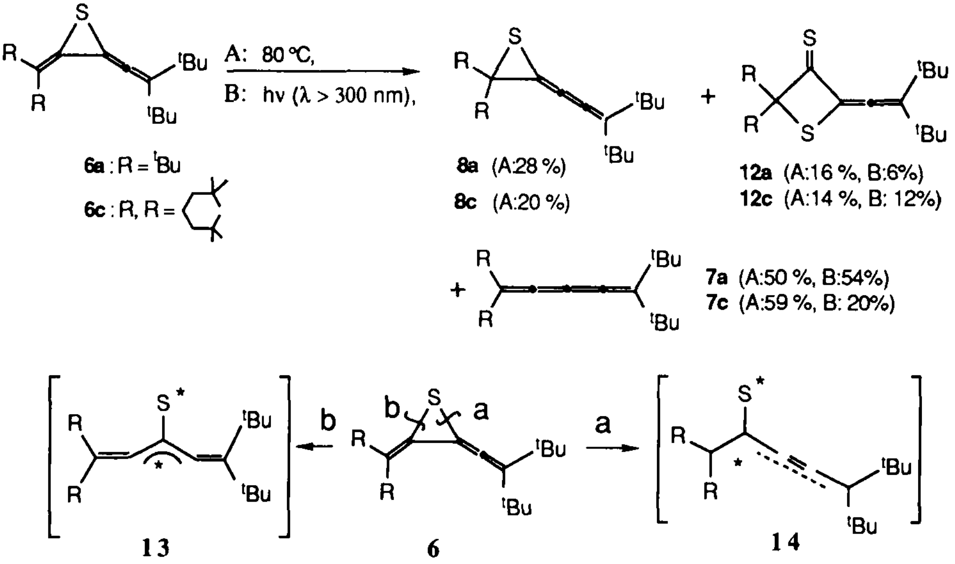
In the tautomerism of allene episulfide with cyclopropanethione, thioallyl intermediate has played a well-fitting and very important roles. Recently we have described the thermal isomerization reactions of different types of substituted allene episulfides (**1a** and **1b**).[6] Since the thermolysis of **1c** gave only the corresponding allene **9** without any isomerization backward into the original allene episulfide (**1a**), the isomerization between **1a** and **1c** was irreversible process. The replacing of two *tert*-butyl groups by more



1a : R = t-Bu Ea = 24.3 kcal/mol, $\Delta H^{\neq}$ = 23.5 kcal/mol, $\Delta S^{\neq}$ = -14.8 e.u. **1c**

1b : R = Me_3Si Ea = 19.2 kcal/mol, $\Delta H^{\neq}$ = 18.4 kcal/mol, $\Delta S^{\neq}$ = -29.0 e.u. **1d**

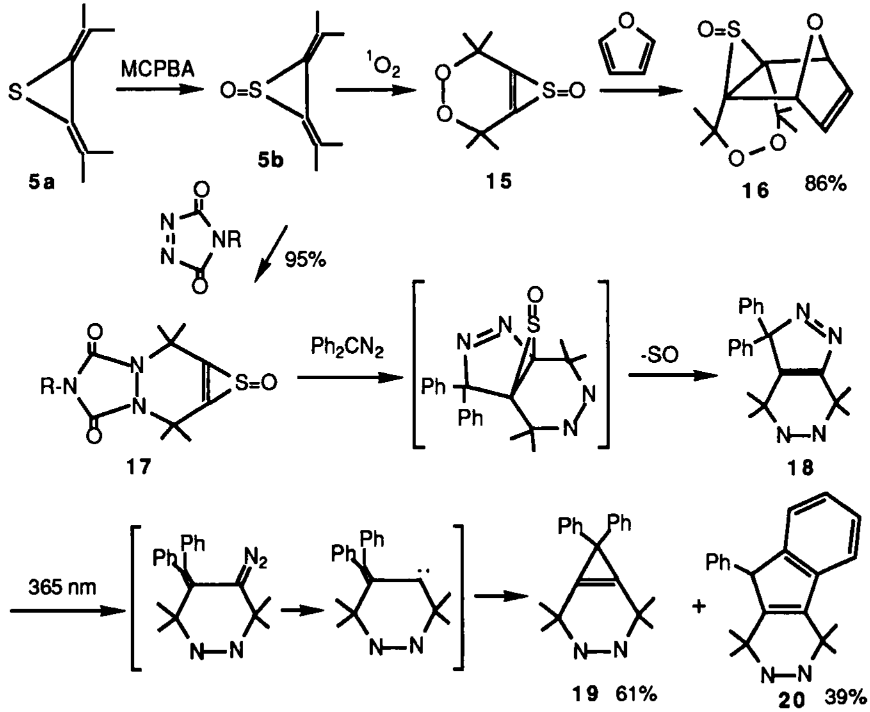
electronegative trimethylsilyl groups resulted in a noticeable decrease of activation energy. This substituent effect reveals that thioallyl is a biradical with partial ionic character, i.e. with a positive charge on sulfur and a negative charge on allylic parts, which is also supported by MCSCF calculation. Photochemically both 1,2,3-butatriene 1-episulfides (**4a-d**) and 2-episulfides (**5a-d**) were easily desulfurized into the corresponding 1,2,3-butatriene (**11a-d**). On the other hand, we found the thermal isomerization between the two types of 1,2,3-butatriene episulfides in the case of **4d** and **5d**.[4] Heating of **4a** or **5d** resulted in a same equilibrated mixture, the equilibrium ratio of **5d** to **4d** were 1.52 (90°C) and 1.1.6 (120°C) respectively. This thermal instability of **5d** might be attributable to the increasing steric repulsion of inner methyl groups on the cisoid butadiene unit of **5d** caused by the augummentative molecular vibration at high temperature. The thermal interconversion between **4d** and **5d** is worthy of attention as the first example of the sulfur-analogous tautomeric system of alkylidene cyclopropane



and bisalkylidene cyclopropane. Pentatetraene 2-episulfides (**6a** and **6c**) readily underwent a thermal C-S bond cleavage (at a-bond) in refluxing benzene to give the corresponding 2-alkylidene thietane-3-thiones (**12a** and **12c**) in addition to the isomerized 1-episulfides (**8a** and **8c**) and desulfurized tetraenes (**7a** and **7c**).[5] Once isolated 1-episulfides (**8a** and **8c**) were also converted into **12a**, **12c**, **7a** and **7c** slowly in refluxing benzene. Meanwhile, similar formation of thietanethiones **12a** and **12c** was attained by the irradiation of **6a** and **6c** with light of hv>300 nm in chloroform at room temperature. The C-S bond cleavage of **6** exclusively occurred along path a, resulting in the formation of thioallyl **14**, because of cumulenic stability of π-conjugated systems of **14** compared to **13**. The formation of **12a** and **12b** might be rationalized by intramolecular sulfur transfer reaction mechanism with intermediacy of **14**, which is also common intermediate for isomerization to **8a** and **8c**.

ADDITION REACTION OF ALKYLIDENE EPISULFIDE S-OXIDE

In the case of the 1,2,3-butatriene 2-episulfide bearing less hindered substituents such as **5a** and its S-oxide (**5b**), intermolecular reaction with a variety of dienophile was realized. In terms of strained alkenes, [2+4] addition of **5a** and **5b** would emerge as powerful method introducing double bond into a three-membered ring fused to a six-membered ring. The compound **5a** reacted with $^1O_2$ to afford a novel fused thiirene sulfoxide



(**15**), while 4-substituted 1,2,4-triazoline-3,5-dione (TAD) as a dienophile also yielded fused thiirene sulfoxide (**17**) quantitatively. Fused thiirene sulfoxides **15** and **17** were shown to be quite reactive. The further reaction of **15** with furan gave **16**, which is the first example of alkyl substituted thiirene S-oxide as well as a propellane containing the thiirene S-oxide moiety.[7] On the other hand, **17** reacted with diphenyldiazomethane to give 3H-pyrazole (**18**), photolysis of which resulted in the quantitative release of nitrogen and gave the bicyclo[4.1.0]alkene (**19**) in addition to the indene (**20**).[8] Inspection of the X-ray analysis data revealed the nonplannar structure of **19** and the angle between two rings is 162.4° shown in Figure 1. The stability of **19** clearly depended on the substitution of four methyl groups, which might fix the bicyclic ring system.

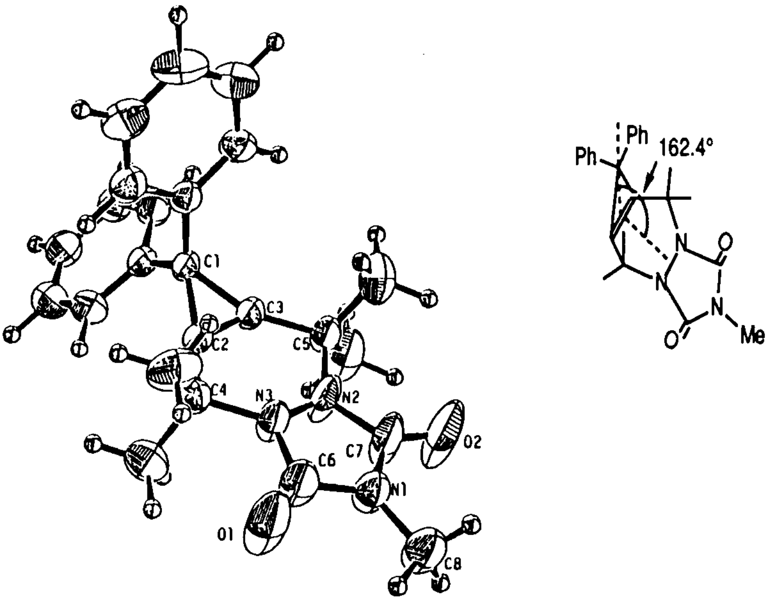
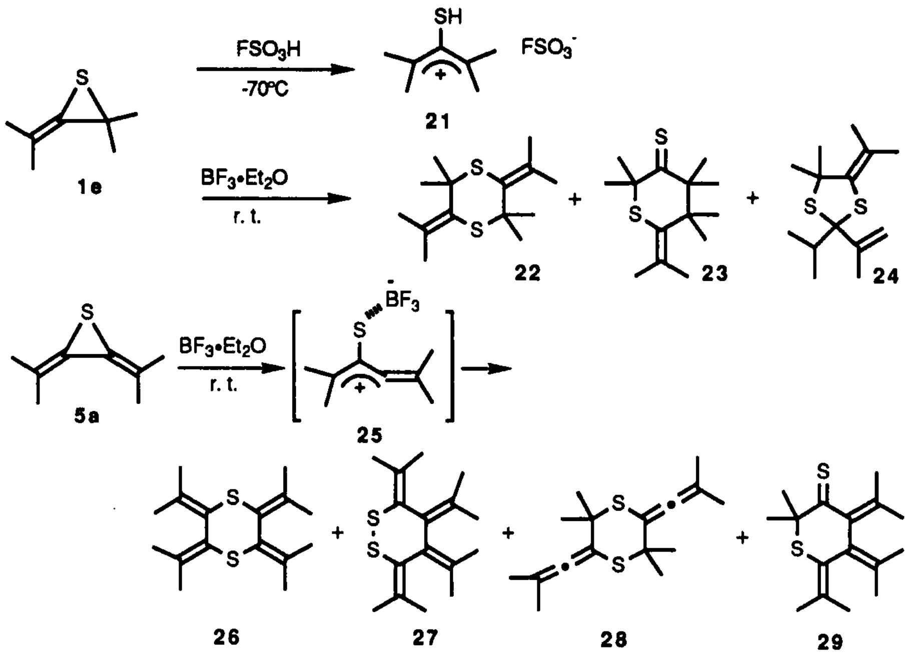


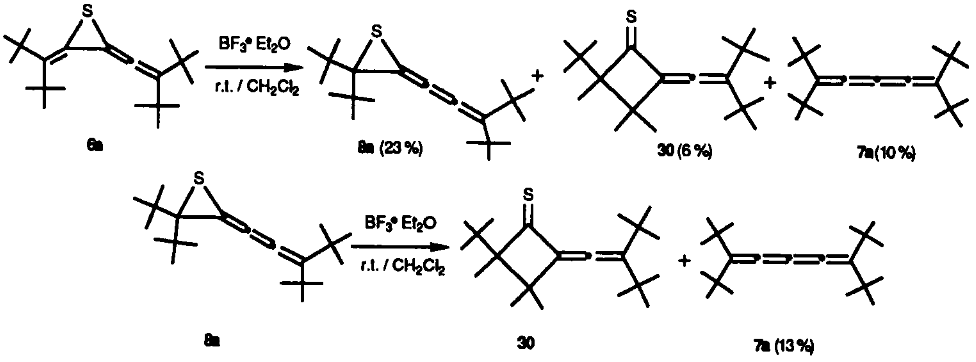
Figure 1. ORTEP Drawing of Six-membered Ring Fused Cyclopropene (19). Selected bond lengths (Å) and angles (degree), C(1)-C(2), 1.521; C(1)-C(3), 1.526; C(2)-C(3), 1.286;C(2)-C(4), 1.491; C(3)-C(5), 1.478. C(2)-C(1)-C(3), 49.92; C(1)-C(2)-C(3), 64.82; C(1)-C(3)-C(2), 65.26; C(2)-C(3)-C(5), 130.23; C(3)-C(2)-C(4), 129.16.

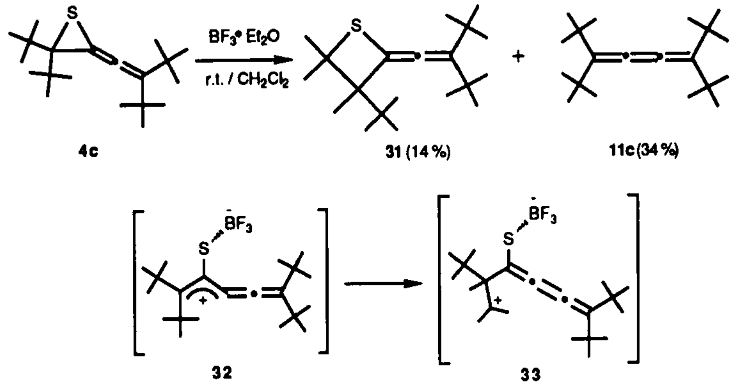
ACID CATALYZED REACTIONS OF ALKYLIDENE EPISULFIDE

The acid ($BF_3{\bullet}Et_2O$) catalyzed reaction of allene episulfide (**1e**) has been reported to yield dimerization products, 1,4-dithiane (**22**), thioketone (**23**) and 1,3-dithiolane (**24**).[9] The formation of these products might be interpreted with a intermediacy of the thioallyl ion (**21**) that undergoes cycloadditions with either **1e** or **21** to give **22** and **23**. In the case of **24**, thioallyl (**21**) undergoes 1,4-hydrogen shift prior to cycloaddition with **1e** or **21**.



The evidence for such a intermediate was observed by spectroscopic studies in super acid (FSO_3H, -70°C). The similar dimerization of 1,2,3-butatriene-2-episulfide (**5a**) does take place readily with acid catalyst via thioallyl ion intermediate (**25**). On the other hand treatment of pentatetraene 2-episulfide (**6a**) with an equimolar amount of $BF_3•Et_2O$ resulted in a formation of 2-alkylidene cyclobutanethione (**30**) with the isomerized 1-episulfide (**8a**) and desulfulized tetraene (**7a**).[5] Similarly 1-episulfide (**8a**) was converted into **30** and **7a** by the action of $BF_3•Et_2O$. The formation of **30** is consistently interpreted with initial generation of the thioallyl cation intermediate **32** followed by the well known methyl group rearrangement in the reaction of di-*t*-butyl





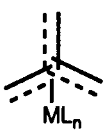
4c **31** (14%) **11c**(34%)

32 **33**

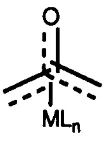
substituted allyl cation systems.[10] This methyl rearrangement also proceeded in the conversion of 1,2,3-butatriene 1-episulfide (**4c**) to **31**.

REACTION OF ALLENE EPISULFIDE WITH $Fe_2(CO)_9$; STABLE (THIOALLYL)IRON TRICARBONYL COMPLEX

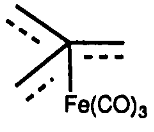
According to the kinetic and MCSCF calculation studies, thioallyl is a biradical with partial ionic character similar to trimethylenemethane rather than ionic oxyallyl. This similarity of thioallyl and trimethylenemethane prompted us to attempt a stabilization of the species by complexation with suitable transition metal, e.g., iron, to obtain the hetero- analogue of well known $(TMM)Fe(CO)_3$ $(34CH_2)$[11], namely (thioallyl)iron tricarbonyl complex



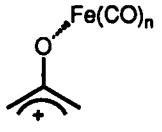
34CH2



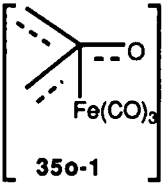
34O



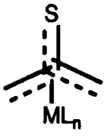
35CH2



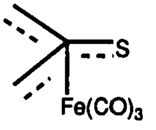
35o-2



35o-1

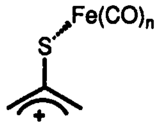


34s

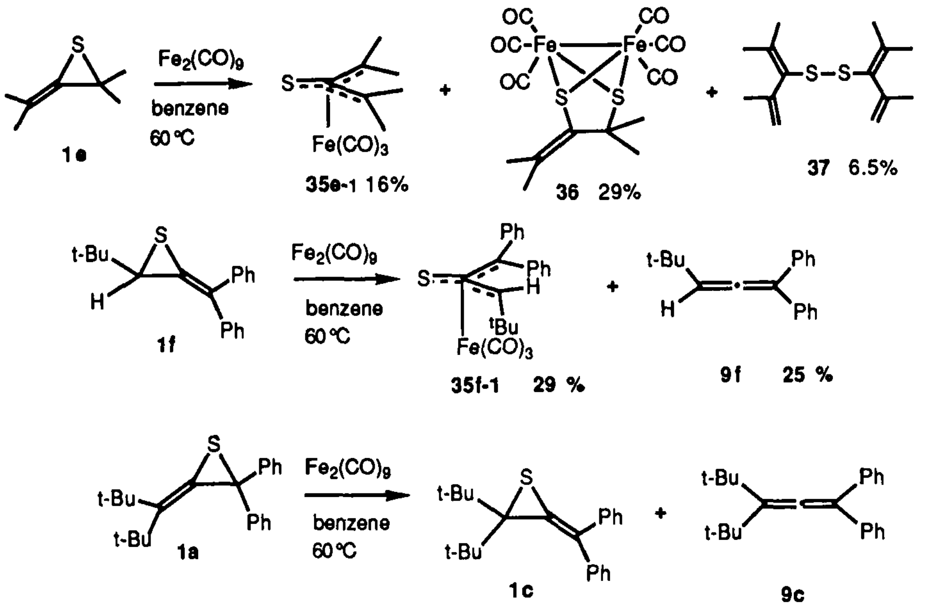


35s-1

or



35s-2



(34S). Although η^4-(oxyallyl)iron complex (34O-1) has not been reported so far, oxyallyl complex has been described as an η^3-(oxyallyl) cation complex (35O-2).[12] Treatment of allene episulfide (1e) with diiron nonacarbonyl ($Fe_2(CO)_9$) in benzene at 60°C gave two iron carbonyl complexes **35e-1**, **36** and disulfide **37**. In contrast, aryl

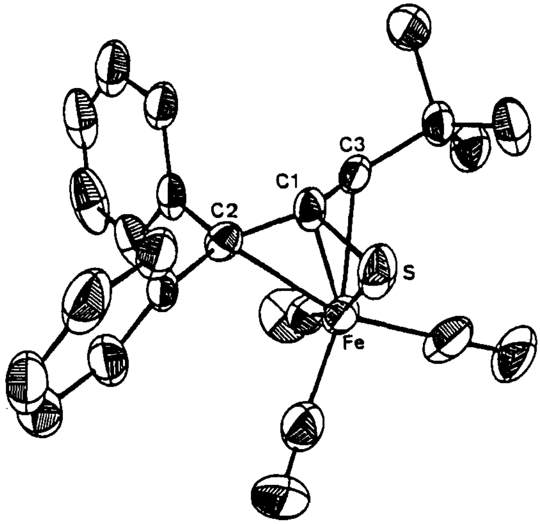
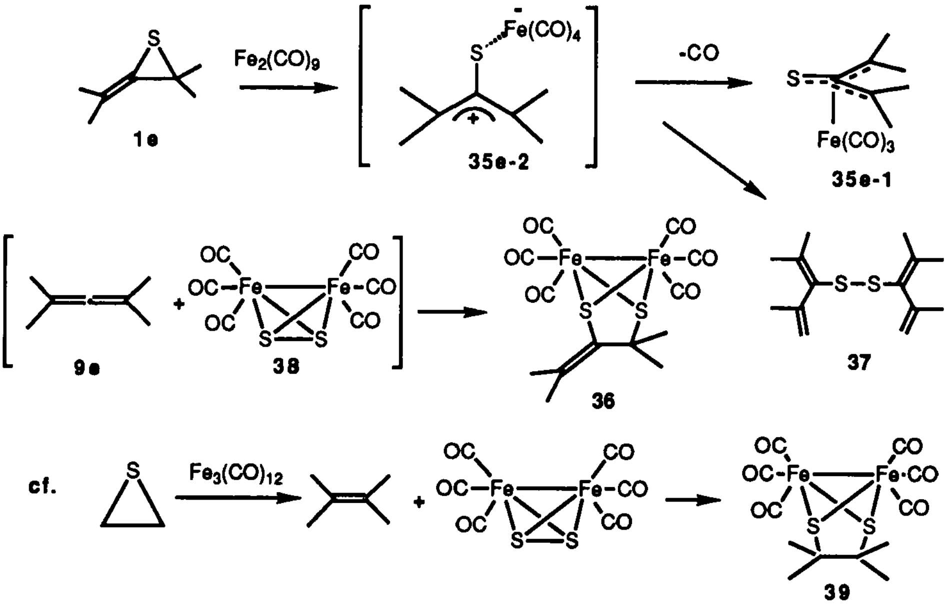


Figure 2. ORTEP Drawing of **35f-1**. Selected bond lengths (Å) and angles (dgree). S-C(1), 1.757(8); C(1)-C(2), 1.41(1); C(1)-C(3), 1.40(1); Fe-S, 2.308; Fe-C(1), 1.938; Fe-C(2), 2.262; Fe-C(3), 2.180; Fe-C(4), 1.80(1); Fe-C(5), 1.84(1); Fe-C(6), 1.76(1). S-C(1)-C(2), 115.2; S-C(1)-C(3), 116.9; C(2)-C(1)-C(3), 119.2; S-C(1)-Fe, 77.2; C(2)-C(1)-Fe, 83.4; C(3)-C(1)-Fe, 79.7.

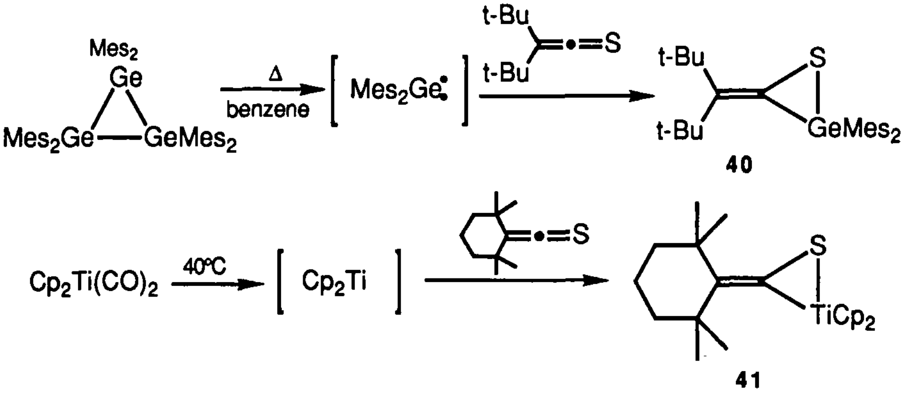
t-butyl substituted allene episulfide (**1f**) provided single iron carbonyl complex (**35f-1**) along with desulfurized allene (**9f**).[13] The X-ray structure determination of **35f-1** confirmed η^4-(thioallyl)iron tricarbonyl structure shown in Figure 2. With the inspection of Figure 2, the iron atom is located directly beneath the central atom (C(1)) of the thioallyl residue π–bonded to three carbon and one sulfur atoms of ligand. This structure was similar to that of (trimethylenemethane)iron complex (**35**CH_2). The relevant bond distances, C(1) to S, C(1) to C(2), and C(1) to C(3) are 1.757, 1.414, 1.40 Å respectively. These may be between C-S or C-C single and double bond. The thioallyl ligand and iron tricarbonyl moiety adopt a mutually staggered conformation. The structure of iron complex **36** was assigned by comparison with the known data of the analogous complex[14] and its butterfly structure was finally confirmed by X-ray analysis. The most reasonable first step of the process by which the complex **35e-1** and **36** are formed is C-S bond cleavage of allene episulfide by $Fe(CO)_4$, which has precedented reactions. Next, the resulting thioallyl cation complex **35e-2** loses carbon monoxide and subsequent coordination transfer to give the complex **35e-1** and **35f-1**. Alternatively, the thioallyl cation complex **35e-2**, on account of the strong sulfur-iron bond, produces allene **9c** and **9f** and iron-bounded sulfur. In the case of less hindered allene episulfide (**1e**), the rupture of C-S bond easily occurred to yield $S_2Fe_2(CO)_6$ (**38**) and tetramethylene (**9e**), which finally coupled to give **36**. The similar butterfly



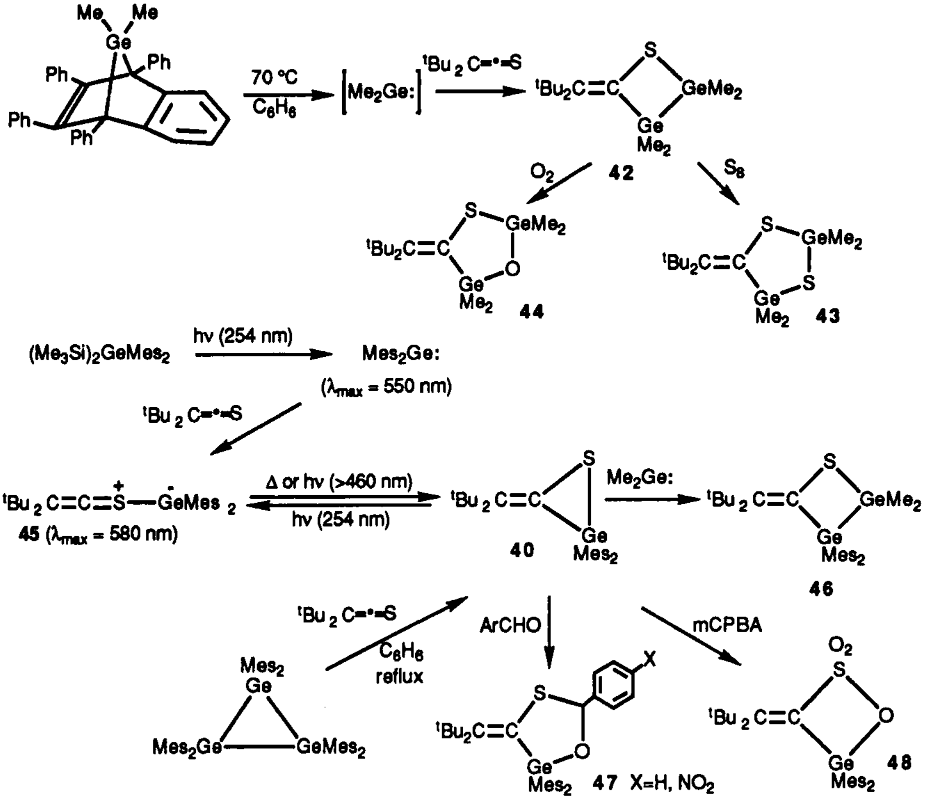
complex (39) is reported to be obtained by thermal fragmentation of thiirane in the presence of $Fe_3(CO)_{12}$ in THF through intermediate complex of $S_2Fe_2(CO)_6$ (38).[15] The compound 37 is thought to come from oxidation of 2,4-dimethyl-1,3-pentadiene-3-thiol, which is formed from thermal 1,2-hydrogen shift of **1e** via thioallyl diradical. When the more hindered allene episulfide, di-*t*-butyldiphenylallene episulfide (**1a**) was treated with diiron nonacarbonyl, no thioallyliron carbonyl complex was detected, but isomer (**1c**) and 1,1-di-*t*-butyl-3,3-diphenylallene (**9c**)were produced. It may be that the sterically hindered allene episulfide moiety of **1a** could not make empty site for $\eta^4(\pi)$-coordination.

METALLIC ANALOGUE OF ALLENE EPISULFIDES

We have already describe the reaction of germylene with thioketene to give 3-alkylidenethiagermirane (40).[16] Berens has been reported the titanocene reacts with thioketene to give titanocene thioketene complex, in other words, alkylidenethiatitanapropane (41), structure of which was characterized by X-ray analysis.[17]

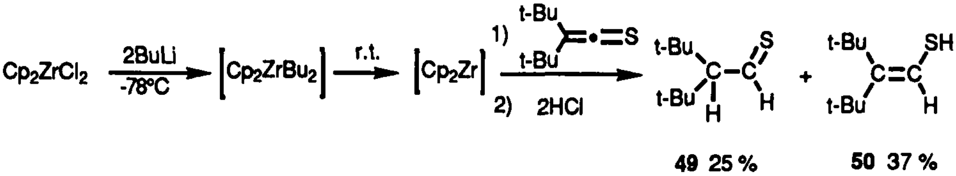


Dimethylgermylene generated by the thermolysis of 7,7-dimethyl-7-germanorbornadiene reacts with di-*t*-butylthioketene to afford 4-alkylidene-1,2,3-hiadigermetane (42), which is the product of insertion of germylene into 3-alkylidenethiagermiranes. Thiadigermetane (42) is extremely sensitive toward oxygen as well as elemental sulfur to yield the corresponding ring expansion products 43 and 44, respectively. Since the introduction of bulky substituents has been widely used for the stabilization of unstable molecules, we tried the reaction of a bulky substituted germylene, dimesitylgermylene, with thioketene. Dimesitylgermylene arising from the photolysis of dimesitylbis (trimethysilyl)germane or the thermolysis of hexamesitylcyclotrigermane react with thioketene to provide the stable 3-alkylidene thiagermirane (40).

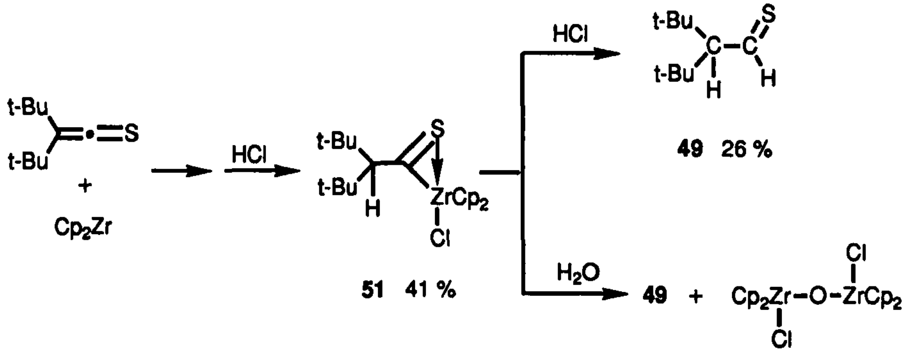


Irradiation of **40** in a 3-methylpentane matrix at 77 K produces germathiocarbonyl ylide (**45**) which is intensely blue in color with a maximum band at 580 nm. The compound **40** undergoes a variety of insertion reactions, with dimethylgermylene, benzaldehyde and *m*-chloroperbenzoic acid to give 4-alkylidene-1,2,3-thiagermetane (**46**), 4-alkylidene-1,3,5-oxathiagermolanes (**47**) and 3-alkylidene-1,2,4-oxathiagermetane S-oxide (**48**) respectively.

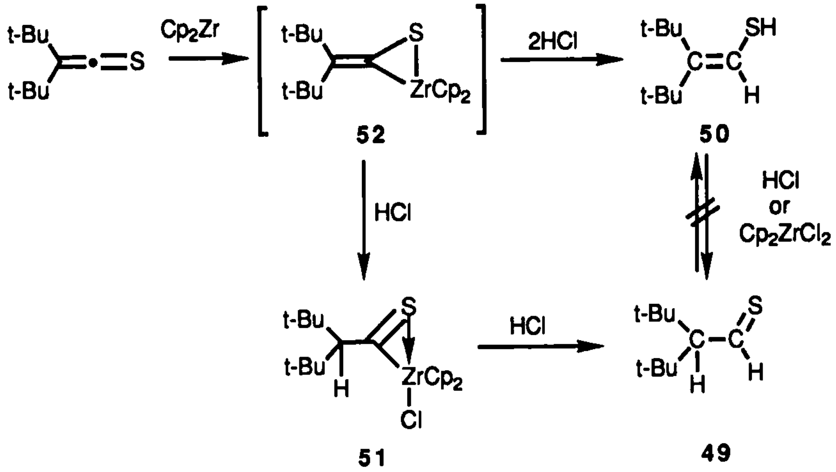
Although the zirconocene has been generated by various method, Negishi has recently reported more convenient method by the reaction of Cp_2ZrCl_2 with 2 equiv of n-BuLi at -78°C, in which $Cp_2Zr(H)Bu$ was obtained by β-elimination of Cp_2ZrBu_2 followed by its reductive elimination to give Cp_2Zr.[18] Accordingly to Negishi's method, addition of n-BuLi to zirconocene dichloride at -78°C under argon followed by introduction of di-*t*-butylthioketene and a work up with 10% HCl gave di-*t*-butylethanethial (**49**) and its isomer, di-*t*-butylethenethiol (**50**).[19] Although Okazaki and Vedejs have been independently reported the stable thioaldehydes,[20] which have no enethiolizable α-protons, **49** is the first example of stable enethiolizable thioaldehyde. The characteristic absorption of 49 at 1110 cm^{-1} (IR) and 536 nm (UV) indicative of thiocarbonyl group and low field shift of the formyl proton and thiocarbonyl carbon in ^{1}H and ^{13}C NMR at 11.58 and 253.3 ppm confirmed the structure of 49. The formulation of 50 was also confirmed by ^{1}H and ^{13}C NMR and furthermore by the reduction of di-*t*-butylthioketene with $LiAlH_4$ and subsequent oxidation with I_2 giving the divinyldisulfide.



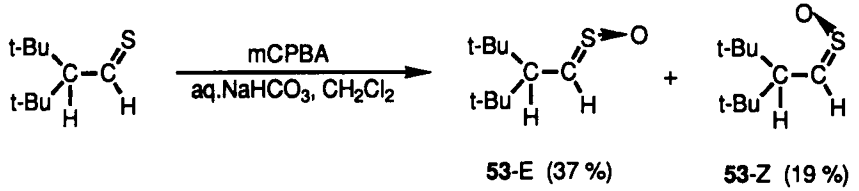
When the reaction mixture was carefully hydrolyzed with a small amount of HCl, zirconocene thioacyl complex (51) was formed in a moderate yield, which has characteristic absorption of thiocarbonyl carbon at 379.3 ppm in ^{13}C NMR comparable to the value of zirconocene acyl complex (314.2 ppm). Similar conversion of niobocene ketene complex into niobocene acyl complex with acid has been reported very recently by Bruno.[21] Since the hydrolysis of 51 produced 49, the origin of thioaldehyde (49) is indeed zirconocene thioacyl complex (51). It is highly likely that zirconocene thioketene



complex (52) is a common intermediate for ethenethiol (50) and zirconocene thioacyl complex (51) and that the hydrolysis of 52 and 51 proceed competitively to yield 50 and 49, respectively. Although the thiocarbonyl is known to isomerize easily to enethiol, the thioaldehyde (49) does not thermally isomerize into ethenethiol even by the addition of acid or Cp_2ZrCl_2 probably because of highly steric hindrance; 50 isomerize little to 49 at

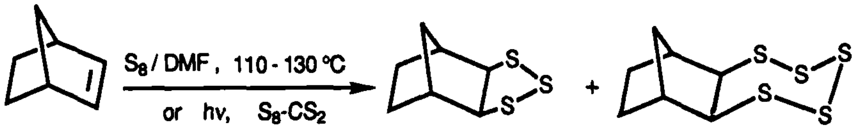


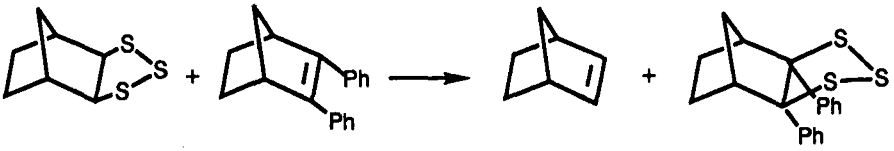
100°C and both **49** and **50** decompose at 150°C. The compound **49** were oxidized by *m*-chloroperbenzoic acid to give E- and Z-sulfines, stereochemistry of which was assigned based on the coupling constants between aldehyde proton and α-proton; $J_{H,H\alpha}$=14Hz for **53E**, $J_{H,H\alpha}$ =12Hz for **53Z**.



2. ELEMENTAL SULFUR IN ORGANIC SYNTHESIS

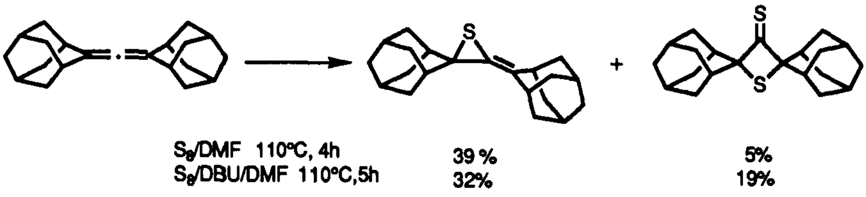
Recently, a detailed study on the sulfurization of norbornene and the inter- molecular sulfur transfer reaction of resulted cyclic trisulfide has been described by Shields, Bartlett and Oae.[22] There have been no reports on the sulfurization of cumulenic carbon-carbon double bond except for the thioallyl intermediate generation in the reaction of peculiarly substituted allene derivative followed by the ketene acetal formation.[23] With a view to providing a new synthetic route for the heteroatom-containing conjugated π-system, we have examined the direct sulfurization of allenes and 1,2,3-butatrienes with elemental sulfur leading to a novel formation of new types of cyclic polysulfides.



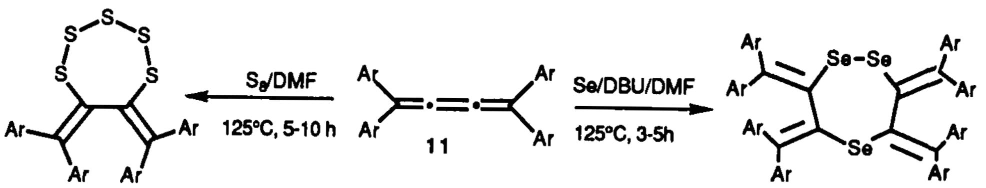


REACTIONS OF ALLENES AND 1,2,3-BUTATRIENES WITH ELEMENTAL SULFUR AND SELENIUM

Sulfurization of bisadamantylideneallene was easily performed by heating with excess of elemental sulfur in N,N-dimethylformamide(DMF) at 110°C for several hours to give the corresponding allene episulfide along with thietanethione. The thietanethione might arise form sulfur transfer reaction of thioallyl intermediate.[24] In contrast, sulfurization of the

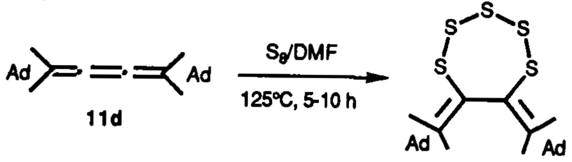


1,2,3-butatrienes (**11a-c**) bearing tetraaryl substituents with excess elemental sulfur gave the 6,7-bis(alkylidene)-1,2,3,4,5-pentathiepane derivatives **54a-c** as yellow crystals in moderate to good yields, respectively.[25] In comparison with the wide chemistry of 1,2,3,4,5-pentathiepins, only a few examples of 1,2,3,4,5-pentathiepane have been reported so far as we know. The structure of this new type of heterocycles **54a-c** was confirmed by spectral and analytical data, and finally determined by X-ray crystallographic analysis. On the other hand, **54a-c** were inert to elemental selenium even in refluxing DMF for several days. However, in the presence of DBU(1,8-diazabicyclo[5.4.0] undec-7-ene) elemental selenium dissolved in DMF at 125 °C and smoothly reacted with **11a-c** to afford the 1,2,5-triselenepane derivatives **55a-c** as a main product. The facile formation of the cyclic polysulfides **54a-c** or cyclic polyselenides **55a-c** were rationalized with an intermediacy of the radical species, though the clear role of DBU cannot be ascertained.

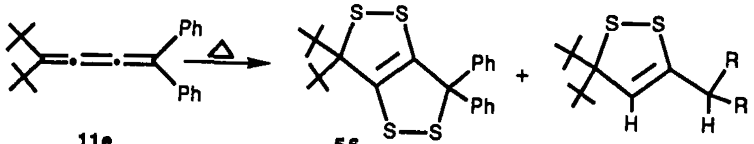


54 a; Ar=p-Tolyl 65%
b; Ar=Phenyl 87%
c; Ar=p-Chlorophenyl 56%

55 a; 64%
b; 55%
c; 25%



54d (19%)



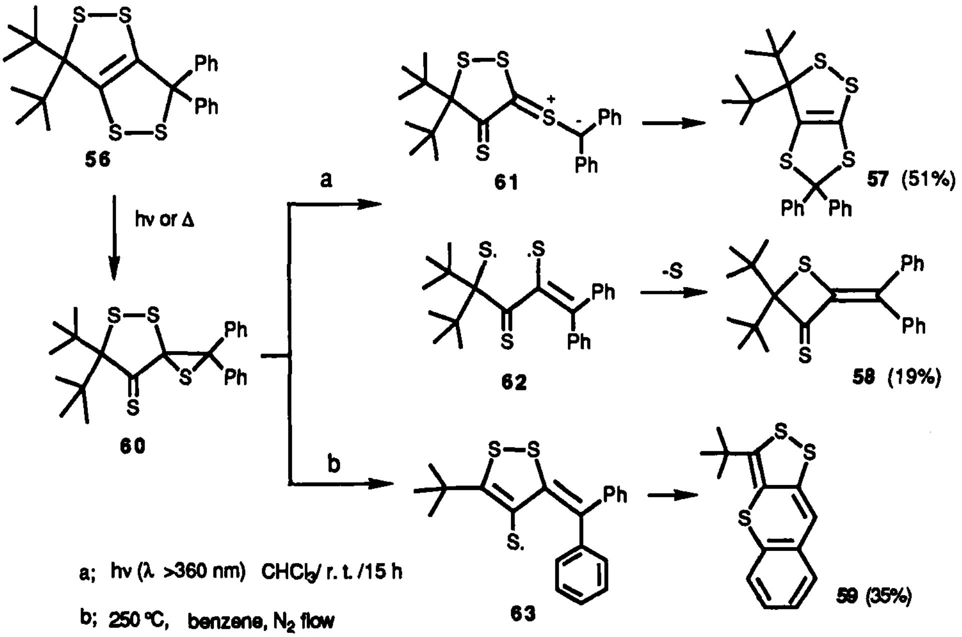
11e **56** **57**

	56	57
S$_8$/DMF at 135°C	19%	52%
S$_8$/Ph$_2$O at 135°C	35%	0
S$_8$ at 120°C	48%	0

Since it is well known that 1,1,4,4-tetraalkyl-1,2,3-butatrienes are less stable than tetraaryl substituted ones, we have tried the sulfurization of tetraalkyl substituted systems using the sterically protected rather stable 1,2,3-butatrienes. When the adamantyl substituted 1,2,3-butatriene **11d** was treated with elemental sulfur in DMF at 125 °C, 1,2,3,4,5-pentathiepane **54d** was isolated in 19 % yield as well as in the case of 1,1,4,4-tetraaryl-1,2,3-butatrienes. Bisadamantyl substitution on 1,2,3-butatriene did not change reaction product from 1,2,3,4,5-pentathiepane to 1,2,3-butatriene 1- or 2-episulfides like bisadamantylideneallene. 1,2-Dithiolo-1,2-dithiole ring system, which is a uniquely fused case of 1,2-dithiole derivative, has never been reported so far as we know. Here, we present a novel formation of the new type of fused 1,2-dithiole 1,2-dithiole **56** by sulfurization of 1,1-di-*t*-butyl-3,3-diphenyl-1,2,3-butatriene **11e** with elemental sulfur.[26] Heating of the butatriene **11e** in an excess amount of molten sulfur at 130 °C for 19 h afforded 3,3-di-*t*-butyl-3',3'-diphenyl[1,2]dithiolo[5,4- *d*][1,2]dithiole (**56**; 48%) as an orange yellow crystalline product. Although the sulfurization of **11e** also proceeded at similar reaction temperature in some organic solvents such as diphenyl ether or DMF, the yield of **56** was found to be somewhat diminished. In the case of DMF another 1,2 - dithiole derivative **57**, which might be a hydrogen abstraction product of the intermediary radical species from the solvent, was obtained as a major product (52%) along with 19% of **56**. The unusual formation of **56** and **57** and the absence of any other sulfurization products in the reaction of **11e** with elemental sulfur, which is in striking contrast to the previously described direct sulfurization of 1,1,4,4-tetraaryl- or 1,1,4,4-tetraalkyl-1,2,3-butatrienes leading to a novel formation of 6,7-bis(alkylidene)-1,2,3,4,5-pentathiepanes, is attributable to the large repulsive steric hindrance between the bulky *t*-butyl group and phenyl group on constructing the cyclopolysulfide skeleton.

THERMOLYSIS AND PHOTOLYSIS OF 1,2-DITHIOLO-1,2-DITHIOLE

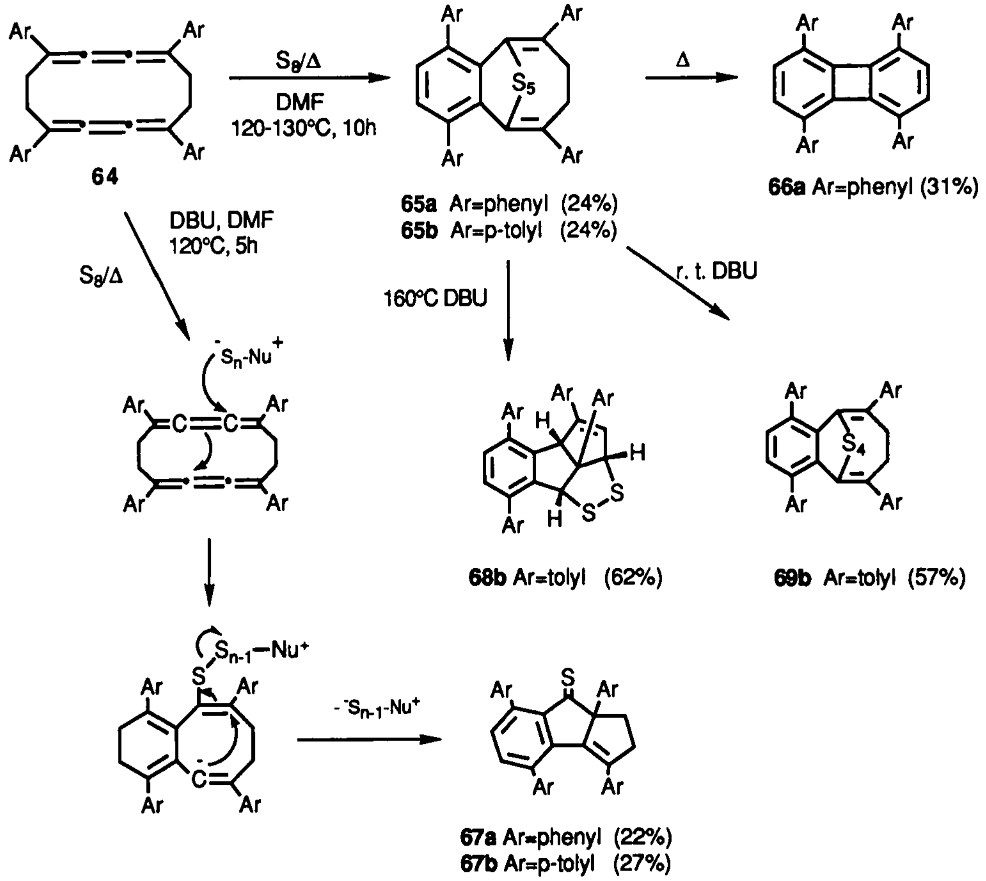
Of particular note among the reactions of the newly obtained fused 1,2-dithiolo-1,2-dithiole **56** is the photochemical transformation into 1,3-dithiole **57** and thietanethione **58**. When the chloroform solution of **56** was irradiated (λ > 360 nm), **57** and **58** were isolated as stable products in 51 and 19% yields, respectively. Since it is hard to discriminate between **57** and **56** spectroscopically, they were subjected to X-ray crystallographic analysis to reveal their final molecular structures.[26] The mechanism of



this unique ring transformation is tentatively rationalized by assuming 1,2-dithione S-ylide **61** derived from the initially formed spirothiirane intermediate **60**, which might also be the key intermediate leading to **58**. On the other hand, in the thermolysis of the fused 1,2-dithiolo-1,2-dithiole **56**, unique ring transformation reaction product (**59**) was also obtained with lack of one sulfur atom and one *t*-butyl group.

SULFURIZATION OF CYCLIC BISCUMULENES

Next, we have extended the study on sulfurization of 1,2,3-butatrienes to cyclic biscumulene **64** in expectation of a novel transannular bridging reaction. Though the two butatriene units in **64** facing each other have a potential suitability for some intramolecular reaction, there have been no reports on the functionalization of the hexaene **64a** except for its complexation with metal carbonyls. When 1,4,7,10-tetraphenylcyclododeca-1,2,3,7,8,9-hexaene (**64a**; Ar = Ph) was treated with an excess amount of sulfur in DMF at 120 - 130 °C for 10 h, a new type of cyclic polysulfide **65a** (24%) was obtained.



Sulfurization of *p*-tolyl substituted hexaene **64b** also readily underwent to give a similar bridged cyclopolysulfide **65b** in 24% yield.[27] The structures of these newly obtained cyclic polysulfides **65a** and **65b** were satisfactorily confirmed by spectroscopic data together with elemental analysis. Final molecular structure of **65a** was determined by X-ray crystallographic analysis as shown in Figure 3, in which the cyclooctatriene ring was fixed in a *quasi*-boat form. On the other hand, the sulfurization of hexaenes **64a**

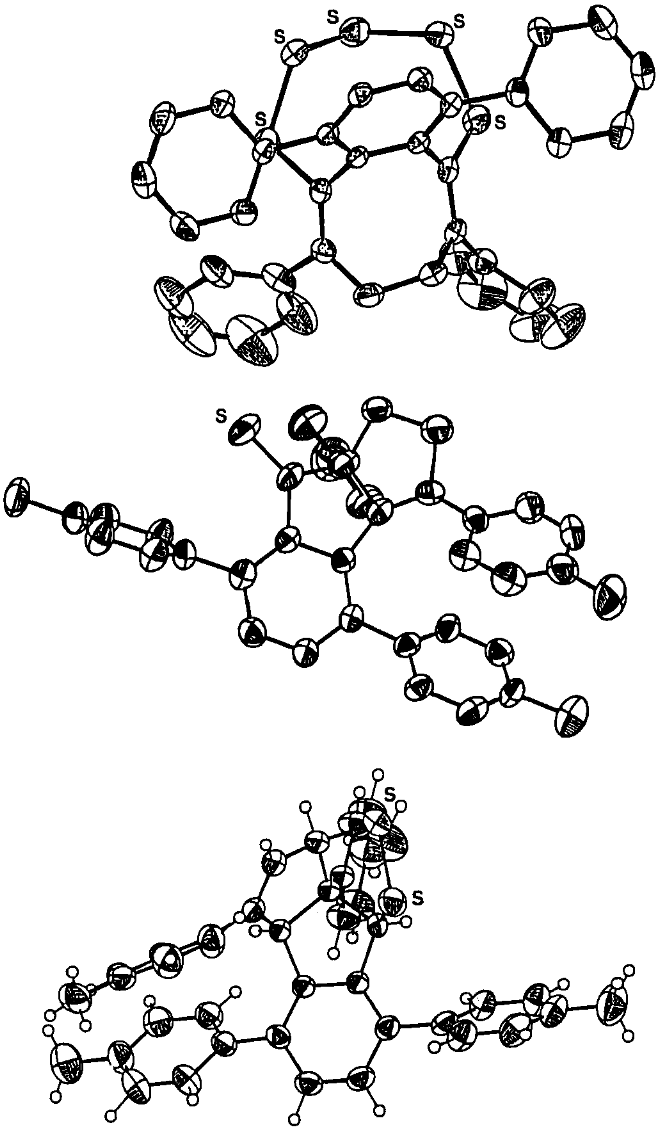
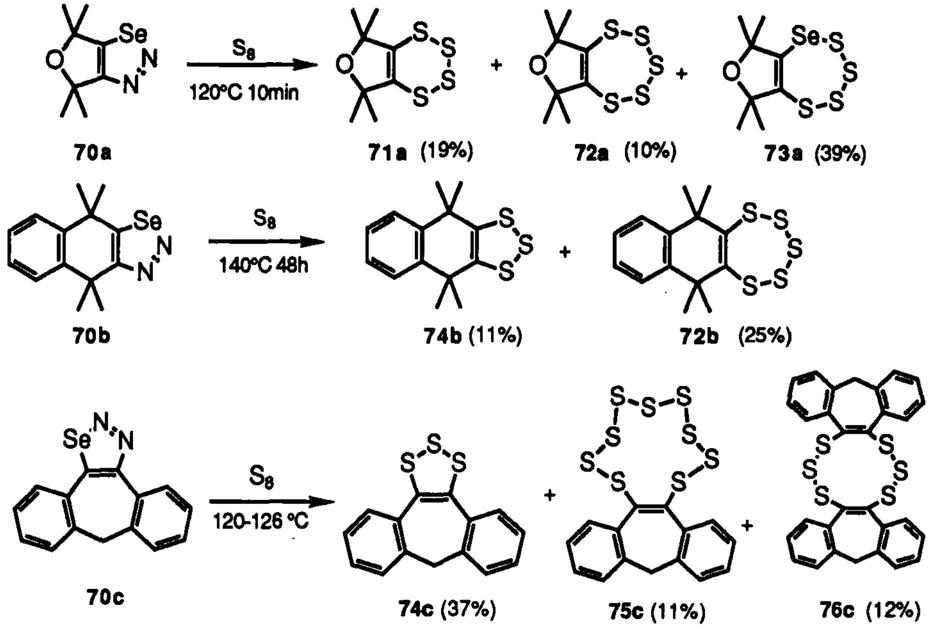


Figure 3. ORTEP Drawings of Sulfurization Products of Cyclododecahexaenes (**64**), **65a** (top), **67b**(middle) and **68b**(bottom).

and **64b** in the presence of an equimolar amount of DBU in DMF at 120 °C resulted in a formation of quite different products, *i.e.* cyclopentenethiones **67a** and **67b** in 22 and 27% yields, respectively. The characteristic color and low field ^{13}C-NMR signals of **67a** [λ_{max} = 599 nm, δ = 248.05 ppm] and **67b** [λ_{max} = 579 nm, δ = 248.65 ppm] are considered to be associated with their conjugated thiocarbonyl unit. The final structure of **67b** was also determined by X-ray crystallographic analysis as shown in Figure 3. The formation mechanism of **65** from **64** can be rationalized by the initial attack of the activated sulfur radical to the cumulenic *sp* carbon of **64** followed by the transannular bridging of the resulting radical reaction centers to another cumulenic unit as illustrated above. Subsequent dehydrogenation by the excess sulfur radicals might result in the final aromatization step leading to the new benzene ring formation. Meanwhile, the cyclopentenethione formation form **64** with S_8/DBU seems to include some ionic sulfur species, since the treatment of once isolated pentasulfide **65b** with DBU under similar reaction conditions did not afford any thiocarbonyl compound but an unusual fused dithiolane **68b** and tetrasulfide **69b** depending on the temperature. In addition, the flow pyrolysis of the bridged pentasulfide **65a** was also examined to give novel 1,4,5,8-tetraarylbiphenylene **66a** in 10% yield.

REACTION OF 1,2,3- SELENADIAZOLES WITH ELEMENTAL SULFUR

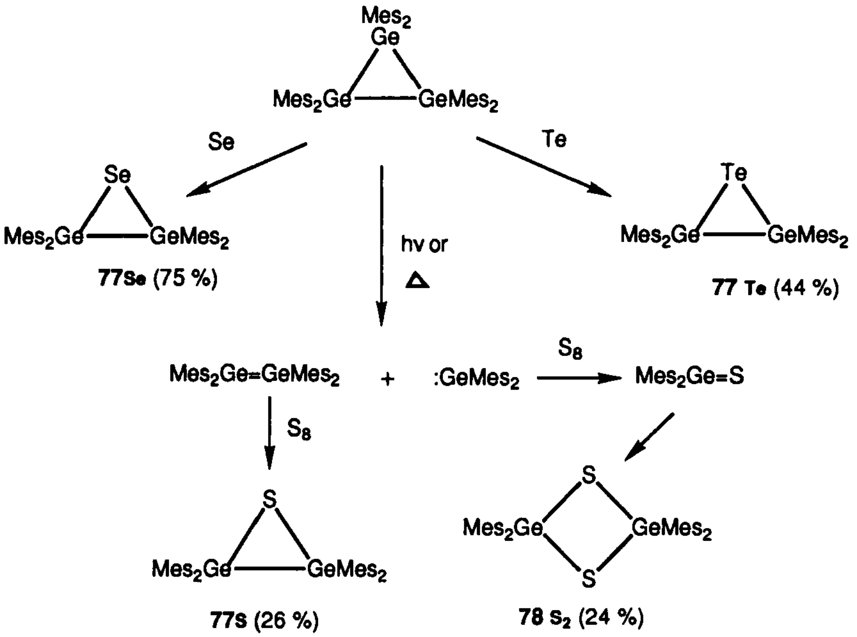
Recent few years have witnessed a number of reports on the synthesis and reactions of new stable cyclic polysulfides. However, most of them are restricted to 1,2,3-trithiole and 1,2,3,4,5-pentathiepin ring systems, and the cyclopolysulfides containing longer sulfur atom linkage than C_2S_5 ring system are much less common. Recently, we have succeeded in the synthesis of novel cyclic polychalcogenides (**71a**,**72a**,**73a**, and **74b**) by the thermal reactions of sterically protected fused 1,2,3-chalcogenadiazoles (**70a** and **70b**) with elemental sulfur.[28, 29] To elucidate the effect of the ring strain and bulkiness of the fused part on the sulfurization of fused 1,2,3-selenadiazole, we have examined the thermal reaction of 8,8-dibenzo[3,4;6,7]cyclohepta[1,2-*d*][1,2,3]selenadiazole **70c** with elemental sulfur.[30] We wish to present here the first synthesis of stable 1,2,3,4,5,6,7,8,9-nonathiacycloundec-10-ene **75c** form **70c**. When the selenadiazole **70c** was treated with an excess amount of molten sulfur at 120-125 °C for 10 h under nitrogen atmosphere, a complicated mixture of sulfurization products was obtained after the separation of excess sulfur. By an exhaustive chromatographic separation (HPLC and TLC) and recrystallization (from hexane), three kinds of cyclopolysulfides, 1,2,3,4,5,6,7,8,9-nonathiacycloundec-10-ene (**75c**; 11%), 1,2,3-trithiole (**74c**; 37%),



and 1,2,3,6,7,8-hexathiecin (**76c**; 7%) were isolated in a stable and colored crystalline form. Although the 1,2,3-trithiole **74c** and 1,2,3,6,7,8-hexathiecin **76c** were thermally stable even in refluxing *o*-dichlorobenzene, nonathiacycloundecene **75c** was fairly labile on heating at 130 °C in *o*-dichlorobenzene to afford an equilibrated mixture of several kinds of polysulfides, the ratio of which was almost the same as that of the crude mixture obtained by the reaction of 1,2,3-selenadiazole **70c** with elemental sulfur. Similar equilibrated mixture of cyclopolysulfides was also obtained by the reaction of 1,2,3-trithiole **74c** with excess amount of molten sulfur at 130 °C. The formation mechanism of these unique cyclopolysulfides from **70c** can be rationalized by the initial attack of the activated sulfur radical to the selenium atom of **70c** followed by the denitrogenation and cyclization leading to the intermediary cyclopolychalcogenide involving selenium. Meanwhile, we have already reported the relative instability of 1,2,3,4,5-tetrathiaselenepin in compared with the corresponding 1,2,3,4,5-pentathiepin resulting in a facile formation of 1,2,3,4-tetrathiin . Therefore, ready thermal deselenation of the intermediate and the subsequent ring closure, dimerization, and/or further reaction with excess activated sulfur radical might result in the final formation of the stable cyclopolysulfides **75c**, **74c**, and **76c**. Successful isolation of these novel cyclopolysulfides without any bulky substituent suggests that the conjugation of the dibenzocycloheptatriene moiety with the polysulfur chain is effective enough to stabilize the cyclopolysulfide ring systems and steric protection is not always essential to the formation and isolation of cyclopolysulfides. The formation of 75c is of great interest as the first example of cyclopolysulfide with an unprecedentedly long sulfur chain, and the molecular structure of 35c was finally determined by X-ray crystallographic analysis.

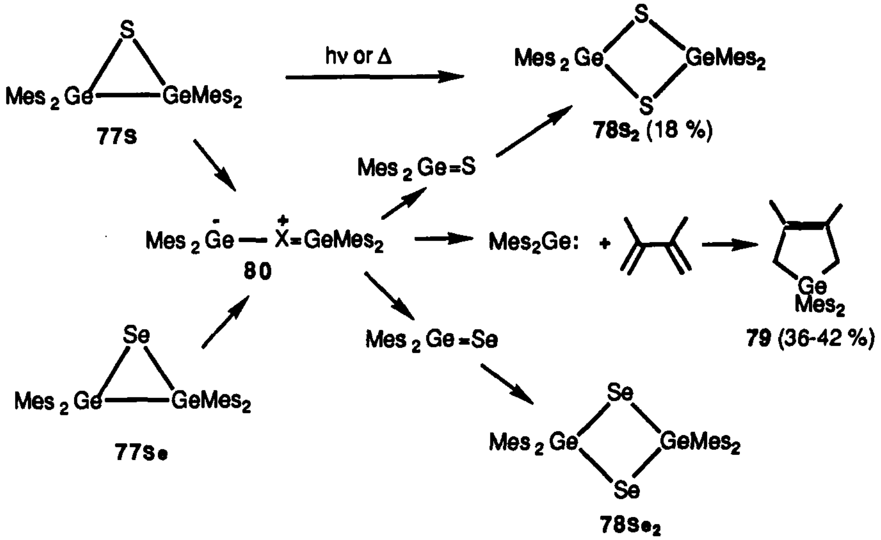
SULFURIZATION OF REACTIVE GERMANIUM AND SILICON SPECIES

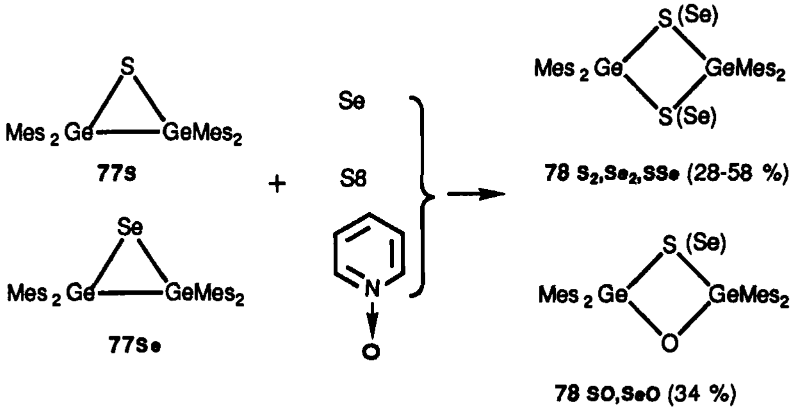
There has been a great interest in the chemistry of stable dimetallene and cyclotrimetallane of group 14 elements for the synthesis of novel heterocyclic systems. Recently the bulky substituted stabilized digermiranes and cyclotrigermanes have been studied on the addition and insertion reactions with a variety of reagents. Here we wish to present novel reactions of digermene and cyclotrigermanes with sulfur, selenium and tellurium. Photolysis or thermolysis of hexamesitylcyclotrigermane with elemental sulfur produced the thiadigermirane (77S) along with dithiadigermetane (78S$_2$).[31] The products 77S and



78S$_2$ are best rationalized as arising from tetramesityldigermene and dimesitylgermylene generated from the fragmentation of cyclotrigermane. Digermene would be expected to react with elemental sulfur to afford 77S.

The formation of dithiadigermetane 78S$_2$ involves the reaction of dimesitylgermylene and

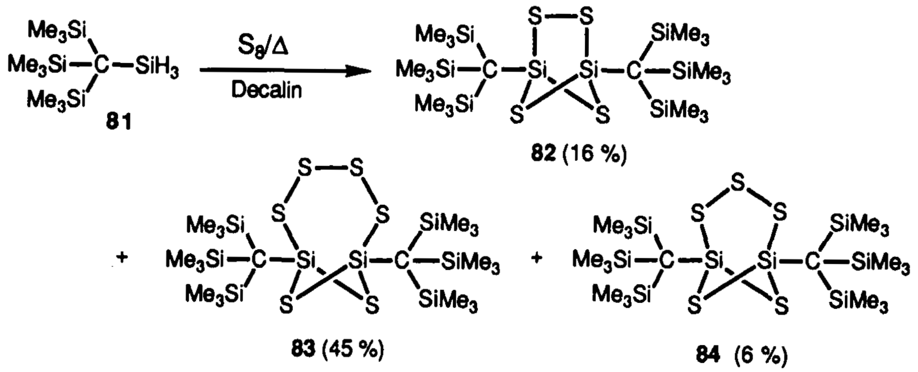


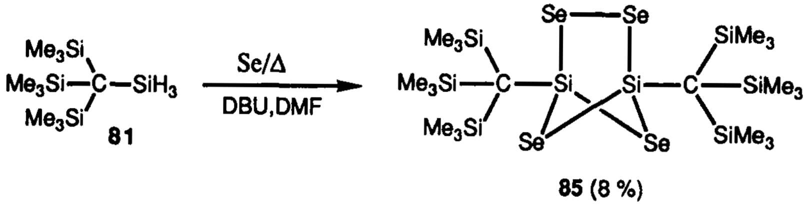


sulfur to dimesitylgermanethione followed by its dimerization in a head-to-tail fashion. Similarly, reactions of cyclotrigermane with selenium and tellurium also gave the selenadigermirane (**77Se**) and telluradigermirane (**77Te**) respectively. Photolysis or pyrolysis of **77S** and **77Se** with 2,3-dimethyl-1,3-butadiene resulted in the formation of germacyclopentene (**79**) and thia- or selenadigermetane (**78S**$_2$ or **78Se**$_2$). The compound **79** arises from addition of dimesithylgermylene to the butadiene and **78S**$_2$ or **78Se**$_2$ is produced by the dimerization of dimesitylgermanethione. The common intermediate for dimesityl digermylene and dimesitylgermanethione appears to be germylene germanethione ylide (**80**). Although **77S** and **70Se** is fairly air stable, the Ge-Ge bond of **77S** and **77Se** was easily oxidized to 1,3-oxathia- or 1,3-oxaselenadigermetane (**78SO** or **78SeO**) by treating **77S** and **77Se** with pyridine

N-oxide in benzene at 80 °C. Elemental sulfur and selenium also reacted with **77S** and **77Se** in refluxing toluene to give the corresponding ring expansion products **78S$_2$**, **78Se$_2$** and **78SSe**, respectively.

Trihydrosilane bearing bulky substituent is known to react with sulfur and selenium under





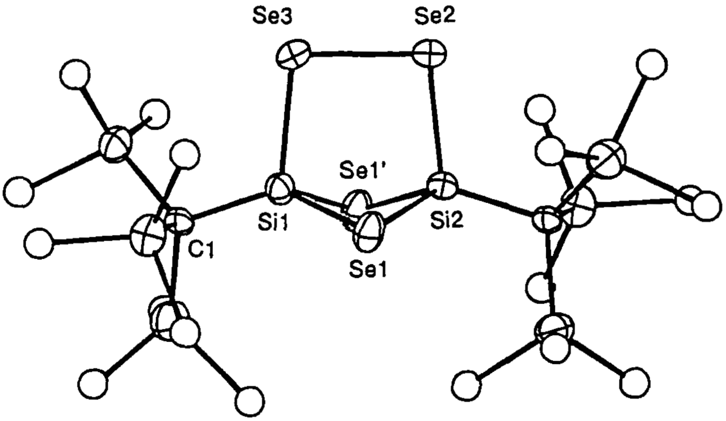


Figure 4. ORTEP Drawing of **85**. Selected bond lengths (Å) and angles (degree). Si(1)-Se(1), 2.252; Si(2)-Se(1), 2.234; Si(1)-Se(3), 2.325; Si(1)-Se(1'), 2.331; Si(2)-Se(1'), 2.312; Si(2)-Se(2), 2.294; Se(2)-Se(3), 2.353; Si(1)-C(1), 1.855; Si(1)-Si(2), 2.820. Si(1)-Se(1)-Si(2), 77.9; Si(1)-Se(1')-Se(2), 74.8; Se(1)-Si(1)-Se(1'), 95.9; Se(1)-Si(1)-Se(3), 100.9; Si(1)-Se(3)-Se(2), 95.7; Si(2)-Se(2)-Se(3), 95.9; Se(1)-Si(2)-Se(2), 100.9.

appropriate conditions to give the cage molecule such as adamantane type silthiane . We found that introduction of trisyl group prevent the silyne unit from oligomerization to yield disilatetrathiabicyclo[2.1.1]hexane(**82**), disilatetraselena[2,1,1]hexane(**85**), disilapentathiabicyclo[3.1.1]heptane (**84**) and disilahexathiabicyclo[4.1.1]octane (**83**).[32] Among them, the structure of **85** was confirmed by X-ray analysis as shown in figure 4. Interestingly, in the presence of sulfur the thermal equilibration between **82** and **83** was observed.

ACKNOWLEDGEMENTS:

The authors are grateful to the collaborators who actually did the work discussed in this article, Dr. Y. Hanyu, Dr. T. Furuhata, Dr. T. Tsumuraya, Dr. H. Yoshida, Mr. A.Itami, Mr. H. Hayakawa, Miss N. Choi, Miss T. Suzuki, Mr. Y. Okano, Miss M. Noguchi, and Mr. S.Imai. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area from the Ministry of Education, Science and Culture of Japan.

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