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Preparation and Reactivity of 1,3-Bis(alkylthio)allenes and Tetrathiacyclic Bisallenes

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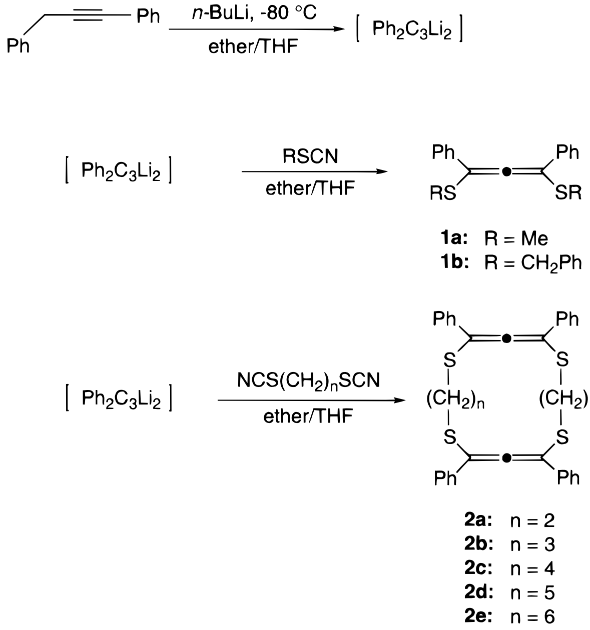
Reactions of Ph_2C_3 dianion, prepared from 1,3-diphenylpropyne and *n*-butyllithium, with alkyl thiocyanates or alkane dithiocyanates gave 1,3-bis(alkylthio)allenes **1** or tetrathiacyclic bisallenes **2**, respectively. Thermal reactions of **1** gave thiophenes **4** and **7**, benzothiepin **5**, 1,2-bis(benzylidene)-cyclobutane **6**, thiete **8**, and α,*β*-unsaturated ketone **9**, and the reactions of tetrathiacyclic bisallenes **2a** gave a cyclic dimer, 1,2-bis(benzylidene)cyclobutane derivative **10**, quantitatively. Irradiation of 1,3-bis(alkylthio)allenes **1** and tetrathiacyclic bisallenes **2a** caused rearrangement to give alkynes **18**, **20**, and **21**. In the irradiation of the cyclic bisallenes **2a**, isomerizations from *dl* to *meso* and *meso* to *dl* isomers were also found. In the reactions of allenes **1** and cyclic bisallenes **2a** with diphenyl diazomethane, the diazomethane reacted selectively with the double bond rather than with the sulfur atom.

Introduction

Allenes are reactive species with cumulated double bonds and are useful intermediates for organic synthesis. Many studies have been performed on their preparation and reactivity.[1−3] Allenes substituted by heteroatoms, such as silicon, phosphorus, and sulfur atoms, have also received attention.[3] Among the sulfur-substituted allenes, mono-,[4,5] 1,1-bis-,[6] tris-,[7] and tetrakis(alkylthio)allenes[7] were synthesized in the 1960s. However, few of their reactivities have been clarified, except for isomerization between the allenes and acetylenes. We succeeded in preparing 1,3-bis(alkylthio)allenes by reacting Ph_2C_3 dianion with the corresponding alkyl thiocyanates, and the introduction of alkylthio groups to the 1- and 3-positions of allenes was found to strongly influence their reactivities. It has also been found that the thermal reactions of 1,3-bis(alkylthio)allenes gave thiophene, benzothiepin, cyclobutane, thiete, and α,*β*-unsaturated ketone derivatives. In this paper, we report the preparation and some reactivities, such as the thermal reaction, photochemical reaction, and reaction with diphenyl diazomethane, of 1,3-bis(alkylthio)allenes and tetrathiacyclic bisallenes.[8]

Scheme 1



Results and Discussion

Preparation of 1,3-Bis(alkylthio)allenes and Tetrathiacyclic Bisallenes. When a THF solution of 2 equiv of methyl thiocyanate was added dropwise to Ph_2C_3 dianion (1,3-dilithiated allene), prepared from 1,3-diphenylpropyne and *n*-butyllithium in ether/THF solution,[9] at −80 °C and allowed to warm to room temperature, 1,3-bis(methylthio)-1,3-diphenylpropadiene (**1a**) was obtained in 62% yield (Scheme 1). A similar reaction of the

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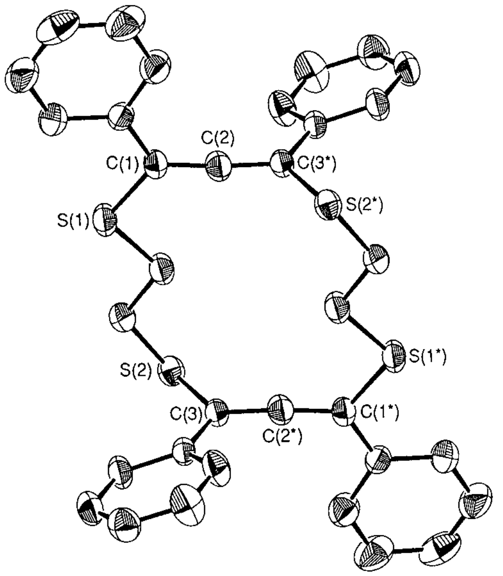
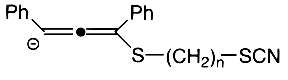


Figure 1. Crystal structure of *meso*-**2a** showing 50% probability displacement ellipsoids with hydrogen atoms removed for clarity; selected bond lengths (Å) and bond angles (deg): S(1)−C(1), 1.7753(7); C(1)−C(2), 1.3095(8); C(2)−C(3*), 1.3162(8); S(2*)−C(3*), 1.7873(7); S(1)−C(1)−C(2), 122.26(6); C(1)−C(2)−C(3*), 175.73(9); S(2*)−C(3*)−C(2), 117.85(6).

dianion with benzyl thiocyanate gave 1,3-bis(benzylthio)-1,3-diphenylpropadiene (**1b**) in 88% yield. 3,3-Bis(alkylthio)-1,3-diphenylpropyne, the formation of which is also anticipated from the reaction, was not obtained in either reaction, whereas reaction of the Ph_2C_3 dianion with ethyl bromide under similar conditions yielded 3,3-diethyl-1,3-diphenylpropyne in 63% yield together with 14% of the 1,3-diethyl-1,3-diphenylpropadiene.

Reaction of the Ph_2C_3 dianion with ethane 1,2-dithiocyanate formed 14-membered cyclic bisallene **2a** in 21% yield (*dl*/*meso* = 41/59), although the reaction with methylene dithiocyanate did not give the corresponding cyclic bisallene. The stereochemistry of one isomer of the cyclic bisallenes, *meso*-**2a**, was determined by X-ray crystallographic analysis, as shown in Figure 1.[8] The bond lengths are almost normal, and the bond angle C(1)−C(2)-C(3*) and torsion angle S(1)−C(1)−C(3*)−S(2*) are 176 and 94°, respectively, indicating a strain-free geometry. Similarly, larger sulfur-substituted cyclic bisallenes **2b**−**e** were also obtained in yields of 25% (*dl*/*meso* = 64/36), 20% (*dl*/*meso* = 75/25), 14% (*dl*/*meso* = 24/76), and 13% (*dl*/*meso* = 67/33), respectively, by reacting the dianion with corresponding alkane dithiocyanates. The structures and the ratios of the *dl*- and *meso*-isomers of **2b**−**e** were estimated by comparison of their ^{13}C NMR spectra with those of *dl*- and *meso*-**2a**. Cyclic monoallenes, which were expected to be formed when using longer alkane dithiocyanates, were not obtained in any of the reactions, whereas the reaction of the dianion with 1,8-dibromooctane gave 1,3-diphenylundeca-1,2-diene although the yield was low (7% yield). The lack of formation of the cyclic monoallene is perhaps due to the conformation in the ring-closure reaction because the reaction of the dianion with 0.5 equiv of methyl thiocyanate gave a ca. 1:1 mixture of the mono(methylthio)allene and the bis(methylthio)allene, and this result indicates that the reactivity of the anion **3** is not low.



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Thermal Reaction of 1,3-Bis(alkylthio)allenes and Tetrathiacyclic Bisallenes. Cyclodimerization reactions of allenes are well-known,[2,10,11] and tetrakis(methylthio)allene[7] and 1,1-bis(alkylthio)allene[12] have also been reported to undergo dimerization even at room temperature to give cyclic dimers. However, 1,3-bis(methylthio)allene **1a** and 1,3-bis(benzylthio)allene **1b** were stable at room temperature. When a *p*-xylene solution of **1a** was refluxed for 3 days, 68% of **1a** was consumed and 2,4-diphenyl thiophene (**4**),[13] 1,3-dihydro-2-benzothiepin **5**, and 1,2-bis(methylthiobenzylidene)-cyclobutane **6** were obtained in 30, 18, and 8% yields, respectively (Scheme 2). The position of the double bond for the thiepin ring of **5** was determined by HMBC NMR measurements. A stereoisomer of **6** was also obtained in this reaction in 8% yield, which showed C_2 or C_s symmetry on ^1H and ^{13}C NMR spectra, although the stereochemistry could not be clarified. The stereochemistry of **6** was determined by X-ray crystallographic analysis, as shown in Figure 2, which showed a trans geometry for the two methylthio groups on the cyclobutane ring and a cis geometry for the olefins. In addition, the crystal was found to be racemic and the cyclobutane ring was nearly planar; dihedral angles in the ring were 4.2−4.6°. 1,3-Bis(benzylthio)allene **1b** also readily underwent a thermal reaction to give 2,3,5-triphenylthiophene (**7**),[14] thiete **8**, and α,*β*-unsaturated ketone **9** in 63, 5, and 11% yields, respectively, under reflux in *p*-xylene for 1 h. It is clear that the thermal reaction of 1,3-bis(alkylthio)allenes is affected by the substituents on the sulfur atoms.

The thermal reaction of cyclic bisallene *dl*-**2a** caused intramolecular cyclization, rather than other reactions found in the case of compounds **1,** to give tricyclic compound **10** in quantitative yield. The isomer *meso*-**2a** also gave an identical compound stereoselectively and quantitatively under similar conditions. In both cases, head-to-head cycloadduct **10** was obtained with the same

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(10) For examples, see: (a) Lebedev, S. V. *J. Russ. Phys. Chem. Soc.* **1913**, *45*, 1249; *Chem. Abstr.* **1914**, *8*, 320. (b) Blomquist, A. T.; Verdol, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 109. (c) Williams, J. K.; Sharkey, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 4269. (d) Pilgram, K.; Korte, F. *Tetrahedron Lett.* **1962**, 883. (e) Roedig, A.; Bischoff, F.; Heinrich, B.; Markl, G. *Ann. Chem.* **1963**, *670*, 8. (f) Slobodin, Y. M.; Khitrov, A. P. *J. Gen. Chem. USSR* **1963**, *33*, 146. (g) Slobodin, Y. M.; Khitrov, A. P. *J. Gen. Chem. USSR* **1963**, *33*, 2748. (h) Roedig, A.; Detzer, N.; Friedrich, H. J. *Angew. Chem.* **1964**, *76*, 379. (i) Fischer, H.; Fischer, H. *Chem. Ber.* **1964**, *97*, 2975. (j) Banks, R. E.; Haszeldine, R. N.; Taylor, D. R. *J. Chem. Soc.* **1965**, 978. (k) Skattebøl, L.; Solomon, S. *J. Am. Chem. Soc.* **1965**, *87*, 4506. (l) Gajewski, J. J.; Shih, C. N. *J. Am. Chem. Soc.* **1969**, *91*, 5900. (m) Jacobs, T. L.; McClenon, J. R.; Muscio, O. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 6038. (n) Gajewski, J. J.; Black, W. A. *Tetrahedron Lett.* **1970**, 899. (o) Jacobs, T. L.; Muscio, O. J., Jr. *Tetrahedron Lett.* **1970**, 4829. (p) Dolbier, W. R., Jr.; Dai, S.-H. *J. Am. Chem. Soc.* **1970**, *92*, 1774. (q) Gajewski, J. J.; Shih, C. N. *J. Org. Chem.* **1972**, *37*, 64. (r) Dai, S.-H.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3946.

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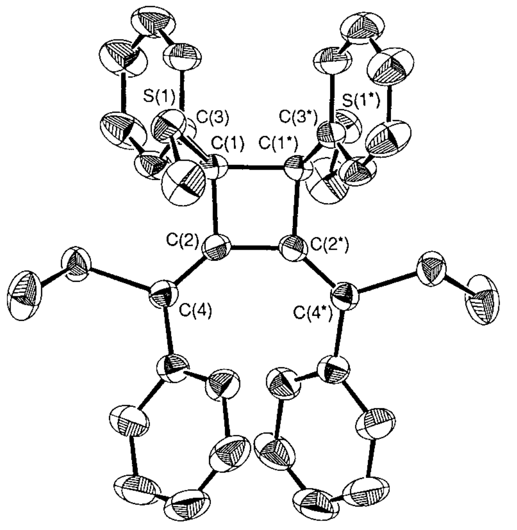
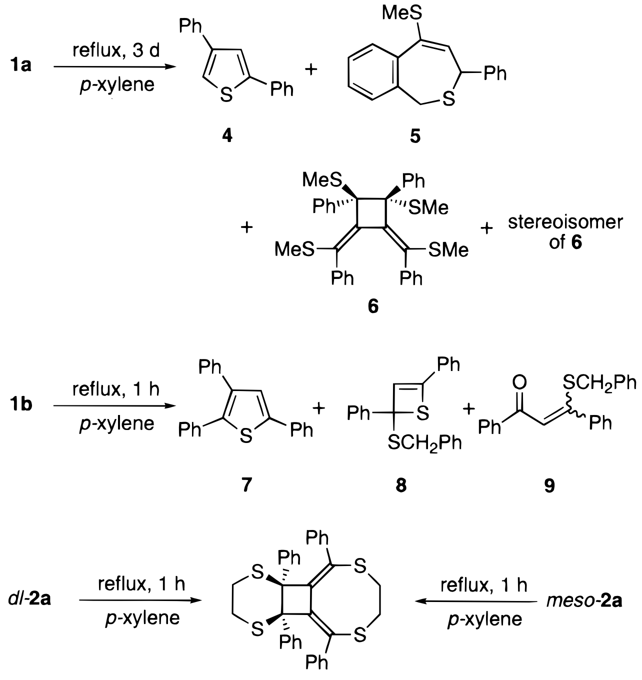


Figure 2. Crystal structure of **6** showing 50% probability displacement ellipsoids with hydrogen atoms removed for clarity; selected bond lengths (Å), bond angles (deg) and dihedral angles (deg): C(1)−C(1*), 1.620(4); C(1)−C(2), 1.533(4); C(2)−C(2*), 1.467(4); C(1)−S(1), 1.851(4); C(1)−C(3), 1.520(5); C(2)−C(4), 1.356(4); C(1*)−C(1)−C(2), 87.1(2); C(1)−C(2)−C(2*), 92.8(2); C(1*)−C(1)−C(3), 115.5(3); C(2)−C(1)−C(3), 119.2(3); C(2)−C(1)−S(1), 114.7(3); C(1)−C(2)−C(4), 129.1(3); C(2*)−C(2)−C(4), 137.6(3); C(2)−C(1)−C(1*)−C(2*), 4.2(3); C(1*)−C(1)−C(2)−C(2*), −4.3(3); C(1)−C(2)−C(2*)−C(1*), 4.6(3); C(3)−C(1)−C(1*)−C(3*), 121.9(3); S(1)−C(1)−C(1*)−S(1*), −123.4(2); C(4)−C(2)−C(2*)−C(4*), 21.2 (9).

Scheme 2



stereochemistry, and the crystal structure of tricyclic compound **10** is given in Figure 3. The crystal structure showed that the ethane dithiolate was fused to the cyclobutane ring with cis geometry, in contrast to that of **6**. The cyclobutane ring had a nonplanar geometry; dihedral angles in the ring were 14.7−16.4°. The geometries of olefin moieties were trans, and the two double bonds were not conjugated; dihedral angle C(5)−C(2)-C(3)−C(6) = −36°.

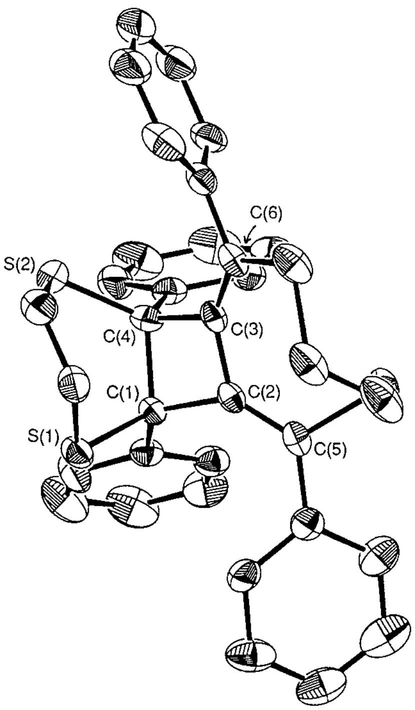
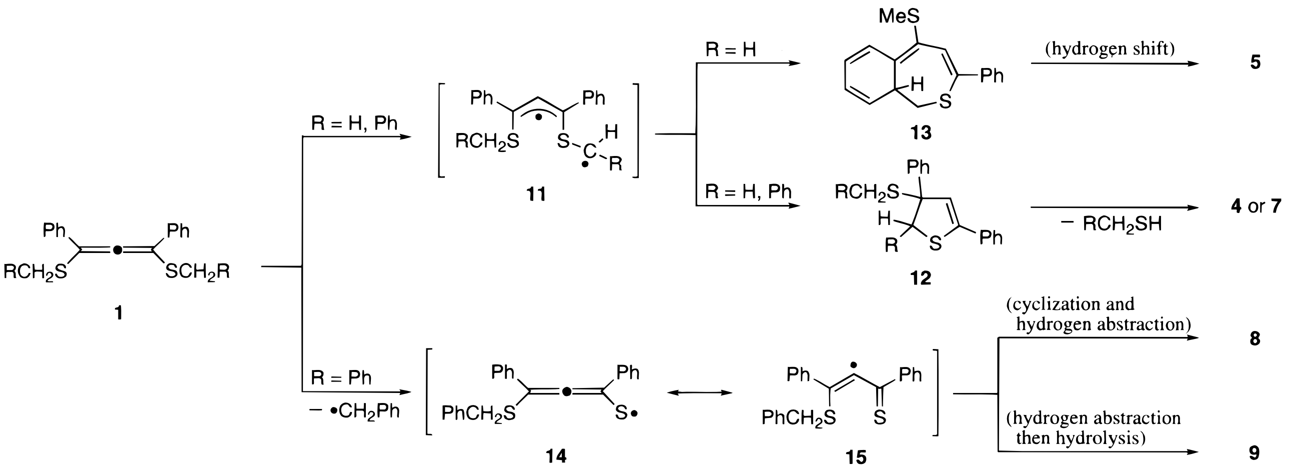


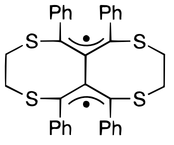
Figure 3. Crystal structure of **10** showing 50% probability displacement ellipsoids with hydrogen atoms removed for clarity; selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): C(1)−C(2), 1.535(9); C(1)−C(4), 1.63(1); C(2)−C(3), 1.46(1); C(3)−C(4), 1.544(9); C(1)−S(1), 1.852(7); C(2)−C(5), 1.33(1); C(3)−C(6), 1.34(1); C(4)−S(2), 1.812(8); C(2)−C(1)−C(4), 85.4(5); C(1)−C(2)−C(3), 92.9(5); C(2)−C(3)−C(4), 91.0(5); C(1)−C(4)−C(3), 86.4(5); C(4)−C(1)−C(2)−C(3), 15.5(5); C(2)−C(1)−C(4)−C(3), −14.7(5); C(1)−C(2)−C(3)−C(4), −16.4(6); C(2)−C(3)−C(4)−C(1), 15.4(5); S(1)−C(1)−C(4)−S(2), −21.2(6); C(5)−C(2)−C(3)−C(6), −36(1).

To examine the reaction mechanism, the thermal reaction of **1a** was carried out in the presence of 1.5 equiv of 1,1-diphenyl-2-picryl hydrazyl (DPPH). After refluxing for 3 days, compounds **4**, **5**, and **6**, which were obtained by the thermal reaction of **1a**, were not detected. In the case of **1b**, addition of 2.5 equiv of DPPH also inhibited the formation of **8** (<1%) and **9** (trace); however, thiophene **7** was obtained in 38% yield. Using 10 equiv of DPPH, thiophene **7** was still formed in 35% yield, although compounds **8** and **9** were not detected. The formation of thiophene **7** can be explained by a fast intramolecular ring-closure reaction in the solvent cage. Thus, the thermal reactions of **1** may proceed via a radical path. One possible mechanism for the formation of thiophene derivatives **4** and **7** is shown in Scheme 3, though the existence of a biradical intermediate could not be clarified. The intramolecular coupling reaction of biradical **11**, generated from **1** by intramolecular hydrogen abstraction, gives dihydrothiophene **12**, and elimination of a thiol gives thiophene **4** or **7**. In the case of **1a** (R = H), a carbon radical of **11** also attacks the ortho position of the phenyl group to yield **13**. Finally, a hydrogen shift of **13** forms 1,3-dihydro-2-benzothiepin **5**. In the case of 1,3-bis(benzylthio)allene **1b** (R = Ph), homolytic cleavage of the carbon−sulfur bond occurs competitively to give thiyl radical **14**, maybe due to the small bonding energy of the sulfur−carbon bond and the stability of the resulting benzyl radical. Intramolecular cyclization of **15** followed by hydrogen abstraction yields thiete **8**. Hydrogen ab-

Scheme 3



straction of **15** followed by hydrolysis gives α,*β*-unsaturated ketone **9**. On the other hand, intramolecular cyclization of *dl*-**2a** and *meso*-**2a** yielded the same compound **10** as a sole product. Therefore, this reaction did not proceed through a concerted path. Tricyclic compound **10** is considered to be formed via 2,2′-bisallyl biradical **16**.[11] Biradical **16** is formed from both the *dl*- and *meso*-isomers **2a**; thus, the tricyclic compound **10** is obtained as a sole product from both isomers. The formation of bismethylidene cyclobutane **6** in the reaction of **1a** can also be explained by a similar mechanism involving the biradical **17**. In this case, two stereoisomers were obtained.



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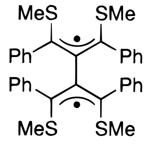

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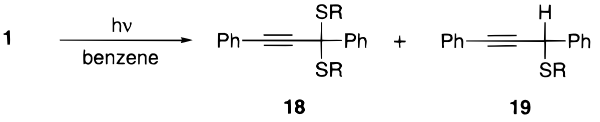
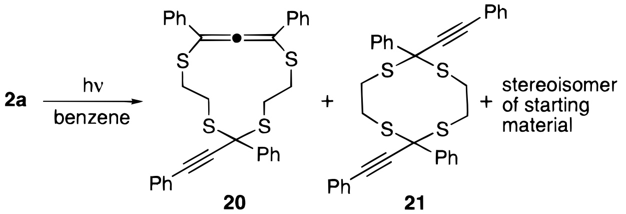
Photochemical Reaction of 1,3-Bis(alkylthio)allenes and Tetrathiacyclic Bisallenes. Irradiation of a benzene solution of allene **1a** through a Pyrex filter gave 3,3-bis(methylthio)-1,3-diphenylpropyne (**18a**) and 3-methylthio-1,3-diphenylpropyne (**19a**) in 13 and 29% yields, as shown in Scheme 4. Similarly, irradiation of allene **1b** yielded bis(methylthio)acetylene **18b** and benzylthioacetylene **19b** in 22 and 23% yields, respectively. Compounds **19** were found to be secondary products from **18** because irradiation of a benzene-d_6 solution of acetylene **18a** yielded compound **19a** (**18a**/**19a** = 3/1 after irradiation for 1 h). Photochemical reaction of cyclic bisallenes *dl*- and *meso*-**2a** also gave rearranged products **20** and **21** from both isomers, and the syn/anti ratios of **21** were ca. 1/1 in both reactions. In these reactions, *meso*-**2a** was also formed from *dl*-**2a**, and *dl*-**2a** was formed from *meso*-**2a**. Cyclopropane derivative,[15,16] which was expected to be formed by the reaction, was not obtained.

Scheme 4



	R	Time (h)	Conversion (%)	Yield (%)[a) 18	Yield (%)[a) 19
1a	Me	3	80	11 (13)	23 (29)
1b	CH$_2$Ph	2.5	89	19 (22)	20 (23)

[a)] In parentheses are conversion yields.



	Time (h)	Conversion (%)	Yield (%)[a) 20	Yield (%)[a) 21	Yield (%)[a) *dl*-2a	Yield (%)[a) *meso*-2a
dl-**2a**	3	94	23 (24)	19 (20)	—	5 (5)
meso-**2a**	2.5	94	21 (22)	22 (23)	6 (6)	—

[a)] In parentheses are conversion yields.

Two possible mechanisms can be considered for this photochemical reaction, as shown in Scheme 5. However, mechanism B involving [1,3]sigmatropic rearrangement via transition state **22** seems to be disadvantageous because the photoisomerization between *dl*-**2a** and *meso*-**2a** cannot be explained since irradiation of **18a** did not give the allene **1a**. Thus, an alternative explanation may be needed for the photorearrangement of **1** (mechanism A). A photoinduced 1,2-rearrangement of the alkylthio group of **1** forms carbene **24** via biradical **23**. Further rearrangement of the alkylthio group of **24** yields acetylene derivative **18**. Photochemical rearrangement of **2a** may also proceed through a similar stepwise mechanism, and photoisomerization of **2a** can be explained as a result of a reverse reaction from the carbene or the biradical.[16]

Reaction of 1,3-Bis(alkylthio)allenes and Tetrathiacyclic Bisallenes with Diphenyl Diazomethane. When a benzene solution of 1,3-bis(methylthio)allene **1a** and diphenyl diazomethane was refluxed for 14 h, 65% of **1a** was consumed and *cis*-butadiene derivative **25** was obtained in 79% yield (Scheme 6). The cis geometry of

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(15) *For examples, see:* (a) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 2492. (b) Murray, R. I.; Sligar, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 2186. (c) Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3963. (d) Price, J. D.; Johnson, R. P. *J. Org. Chem.* **1991**, *56*, 6372.

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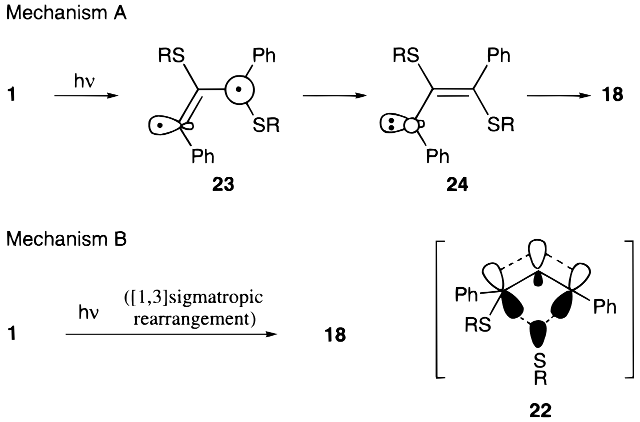
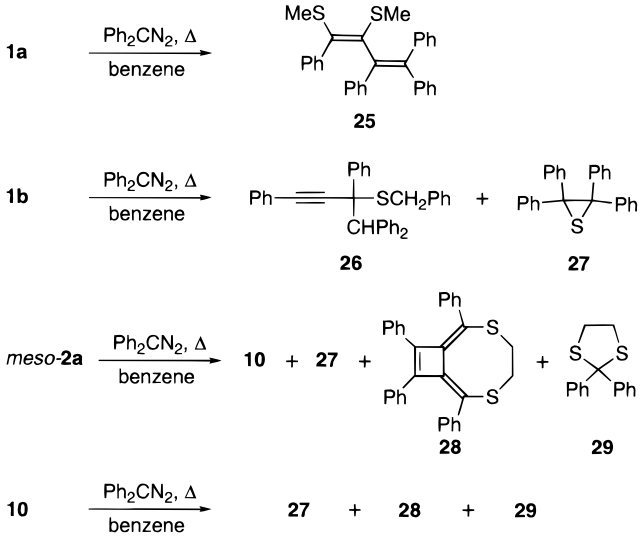
Scheme 5

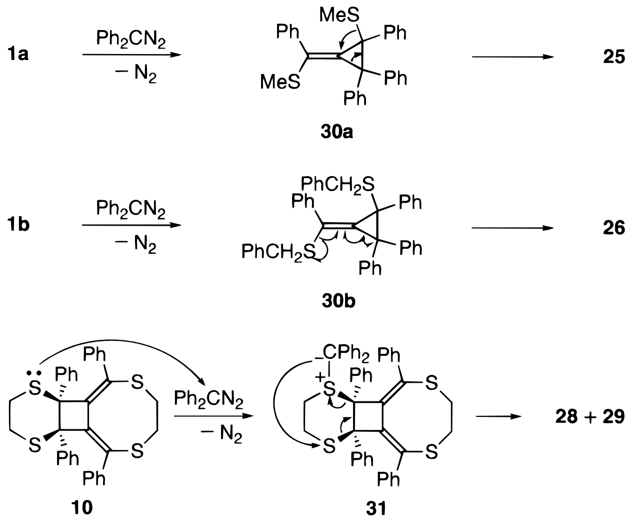


Scheme 6



25 was confirmed by X-ray crystallographic analysis. In the case of allene **1b**, the corresponding butadiene did not form, but 3-benzylthio-1,3,4,4-tetraphenyl-1-butyne (**26**) and episulfide **27** were obtained in 11 and 87% yields, respectively. The alkylidenecyclopropane derivative was not obtained in either reaction, whereas carbon-substituted allenes are known to react with diphenyl diazomethane to give alkylidenecyclopropane derivatives.[18,19] Heating a benzene solution of cyclic bisallene *meso*-**2a** with diphenyl diazomethane gave episulfide **27**, bicyclic compound **28**, and 1,3-dithiolane **29**[17] in 12, 17, and 13% yields, respectively, together with intramolecular cyclization product **10** (48%). In this reaction, the thermal cyclization reaction must occurred in preference to the reaction with diphenyl diazomethane, and products **28** and **29** are considered to be formed as secondary products. In fact, heating a benzene solution of tricyclic compound **10** with diphenyl diazomethane yielded compounds **28** and **29** in 41 and 29% yields, respectively, together with 20% yield of **27**.

Scheme 7



The first step in this reaction is 1,3-dipolar addition of diphenyl diazomethane to the double bond of **1** to give benzylidene cyclopropane derivatives **30** via a five-membered cycloadduct and the subsequent elimination of nitrogen (Scheme 7). In the case of **1a**, the ring-opening reaction of **30a** proceeds with migration of the methylthio group on the cyclopropane ring to give butadiene derivative **25**. On the other hand, in the case of **1b**, the ring-opening reaction of **30b** with elimination of the benzylthio radical followed by hydrogen abstraction yielded acetylene derivative **26**. This behavior may be due to the stability of the benzylthio radical. The product **28** in the reaction of tricyclic compound **10** with diphenyl diazomethane may be accounted for by formation of ylide **31** as an intermediate. In compound **10**, the carbon−carbon double bond may be less reactive than the sulfur atom toward diphenyl diazomethane. The subsequent intramolecular rearrangement of ylide **31** will give products **28** and **29**. Episulfide **27** may be obtained by the further reaction of diphenyl diazomethane and thiobenzophenone, formed by the addition of diphenyl diazomethane and sulfur generated by side reactions from the substrates.[20]

Conclusion

1,3-Bis(alkylthio)allenes and tetrathiacyclic bisallenes could be obtained by the reaction of Ph_2C_3 dianion with the corresponding alkyl thiocyanates and alkane dithiocyanates, respectively. The thermal reaction of 1,3-bis(alkylthio)allenes mainly afforded thiophene derivatives, and the reaction of tetrathiacyclic bisallenes gave a cyclic dimer, 1,2-bis(benzylidene)cyclobutane derivative, quantitatively. Irradiation of 1,3-bis(alkylthio)allenes and tetrathiacyclic bisallenes caused intramolecular rearrangement to give alkynes. Irradiation of the tetrathiacyclic bisallenes also yielded *dl*- and *meso*-isomerized products. Furthermore, the diphenyl diazomethane reacted with the double bonds rather than the sulfur atoms of sulfur-substituted allenes.

Experimental Section

General Methods. TLC was performed with Merck Art. 5554 DC-Alufolien Kieselgel 60 F_{254}. Column chromatography

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[17] Sondej, S. C.; Katzenellenbogen, J. A. *J. Org. Chem.* **1986**, *51*, 3508.

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[19] For examples, see: (a) Blomquist, A. T.; Connolly, D. J. *Chem. Ind.* **1962**, 310. (b) Heinrich, F.; Lüttke, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 234. (c) Fitjer, L.; Conia, J. M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 332. (d) Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611. (e) Kaufmann, D.; de Meijere, A. *Chem. Ber.* **1984**, *117*, 1128.

[20] Schönberg, A.; Frese, E. *Ber.* **1962**, *95*, 2810.

was performed with Merck silica gel 60. Gel-permeation chromatography (GPC) was performed using JAI LC-08 and JAI LC-908 recycling liquid chromatographs with two JAI-GEL-1H columns (20 mm × 600 mm) with chloroform as eluent. All solvents were distilled and stored under nitrogen. Reactions in benzene solution were carried out in a hood.

General Procedure for Preparation of 1,3-Bis(alkylthio)allenes and Tetrathiacyclic Bisallenes. To an ether−THF solution (20 mL/20 mL) of 1,3-diphenylpropyne (1.00 g, 5.21 mmol)[21] was added dropwise at −80 °C *n*-butyllithium (1.59 mol/L, 6.4 mL, 10.2 mmol) under nitrogen, and the solution was stirred for 2 h. A THF solution (20 mL) of alkyl thiocyanate (12.0 mmol) or alkane dithiocyanate (5.70 mmol) was added dropwise to the solution and allowed to warm to room temperature. Water (100 mL) was added to the solution, and products were extracted with ether. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After removal of solvent in vacuo, the residue was subjected to gel-peameation chromatography (GPC). **1a**: 62%; **1b**: 88%; **2a**: 21%; **2b**: 25%; **2c**: 20%; **2d**: 14%; **2e**: 13%.

1,3-Bis(methylthio)-1,3-diphenylpropadiene (1a): yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 6H), 7.26−7.59 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 116.9, 126.4, 128.4, 128.5, 135.0, 194.7; IR (neat) ν_{max} 3050, 3025, 2980, 2910, 1905, 1650, 1630, 1595, 1575, 1550, 1490, 1445, 1310, 1225, 1175, 1075, 1025, 960, 885, 755, 685 cm^{-1}; UV (cyclohexane) λ_{max} 229 (ϵ 2.9 × 10^4), 286 (ϵ 2.3 × 10^4) nm; MS *m/z* 284 (M$^+$, 20), 237 (100), 222 (40), 191 (27). Anal. Calcd for $C_{17}H_{16}S_2$: C, 71.78; H, 5.67. Found: C, 71.92; H, 5.42.

1,3-Bis(benzylthio)-1,3-diphenylpropadiene (1b): pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (d, 2H, J = 13.2 Hz), 3.74 (d, 2H, J = 13.2 Hz), 7.13−7.47 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.9, 113.7, 126.5, 127.1, 128.3, 128.4, 128.5, 129.0, 134.6, 137.1, 197.3; IR (neat) ν_{max} 3055, 3030, 2955, 2930, 1910, 1600, 1495, 1450, 1070, 1030, 860 cm^{-1}; UV (cyclohexane) λ_{max} 228 (ϵ 2.8 × 10^4), 289 (ϵ 1.6 × 10^4) nm; MS *m/z* 345 (M$^+$ − CH_2Ph, 45), 313 (100), 255 (21), 222 (13), 190 (7), 123 (5), 91 (56). Anal. Calcd for $C_{29}H_{24}S_2$: C, 79.77; H, 5.54. Found: C, 79.94; H, 5.40.

***dl*-1,3,8,10-Tetraphenyl-4,7,11,14-tetrathiacyclotetradeca-1,2,8,9-tetraene (*dl*-2a):** mp 144−145 °C (colorless powder from dichloromethane−hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.07 (s, 8H), 7.27 (tt, 4H, J = 1.5, 7.3 Hz), 7.32 (ddd, 8H, J = 1.5, 7.3, 7.3 Hz), 7.53 (dd, 8H, J = 1.5, 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4, 112.4, 126.7, 128.5, 128.6, 134.2, 197.7; IR (KBr) ν_{max} 3060, 3030, 2950, 2920, 2850, 1960, 1910, 1595, 1580, 1485, 1440, 1265, 1210, 1145, 910, 885, 760, 690 cm^{-1}; UV (cyclohexane) λ_{max} 234 (ϵ 4.2 × 10^4), 287 (ϵ 2.7 × 10^4) nm; MS *m/z* 564 (M$^+$, 7), 536 (19), 508 (8), 476 (32), 472 (10), 444 (100), 412 (10), 387 (27), 282 (6). Anal. Calcd for $C_{34}H_{28}S_4$: C, 72.34; H, 4.96. Found: C, 72.59; H, 5.00.

***meso*-1,3,8,10-Tetraphenyl-4,7,11,14-tetrathiacyclotetradeca-1,2,8,9-tetraene (*meso*-2a):** mp 162−163 °C (colorless needles from dichloromethane−hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09−3.23 (m, 8H), 7.25−7.54 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.7, 110.3, 126.9, 128.5, 128.7, 134.0, 200.5; IR (KBr) ν_{max} 3060, 2430, 2175, 1900, 1595, 1580, 1485, 1440, 1425, 1420, 1335, 1310, 890, 760 cm^{-1}; UV (cyclohexane) λ_{max} 238 (ϵ 3.1 × 10^4), 277 (sh, ϵ 2.4 × 10^4) nm; MS *m/z* 564 (M$^+$, 5), 536 (17), 508 (6), 476 (30), 472 (12), 444 (100), 412 (14), 387 (30), 282 (5). Anal. Calcd for $C_{34}H_{28}S_4$: C, 72.34; H, 4.96. Found: C, 72.39; H, 5.05.

1,3,9,11-Tetraphenyl-4,8,12,16-tetrathiacyclohexadeca-1,2,9,10-tetraene (2b). As a *dl*/*meso* (64/36) mixture: colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02−2.08 (m, 4H), 2.73−2.94 (m, 8H), 7.24−7.54 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.4, 29.7, 31.3, 31.6, 109.8, 112.5, 126.9, 127.1, 128.3, 128.4, 128.55, 128.60, 134.3, 134.6, 198.6, 200.5; IR (KBr) ν_{max} 3050, 3020, 2910, 1900, 1595, 1485, 1445, 1070, 1025, 880, 755, 685 cm^{-1}; MS *m/z* 592 (M$^+$, 17), 518 (4), 486 (14), 444 (100), 412 (8), 313 (53), 190 (33); HRMS calcd for $C_{36}H_{32}S_4$ 592.1387, found 592.1403.

1,3,10,12-Tetraphenyl-4,9,13,18-tetrathiacyclooctadeca-1,2,10,11-tetraene (2c). As a *dl*/*meso* (75/25) mixture: colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81−1.92 (m, 8H), 2.72−2.78 (m, 8H), 7.25−7.55 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.2, 27.6, 31.8, 32.0, 113.4, 114.0, 126.45, 126.53, 128.3, 128.4, 128.6 (duplicate), 134.77, 134.81, 196.4, 197.1; IR (KBr) ν_{max} 3025, 2920, 1900, 1595, 1585, 1490, 1445, 1310, 1290, 1210, 1150, 1075, 1030, 895, 760, 690 cm^{-1}; MS *m/z* 620 (M$^+$, 11), 532 (5), 500 (15), 444 (28), 412 (49), 380 (9), 255 (74), 190 (100); HRMS calcd for $C_{38}H_{36}S_4$ 620.1700, found 620.1675.

1,3,11,13-Tetraphenyl-4,10,14,20-tetrathiacycloeicosa-1,2,11,12-tetraene (2d). As a *dl*/*meso* (24/76) mixture: yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39−1.53 (m, 4H), 1.57−1.73 (m, 8H), 2.64−2.75 (m, 8H), 7.23−7.58 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 28.2, 28.75, 28.82, 32.4, 32.6, 112.5, 113.8, 126.6, 126.7, 128.2, 128.3, 128.49, 128.50, 134.8, 134.9, 196.7, 198.2; IR (KBr) ν_{max} 3060, 2925, 1900, 1595, 1585, 1490, 1445, 1305, 1280, 1210, 1150, 1080, 1030, 890, 760, 690 cm^{-1}; MS *m/z* 648 (M$^+$, 19), 546 (3), 514 (6), 444 (11), 412 (13), 380 (3), 255 (100), 190 (52). Anal. Calcd for $C_{40}H_{40}S_4$: C, 74.03; H, 6.21. Found: C, 74.12; H, 6.48.

1,3,12,14-Tetraphenyl-4,11,15,22-tetrathiacyclodocosa-1,2,12,13-tetraene (2e). As a *dl*/*meso* (67/33) mixture: yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39−1.46 (m, 8H), 1.65−1.72 (m, 8H), 2.68−2.71 (m, 8H), 7.25−7.58 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 28.5, 28.6, 28.7, 32.65, 32.66, 113.7, 113.9, 126.5 (duplicate), 128.3 (duplicate), 128.5 (duplicate), 134.98, 135.02, 196.7, 197.0; IR (KBr) ν_{max} 3075, 2960, 2875, 1915, 1605, 1585, 1500, 1470, 1455, 1275, 1220, 1155, 1040, 900, 775, 755, 705 cm^{-1}; MS *m/z* 676 (M$^+$, 27), 528 (10), 445 (13), 412 (30), 380 (8), 339 (19), 255 (100), 191 (46), 116 (35), 84 (12); HRMS calcd for $C_{42}H_{44}S_4$ 676.2326, found 676.2395.

General Procedure for Thermal Reaction of 1,3-Bis(alkylthio)allenes and Tetrathiacyclic Bisallenes. A *p*-xylene solution (2 mL) of 1,3-bis(alkylthio)allene (0.4 mmol) or tetrathiacyclic bisallene (0.2 mmol) was refluxed for the desired period under nitrogen. After removal of solvent in vacuo, the residue was subjected to gel-peameation chromatography (GPC). **1a**: 68% conversion, **4** (30%), **5** (18%), **6** (8%), stereoisomer of **6** (8%); **1b**: 100% conversion, **7** (63%), **8** (5%), **9** (11%); *dl*-**2a**: 100% conversion, **10** (100%); *meso*-**2a**: 100% conversion, **10** (100%).

2,4-Diphenylthiophene (4): mp 115−116 °C (colorless plates from benzene-hexane) (lit.[13] mp 121−121.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.31 (m, 2H), 7.38 (d, 1H, J = 1.5 Hz), 7.39−7.42 (m, 4H), 7.58 (d, 1H, J = 1.5 Hz), 7.60−7.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.7, 121.3, 124.9, 125.3, 126.2, 126.7, 127.8, 127.9, 133.3, 134.8, 142.1, 144.0; IR (KBr) ν_{max} 1595, 1485, 1445, 750, 730, 685 cm^{-1}; MS *m/z* 236 (M$^+$, 100), 202 (9), 191 (10), 165 (5), 121 (5), 77 (5).

1,3-Dihydro-5-methylthio-3-phenyl-2-benzothiepin (5): brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.32 (d, 1H, J = 12.2 Hz), 4.06 (d, 1H, J = 12.2 Hz), 4.42 (d, 1H, J = 7.8 Hz), 5.90 (d, 1H, J = 7.8 Hz), 7.21−7.49 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 33.8, 46.1, 122.0, 127.7, 127.8, 128.4, 128.6, 128.8, 129.0, 129.3, 137.4, 137.8, 138.1, 139.0; IR (neat) ν_{max} 3050, 3005, 2900, 1590, 1485, 1435, 1305, 1235, 1200, 1170, 1065, 1025, 950, 760, 690 cm^{-1}; MS *m/z* 284 (M$^+$, 8), 269 (2), 252 (2), 237 (100), 203 (18), 191 (5), 135 (4), 91 (10), 77 (35); HRMS calcd for $C_{17}H_{16}S_2$ 284.0693, found 284.0713.

1,2-Bis(methylthio)-(*Z*)-3,4-bis(1-methylthiobenzylidene)-1,2-diphenylcyclobutane (6): mp 196−197 °C dec (yellow needles from dichloromethane−hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 6H), 1.58 (s, 6H), 7.01−7.78 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0, 15.9, 72.2, 127.4, 127.7, 127.8, 128.3, 128.6, 129.5, 134.3, 136.9, 137.3, 139.1; IR (KBr) ν_{max} 3050, 3020, 2985, 2920, 1595, 1575, 1555, 1535, 1485, 1445, 1305, 1215, 1175, 1150, 1100, 1075, 1025, 960, 760, 690 cm^{-1}; MS *m/z* 568 (M$^+$, 97), 553 (8), 521 (9), 506 (9), 491 (29), 474 (100), 459 (18), 444 (41), 427 (25), 412 (19), 380 (16), 237 (26); HRMS calcd for $C_{34}H_{32}S_4$ 568.1387, found 568.1419.

Stereoisomer of 6. As a mixture with **6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.53 (s, 6H), 2.26 (s, 6H), 7.01−7.78 (m, 20H);

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[21] Jacobs, T. L.; Dankner, D. *J. Org. Chem.* **1957**, *22*, 1424.

^{13}C NMR (125 MHz, CDCl$_3$) δ 15.4, 17.9, 74.1, 126.4, 127.0, 128.3, 129.4, 129.6, 134.2, 135.2, 138.0, 139.4.

2,3,5-Triphenylthiophene (7): mp 136−137 °C (colorless needles from dichloromethane−hexane) (lit.[14a] mp 127 °C; lit.[14b] mp 157 °C; lit.[14c] mp 132−134 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.14−7.58 (m, 15H), 7.28 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 125.6, 126.5, 127.0, 127.4, 127.6, 128.4, 128.5, 128.9, 129.06, 129.14, 134.1, 134.2, 136.6, 138.0, 139.0, 142.6; IR (KBr) ν_{max} 1600, 1495, 1480, 755, 690 cm^{-1}; MS *m/z* 312 (M$^+$, 100), 278 (6), 235 (3), 192 (3), 121 (3).

4-Benzylthio-2,4-diphenylthiete (8): yellow liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.60 (d, 1H, J = 13.1 Hz), 3.83 (d, 1H, J = 13.1 Hz), 6.18 (s, 1H), 6.92−7.58 (m, 15H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 46.7, 75.8, 123.9, 126.7, 127.1, 127.4, 127.7, 127.8, 128.6, 128.7, 129.2, 130.6, 133.3, 136.2, 142.3, 144.1; IR (neat) ν_{max} 3050, 3020, 2900, 1595, 1570, 1485, 1440, 1255, 1070, 1030, 750, 690 cm^{-1}; MS *m/z* 346 (M$^+$, 2), 313 (21), 256 (100), 224 (5), 192 (5), 91 (3), 77 (2); HRMS calcd for C$_{22}$H$_{18}$S$_2$ 346.0850, found 346.0816.

3-Benzylthio-1,3-diphenyl-2-propene-1-one (9). The stereochemistry has not been clarified: mp 122−123 °C (yellow needles from dichloromethane−hexane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.66 (s, 2H), 7.04 (s, 1H), 7.01−7.96 (m, 15H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 37.7, 119.9, 127.1, 128.07, 128.11, 128.3, 128.47, 128.54, 128.9, 129.0, 132.2, 136.7, 138.4, 139.0, 162.9, 188.4; IR (KBr) ν_{max} 3060, 3030, 2940, 1630, 1600, 1575, 1525, 1485, 1245, 1230, 1045, 1020, 955, 705, 660 cm^{-1}; MS *m/z* 239 (M$^+$ − CH$_2$Ph, 100), 105 (28), 91 (29), 77 (26). Anal. Calcd for C$_{22}$H$_{18}$OS: C, 80.00; H, 5.45. Found: C, 79.65; H, 5.46.

1,3,8,10-Tetraphenyl-4,7,11,14-tetrathiatricyclo[8.4.0.0^{2,9}]-tetradeca-(*E*,*E*)-2,8-diene (10): mp 234−235 °C dec (yellow plates from dichloromethane−hexane); ^{1}H NMR (500 MHz, C$_6$D$_6$, 60 °C) δ 2.54−2.57 (m, 4H), 2.80−2.85 (m, 2H), 3.41 (br s, 2H), 6.73−7.80 (m, 20H); ^{13}C NMR (125 MHz, C$_6$D$_6$, 60 °C) δ 28.2, 29.3, 66.1, 127.0, 127.1, 127.6, 128.4, 128.7, 129.6 (duplicate), 130.6, 138.9, 139.7; IR (KBr) ν_{max} 3050, 2925, 1590, 1555, 1485, 1440, 1400, 1270, 1215, 1175, 1080, 1025, 915, 880, 840, 820, 770, 755, 685 cm^{-1}; MS *m/z* 564 (M$^+$, 9), 536 (28), 508 (11), 476 (51), 472 (98), 444 (100), 412 (76), 387 (43), 366 (51), 334 (51), 302 (51), 221 (16), 189 (15), 145 (20), 121 (72), 77 (14). Anal. Calcd for C$_{34}$H$_{28}$S$_4$: C, 72.23; H, 4.96. Found: C, 72.56; H, 5.15.

General Procedure for Photochemical Reaction of 1,3-Bis(alkylthio)allenes and Tetrathiacyclic Bisallenes. A benzene solution (100 mL) of 1,3-bis(alkylthio)allene (0.4 mmol) or tetrathiacyclic bisallene (0.2 mmol) was irradiated with a 450 W medium-presure mercury lamp through a Pyrex filter under argon for the desired period. After removal of solvent in vacuo, the residue was subjected to gel-peameation chromatography (GPC). **1a**: 80% conversion, **18a** (13%), **19a** (29%); **1b**: 89% conversion, **18b** (22%), **19b** (23%); *dl*-**2a**: 94% conversion, **20** (24%), **21** (20%), *meso*-**2a** (5%); *meso*-**2a**: 94% conversion, **20** (22%), **21** (23%), *dl*-**2a** (6%).

3,3-Bis(methylthio)-1,3-diphenylpropyne (18a): mp 93.5−94 °C (pale yellow solid); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.27 (s, 6H), 7.29−7.91 (m, 10H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 15.8, 55.5, 86.5, 89.1, 122.4, 127.2, 128.2, 128.3, 128.4, 128.7, 131.9, 139.9; IR (KBr) ν_{max} 3060, 3025, 3000, 2925, 2370, 2340, 1600, 1495, 1485, 1445, 1430, 1415, 1315, 1265, 1175, 1075, 1030, 965, 915, 860, 760, 725, 705, 685 cm^{-1}; UV (cyclohexane) λ_{max} 248 (ϵ 1.9 × 10^4) nm; MS *m/z* 284 (M$^+$, 28), 237 (100), 190 (40), 77 (21). Anal. Calcd for C$_{17}$H$_{16}$S$_2$: C, 71.78; H, 5.67. Found: C, 71.67; H, 5.50.

3,3-Bis(benzylthio)-1,3-diphenylpropyne (18b): yellow liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.98 (d, 2H, J = 11.9 Hz), 4.10 (d, 2H, J = 11.9 Hz), 7.09−7.95 (m, 20H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 38.0, 56.3, 87.2, 89.5, 122.4, 127.1, 127.31, 127.32, 128.30, 128.33, 128.4, 128.8, 129.4, 131.9, 136.4, 139.9; IR (neat) ν_{max} 3075, 3050, 3025, 2920, 2350, 2320, 1660, 1595, 1490, 1450, 1445, 1310, 1235, 1175, 1160, 1070, 1025, 915, 840, 755, 740, 685 cm^{-1}; MS *m/z* 435 (M$^+$ − 1, 6), 413 (22), 345 (6), 313 (15), 222 (6), 190 (10), 91 (100); HRMS calcd for C$_{29}$H$_{24}$S$_2$ 436.1319, found 436.1269.

1,3-Diphenyl-3-methylthiopropyne (19a): pale yellow liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.21 (s, 3H), 4.94 (s, 1H), 7.27−7.58 (m, 10H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.2, 40.5, 86.0, 86.7, 122.9, 127.7, 127.9, 128.27, 128.31, 128.5, 131.8, 138.3; IR (neat) ν_{max} 3070, 3040, 2925, 1670, 1605, 1585, 1495, 1455, 1250, 1180, 1080, 1035, 960, 920, 760 cm^{-1}; MS *m/z* 238 (M$^+$, 24), 223 (22), 191 (100), 77 (21); HRMS calcd for C$_{16}$H$_{14}$S 238.0816, found 238.0784.

3-Benzylthio-1,3-diphenylpropyne (19b): yellow liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.81 (d, 1H, J = 13.4 Hz), 4.05 (d, 1H, J = 13.4 Hz), 4.80 (s, 1H), 7.23−7.53 (m, 15H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 36.6, 39.0, 86.3, 87.1, 122.9, 127.1, 127.8, 128.1, 128.3, 128.4, 128.55, 128.57, 129.0, 131.8, 137.7, 137.9; IR (neat) ν_{max} 3075, 3055, 3025, 2925, 2360, 2330, 1600, 1490, 1455, 1440, 1335, 1240, 1070, 1025, 915, 755, 690 cm^{-1}; MS *m/z* 314 (M$^+$, 13), 237 (2), 223 (9), 191 (100), 123 (5), 91 (12), 77 (4); HRMS calcd for C$_{22}$H$_{18}$S 314.1129, found 314.1132.

8-Phenethynyl-1,3,8-triphenyl-4,7,9,12-tetrathiacyclododeca-1,2-diene (20): mp 116−117 °C dec (colorless solid); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.83 (ddd, 1H, J = 5.5, 6.7, 12.2 Hz), 3.01 (ddd, 1H, J = 7.4, 7.4, 14.0 Hz), 3.06−3.15 (m, 2H), 3.22−3.31 (m, 3H), 3.37 (ddd, 1H, J = 8.0, 9.8, 12.2 Hz), 7.24−7.87 (m, 20H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 30.3, 30.5, 32.2, 32.9, 58.1, 87.6, 88.8, 109.1, 109.2, 122.1, 126.2, 127.3, 127.4, 128.30, 128.31, 128.46, 128.50, 128.51, 128.70, 128.72, 128.8, 131.9, 133.9, 134.0, 141.0, 202.5; IR (KBr) ν_{max} 3050, 3025, 2910, 2350, 2325, 1900, 1590, 1575, 1485, 1440, 1425, 1410, 1260, 1200, 1180, 1140, 1110, 1070, 1025, 995, 925, 880, 860, 750, 710, 680 cm^{-1}; MS *m/z* 564 (M$^+$, 100), 536 (23), 504 (21), 476 (32), 472 (55), 444 (98), 412 (72); HRMS calcd for C$_{34}$H$_{28}$S$_4$ 564.1074, found 564.1068.

2,7-Diphenethynyl-2,7-diphenyl-1,3,6,8-tetrathiacyclodecane (21). As a syn/anti (ca. 1/1) mixture: colorless solid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.54 (br s, 8H), 7.25−7.88 (m, 20H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 31.8, 31.9, 59.07, 59.13, 87.35, 87.42, 89.27, 89.31, 122.19, 122.22, 126.04, 126.06, 128.29, 128.30, 128.34, 128.4, 128.5 (duplicate), 128.81, 128.82, 131.9 (duplicate), 141.26, 141.30; IR (KBr) ν_{max} 3050, 3025, 2910, 2345, 1595, 1575, 1490, 1445, 1420, 1400, 1285, 1270, 1180, 1070, 1030, 1000, 920, 855, 840, 755, 715, 685 cm^{-1}; MS *m/z* 564 (M$^+$, 100), 536 (33), 504 (28), 476 (32), 472 (17), 444 (77), 412 (46). Anal. Calcd for C$_{34}$H$_{28}$S$_4$: C, 72.34; H, 4.96. Found: C, 72.85; H, 5.17.

General Procedure for Reaction of 1,3-Bis(alkylthio)-allenes and Tetrathiacyclic Bisallenes with Diphenyl Diazomethane. A benzene solution (10 mL) of diphenyl diazomethane[22] (1.2 mmol) and 1,3-bis(alkylthio)allene (0.6 mmol) or tetrathiacyclic bisallene (0.3 mmol) was refluxed for 14 h under nitrogen. After removal of solvent in vacuo, the residue was subjected to silica gel column chromatography (dichloromethane) followed by gel-peameation chromatography (GPC). **1a**: 65% conversion, **25** (79%); **1b**: 38% conversion, **26** (11%), **27** (87%); *meso*-**2a**: 100% conversion, **10** (48%), **27** (12%), **28** (17%), **29** (13%); **10**: 54% conversion, **27** (20%), **28** (41%), **29** (29%).

1,2-Bis(methylthio)-1,3,4,4-tetraphenyl-(*Z*)-1,3-butadiene (25): mp 169−169.5 °C (yellow prisms from dichloromethane−hexane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.87 (s, 3H), 2.14 (s, 3H), 6.75−7.41 (m, 20H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 15.4, 16.1, 126.79, 126.81, 127.0, 127.2, 127.5, 127.6 (duplicate), 127.7, 128.8, 130.0, 130.97, 131.01, 133.9, 135.1, 137.1, 138.1, 140.2, 142.95, 143.01, 143.5; IR (KBr) ν_{max} 3050, 2930, 1595, 1575, 1540, 1495, 1440, 1320, 1280, 1185, 1075, 1035, 765, 695 cm^{-1}; MS *m/z* 451 (M$^+$ + 1, 100), 436 (7), 403 (6), 388 (10), 356 (30), 279 (15). Anal. Calcd for C$_{30}$H$_{26}$S$_2$: C, 79.95; H, 5.82. Found: C, 79.89; H, 5.82.

3-Benzylthio-1,3,4,4-tetraphenyl-1-butyne (26): yellow liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.33 (d, 1H, J = 11.6 Hz), 3.62 (d, 1H, J = 11.6 Hz), 4.67 (s, 1H), 6.98−7.83 (m, 25H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 36.4, 56.9, 63.3, 89.6, 90.4, 123.2, 126.4, 126.8, 127.18, 127.23, 127.5, 127.9 (duplicate), 128.0,

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[22] (a) Smith, L. I.; Howard, K. L. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 351. (b) Staudinger, H.; Anthes, E.; Pfenninger, F. *Ber.* **1916**, *49*, 1928.

128.1, 128.2, 128.5, 129.3, 129.6, 130.4, 131.5, 137.0, 140.4, 140.5, 141.4; IR (neat) ν_{max} 3060, 3025, 2920, 1595, 1490, 1450, 1265, 1070, 1030, 915, 760, 690 cm^{-1}; MS m/z 479 (M$^+$ − 1), 389, 357, 313, 279, 191, 165, 121, 91, 77; HRMS calcd for $C_{35}H_{28}S$ 480.1912, found 480.1940.

Tetraphenylepisulfide (27): mp 171−172 °C (colorless needles from dichloromethane−hexane) (lit.[20] mp 177−179 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01−7.20 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.7, 126.6, 127.1, 130.9, 140.2; IR (KBr) ν_{max} 3060, 3025, 1595, 1490, 1440, 1315, 1220, 1180, 1075, 1030, 900, 840, 780, 750, 690 cm^{-1}; MS m/z 365 (M$^+$ + 1, 58), 333 (100), 288 (8), 165 (58), 77 (11).

2,7,9,10-Tetraphenyl-3,6-dithiabicyclo[6.2.0]deca-(*Z*,*Z*,*Z*)-1,7,9-triene (28): mp 208−209 °C (yellow solid); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.22 (s, 4H), 6.54−7.32 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.5, 120.6, 127.0, 127.1, 127.3, 127.8, 128.0, 130.8, 131.7, 139.4, 143.8, 152.1; IR (KBr) ν_{max} 2900, 1590, 1570, 1440, 1400, 1260, 1090, 1070, 1025, 800, 770, 750, 690 cm^{-1}; MS m/z 472 (M$^+$, 91), 444 (37), 412 (100), 380 (9), 302 (23), 77 (11). Anal. Calcd for $C_{32}H_{24}S_2$: C, 81.31; H, 5.12. Found: C, 81.23; H, 5.08.

2,2-Diphenyl-1,3-dithiolane (29): mp 95.5−96 °C (lit.[17] mp 105 °C); ^{1}H NMR (500 MHz, C_6D_6) δ 2.81 (s, 4H), 6.98 (t, 2H, J = 7.4 Hz), 7.06 (dd, 4H, J = 7.4, 7.4 Hz), 7.77 (d, 4H, J = 7.4 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 40.1, 77.5, 127.4, 128.3, 128.9, 145.2; MS m/z 258 (M$^+$, 53), 229 (100), 198 (24), 181 (14), 165 (71), 77 (15).

X-ray Analysis: General. Each crystal was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.710 69 Å) on a Mac Science MXC18 diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement. The data were collected at a temperature of 25 ± 1 °C using the $\omega-2\theta$ scan technique. The scan rate varied from 0 to 5 °/min (in omega). Lorentz and polarization corrections were applied to the data. No absorption correction was made. An extinction correction was not necessary. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$, and the weight w is defined as 1.0 for all observed reflections. **Compound *meso*-2a.** A colorless prism of $C_{34}H_{28}S_4$ having approximate dimension of 0.30 × 0.30 × 0.20 mm^3. Triclinic space group $P\bar{1}$ with a = 5.733(1) Å, b = 11.069(3) Å, c = 12.306(3) Å, α = 113.05(2)°, β = 91.25(2)°, γ = 99.24(2)°, V = 706.2(3) Å^3, Z = 1, and ρ(calcd) = 1.328 g cm^{-3}. Of the 3512 unique data, the 2575 with $I > 3\sigma(I)$ were used in the least-squares refinement to yield R = 0.037 and R_w = 0.039. **Compound 6.** A yellow needle of $C_{34}H_{32}S_4$ having approximate dimension of 0.50 × 0.40 × 0.40 mm^3. Monoclinic space group $P2/a$ with a = 18.064(5) Å, b = 11.274(2) Å, c = 16.359(3) Å, β = 116.62(2)°, V = 2978(1) Å^3, Z = 4, and ρ(calcd) = 1.266 g cm^{-3}. Of the 6278 unique data, the 4624 with $I > 3\sigma(I)$ were used in the least-squares refinement to yield R = 0.052 and R_w = 0.053. **Compound 10.** A yellow plate of $C_{34}H_{28}S_4$ having approximate dimension of 0.40 × 0.30 × 0.15 mm^3. Orthorhombic space group $P2_12_12_1$ with a = 9.803(2) Å, b = 32.311(8) Å, c = 8.859(2) Å, V = 2806(1) Å^3, Z = 4, and ρ(calcd) = 1.336 g cm^{-3}. Of the 3351 unique data, the 2412 with $I > 3\sigma(I)$ were used in the least-squares refinement to yield R = 0.057 and R_w = 0.063. **Compound 25.** A yellow prism of $C_{30}H_{26}S_2$ having approximate dimension of 0.60 × 0.30 × 0.25 mm^3. Monoclinic space group $P2_1/n$ with a = 12.994(3) Å, b = 18.214(3) Å, c = 10.907(2) Å, β = 107.68(1)°, V = 2459.5(7) Å^3, Z = 4, and ρ(calcd) = 1.217 g cm^{-3}. Of the 2679 unique data, the 2481 with $I > 3\sigma(I)$ were used in the least-squares refinement to yield R = 0.060 and R_w = 0.108.

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Supporting Information Available: Detailed information of the X-ray crystallographic analysis of **6**, **10**, and **25** including structure diagrams, details of data collection and reduction and structure solution and refinement, tables of positional and thermal parameters, and bond lengths, angles, and torsional angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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