Synthesis and Reactivity of Allenes Substituted by Selenenyl Groups at 1- and 3-Positions

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1,3-Bis(methylseleno)- and 1,3-bis(benzylseleno)-1,3-diphenylpropadienes were synthesized by reaction of Ph_2C_3 dianion, prepared from 1,3-diphenylpropyne and *n*-butyllithium, with dimethyl diselenide or benzylselenocyanate in the presence of TMEDA, and reaction of the dianion with a mixture of dimethyl diselenide and benzylselenocyanate yielded 1-benzylseleno-3-methylselenoallene along with the symmetric allenes. Diselenocyclic allenes and tetraselenocyclic bisallenes were also obtained by reacting the dianion with corresponding alkane diselenocyanates. The thermal reaction of the 1,3-bis(alkylseleno)allenes mainly afforded enediynes through radical pathway, and the nine-membered cyclic allene provided intramolecular cyclization product via an intramolecular rearrangement. Heating of the cyclic bisallenes gave compounds derived from intramolecular cyclization products together with a small amount of the enediynes. Irradiation of allenes caused rearrangement of the selenenyl group to give alkynes, and the alkynes also reacted photochemically to yield the enediynes.

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.[1,2] Sulfur-substituted allenes have also been synthesized in the 1960s,[3] except for 1,3-disulfenyl allene. Recently, we reported the synthesis and reaction of allenes substituted by sulfenyl groups at 1- and 3-positions, and thermal reactions of the 1,3-bis(alkylthio)allenes have been found to give thiophene derivatives, and the irradiation afforded the 1,3-rearrangement products.[4] Several selenium-substituted allenes are also known as isolable compounds or reactive intermediates;[5] however, few of their reactivities have been examined. We synthesized 1,3-bis(alkylseleno)allenes by reacting Ph_2C_3 dianion with the corresponding diselenide or selenocyanates, and it was found that the reactivities of the selenium-substituted allenes are different from those of corresponding sulfur-substituted allenes. In this paper, we report the synthesis, thermal reaction, and photochemical reaction of 1,3-bis(alkylseleno)allenes, diselenocyclic allenes, and tetraselenocyclic bisallenes.[6]

Results and Discussion

Synthesis of Selenium-Substituted Allenes. Reaction of Ph_2C_3 dianion (1,3-dilithiated allene), prepared from 1,3-diphenylpropyne and *n*-butyllithium, with 2 equiv of dimethyl diselenide in the presence of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) yielded 1,3-bis(methylseleno)-1,3-diphenylpropadiene (**1**) in 70% yield (Scheme 1). In this reaction, addition of TMEDA was found to be effective, and the yield was lowered (22%) when the reaction was carried out without TMEDA. Reaction of the dianion with 2 equiv of benzylselenocyanate in the presence of TMEDA also provided 1,3-bis(benzylseleno)-1,3-diphenylpropadiene (**2**) in 64% yield. Similarly, reaction of the dianion with a mixture of dimethyl diselenide and benzylselenocyanate afforded unsymmetric allene **3** in 17% yield along with symmetric allenes **1** (26%) and **2** (5%). 3,3-Bis(alkylseleno)-1,3-diphenylpropyne, formation of which is also anticipated from the reaction, was not found in either reaction, whereas reaction of the dianion with ethyl bromide yielded 1,3-diphenyl-3-ethyl-1-pentyne as a major product.[4] The reason the propyne was not formed might be explained based on the steric effect; the introduction of

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(1) For reviews, see: (a) *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: New York, 1982; Vols. 1−3. (b) *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; Vols. 1 and 2. (c) Brandsma, L.; Verkruijsee, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: New York, 1980. (d) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805. (e) Smadja, W. *Chem. Rev.* **1983**, *83*, 263. (f) Baldwin, J. E.; Fleming, R. H. *Fortschr. Chem. Forsch.* **1970**, *15*, 281. (g) Huché, M. *Tetrahedron* **1980**, *36*, 331. (h) Mavrov, M. V.; Kucherov, V. F. *Russ. Chem. Rev.* **1967**, *36*, 233. (i) Griesbaum, K. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 933.

(2) For reviews, see: (a) Bruneau, C.; Dixneuf, P. H. *Compr. Org. Funct. Group Transform.* **1995**, *1*, 953. (b) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31. (c) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley: New York, 1984. (d) Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317.

(3) (a) Pourcelot, G.; Cadiot, P.; Willemart, A. *Compt. Rend. Acad. Sci.* **1961**, *252*, 1630. (b) Pourcelot, G.; Le Quan, M.; Simonnin, M.-P.; Cadiot, P. *Bull. Soc. Chim. France* **1962**, 1278. (c) Brandsma, L.; Wijers, H. E.; Arens, J. F. *Rec. Trav. Chim. Pays-Bas* **1963**, *82*, 1040. (d) Wildschut, G. A.; van Boom, J. H.; Brandsma, L.; Arens, J. F. *Rec. Trav. Chim. Pays-Bas* **1968**, *87*, 1447. (e) Wildschut, G. A.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1132.

(4) (a) Shimizu, T.; Sakamaki, K.; Kamigata, N. *Tetrahedron Lett.* **1997**, *38*, 8529. (b) Shimizu, T.; Sakamaki, K.; Miyasaka, D.; Kamigata, N. *J. Org. Chem.* **2000**, *65*, 1721.

(5) (a) Pourcelot, G.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 3016; 3024. (b) Petrov, M. L.; Radchenko, S. I.; Kupin, V. S.; Petrov, A. A. *J. Org. Chem. U.S.S.R.* **1973**, *9*, 683. (c) Braverman, S.; Duar, Y. *Tetrahedron Lett.* **1978**, 1493. (d) Braverman, S.; Freund, M.; Goldberg, I. *Tetrahedron Lett.* **1980**, *21*, 3617. (e) Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 3112. (f) Reich, H. J.; Kelly, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 1119. (g) Tada, M.; Nagasaka, R. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3221.

(6) For a preliminary communication, see: Shimizu, T.; Miyasaka, D.; Kamigata, N. *Org. Lett.* **2000**, *2*, 1923.

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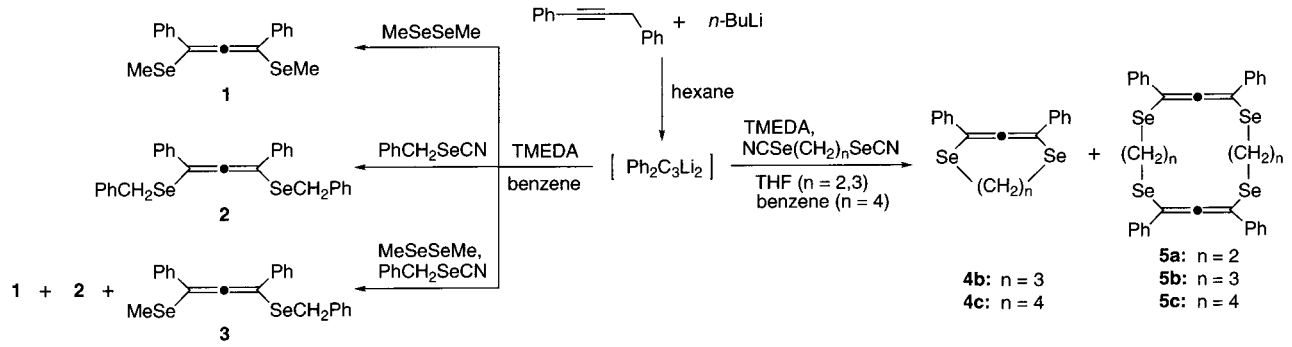
Scheme 1



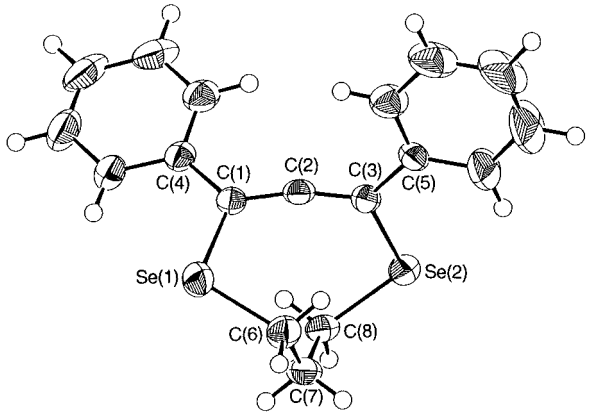


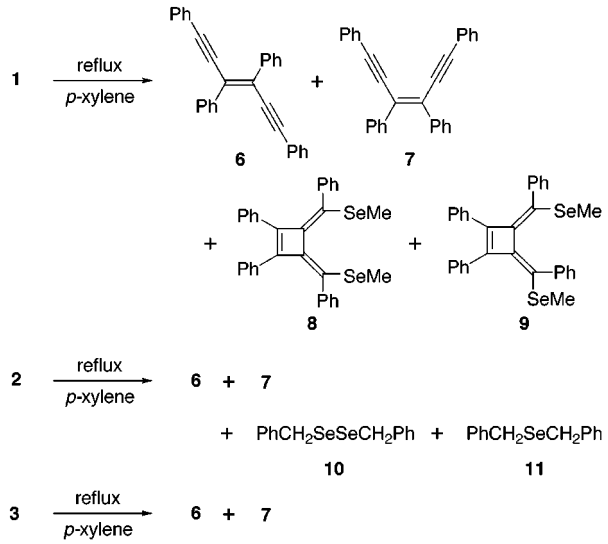
Figure 1. Crystal structure of **4b** showing 50% probability displacement ellipsoids. Selected bond lengths (Å) and bond angles (deg): Se(1)−C(1), 1.944(4); Se(1)−C(6), 1.950(4); Se(2)−C(3), 1.947(4); Se(2)−C(8), 1.952(4); C(1)−C(2), 1.312(5); C(1)−C(4), 1.472(5); C(2)−C(3), 1.303(5); C(3)−C(5), 1.467(5); C(1)−Se(1)−C(6), 99.3(2); C(3)−Se(2)−C(8), 98.5(1); Se(1)−C(1)−C(2), 116.6(3); Se(1)−C(1)−C(4), 118.0(3); C(2)−C(1)−C(4), 125.4(4); C(1)−C(2)−C(3), 166.5(4); Se(2)−C(3)−C(2), 117.3(3); Se(2)−C(3)−C(5), 118.2(3); C(2)−C(3)−C(5), 124.5(3).

two bulky selenenyl groups on the same carbon would be difficult.

The dianion also reacted with ethane 1,2-diselenocyanate to afford 14-membered cyclic bisallene **5a** in 26% yield (*dl*/*meso* ≈ 1/2). Stereochemistry of the *dl*- and *meso*-isomers was assigned in comparison of their ^{1}H NMR spectra with those of sulfur analogue, whose structure has been determined by X-ray analysis of the *meso*-isomer.[4] Similarly, selenium-substituted, larger-membered cyclic bisallenes **5b** and **5c** were also obtained in yields of 1% (*dl*/*meso* ≈ 1/1) and 14% (*dl*/*meso* ≈ 1/1), respectively, by reacting the dianion with corresponding alkane diselenocyanates. In these reactions, cyclic monoallenes **4b** and **4c** were also obtained in 57% and 14% yields, respectively, whereas the corresponding sulfur-substituted cyclic monoallene has not been obtained by the reaction of the dianion with corresponding alkane dithiocyanates.[4] This difference is maybe due to the difference of configuration in the ring-closure reaction. The crystal structure of eight-membered cyclic monoallene **4b** was determined by X-ray analysis, as shown in Figure 1. The bond lengths are almost normal, and bond angle C(1)−C(2)−C(3) and torsion angle Se(1)−C(1)−C(3)−Se(2) are 167° and 75°, respectively, indicating a slightly strained structure.

Thermal Reaction of Selenium-Substituted Allenes. When a *p*-xylene solution of 1,3-bis(methylseleno)allene **1** was refluxed for 3 d, (*E*)- and (*Z*)-1,3,4,6-tetraphenyl-3-hexen-1,5-diynes (**6** and **7**), the framework of which is known as an important building block of several naturally occurring antitumor antibiotics[7] and as a substrate of the Masamune−Bergman reaction,[8] were obtained in 34% and 7% yields, respectively, together with (*Z*,*Z*)-3,4-bis{α-(methylseleno)benzylidene}-1,2-diphenylcyclobutene (**8**) (21%) and the *E*,*Z*-isomer **9** (9%) (Scheme 2). The structure of enediynes **6** and **7** was confirmed by X-ray crystallographic analysis of *E*-isomer **6**.[6] The stereochemistry of *Z*,*Z*-isomer **8** was also determined by X-ray analysis, as shown in Figure 2. Dihedral angle C(5)−C(3)−C(4)−C(6) of **8** is twisted (24°) in the crystalline state perhaps due to repulsion of two selenium

Scheme 2



(7) (a) Golik, J.; Clardy, J.; Dubay, G.; Groenewold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3461. (b) Nicolaou, K. C.; Ogawa, Y.; Zuccarello, G.; Kataoka, H. *J. Am. Chem. Soc.* **1988**, *110*, 7247. (c) Nicolaou, K. C.; Dai, W.-M.; Wendeborn, S. V.; Smith, A. L.; Torisawa, Y.; Maligres, P.; Hwang, C.-K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1032. (d) Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387. (e) Nicolaou, K. C.; Smith, A. L. *Acc. Chem. Res.* **1992**, *25*, 497. (f) Nicolaou, K. C.; Liu, A.; Zeng, Z.; McComb, S. *J. Am. Chem. Soc.* **1992**, *114*, 9279. (g) Nicolaou, K. C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1377. (h) Kagan, J.; Wang, X. D.; Chen, X. S.; Lau, K. Y.; Batac, I. V.; Tuveson, R. W.; Hudson, J. B. *J. Photochem. Photobiol., B* **1993**, *21*, 135. (i) Wender, P. A.; Zercher, C. K.; Beckham, S.; Haubold, E.-M. *J. Org. Chem.* **1993**, *58*, 5867.

(8) (a) Darby, N.; Kim, C. U.; Salaün, J. A.; Shelton, K. W.; Takada, S.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1971**, 1516. (b) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660. (c) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25. (d) Wong, H. N. C.; Sondheimer, F. *Tetrahedron Lett.* **1980**, *21*, 217. (e) Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4091. (f) Ramkumar, D.; Kalpana, M.; Varghese, B.; Sankararaman, S.; Jagadeesh, M. N.; Chandrasekhar, J. *J. Org. Chem.* **1996**, *61*, 2247. (g) Evenzahav, A.; Turro, N. J. *J. Am. Chem. Soc.* **1998**, *120*, 1835.

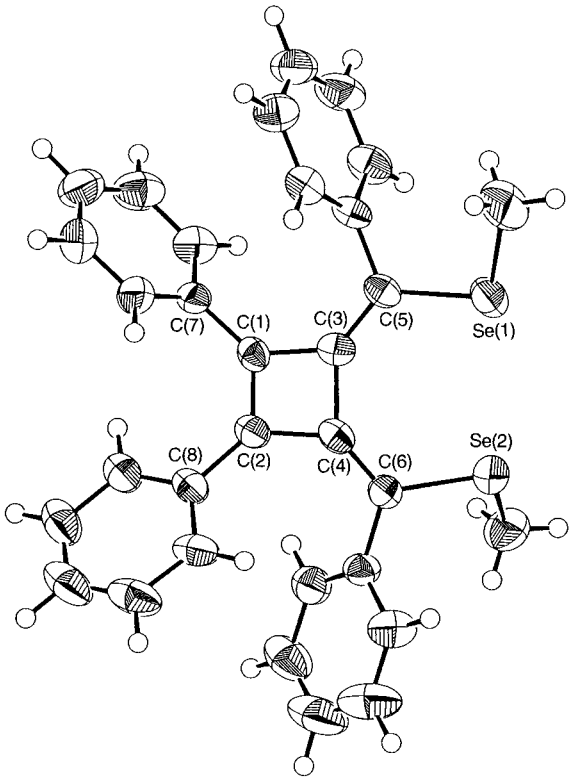


Figure 2. Crystal structure of **8** (one of unequivalent two molecules) showing 50% probability displacement ellipsoids. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): C(1)−C(2), 1.368(6); C(1)−C(3), 1.492(6); C(1)−C(7), 1.478(6); C(2)−C(4), 1.507(7); C(2)−C(8), 1.462(6); C(3)−C(4), 1.537(6); C(3)−C(5), 1.344(6); C(4)−C(6), 1.334(6); C(2)−C(1)−C(3), 93.4(4); C(2)−C(1)−C(7), 133.2(4); C(1)−C(2)−C(4), 92.8(4); C(1)−C(2)−C(8), 132.0(5); C(1)−C(3)−C(4), 86.9(4); C(1)−C(3)−C(5), 131.7(4); C(2)−C(4)−C(3), 86.4(4); C(2)−C(4)−C(6), 134.0(4); C(7)−C(1)−C(2)−C(8), −3.3(9); C(3)−C(1)−C(2)−C(4), −5.3(4); C(1)−C(3)−C(4)−C(2), −4.7(3); C(5)−C(3)−C(4)−C(6), −24(1).

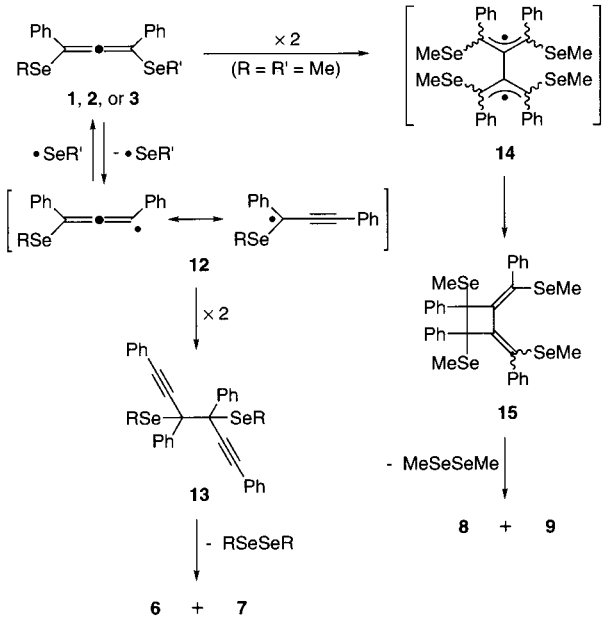
atoms, whereas the four-membered ring has almost planar geometry {C(1)−C(3)−C(4)−C(2) = 5°}. It was also found that isomerization from *Z*-isomer **7** to *E*-isomer **6** occurred between enediynes **6** and **7** under the refluxing conditions in *p*-xylene; ca. a 2:1 mixture of **6** and **7** was obtained from **7** after 1.5 h.

Thermal reaction of 1,3-bis(benzylseleno)allene **2** proceeded smoothly under similar conditions, and enediynes **6** and **7** were formed in 36% and 8% yields, respectively, along with dibenzyl diselenide **10** (57%) and dibenzyl selenide **11** (25%). In this reaction, cyclic compound corresponding to **8** or **9** was not obtained. In the thermal reaction of unsymmetric allene **3**, the reaction was intricate, and only enediynes **6** and **7** could be isolated in 28% and 7% yields, respectively. The thermal reactivities of selenium-substituted allenes **1** and **2** were found to be different from those of the corresponding sulfur-substituted allenes, i.e., thermal reactions which afforded thiophene derivatives as major products.[4] The difference of the reactivities must be due to the smaller bond dissociation energy of the carbon−selenium bond than that of the carbon−sulfur bond. The formation of the enediynes in the thermal reactions of **1** and **2** was inhibited by addition of galvinoxyl (Table 1). Therefore, the thermal reactions of the selenium-substituted allenes to give the enediynes were found to proceed through radical mechanism. Addition of galvinoxyl also accelerated disappearance of the allenes. This means the existence of reverse radical coupling reaction of allenyl radical and selenenyl radical, formed by homolytic cleavage of the carbon−selenium bond of the starting materials, to give the allenes, and the acceleration of the disappearance may be a result from the radical trapping by galvinoxyl.

Table 1. Thermal Reaction of Allenes 1, 2, and 3 in Refluxing *p*-Xylene

allene	reaction time	galvinoxyl	conversion (%)	product (%) 6	7	8	9	10	11
1	3 d		79	34	7	21	9		
1	3 d	5 equiv	100						
2	1.5 h		90	36	8			57	25
2	1.5 h	5 equiv	100	4	2			41	
2	1.5 h	10 equiv	100					11	
3	1.5 h		40	28	7				

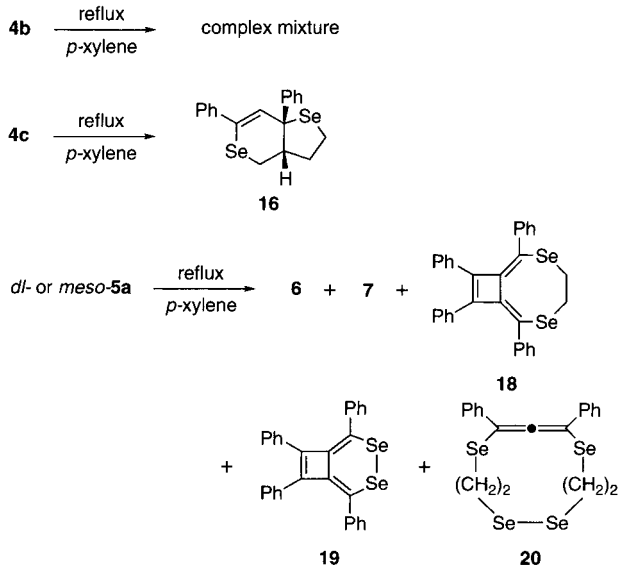
Scheme 3



The mechanism for the formation of enediynes **6** and **7** is considered as follows (Scheme 3). Homolytic cleavage of the carbon−selenium bond of allene **1**, **2**, or **3** gives radical **12** and the selenenyl radical. Dimerization of radical **12** yields hexadiyne **13** followed by elimination of diselenide to afford enediynes **6** and **7**. In the case of allene **1**, addition between *sp*-hybridized carbons also occurs to give biradical intermediate **14** followed by intramolecular cyclization to form cycloadduct **15**. Under the conditions, further reaction occurs to give cyclobutene derivatives **8** and **9** with extrusion of dimethyl diselenide. The reason cyclobutene derivative was not obtained in the case of allene **2** is maybe due to fast cleavage of the carbon−selenium bond and/or repulsion between two benzyl groups in formation of the carbon−carbon bond. Another mechanism for formation of enediynes **6** and **7** is also plausible, that is, elimination of diselenide from cyclobutene derivative **8** or **9**. However, enediyne **6** or **7** was not obtained from isolated **8** under the conditions.

The thermal reactivity of cyclic monoallenes **4b** and **4c** was also investigated in *p*-xylene solution under reflux. In the case of **4c**, bicyclic compound **16** was obtained in 59% yield, whereas the reaction of **4b** was intricate, and no identified compound was obtained (Scheme 4). The structure of **16** was determined by X-ray

Scheme 4



allene	reaction time	conversion (%)	product (%)						
			6	**7**	**18**	**19**	**20**	*dl*-**5a**	*meso*-**5a**
dl-**5a**	8 h	96	3	1	41	11	6		10
meso-**5a**	8 h	84	5	3	36	4	7	7	

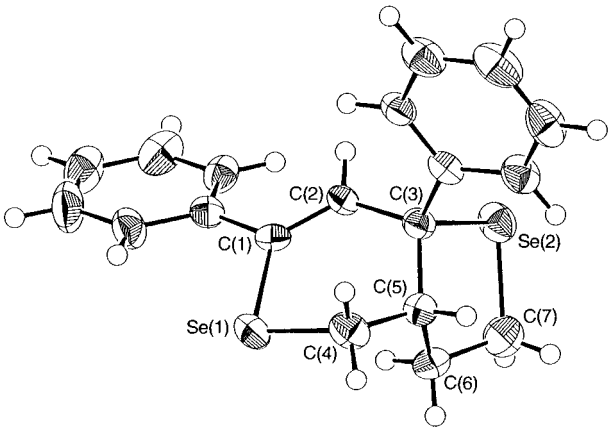
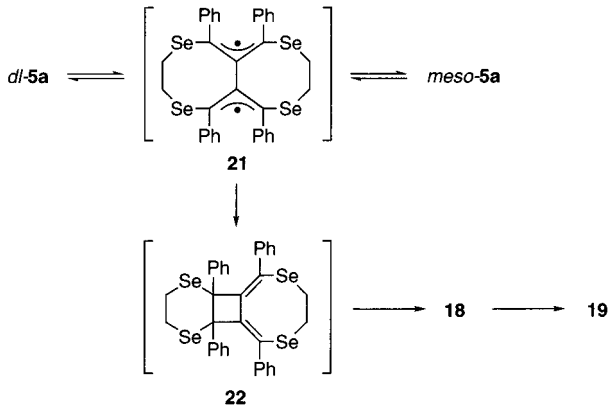


Figure 3. Crystal structure of **16** (one of unequivalent two molecules) showing 50% probability displacement ellipsoids. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): Se(1)−C(1), 1.908(6); Se(1)−C(4), 1.967(6); Se(2)−C(3), 2.019(7); Se(2)−C(7), 1.946(7); C(1)−C(2), 1.351(8); C(1)−Se(1)−C(4), 96.2(2); C(3)−Se(2)−C(7), 91.3(3); Se(1)−C(1)−C(2), 122.8(4); C(1)−C(2)−C(3), 130.2(5); Se(1)−C(1)−C(2)−C(3), 7.0(8).

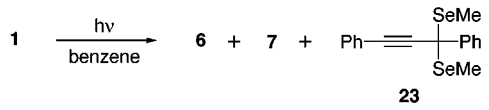
analysis, and the stereochemical relationship between the hydrogen and phenyl group at the bridge head was determined to be syn geometry, as shown in Figure 3. In this reaction, an intramolecular hydrogen-abstraction reaction by *sp*-hybridized carbon from methylene may be occurring at the initial stage to give biradical intermediate **17** and the subsequent intramolecular radical-coupling reaction yields bicyclic compound **16**. Heating of cyclic bisallenes *dl*- and *meso*-**5a** in a *p*-xylene solution caused an intramolecular cyclization reaction and the subsequent elimination of the $SeCH_2CH_2Se$ moiety to give bicyclic product **18** in 41% and 36% yields, respectively, together with small amounts of enediynes **6** and **7**, 1,2-diselenine **19**, and cyclic diselenide **20**. In these reactions, *meso*-**5a** was also formed from *dl*-**5a**, and *dl*-**5a** was formed from *meso*-**5a**. This observation indicates that a reverse reaction is occurring from the common intermediate to give the stereoisomer of *dl*- or *meso*-**5a**. Therefore, bicyclic compound **18** is considered to be formed via 2,2′-bisallyl biradical **21** followed by subsequent carbon−carbon bond formation and elimination of the selenium substituent, as shown in Scheme 5. In the case of corresponding tetrathiacyclic bisallenes, the sulfur analogue corresponding to compound **22** was obtained quantitatively.[4] This difference may be explained by the small bond dissociation energy of carbon−selenium bond. Reverse reaction from **21** to the starting material may yield *dl*- and *meso*-**5a**. Compound **19** will be formed from **18** with extrusion of ethylene under the conditions, since isolated **18** gave compound **19** under the conditions although the reaction was slow (8 h; 18% conversion, 88% yield). Formation of cyclic monoallene **20** is also considered as a result of homolytic cleavage of the carbon−selenium bond of the starting materials, and the subsequent reaction will form the enediynes.

Scheme 5



Photochemical Reaction of Selenium-Substituted Allenes. Irradiation of a benzene solution of allene **1** for 15 min through a Pyrex filter afforded enediynes **6** and **7** and 3,3-bis(methylseleno)-1,3-diphenylpropyne **23** in 14%, 11%, and 16% yields, respectively (Scheme 6). The longer irradiation time (1 h) increased the formation of enediynes **6** and **7** with decreasing rearrangement product **23**. Irradiation of **2** also yielded enediynes **6** and **7** in yields of 22% and 16% together with 57% of dibenzyl diselenide **10**. In this reaction, 3,3-bis(benzylseleno)-1,3-diphenylpropyne was not obtained unlike the sulfur analogue, which has been obtained by irradiation of 1,3-bis(benzylthio)-1,3-diphenylpropadiene.[4] Lack of formation of the 1,3-diphenylpropyne in the reaction of **2** may be due to further photochemical reaction of the propyne to give the enediynes. No formation of enediynes **6** and **7** was found when allene **2** was irradiated under oxygen bubbling, and 1,3-diphenylpropynone **24** was obtained in 63% yield. Irradiation of cyclic monoallenes **4b** and **4c** also gave enediynes **6** and **7** along with rearrangement compounds **25** and **26**, respectively (Scheme 7). In the case of **4b**, longer irradiation time also increased the

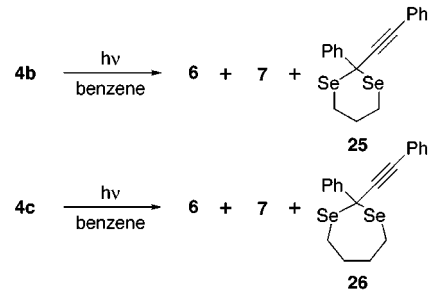
Scheme 6



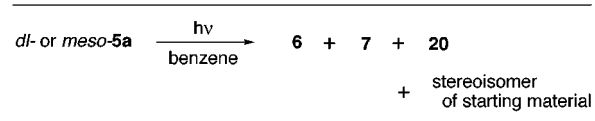
allene	reaction time	conversion (%)	product (%)				
			6	**7**	**10**	**23**	**24**
1	15 min	54	14	11		16	
1	60 min	82	20	20		10	
2	60 min	79	22	16	57		
2[a]	60 min	100			52		63

[a] under bubbling of oxygen.

Scheme 7

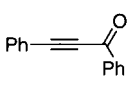


allene	reaction time	conversion (%)	product (%)			
			6	**7**	**25**	**26**
4b	20 min	75	6	4	22	
4b	60 min	95	29	23	8	
4c	60 min	69	8	7		51



allene	reaction time	conversion (%)	product (%)				
			6	**7**	**20**	*dl*-**5a**	*meso*-**5a**
dl-**5a**	100 min	86	19	16	11		8
meso-**5a**	90 min	96	18	17	15	9	

formation of enediynes **6** and **7** with decreasing rearrangement product **25**, indicating the endiynes are secondary products from the rearrangement product. Irradiation of isolated **25** yielded enediynes **6** and **7** and cyclic monoallene **4b** in 18%, 16%, and 13% yields, respectively, which confirms the hypothesis and also indicates the existence of a photochemical reverse reaction from **25** to cyclic monoallene **4b**. Similarly, cyclic bisallenes *dl*- and *meso*-**5a** were also irradiated and afforded enediynes **6** and **7** together with cyclic monoallene **20**. In these reactions, *meso*-**5a** was also formed from *dl*-**5a**, and *dl*-**5a** was formed from *meso*-**5a**.



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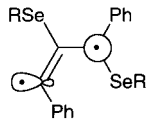
In the photochemical reactions, the first step is photorearrangement to give alkynes, such as **23**, **25**, and **26**. The photorearrangement may proceed via photoinduced 1,2-rearrangement of the alkylselenenyl group of the allenes to give biradical **27**, which yields carbene **28**.[9] Further rearrangement of the selenenyl group gives the alkynes. The alkynes also react photochemically to give a carbon radical by homolytic cleavage of carbon−selenium bond. A radical-coupling reaction of the carbon radical followed by subsequent elimination of diselenide yields enediynes **6** and **7**.



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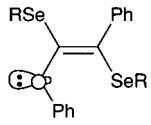

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Conclusion

1,3-Bis(methylseleno)-, 1,3-bis(benzylseleno)-, and 1-benzylseleno-3-methylseleno-1,3-diphenylpropadienes were synthesized by reaction of Ph_2C_3 dianion with dimethyl diselenide and/or benzylselenocyanate. Diselenocyclic allenes, a type of compounds which has not been obtained in the case of corresponding sulfur analogue, and tetraselenocyclic bisallenes were also obtained by reacting the dianion with alkane diselenocyanates. Thermal reaction of the allenes afforded enediynes, which were not obtained in the case of sulfur analogue, through a radical pathway. Irradiation of allenes caused rearrangement of the selenenyl group to give alkynes, and the alkynes also reacted photochemically to yield the enediynes whereas corresponding sulfur-substituted alkynes did not react photochemically.

Experimental Section

General Methods. Tetrahydrofuran, *n*-hexane, and benzene were distilled from sodium metal before use. *p*-Xylene was freshly distilled from calcium hydride. Column chromatography was performed with silica gel (70−230 mesh). Gel permeation chromatography (GPC) was performed with two JAIGEL-1H columns (20 mm × 600 mm), and the products were eluted with chloroform. All reactions were carried out under nitrogen. ^{1}H and ^{13}C NMR spectra were measured with Me_4Si as internal standard.

Synthesis of 1,3-Bis(methylseleno)-1,3-diphenylpropadiene (1). To a hexane solution (40 mL) of 1,3-diphenylpropyne[10] (1.00 g, 5.21 mmol) was added dropwise *n*-butyllithium (1.54 mol/L, 6.6 mL, 10.2 mmol) under nitrogen at room temperature,[11] and the solution was stirred for 1 h. TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (0.80 mL, 5.32 mmol) was added to the mixture, and stirring was continued for an additional 1 h. A benzene solution (20 mL) of dimethyl diselenide (2.06 g, 11.0 mmol) was added dropwise to the solution and stirred for 30 min. Water (100 mL) was added to the solution, and the product was extracted with benzene. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After removal of the solvent in vacuo, the product was purified by silica gel column chromatography (benzene/hexane = 1/8) to give allene **1** (1.36 g, 70%).

1,3-Bis(methylseleno)-1,3-diphenylpropadiene (1). Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 6H), 7.26 (t, 2H, J = 7.3 Hz), 7.33 (t, 4H, J = 7.3 Hz), 7.53 (d, 4H, J = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.1, 106.9, 127.0, 128.2, 128.6, 135.2, 193.4; IR (neat) ν_{max} 3052, 2926, 1906, 1595, 1491,

(9) (a) Steinmetz, M. G.; Mayes, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 2111. (b) Stierman, T. J.; Johnson, R P. *J. Am. Chem. Soc.* **1985**, *107*, 3971. (c) Stierman, T. J.; Shakespeare, W. C.; Johnson, R P. *J. Org. Chem.* **1990**, *55*, 1043.
(10) Jacobs, T. L.; Dankner, D. *J. Org. Chem.* **1957**, *22*, 1424.
(11) (a) Klein, J.; Backer, J. Y. *J. Chem. Soc., Chem. Commun.* **1973**, 576. (b) Leroux, Y.; Mantione, R. *Tetrahedron Lett.* **1971**, 591.

1444, 1420, 1273, 1211, 1029, 911, 857, 760, 690 cm^{-1}; UV (cyclohexane) λ_{max} 205 (ϵ 3.69 × 10^4), 236 (ϵ 2.37 × 10^4), 250 (sh, ϵ 2.14 × 10^4), 298 (ϵ 1.54 × 10^4) nm; MS *m*/*z* 378 (M^+, 5%), 285 (100%), 270 (14%), 189 (35%). Anal. Calcd for $C_{17}H_{16}Se_2$: C, 53.98; H, 4.26. Found: C, 54.27; H, 4.24.

Synthesis of 1,3-Bis(benzylseleno)-1,3-diphenylpropadiene (2). To a hexane solution (45 mL) of 1,3-diphenylpropyne (1.50 g, 7.81 mmol) was added dropwise *n*-butyllithium (1.54 mol/L, 10.0 mL, 15.4 mmol) under nitrogen at room temperature, and the solution was stirred for 1 h. TMEDA (1.20 mL, 7.98 mmol) was added to the mixture, and stirring was continued for an additional 1 h. A benzene solution (45 mL) of benzylselenocyanate (3.34 g, 17.0 mmol) was added dropwise at −20 °C to the solution and allowed to warm to room temperature. Water (100 mL) was added to the solution, and the product was extracted with benzene. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After removal of solvent in vacuo, the product was purified by silica gel column chromatography (benzene/hexane = 1/6) to give allene **2** (2.60 g, 64%).

1,3-Bis(benzylseleno)-1,3-diphenylpropadiene (2). Mp 100.0−100.7 °C (pale yellow prisms from ethanol−hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 4H), 7.16−7.28 (m, 12H), 7.31 (t, 4H, J = 7.7 Hz), 7.46 (d, 4H, J = 7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 103.3, 126.9, 127.4, 128.2, 128.5, 128.7, 129.1, 134.8, 138.0, 197.6; IR (KBr) ν_{max} 3076, 3027, 1904, 1594, 1490, 1453, 1444, 1172, 1029, 912, 862, 761, 697, 629 cm^{-1}; UV (cyclohexane) λ_{max} 203 (ϵ 5.77 × 10^4), 229 (sh, ϵ 3.98 × 10^4), 266 (sh, ϵ 2.35 × 10^4), 307 (ϵ 1.38 × 10^4) nm; MS *m*/*z* 530 (M^+, 8%), 439 (100%), 359 (54%). Anal. Calcd for $C_{29}H_{24}Se_2$: C, 65.67; H, 4.56. Found: C, 65.79; H, 4.66.

Synthesis of 1-Benzylseleno-3-methylseleno-1,3-diphenylpropadiene (3). To a hexane solution (30 mL) of 1,3-diphenylpropyne (1.00 g, 5.21 mmol) was added dropwise *n*-butyllithium (1.54 mol/L, 6.6 mL, 10.2 mmol) under nitrogen at room temperature, and the solution was stirred for 1 h. TMEDA (0.80 mL, 5.32 mmol) was added to the mixture, and stirring was continued for an additional 1 h. A benzene solution (30 mL) of dimethyl diselenide (1.06 g, 5.63 mmol) and benzylselenocyanate (1.23 g, 6.26 mmol) was added dropwise to the solution and stirred for 30 min. Water (100 mL) was added to the solution, and the product was extracted with benzene. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After removal of solvent in vacuo, the product was purified by silica gel column chromatography (benzene/hexane = 1/8) to give unsymmetric allene **3** (402 mg, 17%) together with symmetric allenes **1** (520 mg, 26%) and **2** (128 mg, 5%).

1-Benzylseleno-3-methylseleno-1,3-diphenylpropadiene (3). Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.06 (s, 3H), 3.97 (s, 2H), 7.14−7.35 (m, 11H), 7.45 (dd, 2H, J = 1.5, 7.8 Hz), 7.54 (dd, 2H, J = 1.2, 7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.2, 31.0, 105.2, 105.3, 126.9, 127.1, 127.2, 128.17, 128.20, 128.5, 128.6, 128.7, 129.1, 134.9, 135.0, 137.9, 195.3; IR (neat) ν_{max} 3057, 3027, 2925, 1906, 1594, 1490, 1445, 1029, 911, 860, 760, 692 cm^{-1}; MS *m*/*z* 454 (M^+, 2%), 361 (34%), 285 (100%), 269 (52%), 189 (69%). Anal. Calcd for $C_{23}H_{20}Se_2$: C, 60.81; H, 4.44. Found: C, 60.90; H, 4.41.

General Procedure for the Synthesis of Diselenocyclic Allene (4b) and Tetraselenocyclic Bisallenes (5a and 5b). To a hexane solution (40 mL) of 1,3-diphenylpropyne (1.00 g, 5.21 mmol) was added dropwise *n*-butyllithium (1.54 mol/L, 6.6 mL, 10.2 mmol) under nitrogen at room temperature, and the solution was stirred for 1 h. TMEDA (0.80 mL, 5.32 mmol) was added to the mixture, and stirring was continued for an additional 1 h. A THF solution (120 mL) of alkane diselenocyanate (1.1 equiv) was added dropwise to the solution at −80 °C, and the solution was allowed to warm to room temperature. Stirring was continued for an additional 2 d. Water (100 mL) was added to the solution, and the product was extracted with benzene. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After removal of solvent in vacuo, the products were separated by gel permeation chromatography (chloroform). Compound **5a** was recrystallized from chloroform−hexane to give yellow prisms (*meso*-**5a**) and yellow solid (*dl*-**5a**). **5a**, 26% (511 mg, *dl*/*meso* ≈ 1/2); **4b**, 57% (1.16 g); **5b**, 1% (29 mg, *dl*/*meso* ≈ 1/1).

1,3-Diphenyl-4,8-diselenocycloocta-1,2-diene (4b). Mp 173.9−175.0 °C (orange needles from chloroform−hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42−2.46 (m, 2H), 2.86−2.90 (m, 2H), 3.14−3.20 (m, 2H), 7.30 (tt, 2H, J = 1.6, 7.2 Hz), 7.38 (t, 4H, J = 7.2 Hz), 7.62 (dd, 4H, J = 1.6, 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.8, 40.3, 108.3, 127.9, 128.5, 128.6, 135.0, 192.4; IR (KBr) ν_{max} 3068, 3037, 2937, 1887, 1591, 1490, 1443, 1408, 1290, 855, 760, 689 cm^{-1}; UV (cyclohexane) λ_{max} 236 (ϵ 2.05 × 10^4), 250 (ϵ 2.16 × 10^4), 317 (ϵ 1.22 × 10^4) nm; MS *m*/*z* 390 (M^+, 8%), 349 (1%), 270 (60%), 190 (100%). Anal. Calcd for $C_{18}H_{16}Se_2$: C, 55.40; H, 4.13. Found: C, 55.38; H, 4.16.

***dl*-1,3,8,10-Tetraphenyl-4,7,11,14-tetraselenocyclotetradeca-1,2,8,9-tetraene (*dl*-5a).** Mp 168.8−170.5 °C (decomp, yellow solid); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35 (s, 8H), 7.26 (t, 4H, J = 7.9 Hz), 7.33 (t, 8H, J = 7.9 Hz), 7.52 (d, 8H, J = 7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.7, 100.2, 127.6, 128.2, 128.7, 134.4, 199.3; IR (KBr) ν_{max} 3020, 1903, 1593, 1488, 1444, 1159, 865, 757, 689, 640, 581 cm^{-1}; UV (cyclohexane) λ_{max} 208 (ϵ 4.87 × 10^4), 236 (sh, ϵ 4.19 × 10^4), 258 (ϵ 4.35 × 10^4), 304 (sh, ϵ 1.76 × 10^4) nm; MS *m*/*z* 724 (M^+-2(CH_2), 0.2%), 696 (0.2%), 617 (1%), 270 (78%), 190 (100%). Anal. Calcd for $C_{34}H_{28}Se_4$: C, 54.27; H, 3.75. Found: C, 54.13; H, 3.88.

***meso*-1,3,8,10-Tetraphenyl-4,7,11,14-tetraselenocyclotetradeca-1,2,8,9-tetraene (*meso*-5a).** Mp 159.0−160.0 °C (yellow prisms from chloroform−hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.10−3.24 (m, 8H), 7.26 (t, 4H, J = 7.4 Hz), 7.32 (t, 8H, J = 7.4 Hz), 7.49 (d, 8H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.3, 103.9, 127.3, 128.4, 128.7, 134.8, 196.3; IR (KBr) ν_{max} 3022, 1906, 1593, 1488, 1442, 1160, 864, 757, 694, 641, 619 cm^{-1}; UV (cyclohexane) λ_{max} 206 (ϵ 7.19 × 10^4), 238 (ϵ 4.57 × 10^4), 250 (sh, ϵ 4.45 × 10^4), 303 (sh, ϵ 1.95 × 10^4) nm; MS *m*/*z* 696 (M^+-4(CH_2), 0.2%), 616 (0.7%), 536 (3%), 460 (11%), 380 (23%), 270 (79%), 190 (100%). Anal. Calcd for $C_{34}H_{28}Se_4$: C, 54.27; H, 3.75. Found: C, 54.32; H, 3.71.

1,3,9,11-Tetraphenyl-4,8,12,16-tetraselenocyclohexadeca-1,2,9,10-tetraene (5b). As a *dl*/*meso* mixture (≈1/1): mp 98.5−112.5 °C (colorless solid); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.08−2.26 (m, 4H), 2.76−2.92 (m, 8H), 7.23−7.33 (m, 12H), 7.49−7.53 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.7, 27.2, 31.0, 31.3, 100.7, 103.1, 127.4, 127.5, 128.0, 128.1, 128.60, 128.64, 134.7, 134.9, 197.1, 198.4; IR (KBr) ν_{max} 3051, 3022, 2920, 1903, 1593, 1489, 1443, 1210, 1074, 1028, 859, 757, 691, 639 cm^{-1}; MS *m*/*z* 540 (M^+-6(CH_2)-2Se, 1%), 460 (2%), 380 (31%), 190 (100%). Anal. Calcd for $C_{36}H_{32}Se_4$: C, 55.40; H, 4.13. Found: C, 54.94; H, 4.27.

Synthesis of Diselenocyclic Allene (4c) and Tetraselenocyclic Bisallene (5c). To a hexane solution (60 mL) of 1,3-diphenylpropyne (1.50 g, 7.81 mmol) was added dropwise *n*-butyllithium (1.57 mol/L, 10.0 mL, 15.7 mmol) under nitrogen at room temperature, and the solution was stirred for 1 h. TMEDA (1.20 mL, 7.98 mmol) was added to the mixture, and stirring was continued for an additional 1 h. A benzene solution (180 mL) of butane-1,4-diselenocyanate (2.35 g, 8.83 mmol) was added dropwise to the solution at −20 °C and allowed to warm to room temperature. Stirring was continued for an additional 1 d. Water (100 mL) was added to the solution, and the products were extracted with THF. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After removal of solvent in vacuo, the product was purified by silica gel column chromatography (benzene/hexane = 1/5) to give cyclic allene **4c** (442 mg, 14%) and cyclic bisallene **5c** (447 mg, 14%) (*dl*/*meso* ≈ 1/1). One stereoisomer of **5c** was obtained by washing the *dl*- and *meso*-mixture of **5c** with chloroform.

1,3-Diphenyl-4,9-diselenocyclonona-1,2-diene (4c). Mp 136.5−137.8 °C (yellow needles from chloroform−hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.87−1.96 (m, 2H), 2.14−2.24 (m, 2H), 2.80−2.92 (m, 4H), 7.26 (t, 2H, J = 8.3 Hz), 7.35 (t, 4H, J = 8.3 Hz), 7.65 (d, 4H, J = 8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.5, 28.7, 99.1, 127.8, 128.0, 128.6, 134.8, 201.5; IR (KBr) ν_{max} 3052, 2926, 1947, 1591, 1492, 1487, 1441, 1264, 1072, 854, 758, 691 cm^{-1}; UV (cyclohexane) λ_{max} 228 (sh, ϵ 2.18

× 10^4), 264 (ϵ 2.38 × 10^4), 304 (sh, ϵ 1.23 × 10^4) nm; MS *m*/*z* 404 (M^+, 17%), 349 (21%), 270 (100%), 190 (80%). Anal. Calcd for $C_{19}H_{18}Se_2$: C, 56.45; H, 4.49. Found: C, 56.71; H, 4.50.

1,3,10,12-Tetraphenyl-4,9,13,18-tetraselenocyclooctadeca-1,2,10,11-tetraene (5c). As a *dl*/*meso* mixture (≈ 1/1): mp 144.9−172.0 °C (colorless solid); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.84−1.92 (m, 8H), 2.72−2.86 (m, 8H), 7.23−7.35 (m, 12H), 7.50−7.54 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.6, 26.8, 30.0, 30.2, 103.0, 103.8, 127.1, 127.2, 128.08, 128.14, 128.6 (duplicate), 135.0 (duplicate), 196.3, 196.9; IR (KBr) ν_{max} 3051, 3022, 2925, 1901, 1593, 1489, 1443, 1172, 1076, 1027, 865, 761, 691, 640 cm^{-1}; MS *m*/*z* 540 (M^+-8(CH_2)-2Se, 1%), 460 (3%), 380 (35%), 190 (100%). Anal. Calcd for $C_{38}H_{36}Se_4$: C, 56.45; H, 4.49. Found: C, 55.94; H, 4.47. One stereoisomer of **5c**: mp 170.2−171.9 °C (colorless solid); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83−1.93 (m, 8H), 2.72−2.87 (m, 8H), 7.26 (t, 4H, *J* = 7.9 Hz), 7.33 (t, 8H, *J* = 7.9 Hz), 7.53 (d, 8H, *J* = 7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.8, 30.2, 103.0, 127.3, 128.1, 128.6, 135.1, 197.0; IR (KBr) ν_{max} 3055, 3027, 2940, 1909, 1593, 1490, 1444, 1173, 1075, 1027, 865, 761, 690, 640 cm^{-1}; MS *m*/*z* 596 (M^+− 4(CH_2) − 2Se, 0.3%), 460 (5%), 380 (32%), 302 (3%), 190 (100%).

General Procedure for the Thermal Reaction of Selenium-Substituted Allenes. A *p*-xylene solution (20 mL) of selenium-substituted allene (1.0 mmol) was refluxed for a desired period under nitrogen. After removal of solvent in vacuo, the residue was subjected to silica gel column chromatography (benzene/hexane). **1**: 79% conversion (3 d), **6**[6,12] (34%), **7**[6,12] (7%), **8** (21%), **9** (9%). **2**: 90% conversion (1.5 h), **6** (36%), **7** (8%), **10**[13] (57%), **11**[13] (25%). **3**: 40% conversion (1.5 h), **6** (28%), **7** (7%). **4c**: 34% conversion (55 h), **16** (59%). *dl*-**5a**: 96% conversion (8 h), **6** (3%), **7** (1%), **18** (41%), **19** (11%), **20** (6%), *meso*-**5a** (10%). *meso*-**5a**: 84% conversion (8 h), **6** (5%), **7** (3%), **18** (36%), **19** (4%), **20** (7%), *dl*-**5a** (7%).

***(Z,Z)*-3,4-Bis{α-(methylseleno)benzylidene}-1,2-diphenylcyclobutene (8).** Mp 153.6−155.0 °C (yellow needles from chloroform−methanol); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 6H), 6.64 (dd, 4H, *J* = 1.2, 7.9 Hz), 6.81 (t, 4H, *J* = 7.9 Hz), 6.90−6.96 (m, 8H), 7.10 (dd, 4H, *J* = 1.2, 7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.9, 114.8, 126.66, 126.72, 127.1, 127.2, 127.8, 130.3, 131.9, 138.4, 142.2, 151.6; IR (KBr) ν_{max} 3050, 2920, 1600, 1480, 1440, 1410, 1260, 1070, 1025, 910, 770, 700 cm^{-1}; MS *m*/*z* 568 (M^+, 26%), 475 (100%), 460 (33%), 380 (97%). Anal. Calcd for $C_{32}H_{26}Se_2$: C, 67.61; H, 4.61. Found: C, 67.38; H, 4.71.

***(E,Z)*-3,4-Bis{α-(methylseleno)benzylidene}-1,2-diphenylcyclobutene (9).** Mp 112.1−113.8 °C (yellow solid); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (s, 3H), 1.53 (s, 3H), 6.59 (dd, 2H, *J* = 1.1, 7.9 Hz), 6.80 (t, 2H, *J* = 7.9 Hz), 6.87−6.97 (m, 6H), 7.27−7.34 (m, 4H), 7.41−7.45 (m, 4H), 7.54 (dd, 2H, *J* = 1.2, 8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.4, 7.8, 116.9, 117.8, 126.6, 126.7, 127.1, 127.2, 127.4, 127.6, 127.7, 127.8, 128.6, 129.1, 130.3, 131.1, 131.9, 133.1, 138.3, 139.7, 140.3, 141.3, 152.5, 152.9; IR (KBr) ν_{max} 3076, 3017, 2999, 1595, 1489, 1442, 1305, 1160, 1070, 1028, 923, 772, 755, 727, 699, 685 cm^{-1}; MS *m*/*z* 568 (M^+, 4%), 475 (100%), 460 (25%), 380 (85%). Anal. Calcd for $C_{32}H_{26}Se_2$: C, 67.61; H, 4.61. Found: C, 67.58; H, 4.64.

***cis*-1,3-Diphenyl-4,9-diselenobicyclo[4.3.0]nona-2-ene (16).** Mp 92.5−93.5 °C (pale yellow plates from benzene−hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46−2.57 (m, 3H), 2.73 (dd, 1H, *J* = 4.2, 12.1 Hz), 2.93 (dd, 1H, *J* = 2.2, 12.1 Hz), 3.23−3.28 (m, 1H), 3.38−3.44 (m, 1H), 6.58 (s, 1H), 7.21 (tt, 1H, *J* = 1.5, 7.6 Hz), 7.28−7.32 (m, 3H), 7.36 (t, 2H, *J* = 7.3 Hz), 7.54 (d, 2H, *J* = 7.3 Hz), 7.70 (dd, 2H, *J* = 1.5, 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.9, 23.4, 36.7, 49.8, 60.9, 125.1, 126.7, 126.9, 128.0, 128.3, 128.5, 128.7, 129.1, 140.8, 144.8; IR (KBr) ν_{max} 3050, 2949, 1595, 1487, 1442, 1279, 964, 758, 747, 733, 704, 693 cm^{-1}; MS *m*/*z* 404 (M^+, 11%), 351 (6%), 297 (100%), 269 (7%), 189 (36%). Anal. Calcd for $C_{19}H_{18}Se_2$: C, 56.45; H, 4.49. Found: C, 56.44; H, 4.49.

2,7,9,10-Tetraphenyl-3,6-diselenobicyclo[6.2.0]deca-(*Z*,*Z*,*Z*)-1,7,9-triene (18). Mp 196.0−197.0 °C (yellow solid); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.37 (s, 4H), 6.54 (d, 4H, *J* = 7.6 Hz), 6.82 (t, 4H, *J* = 7.6 Hz), 6.93−6.99 (m, 6H), 7.05 (t, 2H, *J* = 7.6 Hz), 7.26 (d, 4H, *J* = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.7, 115.3, 126.9, 127.1, 127.3, 127.6, 127.9, 130.6, 131.8, 140.8, 145.3, 152.9; IR (KBr) ν_{max} 3058, 2909, 1598, 1479, 1440, 1409, 1227, 1074, 1028, 882, 768, 756, 696, 677 cm^{-1}; MS *m*/*z* 566 (M^+, 26%), 540 (42%), 460 (100%), 380 (31%), 302 (31%); HRMS calcd for $C_{32}H_{24}{}^{80}Se_2$ 568.0208, found 568.0203.

2,5,7,8-Tetraphenyl-3,4-diselenobicyclo[4.2.0]octa-(*Z*,*Z*,*Z*)-1,5,7-triene (19). Mp 196.0−196.5 °C (red needles from chloroform−hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, 4H, *J* = 7.7 Hz), 7.01 (t, 4H, *J* = 7.7 Hz), 7.11−7.14 (m, 6H), 7.22 (t, 2H, *J* = 7.7 Hz), 7.29 (d, 4H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 105.8, 127.6, 127.9, 128.0, 128.3, 128.6, 130.2, 131.6, 135.6, 136.8, 145.8; IR (KBr) ν_{max} 3046, 1486, 1439, 1066, 1027, 767, 758, 694, 538 cm^{-1}; MS *m*/*z* 538 (M^+, 100%), 460 (30%), 380 (23%), 302 (63%). Anal. Calcd for $C_{30}H_{20}Se_2$: C, 66.92; H, 3.74. Found: C, 66.87; H, 3.85.

1,3-Diphenyl-4,7,8,11-tetraselenocycloundeca-1,2-diene (20). Mp 112.3−114.2 °C (yellow solid); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.07−3.12 (m, 2H), 3.24−3.37 (m, 4H), 3.53−3.58 (m, 2H), 7.27 (t, 2H, *J* = 7.0 Hz), 7.35 (t, 4H, *J* = 7.0 Hz), 7.53 (d, 4H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.8, 31.9, 102.3, 127.8, 128.3, 128.7, 134.6, 198.1; IR (KBr) ν_{max} 3055, 3019, 2916, 1904, 1594, 1489, 1444, 1408, 1231, 1158, 1075, 1029, 858, 755, 693 cm^{-1}; MS *m*/*z* 562 (M^+, 7%), 378 (8%), 350 (23%), 270 (87%), 189 (100%); HRMS calcd for $C_{19}H_{18}{}^{80}Se_4$ 565.8069, found 565.8106.

General Procedure for the Photochemical Reaction of Selenium-Substituted Allenes. A benzene solution (100 mL) of selenium-substituted allene (0.4 mmol) was irradiated with a 450 W medium-pressure mercury lamp through a Pyrex filter under argon for a desired period. After removal of solvent in vacuo, the residue was subjected to gel-permeation chromatography (chloroform) or silica gel column chromatography (benzene/hexane). **1**: 82% conversion (1 h), **6** (20%), **7** (20%), **23** (10%). **2**: 79% conversion (1 h), **6** (22%), **7** (16%), **10** (57%). **4b**: 95% conversion (1 h), **6** (29%), **7** (23%), **25** (8%). **4c**: 69% conversion (1 h), **6** (8%), **7** (7%), **26** (51%). *dl*-**5a**: 86% conversion (100 min), **6** (19%), **7** (16%), **20** (11%), *meso*-**5a** (8%). *meso*-**5a**: 96% conversion (90 min), **6** (18%), **7** (17%), **20** (15%), *dl*-**5a** (9%).

3,3-Bis(methylseleno)-1,3-diphenylpropyne (23). Mp 98.5−101.0 °C (pale yellow solid); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 6H), 7.26 (t, 1H, *J* = 7.4 Hz), 7.33−7.56 (m, 7H), 7.89 (d, 2H, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.7, 34.0, 88.5, 89.8, 122.7, 127.2, 127.8, 128.3, 128.4, 128.5, 131.8, 141.4; IR (KBr) ν_{max} 3050, 3011, 2913, 1594, 1489, 1445, 1269, 1031, 910, 758, 699, 691, 520 cm^{-1}; UV (cyclohexane) λ_{max} 250 (ϵ 4.41 × 10^3), 302 (sh, ϵ 7.20 × 10^2) nm; MS *m*/*z* 378 (M^+, 5%), 285 (100%), 270 (44%), 189 (50%); HRMS calcd for $C_{17}H_{16}{}^{80}Se_2$ 379.9582, found 379.9626.

2-Phenethynyl-2-phenyl-1,3-diselenane (25). Pale yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10−2.22 (m, 1H), 2.29−2.36 (m, 1H), 3.07−3.12 (m, 2H), 3.73 (dt, 2H, *J* = 2.2, 13.3 Hz), 7.30−7.42 (m, 6H), 7.56−7.58 (m, 2H), 7.98 (dd, 2H, *J* = 1.2, 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.3, 26.4, 26.7, 89.2, 91.4, 122.9, 127.1, 128.4, 128.45, 128.47, 128.7, 131.7, 140.6; IR (neat) ν_{max} 3056, 2915, 1596, 1489, 1446, 1242, 1030, 859, 756, 691 cm^{-1}; UV (cyclohexane) λ_{max} 224 (ϵ 2.13 × 10^4), 251 (ϵ 2.32 × 10^4) nm; MS *m*/*z* 390 (M^+, 2%), 270 (21%), 190 (100%); HRMS calcd for $C_{18}H_{16}{}^{80}Se_2$ 391.9582, found 391.9566.

2-Phenethynyl-2-phenyl-1,3-diselenepane (26). Pale yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.35−2.50 (m, 4H), 3.18−3.28 (m, 2H), 3.35−3.45 (m, 2H), 7.28 (t, 1H, *J* = 7.4 Hz), 7.34−7.38 (m, 5H), 7.54−7.57 (m, 2H), 7.98 (dd, 2H, *J* = 1.1, 8.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.0, 31.3, 35.4, 90.1, 91.4, 122.9, 126.8, 128.1, 128.3, 128.5 (duplicate), 131.7, 141.4; IR (neat) ν_{max} 3055, 2919, 2847, 1596, 1489, 1443, 1261, 1030, 757, 694 cm^{-1}; MS *m*/*z* 404 (M^+, 4%), 351 (15%), 270

(12) Isagawa, K.; Mizuno, K.; Majima, T. *Tetrahedron Lett.* **1999**, *40*, 9051.

(13) Painter, E. P.; Franke, K. W.; Gortner, R. A. *J. Org. Chem.* **1940**, *5*, 579.

(69%), 189 (100%); HRMS calcd for $C_{19}H_{18}{}^{80}Se_2$ 405.9739, found 405.9777. Anal. Calcd for $C_{19}H_{18}Se_2$: C, 56.45; H, 4.49. Found: C, 55.88; H, 4.27.

X-ray Analysis: Compound 4b. Orange needle of $C_{18}H_{16}Se_2$ having approximate dimensions of 0.80 × 0.80 × 0.75 mm^3. Monoclinic space group $P2_1/n$ with a = 17.438 (9) Å, b = 8.90 (1) Å, c = 10.622 (6) Å, β = 105.424 (2)°, V = 1588 (2) Å^3, Z = 4, and ρ(calcd) = 1.632 g cm^{-3}. Of the 7281 unique data, 4486 with $I > 2\sigma(I)$ were used in the least-squares refinement to yield $R1$ = 0.050 (R = 0.121 and Rw = 0.129 for all data). **Compound 8.** Yellow needle of $C_{32}H_{26}Se_2$ having approximate dimensions of 0.30 × 0.20 × 0.30 mm^3. Monoclinic space group $P2/c$ with a = 18.6330 (9) Å, b = 10.3138 (5) Å, c = 27.749 (2) Å, β = 100.364 (2)°, V = 5245.7 (4) Å^3, Z = 8, and ρ(calcd) = 1.440 g cm^{-3}. Of the 11 951 unique data, 4872 with $I > 2\sigma(I)$ were used in the least-squares refinement to yield $R1$ = 0.048 (R = 0.096 and Rw = 0.120 for all data). **Compound 16.** Pale yellow plate of $C_{38}H_{36}Se_4$ having approximate dimensions of 0.80 × 0.70 × 0.55 mm^3. Triclinic space group $P\bar{1}$ with a = 10.19 (3) Å, b = 8.17 (3) Å, c = 20.2 (1) Å, α = 89.5 (4)°, β = 97.7 (3)°, γ = 90.1 (3)°, V = 1670 (11) Å^3, Z = 2, and ρ(calcd) = 1.607 g cm^{-3}. Of the 7560 unique data, 4454 with $I > 2\sigma(I)$ were used in the least-squares refinement to yield $R1$ = 0.044 (R = 0.114 and Rw = 0.133 for all data).

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Supporting Information Available: Detailed information of the X-ray crystallographic analysis of **4b**, **8**, and **16** including structure diagram, 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 information is available free of charge via the Internet at http://pubs.acs.org.

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