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Thermal [2+2] Cycloaddition of Allenynes: Easy Construction of Bicyclo[6.2.0]deca-1,8-dienes, Bicyclo[5.2.0]nona-1,7-dienes, and Bicyclo[4.2.0]octa-1,6-dienes

Chisato Mukai,* Yasuyuki Hara, Yusuke Miyashita, and Fuyuhiko Inagaki

Division of Pharmaceutical Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

cmukai@kenroku.kanazawa-u.ac.jp

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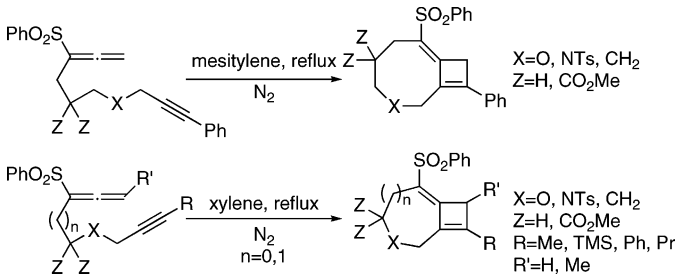

The simple refluxing of allenynes, having a phenylsulfonyl functionality on the allenyl group, in xylene (or mesitylene) without microwave irradiation resulted in the efficient formation of bicyclo[5.2.0]nona-1,7-dienes and bicyclo[4.2.0]octa-1,6-dienes in high yields. This method was shown to be successfully applicable to the first construction of bicyclo[6.2.0]deca-1,8-dienes. Construction of the corresponding oxa- and azabicyclo[*m*.2.0] frameworks could also be attained. This thermal ring-closing reaction involves the formal [2+2] cycloaddition in which the distal double bond of an allenyl moiety exclusively served as one of the π-components regardless of the position of the phenysulfonyl functionality on the allenyl moiety.

Introduction

A novel method for the preparation of bicyclo[5.2.0]nona-1,7-diene skeletons[1] based on the intramolecular [2+2] cycloaddition reaction of allenynes[2,3] with use of microwave irradiation has recently been independently developed by two groups: Brummond and Chen[1a] reported the construction of the bicyclo[5.2.0] derivative **2** from the allene-alkynone derivative **1**, while two successful examples forming other types of bicyclo-[5.2.0] derivatives **4** from the allene-propiolate derivatives **3** under similar conditions were described by Oh and co-workers.[1b] They claimed that the transformation of **3** into **4** could not occur under the stated conditions[1b] without microwave irradiation (Scheme 1).

On the other hand, during our studies on the scope and limitations of the Rh(I)-catalyzed intramolecular Pauson−Khand-type reaction of phenylsulfonylallenynes,[4,5] compound **5a** was exposed to a catalytic amount of $[RhCl(CO)dppp]_2$ in

* To whom correspondence should be addressed. Phone: +81-76-234-4411. Fax: +81-76-234-4410.

(1) (a) Brummond, K. M.; Chen, D. *Org. Lett.* **2005**, *7*, 3473−3475. (b) Oh, C. H.; Gupta, A. K.; Park, D. I.; Kim, N. *Chem. Commun.* **2005**, 5670−5672. In both references, the preparation of bicyclo[4.2.0]octa-1,6-dienes skeleton with microwave irradiation conditions was also reported.

(2) For the intramolecular thermal [2+2] cycloaddition of allenynes for the construction of the bicyclo[3.2.0]hepta-1,5-diene skeleton without microwave irradiation, see: (a) Gillmann, T.; Hülsen, T.; Massa, W.; Wocadlo, S. *Synlett* **1995**, 1257−1259. (b) Cao, H.; Flippen-Anderson, J.; Cook, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 3230−3231. (c) Cao, H.; Van Ornum, S. G.; Deschamps, J.; Flippen-Anderson, J.; Laib, F.; Cook, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 933−943.

(3) For the intramolecular thermal [2+2] cycloaddition of allenynes for the construction of the bicyclo[4.2.0]octa-1,6-diene skeleton without microwave irradiation, see: (a) Ikemoto, C.; Kawano, T.; Ueda, I. *Tetrahedron Lett.* **1998**, *39*, 5053−5056. (b) Ohno, H.; Mizutani, T.; Kadoh, Y.; Miyamura, K.; Tanaka, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 5113−5115.

(4) For the Rh(I)-catalyzed Pauson−Khand reaction of phenylsulfonylallenynes, see: (a) Mukai, C.; Nomura, I.; Yamanishi, K.; Hanaoka, M. *Org. Lett.* **2002**, *4*, 1755−1758. (b) Mukai, C.; Nomura, I.; Kitagaki, S. *J. Org. Chem.* **2003**, *68*, 1376−1385. (c) Mukai, C.; Inagaki, F.; Yoshida, T.; Kitagaki, S. *Tetrahedron Lett.* **2004**, *45*, 4117−4121. (d) Mukai, C.; Inagaki, F.; Yoshida, T.; Yoshitani, K.; Hara, Y.; Kitagaki, S. *J. Org. Chem.* **2005**, *70*, 7159−7171. (e) Mukai, C.; Hirose, T.; Teramoto, S.; Kitagaki, S. *Tetrahedron* **2005**, *61*, 10983−10994.

(5) For the Rh(I)-catalyzed Pauson−Khand reaction of phenylsulfonylallenenes, see: Inagaki, F.; Mukai, C. *Org. Lett.* **2006**, *8*, 1217−1220.

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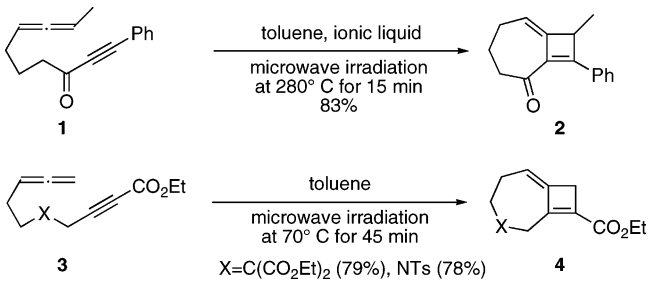
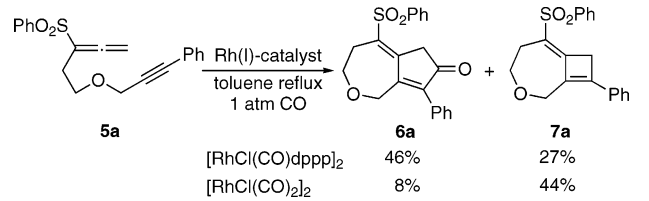
SCHEME 1

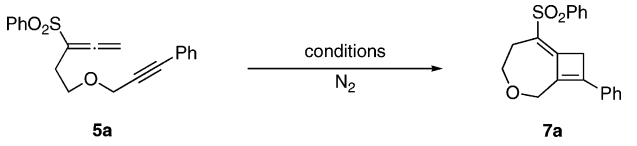


SCHEME 2



refluxing toluene under an atmosphere of CO (optimized conditions[4] for Rh(I)-catalyzed Pauson−Khand-type reaction of other allenynes) that produced the Pauson−Khand product **6a** in 46% yield along with the unexpected 5-oxabicyclo[5.2.0]-nona-1,7-diene derivative **7a** in 27% yield as a byproduct.[6] Compound **7a** became a major product (44%) when [RhCl-$(CO)_2]_2$ was used instead of $[RhCl(CO)dppp]_2$[6] (Scheme 2). Thus, the formation of the oxabicyclo[5.2.0]nona-1,7-diene skeleton **7a** by the simple heating of the allenyne **5a** in toluene without any microwave irradiation prompted us to search for the optimal conditions for this conversion[7−9] as well as study its scope and limitations. We now describe an efficient and very simple procedure for the construction of bicyclo[4.2.0]octa-1,6-dienes, bicyclo[5.2.0]nona-1,7-dienes, and bicyclo[6.2.0]deca-1,8-dienes. We note, in advance, that this is the first example of the construction of the bicyclo[6.2.0]deca-1,8-diene frameworks by the [2+2] cycloaddition of allenynes.

TABLE 1. Thermal [2+2] Cycloaddition of 5a



entry	solvent	*T* (°C)	*t* (h)	Rh(I)-catalyst[a]	yield (%)
1	toluene	80	40	none	23[b]
2	toluene	reflux	25	none	86
3	xylene	reflux	2	none	91
4	toluene	100	20	$[RhCl(CO)_2]_2$	40[c]
5	xylene	reflux	1	$[RhCl(CO)_2]_2$	46

[a] 2.5 mol % of Rh(I)-catalyst was used. [b] The starting material **5a** was recovered in 53% yield. [c] The starting material **5a** was recovered in 38% yield.

Results and Discussion

Our initial evaluation for the intramolecular [2+2] cycloaddition of a phenylsulfonylallenyne **5a**[10] was carried out in toluene at 80 °C in a nitrogen atmosphere instead of CO to give **7a** in 23% yield together with the recovery of the starting material in 53% yield after a prolonged reaction time (Table 1, entry 1). Refluxing of **5a** in toluene for 25 h significantly improved the chemical yield (86%) (entry 2). Changing the solvent from toluene to xylene led to a shortening of the reaction time and the highest yield (91%) (entry 3). When this cycloaddition reaction was carried out in the presence of a rhodium catalyst, significantly lower yields were observed (entries 4 and 5). These results indicated that the transformation of **5a** into **7a** would mainly proceed via the thermal [2+2] cycloaddition rather than the rhodium catalyst-mediated ring-closing reaction.[11−13]

We next investigated the scope of this thermal [2+2] ring-closing reaction using several substrates **5b**−**f** under xylene refluxing conditions. These results are summarized in Table 2. The allenynes **5b**[4d] and **5c**,[10] having an oxygen atom on the alkyl tether and a substituent at the alkyne terminus, consistently produced the corresponding oxabicyclic compounds **7b** and **7c** in reasonable yields, although prolonged reaction times, compared to that of **5a** (2 h), were required (entries 1 and 2). When compound **5d**,[4d] which has a terminal alkyne group, was exposed to the standard conditions, no formation of the oxabicyclo[5.2.0] derivative could be detected and the gradual decomposition of the starting material was observed (entry 3). Both the aza- and carbon-congeners **5e**[4d] and **5f**[10] are also susceptible to this ring-closing reaction that produced the corresponding 5-azabicyclo-[5.2.0]nona- and bicyclo[5.2.0]nona-1,7-dienes **7e**,**f** in high yields (entries 4 and 5). On the basis of the results in Tables 1 and 2, it might be concluded that the thermal [2+2] cycloaddition of 3-phenylsulfonyl-9-substituted-1,2-nonadien-8-yne and its congeners possessing a heteroatom on the alkyl appendage

(6) Under similar Pauson−Khand-type conditions, the homologues of **5a**, having a carbon or nitrogen atom instead of an oxygen atom with a different kind of terminal substituent, did not produce the corresponding bicyclo[5.2.0]nona-1,7-diene compounds, see ref 4.

(7) For reviews of the [2+2] cycloaddition of allenes, see: (a) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805−2827. (b) Murakami, M.; Matsuda, T. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 2, pp 727−815. (c) Ma, S. *Chem. Rev.* **2005**, *105*, 2829−2872.

(8) Extensive studies of the intramolecular thermal [2+2] cycloaddition of phenylsulfonylallenenes have been made by Padwa; see: (a) Padwa, A.; Filipkowski, M. A.; Meske, M.; Watterson, S. H.; Ni, Z. *J. Am. Chem. Soc.* **1993**, *115*, 3776−3777. (b) Padwa, A.; Meske, M.; Murphree, S. S.; Watterson, S. H.; Ni, Z. *J. Am. Chem. Soc.* **1995**, *117*, 7071−7080. (c) Padwa, A.; Lipka, H.; Watterson, S. H.; Murphree, S. S. *J. Org. Chem.* **2003**, *68*, 6238−6250 and references cited therein.

(9) Additional examples for intramolecular thermal [2+2] cycloaddition of allenenes; see: (a) Yeo, S.-K.; Shiro, M.; Kanematsu, K. *J. Org. Chem.* **1994**, *59*, 1621−1632. (b) Yoshida, M.; Hidaka, Y.; Nawata, Y.; Rudzinski, J. M.; Osawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* **1988**, *110*, 1232−1238. (c) Hansen, T. V.; Skattebol, L.; Stenstrom, Y. *Tetrahedron* **2003**, *59*, 3461−3466. (d) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Org. Lett.* **2003**, *5*, 3795−3798. (e) Alcaide, B.; Almendros, P.; Aragoncillo, C.; Redondo, M. C.; Torres, M. R. *Chem. Eur. J.* **2006**, *12*, 1539−1546. (f) Närhi, K.; Franzén, J.; Bäckvall, J.-E. *J. Org. Chem.* **2006**, *71*, 2914−2917 and references cited therein.

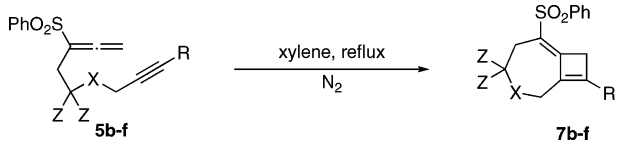
(10) The preparation and characterization of the unknown allenynes are described in the Supporting Information.

(11) The $Mo(CO)_6$-catalyzed intramolecular [2+2] cycloaddition reaction of allenynes resulting in the formation of bicyclo[4.2.0]octa-1,6-dienes was reported; see: Shen, Q.; Hammond, G. B. *J. Am. Chem. Soc.* **2002**, *124*, 6534−6535.

(12) The $PdCl_2(PPh_3)_2$-catalyzed intramolecular [2+2] cycloaddition reaction of allenynes resulting in the formation of bicyclo[*m*.2.0]-1,(*m*+2)-diene derivatives ($m = 3, 4$) was reported, see ref 1b.

(13) The $PtCl_2$-catalyzed cycloisomerization of allenynes resulting in the formation of bicyclo[3.2.0] frameworks was reported; see: Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Synlett* **2006**, 575−578.

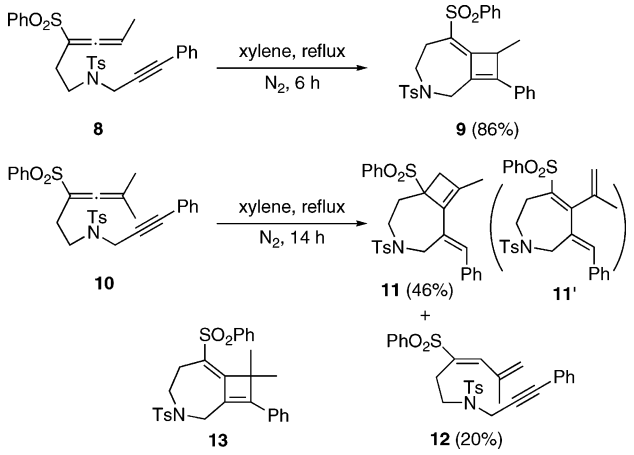
TABLE 2. Thermal [2+2] Cycloaddition of 5b−f



entry	substrate	R	X	Z	*t* (h)	product	yield (%)
1	**5b**	TMS	O	H	20	**7b**	62[a]
2	**5c**	Me	O	H	40	**7c**	63[b]
3	**5d**	H	O	H	20	**7d**	−[c]
4	**5e**	TMS	NTs	H	11	**7e**	91
5	**5f**	TMS	CH_2	CO_2Me	10	**7f**	80

[a] The starting material **5b** was recovered in 4% yield. [b] The starting material **5c** was recovered in 10% yield. [c] The starting material **5d** was recovered in 26% yield.

SCHEME 3



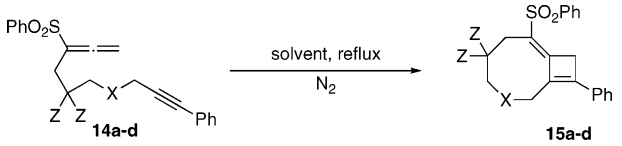
produces the corresponding bicyclo[5.2.0] frameworks in good to high yields by simply refluxing in xylene.

The next phase of this investigation was to confirm the compatibility of the substituent at the allenic terminus of **5** during this ring-closing reaction. A solution of the monomethyl derivative **8**[4d] in xylene was refluxed in a nitrogen atmosphere for 6 h to give the bicyclo[5.2.0] derivative **9** in 86% yield (Scheme 3). The dimethyl derivative **10**,[10] however, was transformed into two different products **11**[4d] and **12**.[14] The expected [2+2] compound **13** could not be detected in the reaction mixture. The formation of another type of bicyclo[5.2.0] skeleton **11** could be rationalized in terms of the intermediacy of the triene derivative **11′**,[4d] which should be formed via the thermal ene-type reaction of **10**, the former of which would simultaneously undergo the 4π-electronic cyclization reaction and collapse into **11**. These observations obviously indicated that allenynes having a tetrasubstituted-allenyl moiety, such as **10**, seem to be unsuitable substrates for this thermal [2+2] cycloaddition reaction (Scheme 3).

The thermal [2+2] cycloaddition of the one-carbon homologated allenynes **14**[10] for the synthesis of the bicyclo[6.2.0]-decadienes was the next subject. Thus, a solution of **14a** in xylene was refluxed for 30 h to afford 2-phenylsulfonyl-6-oxabicyclo[6.2.0]deca-1,8-diene (**15a**) in 41% yield along with **14a** in 28% yield (Table 3, entry 1). Similarly, the aza-congener **15b** was obtained from **14b** in 74% yield (entry 2). Improvement

(14) The stereochemistry was determined by an NOE analysis.

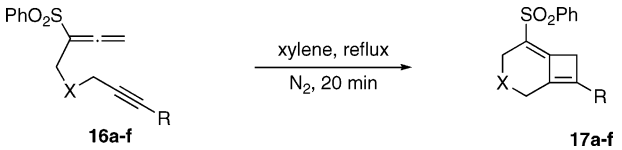
TABLE 3. Thermal [2+2] Cycloaddition of 14a−d



entry	substrate	X	Z	solvent	*t* (h)	product	yield (%)
1	**14a**	O	H	xylene	30	**15a**	41[a]
2	**14b**	NTs	H	xylene	28	**15b**	74
3	**14a**	O	H	mesitylene	10	**15a**	75
4	**14b**	NTs	H	mesitylene	7	**15b**	88
5	**14c**	CH_2	CO_2Me	mesitylene	11	**15c**	60[b]
6	**14d**	CH_2	H	mesitylene	18	**15d**	−[c]

[a] The starting material **14a** was recovered in 28% yield. [b] The starting material **14c** was recovered in 9% yield. [c] The starting material **14d** was recovered in 70% yield.

TABLE 4. Thermal [2+2] Cycloaddition of 16a−f



entry	substrate	R	X	product	yield (%)
1	**16a**	Ph	O	**17a**	64[a]
2	**16b**	Me	O	**17b**	98
3	**16c**	TMS	O	**17c**	90
4	**16d**	H	NTs	**17d**	−[b]
5	**16e**	^{n}Pr	NTs	**17e**	100
6	**16f**	^{n}Bu	$C(CO_2Me)_2$	**17f**	94

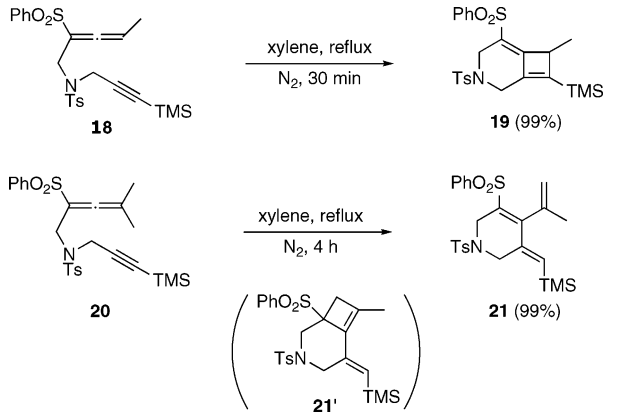
[a] The allene **16a** was too reactive to purify. Thus, the crude **16a** was heated in toluene at 40 °C for 18 h to give compound **17a** in 64% overall yield from the corresponding propargyl alcohol precursor. [b] The starting material was completely decomposed.

of the chemical yield for both compounds, accompanied by a significant shortening of the reaction time, was realized by using mesitylene instead of xylene to furnish **15a** and **15b** in the respective yields of 75% and 88% (entries 3 and 4). Furthermore, the carbon homologue **15c** could be synthesized in a good yield under similar conditions (entry 5). However, the simpler carbon analogue **14d** without a bis(methoxycarbonyl) group did not give the ring-closed product **15d**, presumably due to the loss of the Thorpe−Ingold-type effects (entry 6).[15]

To further extend the scope of this simple method, we examined the construction of the bicyclo[4.2.0]octa-1,6-diene derivative. The results are summarized in Table 4. As can be predicted from the literature,[2,3] the easy formation of the bicyclo-[4.2.0]octa-1,6-diene frameworks **17** from allenynes **16** could be attained in high yields except for compound **16d**, and the reaction occurred much faster than those of the bicyclo[5.2.0]-nona-1,7-dienes and bicyclo[6.2.0]deca-1,8-dienes. Because the phenyl derivative **16a** was extremely reactive and gradually transformed into the cyclized product **17a** during its preparation steps, compound **17a** was straighforwardly synthesized in a 64% overall yield from the propargyl alcohol precursor by successive treatment with PhSCl and *m*CPBA, followed by heating in toluene at 40 °C for 18 h (entry 1). In the case of compound

(15) For a recent review, see: Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735−1766.

SCHEME 4



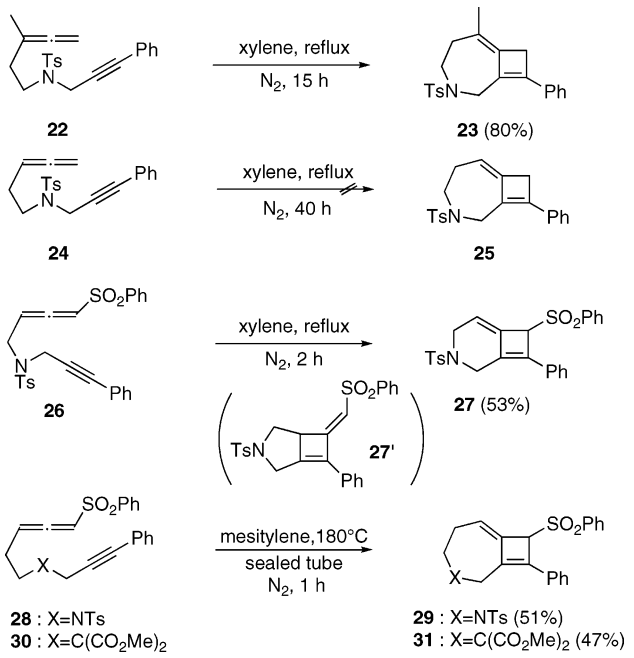
16d (entry 4), no characteristic products could be isolated from the reaction mixture after refluxing in xylene for 20 min. This result is in good accordance with the result of compound **5d** in Table 2, entry 3. Two additional examples of the thermal [2+2] cycloaddition are depicted in Scheme 4. The monomethyl derivative **18**[10] underwent the [2+2] cycloaddition in refluxing xylene to afford the bicyclo[4.2.0] compound **19** in 99% yield, whereas the dimethyl congener **20** under similar conditions provided the triene derivative **21** via the thermal ene-type reaction. The bicyclo[4.2.0] derivative **21′**, which may be formed via the 4π-electronic cyclization reaction of **21**, could never be detected. This result is in good agreement with the previous observations.[4c,d]

The thermal [2+2] cycloaddition of the phenylsulfonylallenynes, such as compounds **5**, **14**, and **16** (1-phenylsulfonyl-1-substituted-allene species) as well as **8** and **18** (1-phenylsulfonyl-1,3-disubstituted-allene species), exclusively gave the corresponding bicyclo[*m*.2.0] derivatives (m = 4, 5, 6), in which the distal double bond of the allenyl moiety consistently took part in the ring-closing process. Some additional experiments with various allenynes were performed to confirm the effect of a phenylsulfonyl group on the allenyl moiety in this ring-closing reaction (Scheme 5). The allenyne **22**,[10] having a methyl group instead of a phenylsulfonyl one, was submitted to the xylene refluxing conditions to furnish the bicyclo[5.2.0] compound **23** in 80% yield along with the recovery of the starting material (10%), strongly indicating that a phenylsulfonyl group on the allenyl moiety seems not to be mandatory for this regioselective thermal [2+2] cycloaddition. Upon heating in refluxing xylene for 40 h, however, compound **24**,[10] without an additional functional group at the C_1-position of the allenyl moiety (1-substituted-allene), gradually decomposed and no expected products like **25** could be found except for the starting material. Presumably, the instability of **24** and/or **25** under high-temperature conditions, compared to those of the phenysulfonylallenynes,[16] may have caused the decomposition.

To obtain more information on the effect of the phenylsulfonyl group, it would be interesting to investigate the thermal [2+2] cycloaddition of the 1-phenylsulfonyl-3-substituted species, which might clarify the role of the phenylsulfonyl group in the regioselectivity observed in this ring-closing reaction. Thus, compound **26**,[10] possessing the 1-phenylsulfonyl-3-substituted framework, was refluxed in xylene until the starting

(16) The easy formation of phenylsulfonylbicyclo[*m*.2.0] skeletons might reflect the marked stability of phenylsulfonylallenes under high-temperature conditions.

SCHEME 5

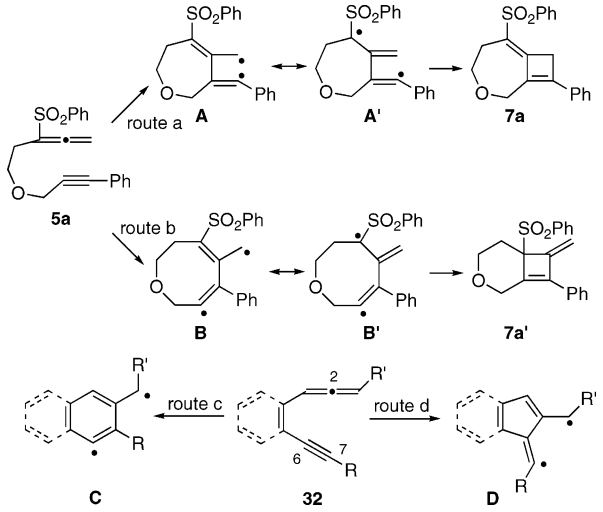


material completely disappeared (2 h) to give the bicyclo[4.2.0] derivative **27** in 53% yield through the [2+2] cycloaddition between a distal double bond of an allenyl functionality and a triple bond. The corresponding azabicyclo[3.2.0]heptene skeleton **27′** with an exomethylene group, which should have been formed by the reaction of a triple bond with the proximal double bond of the allenyl group, could not be obtained. This experiment revealed that the thermal reaction of the 1-phenylsulfonyl-3-substituted-allene **26** required a longer reaction time and resulted in a lower chemical yield in comparison to those of the 1-phenylsulfonyl-1-substituted-allenes depicted in Table 4 (20 min, 90−100%). For the one-carbon homologated 1-phenylsulfonyl-3-substituted-allenes **28**[10] and **30**,[10] a much higher temperature (180 °C), compared to that for the 1-phenylsulfonyl-1-substituted-allenes **5** (xylene reflux, see Table 2, e.g.), was necessary to produce the ring-closed products **29** and **31** in moderate yields (51% and 47% yield, respectively). In fact, **29** was obtained in only13% yield when **28** was treated in refluxing xylene for 6 h. Thus, it was found that the [2+2] cycloaddition of the phenylsulfonylallenynes exclusively occurred between the distal double bond of the allenyl functionality and a triple bond irrespective of the position of the phenylsulfonyl group in sharp contrast to the [2+2] cycloaddition of the allenenes reported by Padwa,[8] in which a distal or a proximal double bond of the allenyl moiety reacted with an olefin depending on the position of the phenylsulfonyl group on the allenyl moiety.

The mechanism for the regioselective formation of the bicyclo[*m*.2.0] frameworks is uncertain at this stage, but a simple explanation involving biradical intermediates might be tentatively rationalized based on the literature precedents.[1−3,7−9] For the thermal reaction of **5a**, for instance, there are two pathways via biradical intermediates that can be considered. One is route a in which the allyl radical intermediate **A** (**A′**) would be formed by the initial combination between the sp-hybridized carbon center of the allenyl moiety and that of the internal alkyne carbon. The resulting seven-membered biradical intermediate **A** (**A′**), having an allyl as well as phenylvinyl radical species, would immediately collapse into compound **7a**. An alternative

initial connection of the sp-hybridized carbon of the allenyl moiety with the external alkyne carbon might lead to the eight-membered intermediate **B** (**B′**) containing allyl and vinyl radicals. The ring-closing reaction of **B** (**B′**) would give rise to the production of compound **7a′** (route b). The fact that compound **5a** exclusively gave **7a** in a high yield (Table 1) would strongly reflect the preferential formation of **A** (**A′**) over **B** (**B′**) due to its easier formation, the latter of which has an eight-membered ring, while the former has a seven-membered one. Similarly, the exclusive formation of bicyclo[4.2.0]-octadiene derivatives **17** and the bicyclo[6.2.0]decadiene derivatives **15** would be interpreted by considering the ring size of the biradical species (6- versus 7-membered ring and 8- versus 9-membered ring).[17] It is well-known that the Myers−Saito cycloaromatization (C^2-C^7 cyclization)[18] of enyne-allenes **32** predominantly proceeds via the biradical **C** when **32** does not have a substituent at the alkyne terminus (route c), whereas aryl groups or sterically demanding substituents at the acetylene terminus of compound **32** change the reaction pathway from the C^2-C^7 mode combination to the C^2-C^6 one (Schmittel cyclization)[19] resulting in the formation of biradical **D**, the vinyl radical center of which is stabilized by the attached substituent (R).[19] The plausible route a, leading to **7a**, might be regarded as an analogy to route d (C^2-C^6 cyclization), both of which produce a vinyl radical center stabilized by the phenyl group (when R = Ph), although the nonconjugated allenyne group of compound **5a** is not the same as that of **32** having a conjugated enyne-allene functionality. As mentioned in Tables 2 and 4, compounds **5d** and **16d**, both of which have a terminal acetylene moiety, did not provide the corresponding [2+2] cycloadducts unlike the other substrates possessing a substituent at the triple bond terminus. This observation might be rationalized by considering the stability of the vinyl radical center due to the attached substituents.[20] On the other hands, route b would be regarded as analogous to route c (C^2-C^7 cyclization). In contrast to the biradical intermediate **A** (**A′**), the stability of the vinyl radical center of the biradical intermediate **B** (**B′**) could not be directly increased by the presence of the attached substituent (a terminal substituent of the acetylene group of the starting allenyne). As a result, route a would become a favorable pathway over route b due to (i) the ring size of the biradical intermediate and/or (ii) the stabilization of the vinyl radical by the attached substituent resulting in the exclusive formation of compound **7a**.

SCHEME 6



Our next effort involved capturing the possible biradical intermediate **A** (**A′**). Thus, compound **18** was refluxed in xylene in the presence of TEMPO (7 equiv) for 1 h, hoping to obtain compound **33**, but the only isolatable compound from the reaction mixture was **19** in a rather lower yield (57%), compared to the reaction without TEMPO (99%, Scheme 4). When **18** was treated with 1,4-cyclohexadiene (1,4-CHD) (20 equiv) in refluxing toluene, compound **19** was again isolated in 63% yield. Furthermore, refluxing of compound **8** in 1,4-CHD[19f,h] did not afford compound **34** at all.[21]

Schemittel[19] reported that the phenyl group of the benzene-conjugated allenynes, such as compound **32** (R′ = Ph) in Scheme 6, participated in the ring-closing reaction through a biradical intermediate **D**. Wang[22] also described similar ring-closing reactions of the benzene-conjugated aza-allenyne congeners.[23] On the basis of these results, we presumed that the allyl-benzyl radical intermediate **E** (**F**) resulting from the allenyne **35** having a phenyl group at the allenic terminus would be susceptible to a subsequent ring-closing reaction to produce the tricyclic product **37** via the 1,5-hydrogen-shift of **36** (Scheme 8).

Thus, the allenyne **38**[10] was heated in toluene under reflux to give the [2+2] cycloadduct **39** in 72% yield along with the expected tricyclic derivative **40** in 18% yield (Scheme 9). Refluxing of **38** in xylene afforded a similar result. The low

(17) The exclusive formation of **27**, **29**, and **31** from the corresponding 1-phenylsulfonyl-1,3-disubstituted-allenes **26**, **28**, and **30** would also be interpreted by a similar consideration on the stability of the biradical intermediates.

(18) (a) Myers, A. G. *Tetrahedron Lett.* **1987**, *28*, 4493−4496. (b) Myers, A. G.; Kuo, E. Y.; Finney, N. S. *J. Am. Chem. Soc.* **1989**, *111*, 8057−8059. (c) Nagata, R.; Yamanaka, H.; Okazaki, E.; Saito, I. *Tetrahedron Lett.* **1989**, *30*, 4995−4998. (d) Nagata, R.; Yamanaka, H.; Murahashi, E.; Saito, I. *Tetrahedron Lett.* **1990**, *31*, 2907−2910. (e) Myers, A. G.; Dragovich, P. S.; Kuo, E. Y. *J. Am. Chem. Soc.* **1992**, *114*, 9369−9386.

(19) (a) Schmittel, M.; Strittmatter, M.; Kiau, S. *Tetrahedron Lett.* **1995**, *36*, 4975−4978. (b) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, *37*, 999−1002. (c) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1843−1845. (d) Schmittel, M.; Maywald, M.; Strittmatter, M. *Synlett* **1997**, 165−166. (e) Schmittel, M.; Keller, M.; Kiau, S.; Strittmatter, M. *Chem. Eur. J.* **1997**, *3*, 807−816. (f) Schmittel, M.; Steffen, J.-P.; Auer, D.; Maywald, M. *Tetrahedron Lett.* **1997**, *38*, 6177−6180. (g) Schmittel, M.; Steffen, J.-P.; Wencesla Ángel, M. Á.; Engels, B.; Lennartz, C.; Hanrath, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1562−1564. (h) Engels, B.; Lennartz, C.; Hanrath, M.; Schmittel, M.; Strittmatter, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1960−1963. (i) Schmittel, M.; Steffen, J.-P.; Engels, B.; Lennartz, C.; Hanrath, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2371−2373.

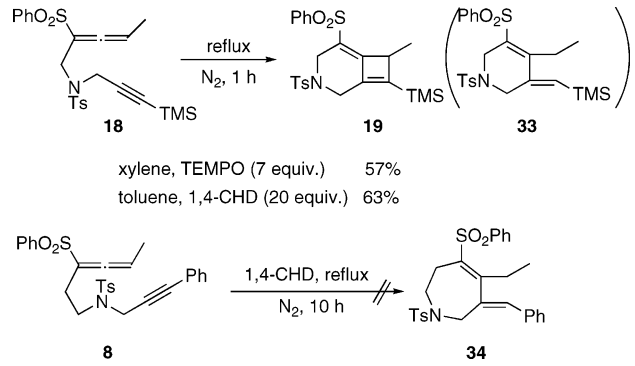
(20) Proton transfer from plausible biradical intermediates, similar to **A** with a dimethyl substituent at the allenic terminus, generated from allenes **10** and **20** may rationalize the formation of triene derivatives **11′** (actually, compound **11** was isolated instead of **11′**) and **21**, see refs 17a,c,e.

(21) Reaction was monitored by ^{1}H NMR, and no peaks due to compound **35** could be detected except for those of **8** and **9**.

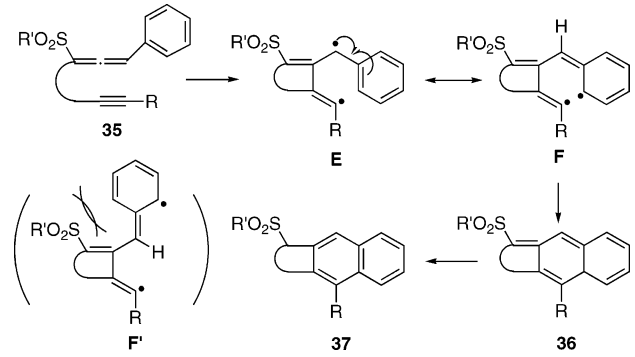
(22) (a) Shi, C.; Wang, K. K. *J. Org. Chem.* **1998**, *63*, 3517−3520. (b) Shi, C.; Zhang, Q.; Wang, K. K. *J. Org. Chem.* **1999**, *64*, 925−932. (c) Zhang, Q.; Shi, C.; Zhang, H.-R.; Wang, K. K. *J. Org. Chem.* **2000**, *65*, 7977−7983. (d) Lu, X.; Peterson, J. L.; Wang, K. K. *J. Org. Chem.* **2002**, *67*, 5412−5415. (e) Lu, X.; Peterson, J. L.; Wang, K. K. *J. Org. Chem.* **2002**, *67*, 7797−7801. (f) Dai, W.; Peterson, J. L.; Wang, K. K. *J. Org. Chem.* **2005**, *70*, 6647−6652.

(23) A similar ring-closing reaction of benzene-conjugated allenynes was used for preparation of polycyclic aromatics; see: (a) Wang, K. K.; Zhang, H.-R.; Peterson, J. L. *J. Org. Chem.* **1999**, *64*, 1650−1656. (b) Li, H.; Zhang, H.-R.; Peterson, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 6662−6668. (c) Li, H.; Peterson, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 7804−7810. (d) Yang, Y.; Peterson, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, *68*, 5832−5837. (e) Yang, Y.; Peterson, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, *68*, 8545−8549. (f) Han, X.; Zhang, Y.; Wang, K. K. *J. Org. Chem.* **2005**, *70*, 2406−2408.

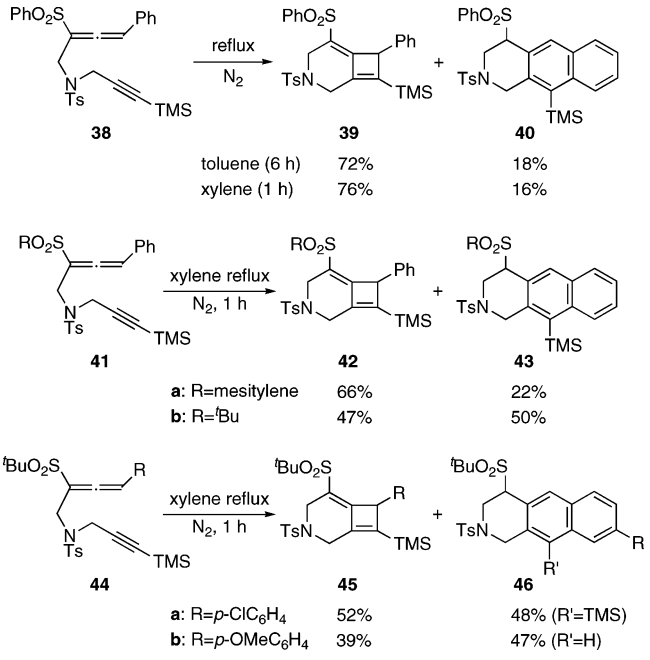
SCHEME 7



SCHEME 8



SCHEME 9



yield of **40** may be attributed to the low ratio of the intermediate **F** (R′ = Ph) compared to its isomer **F′** (see Scheme 8). We thought that the substituent (R′) sterically more hindered than a phenyl group on the sulfonyl functionality would significantly increase the nonbonding interaction with the pentadienyl radical moiety as shown in the structure of intermediate **F′** resulting in the increased ratio of intermediate **F**. As a result, the mesitylenesulfonyl drivative **41a**[10] was reacted under standard conditions (refluxed in xylene for 1 h) to afford the tricyclic compound **43a** in a slightly higher yield (22%) and the normal [2+2] cycloadduct **42a** in 66% yield. When a substituent on the sulfonyl group was changed to the sterically more hindered *tert*-butyl group, a remarkable improvement in the chemical yield of the tricyclic compound was attained. In fact, the *tert*-butylsulfonyl derivative **41b**[10] provided a tricyclic compound **43b** in 50% yield along with **42b** in 47% yield. Finally, we examined the electronic effect of a substituent on the phenyl group at the allenic terminus using the *tert*-butylsulfonyl derivative, which gave the highest yield of the tricyclic compound. As depicted in Scheme 9, the behavior of **44**[10] similar to that of **41b** was observed irrespective of the electronic property of substituent on the benzene ring. In the case of **44b**, the tricyclic compound **46b** was formed in 47% yield accompanied by desilylation. Although direct evidence for the intermediacy of the biradical species such as **A** during the thermal transformation of the allenynes to the bicyclo[m.2.0] skeletons could not yet be obtained, a series of experiments in Scheme 9 indirectly but strongly suggested the possibility of the intermediacy of the biradical species because the ratio of the azabicyclo[4.2.0]octadienes **39**, **42**, and **45** to tricyclic compounds **40**, **43**, and **46** obviously depended on the bulkiness of a substituent on the sulfonyl group of starting allenynes **38**, **41**, and **44**. These results would not only support the ring-closing process via biradical intermediates leading to the [2+2] cycloadducts, but it would also rule out the possibility of a concerted [4+2] cycloaddition pathway for the formation of tricyclic compounds.[24]

In summary, we have described the thermal [2+2] cycloaddition of allenynes by refluxing in xylene that leads to the formation of the bicyclo[5.2.0]nona-1,7-dienes, in which the distal double bond of the allenyl moiety exclusively served as the π-component irrespective of the position of the sulfonyl group on the allenyl moiety. This simple method was shown to be successfully applicable to the first construction of the one-carbon homologated bicyclo[6.2.0]deca-1,8-dienes. One-carbon smaller-sized bicyclo[4.2.0]octa-1,6-dienes could also be obtained in high yields. When the starting allenynes have a phenyl group at the allenic terminus, tricyclic compounds incorporating a terminal phenyl group were obtained along with the normal [2+2] cycloadducts. Thus, we developed a general procedure for the preparation of bicyclo[*m*.2.0]alka-1,(*m*+2)-diene skeletons ($m = 4-6$). Further studies on the scope and limitations of this method are now in progress.

Experimental Section

8-Phenyl-2-(phenylsulfonyl)-5-oxabicyclo[5.3.0]deca-1,7-dien-9-one (6a) and 8-Phenyl-2-(phenylsulfonyl)-5-oxabicyclo[5.2.0]-nona-1,7-diene (7a). [RhCl(CO)dppp]$_2$ (2.9 mg, 2.5×10^{-3} mmol) was added to a solution of allenyne **5a** (33.9 mg, 0.100 mmol) in toluene (1.0 mL). The reaction mixture was refluxed under a CO atmosphere for 1 h. Toluene was evaporated off, and the residual oil was chromatographed with CH_2Cl_2 to afford **6a** (16.9 mg, 46%) and **7a** (9.0 mg, 27%); **6a**: colorless needles, mp 203−204 °C (AcOEt), IR 1713, 1308, 1151 cm^{-1}; ^{1}H NMR δ 7.94−7.91 (m, 2H), 7.70−7.55 (m, 3H), 7.46−7.40 (m, 3H), 7.28−7.24 (m, 2H), 4.70 (s, 2H), 3.92 (t, 2H, J = 6.1 Hz), 3.76 (s, 2H), 3.06 (t, 2H, J = 6.1 Hz); ^{13}C NMR δ 200.6, 163.4, 145.83, 145.78, 140.3, 133.8,

(24) If the ring-closing reaction of **38**, **41**, and **44** leading to tricyclic compounds **40**, **43**, and **46** proceeds via a concerted [4+2] cycloaddition pathway in which the distal double bond of the allenyl moiety and one of the π bonds of the benzene ring serve as a 1,3-diene part and an alkyne group functions as a dienophile, the bulkiness of the substituent on the sulfonyl functionality should not affect their reactivity.

133.3, 129.6, 129.5, 129.2, 128.5, 127.6, 69.2, 63.9, 41.1, 29.3; MS *m*/*z* 366 (M^+, 8.7). HRMS calcd for $C_{21}H_{18}O_4S$ 366.0926, found 366.0925. Anal. Calcd for $C_{21}H_{18}O_4S$: C, 68.83; H, 4.95. Found: C, 68.53; H, 5.04. **7a**: colorless needles, mp 216−218 °C (AcOEt); IR 1680, 1304, 1151 cm^{-1}; ^1H NMR δ 7.92−7.90 (m, 2H), 7.61−7.52 (m, 3H), 7.45−7.36 (m, 3H), 7.28−7.24 (m, 2H), 4.60 (t, 2H, J = 3.2 Hz), 3.92 (t, 2H, J = 4.9 Hz), 3.70 (t, 2H, J = 3.2 Hz), 2.69 (t, 2H, J = 4.9 Hz); ^{13}C NMR δ 148.5, 147.4, 141.2, 139.9, 132.94, 132.88, 129.7, 129.1, 128.9, 127.6, 127.5, 122.7, 70.5, 68.9, 36.3, 33.5; MS *m*/*z* 338 (M^+, 79.4). HRMS calcd for $C_{20}H_{18}O_3S$ 338.0977, found 338.0977. Anal. Calcd for $C_{20}H_{18}O_3S$: C, 70.98; H, 5.36. Found: C, 70.70; H, 5.46.

General Procedure for Ring-Closing Reaction of Allenynes under an Atmosphere of N_2. To a solution of allenyne (0.10 mmol) in toluene was added xylene or mesitylene (1 mL) with refluxed under a N_2 atmosphere until the starting material completely disappeared (monitored by TLC). Solvent was evaporated off, and the residual oil was chromatographed with hexane−AcOEt to afford cyclized products. Chemical yields are summarized in Tables 1−4 and Schemes 3−5 and 9.

***N*-(4-Methylbenzenesulfonyl)-2-(phenylsulfonyl)-8-(trimethylsilyl)-5-azabicyclo[5.2.0]nona-1,7-diene (7e):** colorless plates, mp 134−136 °C (AcOEt); IR 1666, 1350, 1306, 1159 cm^{-1}; ^1H NMR δ 7.83−7.82 (m, 2H), 7.63−7.53 (m, 5H), 7.26−7.25 (m, 2H), 3.96 (br s, 2H), 3.39 (t, 2H, J = 5.0 Hz), 3.26 (br s, 2H), 2.66 (t, 2H, J = 5.0 Hz), 2.42 (s, 3H), 0.16 (s, 9H); ^{13}C NMR δ 160.5, 151.9, 149.2, 143.7, 140.7, 135.5, 133.1, 129.8, 129.2, 127.7, 127.0, 121.8, 49.6, 48.6, 37.9, 32.2, 21.5, −2.2; MS *m*/*z* 487 (M^+, 2.0). HRMS calcd for $C_{24}H_{29}NO_4S_2Si$ 487.1307, found 487.1303. Anal. Calcd for $C_{24}H_{29}NO_4S_2Si$: C, 59.10; H, 5.99; N, 2.87. Found: C, 58.77; H, 6.08; N, 2.86.

4,4-Bis(methoxycarbonyl)-8-(trimethylsilyl)-2-(phenylsulfonyl)-bicyclo[5.2.0]nona-1,7-diene (7f): colorless needles, mp 133−135 °C (AcOEt); IR 1734, 1304, 1155 cm^{-1}; ^1H NMR δ 7.93−7.90 (m, 2H), 7.61−7.52 (m, 3H), 3.58 (s, 6H), 3.27−3.25 (m, 2H), 2.97 (s, 2H), 2.50−2.43 (m, 2H), 2.24−2.19 (m, 2H), 0.14 (s, 9H); ^{13}C NMR δ 170.7, 160.3, 155.7, 151.0, 141.2, 132.8, 129.0, 127.8, 117.9, 57.3, 52.7, 37.7, 36.1, 30.9, 25.1, −2.0; MS *m*/*z* 448 (M^+, 10.4). HRMS calcd for $C_{22}H_{28}O_6SSi$ 448.1376, found 448.1376. Anal. Calcd for $C_{22}H_{28}O_6SSi$: C, 58.90; H, 6.29. Found: C, 58.53; H, 6.38.

9-Methyl-*N*-(4-methylbenzenesulfonyl)-8-phenyl-2-(phenylsulfonyl)-5-azabicyclo[5.2.0]nona-1,7-diene (9): colorless plates, mp 205.5−207 °C (AcOEt); IR 1344, 1304, 1153 cm^{-1}; ^1H NMR δ 7.86 (d, 2H, J = 7.6 Hz), 7.64−7.60 (m, 3H), 7.56−7.53 (m, 2H), 7.48−7.39 (m, 3H), 7.31 (d, 2H, J = 7.6 Hz), 7.27−7.25 (m, 2H), 4.37−4.26 (m, 2H), 4.09−4.07 (m, 1H), 3.52−3.48 (m, 1H), 3.42−3.38 (m, 1H), 2.74−2.69 (m, 1H), 2.63−2.58 (m, 1H), 2.41 (s, 3H), 1.59 (d, 3H, J = 6.6 Hz); ^{13}C NMR δ 155.2, 152.3, 143.7, 140.7, 135.5, 134.3, 133.1, 131.6, 129.9, 129.13, 129.05, 127.8, 127.5, 127.0, 121.2, 48.6, 48.2, 43.9, 32.5, 21.5, 17.4; MS *m*/*z* 505 (M^+, 3.5). Anal. Calcd for $C_{28}H_{27}NO_4S_2$: C, 66.51; H, 5.38; N, 2.77. Found: C, 66.29; H, 5.50; N, 2.73.

9-Methyl-*N*-(4-methylbenzenesulfonyl)-2-[(*Z*)-phenylmethylene]-7-(phenylsulfonyl)-4-azabicyclo[5.2.0]non-1(9)-ene (11): colorless needles, mp 153−154 °C (AcOEt); IR 1360, 1157, 1146 cm^{-1}; ^1H NMR δ 7.88−7.84 (m, 2H), 7.66−7.20 (m, 12H), 6.47 (s, 1H), 4.98 (d, 1H, J = 16.8 Hz), 4.17−4.08 (m, 2H), 3.74−3.63 (m, 1H), 2.75−2.69 (m, 1H), 2.53 (d, 1H, J = 14.9 Hz), 2.39 (s, 3H), 2.16−2.04 (m, 2H), 1.60 (s, 3H); ^{13}C NMR δ 143.0, 142.9, 138.8, 137.5, 136.1, 135.8 134.3, 133.8, 129.6, 129.5, 128.9, 128.8, 128.5, 128.4, 127.5, 126.9, 68.8, 50.0, 49.9, 42.6, 34.0, 21.4, 15.2; MS *m*/*z* 519 (M^+, 0.7). Anal. Calcd for $C_{29}H_{29}NO_4S_2$: C, 67.02; H, 5.62; N, 2.70. Found: C, 66.81; H, 5.67; N, 2.66.

***N*-[(*E*)-5-Methyl-3-(phenylsulfonyl)hexa-3,5-dienyl]-*N*-(3-phenyl-2-propynyl)-(4-methylbenzene)sulfonamide (12):** colorless plates, mp 102−103.5 °C (AcOEt); IR 1599, 1491, 1348, 1306, 1161 cm^{-1}; ^1H NMR δ 7.89−7.87 (m, 2H), 7.73−7.71 (m, 2H), 7.58−7.55 (m, 1H), 7.48−7.44 (m, 2H), 7.40 (s, 1H), 7.32−7.23 (m, 5H), 7.13−7.11 (m, 2H), 5.32−5.31 (m, 2H), 4.27 (s, 2H), 3.42−3.38 (m, 2H), 2.80−2.77 (m, 2H), 2.34 (s, 3H), 2.01 (s, 3H); ^{13}C NMR δ 143.6, 142.1, 139.1, 138.8, 137.1, 135.6, 133.3, 131.6, 129.6, 129.3, 128.5, 128.3, 128.1, 127.7, 123.2, 122.1, 85.6, 82.0, 46.6, 38.2, 26.7, 21.7, 21.4; MS *m*/*z* 519 (M^+, 0.6). HRMS calcd for $C_{29}H_{29}NO_4S_2$ 519.1538, found 519.1541.

9-Phenyl-2-(phenylsulfonyl)-6-oxabicyclo[6.2.0]deca-1,8-diene (15a): colorless needles, mp 175−176.5 °C (AcOEt); IR 1302, 1150 cm^{-1}; ^1H NMR δ 7.92−7.91 (m, 2H), 7.59−7.56 (m, 1H), 7.54−7.51 (m, 2H), 7.45−7.42 (m, 2H), 7.40−7.37 (m, 1H), 7.34−7.32 (m, 2H), 4.55 (t, 2H, J = 3.1 Hz), 3.75 (t, 2H, J = 3.1 Hz), 3.70 (t, 2H, J = 6.1 Hz), 2.62−2.60 (m, 2H), 1.77−1.72 (m, 2H); ^{13}C NMR δ 151.3, 148.4, 141.8, 139.5, 133.0, 132.7, 129.8, 129.1, 128.9, 127.9, 127.6, 123.4, 69.0, 65.4, 37.1, 28.0, 24.5; MS *m*/*z* 352 (M^+, 0.1). HRMS calcd for $C_{21}H_{20}O_3S$ 352.1133, found 352.1134.

***N*-(4-Methylbenzenesulfonyl)-9-phenyl-2-(phenylsulfonyl)-6-azabicyclo[6.2.0]deca-1,8-diene (15b):** colorless needles, mp 198.5−200 °C (AcOEt); IR 1346, 1304, 1157 cm^{-1}; ^1H NMR δ 7.89−7.86 (m, 2H), 7.69−7.29 (m, 12H), 4.28−4.26 (m, 2H), 3.70−3.69 (m, 2H), 3.26 (t, 2H, J = 5.9 Hz), 2.58−2.54 (m, 2H), 2.42 (s, 3H), 1.79−1.70 (m, 2H); ^{13}C NMR δ 153.0, 148.3, 143.7, 141.3, 135.3, 134.6, 132.9, 132.5, 130.2, 129.8, 129.1, 129.0, 127.8, 127.6, 127.2, 122.8, 46.3, 45.4, 37.3, 28.2, 24.3, 21.5; MS *m*/*z* 505 (M^+, 0.5). Anal. Calcd for $C_{28}H_{27}NO_4S_2$: C, 66.51; H, 5.38; N, 2.77. Found: C, 66.24; H, 5.56; N, 2.86.

4,4-Bis(methoxycarbonyl)-9-phenyl-2-(phenylsulfonyl)bicyclo-[6.2.0]deca-1,8-diene (15c): pale yellow plates, mp 183−185 °C (AcOEt); IR 1728, 1306, 1151 cm^{-1}; ^1H NMR δ 7.87−7.86 (m, 2H), 7.59−7.36 (m, 8H), 3.80 (s, 6H), 3.64 (s, 2H), 3.20 (s, 2H), 2.67−2.64 (m, 2H), 2.27−2.24 (m, 2H), 1.68−1.66 (m, 2H); ^{13}C NMR δ 171.4, 155.3, 151.6, 141.8, 140.9, 133.4, 132.7, 129.7, 129.1, 128.8, 127.7, 127.4, 117.9, 57.9, 52.8, 36.7, 30.7, 28.0, 24.3, 22.6; MS *m*/*z* 466 (M^+, 0.2). Anal. Calcd for $C_{26}H_{26}O_6S$: C, 66.93; H, 5.62. Found: C, 66.69; H, 5.81.

***N*-(4-Methylbenzenesulfonyl)-2-(phenylsulfonyl)-7-propyl-4-azabicyclo[4.2.0]octa-1,6-diene (17e):** a colorless oil; IR 1350, 1306, 1159 cm^{-1}; ^1H NMR δ 7.87−7.83 (m, 2H), 7.67−7.46 (m, 5H), 7.20−7.17 (m, 2H), 4.07 (s, 2H), 3.95−3.94 (m, 2H), 3.02 (s, 2H), 2.40 (s, 3H), 2.21−2.15 (m, 2H), 1.56−1.42 (m, 2H), 0.96−0.90 (m, 3H); ^{13}C NMR δ 155.1, 146.9, 143.6, 140.5, 134.54, 134.49, 133.3, 129.5, 129.3, 127.6, 127.4, 114.0, 42.8, 41.8, 38.5, 32.6, 21.5, 19.8, 14.0; MS *m*/*z* 443 (M^+, 0.4). HRMS calcd for $C_{23}H_{25}NO_4S_2$ 443.1225, found 443.1218.

4,4-Bis(methoxycarbonyl)-7-butyl-2-(phenylsulfonyl)bicyclo-[4.2.0]nona-1,6-diene (17f): a colorless oil; IR 1736, 1306, 1155 cm^{-1}; ^1H NMR δ 7.88−7.87 (m, 2H), 7.61−7.58 (m, 1H), 7.55−7.52 (m, 2H), 3.49 (s, 6H), 3.28 (br s, 2H), 2.89 (s, 2H), 2.70 (br s, 2H), 2.33 (t, 2H, J = 7.3 Hz), 1.55 (quin, 2H, J = 7.3 Hz), 1.37 (sex, 2H, J = 7.3 Hz), 0.93 (t, 3H, J = 7.3 Hz); ^{13}C NMR δ 170.1, 155.8, 148.4, 140.8, 137.5, 132.7, 128.9, 127.8, 113.6, 55.5, 52.8, 38.2, 30.3, 29.2, 28.4, 28.0, 22.5, 13.7; MS *m*/*z* 418 (M^+, 87.2). HRMS calcd for $C_{22}H_{26}O_6S$ 418.1450, found 418.1438.

8-Methyl-*N*-(4-methylbenzenesulfonyl)-2-(phenylsulfonyl)-7-(trimethylsilyl)-4-azabicyclo[4.2.0]octa-1,6-diene (19): colorless plates, mp 119−120 °C (AcOEt); IR 1346, 1306, 1157 cm^{-1}; ^1H NMR δ 7.89−7.86 (m, 2H), 7.71−7.57 (m, 3H), 7.39−7.36 (m, 2H), 7.16−7.13 (m, 2H), 4.23−4.13 (m, 2H), 4.02−3.96 (m, 1H), 3.86 (dd, 1H, J = 17.3, 3.5 Hz), 3.58−3.54 (m, 1H), 2.39 (s, 3H), 1.12 (d, 3H, J = 6.9 Hz), 0.12 (s, 9H); ^{13}C NMR δ 164.0, 153.1, 148.3, 143.6, 140.2, 135.0, 133.6, 129.6, 129.4, 127.6, 127.4, 114.7, 48.0, 42.9, 42.7, 21.4, 17.5, −1.8; MS *m*/*z* 487 (M^+, 1.6). HRMS calcd for $C_{24}H_{29}NO_4S_2Si$ 487.1307, found 487.1311. Anal. Calcd for $C_{24}H_{29}NO_4S_2Si$: C, 59.10; H, 5.99; N, 2.87. Found: C, 58.79; H, 6.05; N, 2.87.

1-(4-Methylbenzenesulfonyl)-5-(phenylsulfonyl)-4-(1-propen-2-yl)-3-[(*Z*)-(trimethylsilyl)methylene]-1,2,3,6-tetrahydropyridine (21): colorless plates, mp 144−145.5 °C (AcOEt); IR 1352, 1308, 1161, 1153 cm^{-1}; ^1H NMR δ 7.88−7.85 (m, 2H), 7.69−

7.63 (m, 1H), 7.57−7.48 (m, 4H), 7.16−7.13 (m, 2H), 6.01 (s, 1H), 5.07 (s, 1H), 4.25 (br s, 3H), 4.08 (s, 1H), 3.63 (br s, 1H), 2.37 (s, 3H), 1.73 (s, 3H), 0.21 (s, 9H); ^{13}C NMR δ 149.8, 143.8, 141.2, 140.8, 139.3, 137.8, 134.1, 133.6, 131.3, 129.6, 129.1, 128.2, 127.6, 117.3, 47.6, 45.6, 23.9, 21.4, −0.4; MS *m*/*z* 501 (M^+, 76.5). HRMS calcd for $C_{25}H_{31}NO_4S_2Si$ 501.1464, found 501.1466.

2-Methyl-*N*-(4-methylbenzenesulfonyl)-8-phenyl-5-azabicyclo-[5.2.0]nona-1,7-diene (23): colorless needles, mp 193−194.5 °C (AcOEt); IR 1344, 1159 cm^{-1}; ^{1}H NMR δ 7.72−7.71 (m, 2H), 7.38−7.20 (m, 7H), 4.32−4.31 (m, 2H), 3.48−3.46 (m, 2H), 2.99−2.98 (m, 2H), 2.44−2.42 (m, 5H), 1.64 (s, 3H); ^{13}C NMR δ 143.2, 137.5, 137.0, 136.3, 134.6, 131.5, 129.6, 128.6, 127.4, 127.1, 126.0, 121.0, 49.5, 49.1, 37.9, 33.0, 21.5, 18.2; MS *m*/*z* 365 (M^+, 12.0). Anal. Calcd for $C_{22}H_{23}NO_2S$: C, 72.30; H, 6.34; N, 3.83. Found: C, 72.12; H, 6.35; N, 3.95.

***N*-(4-Methylbenzenesulfonyl)-7-phenyl-8-(phenylsulfonyl)-4-azabicyclo[4.2.0]octa-1,6-diene (27):** a pale yellow oil; IR 1350, 1307, 1163, 1138 cm^{-1}; ^{1}H NMR δ 7.65 (d, 2H, J = 8.1 Hz), 7.61−7.57 (m, 3H), 7.41−7.34 (m, 7H), 7.24 (d, 2H, J = 7.8 Hz), 5.41−5.39 (m, 1H), 4.97 (s, 1H), 4.34−4.30 (m, 1H), 3.98 (dd, 1H, J = 17.1, 4.4 Hz), 3.89 (d, 1H, J = 17.1 Hz), 3.75 (dd, 1H, J = 17.1, 3.2 Hz), 2.41 (s, 3H); ^{13}C NMR δ 143.8, 140.6, 136.4, 136.0, 134.3, 134.0, 132.1, 131.2, 129.6, 129.1, 128.9, 128.4, 127.4, 127.0, 109.6, 70.2, 44.1, 42.7, 21.5; MS *m*/*z* 477 (M^+, 5.5); HRMS calcd for $C_{26}H_{23}NO_4S_2$ 477.1069, found 477.1070.

***N*-(4-Methylbenzenesulfonyl)-8-phenyl-2-(phenylsulfonyl)-7-(trimethylsilyl)-4-azabicyclo[4.2.0]octa-1,6-diene (39):** colorless plates, mp 189−190.5 °C (AcOEt); IR 1348, 1308, 1157 cm^{-1}; ^{1}H NMR δ 7.52−7.49 (m, 1H), 7.43 (d, 2H, J = 8.3 Hz), 7.31−7.17 (m, 7H), 7.05 (d, 2H, J = 7.1 Hz), 6.90 (d, 2H, J = 7.1 Hz), 4.61 (d, 1H, J = 2.4 Hz), 4.38 (dd, 1H, J = 17.1, 1.5 Hz), 4.15 (ABq, 2H, J = 17.1 Hz), 3.89 (dd, 1H, J = 17.3, 3.7 Hz), 2.46 (s, 3H), −0.03 (s, 9H); ^{13}C NMR δ 162.4, 151.9, 150.6, 143.6, 139.8, 138.4, 135.1, 133.1, 129.9, 129.0, 128.2, 128.1, 127.44, 127.37, 127.2, 114.8, 56.4, 42.7, 42.5, 21.6, −1.9; MS *m*/*z* 549 (M^+, 1.2). HRMS calcd for $C_{29}H_{31}NO_4S_2Si$ 549.1464, found 549.1472.

***N*-(4-Methylbenzenesulfonyl)-4-(phenylsulfonyl)-10-trimethylsilyl-1,2,3,4-tetrahydrobenz[*g*]isoquinoline (40):** colorless plates, mp 228−229 °C (AcOEt); IR 1348, 1308, 1163, 1134 cm^{-1}; ^{1}H NMR δ 8.13 (d, 1H, J = 8.3 Hz), 7.88 (s, 1H), 7.79−7.77 (m, 1H), 7.53−7.45 (m, 5H), 7.38−7.37 (m, 2H), 7.26−7.23 (m, 2H), 7.15 (d, 2H, J = 8.1 Hz), 4.56−4.52 (m, 2H), 4.06 (ABq, 2H, J = 15.1 Hz), 3.37−3.34 (m, 1H), 2.33 (s, 3H), 0.46 (s, 9H); ^{13}C NMR δ 143.9, 137.14, 137.06, 136.7, 134.9, 133.8, 133.6, 132.7, 131.9, 130.1, 129.6, 129.3, 128.3, 127.8, 127.6, 126.5, 125.6, 121.8, 65.2, 49.2, 43.3, 21.4, 3.8; MS *m*/*z* 549 (M^+, 0.9). HRMS calcd for $C_{29}H_{31}NO_4S_2Si$ 549.1464, found 549.1480.

7-Phenyl-2-(phenylsulfonyl)-4-oxabicyclo[4.2.0]octa-1,6-diene (17a). PhSCl (90 mg, 0.62 mmol) was gradually added to a solution of 4-(3-phenyl-2-propynyloxy)-2-butyn-1-ol (31.0 mg, 0.155 mmol) and Et_3N(0.1 mL, 0.71 mmol) in THF (1.5 mL) at −78 °C. After being stirred for 2 h at the same temperature, the mixture was quenched by addition of saturated aqueous $NaHCO_3$. The resulting mixture was extracted with AcOEt, which was washed with water and brine, dried, and concentrated to dryness. The residual oil was passed through a short pad of silica gel with hexane−AcOEt (2:1) to afford the crude sulfoxide. *m*CPBA (35 mg, 0.20 mmol) was added to a solution of the crude sulfoxide in CH_2Cl_2 (1.3 mL) at 0 °C. After being stirred for 1 h at the same temperature, the mixture was quenched by addition of saturated aqueous $Na_2S_2O_3$ and $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2, which was washed with water and brine, dried, and concentrated to dryness. The residual oil was passed through a short pad of silica gel with hexane−AcOEt (7:3) to afford the crude allenyne **16a**. A solution of the crude allenyne **16a** in toluene (1.0 mL) was stirred for 18 h at 40 °C under a N_2 atmosphere. The solvent was evaporated off, and the residual oil was chromatographed with hexane−AcOEt (7:3) to afford **17a** (32.0 mg, 64%, for three steps) as pale yellow plates: mp 188−189.5 °C (AcOEt); IR 1306, 1157 cm^{-1}; ^{1}H NMR δ 7.93−7.91 (m, 2H), 7.63−7.60 (m, 1H), 7.56−7.53 (m, 2H), 7.43−7.35 (m, 3H), 7.28−7.26 (m, 2H), 4.52 (t, 2H, J = 2.9 Hz), 4.34 (s, 2H), 3.75 (t, 2H, J = 2.9 Hz); ^{13}C NMR δ 145.4, 145.1, 140.9, 136.1, 133.2, 132.7, 129.8, 129.3, 128.9, 127.5, 127.3, 119.0, 62.44, 62.39, 37.0; MS *m*/*z* 324 (M^+, 48.1). HRMS calcd for $C_{19}H_{16}O_3S$ 324.0820, found 324.0813.

***N*-[(4-Methylbenzene)sulfonyl]-8-phenyl-9-(phenylsulfonyl)-5-azabicyclo[5.2.0]]nona-1,7-diene (29).** A solution of **28** (15 mg, 3.0×10^{-2} mmol) in mesitylene (2 mL) was heated at 180 °C in a sealed tube for 1 h. Mesitylene was evaporated off, and the residual oil was chromatographed with hexane−AcOEt (3:1) to afford **29** (7.6 mg, 51%) as a pale yellow oil: IR 1361, 1340, 1159, 1136 cm^{-1}; ^{1}H NMR δ 7.66−7.54 (m, 5H), 7.41−7.28 (m, 9H), 5.60 (t, 1H, J = 4.2 Hz), 4.91−4.90 (m, 1H), 4.33 (dd, 1H, J = 17.7, 2.4 Hz), 3.76 (dd, 1H, J = 17.7, 1.8 Hz), 3.56−3.51 (m, 1H), 2.99−2.93 (m, 1H), 2.60−2.53 (m, 1H), 2.47−2.39 (m, 4H); ^{13}C NMR δ 145.1, 143.6, 137.5, 136.1, 135.6, 133.8, 132.2, 131.3, 129.8, 129.4, 129.0, 128.8, 128.1, 127.2, 127.0, 118.8, 67.7, 49.2, 48.6, 32.6, 21.5; MS *m*/*z* 491 (M^+, 47.9); HRMS calcd for $C_{27}H_{25}O_4S_2N$ 491.1225, found 491.1223.

Ring-Closing Reaction of 18 with TEMPO under an Atmosphere of N_2. To a solution of **18** (48.0 mg, 9.85×10^{-2} mmol) in xyene (1.0 mL) was added TEMPO (110 mg, 0.70 mmol) at room temperature. The reaction mixture was refluxed under a N_2 atmosphere for 1 h and toluene was evaporated off. The residual oil was chromatographed with hexane−AcOEt to afford **19** (27.2 mg, 57%).

Ring-Closing Reaction of 18 with 1,4-CHD under an Atmosphere of N_2. To a solution of **18** (55.0 mg, 0.113 mmol) in xyene (1.1 mL) was added 1,4-CHD (0.21 mL, 2.3 mmol). The reaction mixture was refluxed under a N_2 atmosphere for 1 h and toluene was evaporated off. The residual oil was chromatographed with hexane−AcOEt to afford **19** (34.9 mg, 63%).

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Supporting Information Available: ^{1}H spectra for compounds **6a**, **7a**,**e**,**f**, **9**−**11**, **14b**, **15b**,**c**, **16e**, **18**, **19**, **22**, **23**, and **55**, ^{1}H and ^{13}C NMR spectra for compounds **5a**,**c**,**f**, **7b**,**c**, **12**, **14a**, **15a**, **16b**−**d**,**f**, **17a**−**c**,**e**,**f**, **20**, **21**, **24**, **26**−**31**, **38**−**40**, **41a**,**b**, **42a**,**b**, **43a**,**b**, **44a**,**b**, **45a**,**b**, **46a**,**b**, **49**, **50**, **54**, **57**, **58**, **60**, **65**, **67**, **69**, **70**, **73**, **76**, **77**, **80**, **81**, **84**, **89**, and **90**, characterization data for compounds **7b**,**c** **17b**,**c**, **31**, **42a**,**b**, **43a**,**b**, **45a**,**b**, and **46a**,**b**, and preparation and characterization data for compounds **5a**−**f**, **8**, **10**, **14a**−**d**, **16b**−**f**, **18**, **20**, **22**, **24**, **26**, **28**, **30**, **38**, **41a**,**b**, and **44a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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