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# Cu-Promoted [2 + 2] Cycloaddition of 1,4-Bisallenes

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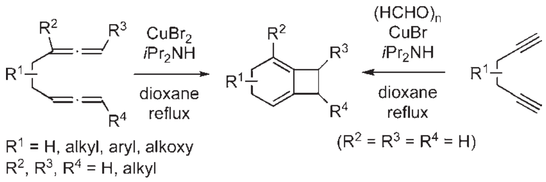
## ABSTRACT



**The thermal reaction of 1,4-bisallenes with the aid of Cu salt/amine significantly suppressed the formal [3,3] sigmatropic rearrangement resulting in the highly selective formation of the bicyclo[4.2.0]octadiene framework. This reaction could be applied to the one-pot synthesis of bicyclo[4.2.0]octadienes from 1,5-hexadiynes via the Crabbé homologation.**

The allene functionality is well-known to serve as a powerful $\pi$-component in the [2 + 2] cycloaddition.[1] There are many examples of efficient constructions of bicyclo[$n$.2.0] skeletons based on the thermal, photochemical, or metal-catalyzed intramolecular [2 + 2] cycloaddition of allene–alkenes[2] and allene–alkynes.[3] The analogous allene–allenes (1,$n$-bisallenes) **I** ($n$ = 3–7) selectively produced bicyclo[$n$.2.0]alkadienes **II** or dimethylenebicyclo[$n$-2.2.0]alkanes **III** upon exposure to thermal or metal-catalyzed conditions (Scheme 1).[4–7] The 1,4-bisallene (exemplified by **1a**), however, has often been found to provide the [2 + 2] cycloadduct **3a** in low yield under thermal conditions due to the preferential formation of the formal [3,3]-sigmatropic rearrangement product **4a** via the biradical intermediate **2a**.[8] Thus, it is obvious that no

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(1) (a) Murakami, M.; Matsuda, T. Cycloadditions of Allenes. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 727–816. (b) Ma, S. *Chem. Rev.* **2005**, *105*, 2829–2872. (c) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Soc. Rev.* **2010**, *39*, 783–816. (d) Aubert, C.; Fensterbank, L.; Garcia, P.; Malacria, M.; Simonneau, A. *Chem. Rev.* **2011**, *111*, 1954–1993.

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(3) For recent examples of thermal reaction, see: (a) Brummond, K. M.; Osbourn, J. M. *Beilstein J. Org. Chem.* **2011**, *7*, 601–605. (b) Siebert, M. R.; Osbourn, J. M.; Brummond, K. M.; Tantillo, D. J. *J. Am. Chem. Soc.* **2010**, *132*, 11952–11966. (c) Ovaska, T. V.; Kyne, R. E. *Tetrahedron Lett.* **2008**, *49*, 376–378. (d) Mukai, C.; Hara, Y.; Miyashita, Y.; Inagaki, F. *J. Org. Chem.* **2007**, *72*, 4454–4461. (e) Jiang, X.; Ma, S. *Tetrahedron* **2007**, *63*, 7589–7595. (f) Oh, C. H.; Gupta, A. K.; Park, D. I.; Kim, N. *Chem. Commun.* **2005**, 5670–5672. For recent examples of metal-catalyzed reaction, see: (g) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem.—Eur. J.* **2009**, *15*, 9987–9989. (h) Saito, N.; Tanaka, Y.; Sato, Y. *Org. Lett.* **2009**, *11*, 4124–4126. (i) Oh, C. H.; Kim, A. *Synlett* **2008**, 777–781. (j) Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Synlett* **2006**, 575–578. (k) Oh, C. H.; Park, D. I.; Jung, S. H.; Reddy, V. R.; Gupta, A. K.; Kim, Y. M. *Synlett* **2005**, 2092–2094. (l) Ohno, H.; Mizutani, T.; Kadoh, Y.; Miyamura, K.; Tanaka, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 5113–5115. (m) Cao, H.; Van Ornum, S. G.; Deschamps, J.; Flippen-Anderson, J.; Laib, F.; Cook, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 933–943. (n) Shen, Q.; Hammond, G. B. *J. Am. Chem. Soc.* **2002**, *124*, 6534–6535.

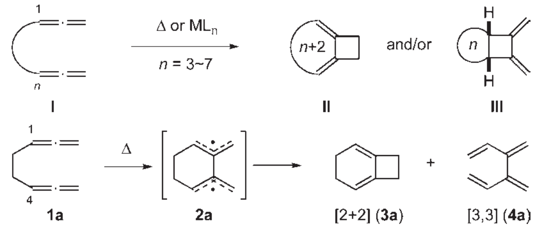
(4) For 1,3-bisallenes, see: (a) Garratt, P. J.; Neoh, S. B. *J. Am. Chem. Soc.* **1975**, *97*, 3255–3257. (b) Bui, B. H.; Schreiner, P. R. *Eur. J. Org. Chem.* **2006**, 4187–4192.

(5) For 1,5-bisallenes, see: (a) Jiang, X.; Cheng, X.; Ma, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 8009–8013. (b) Lu, P.; Ma, S. *Chin. J. Chem.* **2010**, *28*, 1600–1606. (c) Hong, Y.-T.; Yoon, S.-K.; Kang, S.-K.; Yu, C.-M. *Eur. J. Org. Chem.* **2004**, 4628–4635. (d) Kim, S. M.; Park, J. H.; Kang, Y. K.; Chung, Y. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 4532–4535.

(6) For 1,6-bisallenes, see: Shimizu, T.; Sakamaki, K.; Kamigata, N. *Tetrahedron Lett.* **1997**, *38*, 8529–8532. See also ref 5b.

10.1021/ol300096u

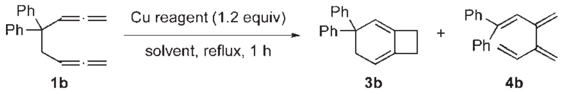
**Scheme 1.** [2 + 2] Cycloaddition Reaction of 1,*n*-Bisallenes



reliable method for the direct production of the bicyclo[4.2.0]octadiene skeleton **3a** from 1,4-bisallene **1a** is available except for a few limited cases, in which the benzocyclobutene derivatives were obtained from (i) ene-bisallenes, *in situ* generated from (*Z*)-ethylene-bridged bis(propargyl alcohol)s,[9,10] and (ii) 1,4-bisallenes having an alkoxymethyl group at the C1 and C4 positions.[11] We now report a new reliable method for the preparation of the bicyclo[4.2.0] framework that involves the copper-promoted, aromatization-independent [2 + 2] cycloaddition of 1,4-bisallenes.

We first investigated the [2 + 2] cycloaddition of 4,4-diphenylocta-1,2,7,8-tetraene (**1b**) using inexpensive and easy to use transition metal complexes.[12] The use of Mo(CO)$_6$[3m,n] or PdCl$_2$(PPh$_3$)$_2$,[3k] both of which have been proven to catalyze the allene–alkyne [2 + 2] cycloaddition reactions, in heated toluene afforded the corresponding tetraene compound **4b** as the only isolated product, and the desired cycloadduct **3b** could not be detected at all. The reaction with Pd(PPh$_3$)$_4$ in the presence of K$_2$CO$_3$ and *n*Bu$_4$NI[5a] or with the cationic Au(I) complex,[5d] both of which are known to convert the 1,5-bisallenes to the corresponding [2 + 2] cycloadducts, produced no desired product. Several transition metal salts such as AuCl$_3$, PtCl$_2$, and FeCl$_3$ were also ineffective for this cycloaddition, except for the Cu salt. In fact, a solution of **1b** in 1,4-dioxane was refluxed in the presence of 1.2 equiv of CuBr$_2$ for 1 h to produce the [2 + 2] cycloadduct **3b** in 31% yield along with the tetraene **4b** (6%) (Table 1, entry 1).

**Table 1.** Cu-Mediated Reaction of Bisallene **1b**



| entry | Cu salt | additive (equiv) | solvent | product (% yield)[a] 3b | 4b |
|---|---|---|---|---|---|
| 1 | CuBr$_2$ | none | dioxane | 31 | 6 |
| 2 | CuBr$_2$ | *i*Pr$_2$NH (1.2) | dioxane | 55 | 11 |
| 3 | CuBr$_2$ | *i*Pr$_2$NH (3.6) | dioxane | 58 | 12 |
| 4 | CuBr$_2$ | *i*Pr$_2$NH (7.2) | dioxane | 80<br>(81)[b] | 17<br>(16)[b] |
| 5 | CuBr$_2$ | *i*Pr$_2$NH (10) | dioxane | 74 | 15 |
| 6[c] | CuBr$_2$ | *i*Pr$_2$NH (3.0) | dioxane | 54 | 12 |
| 7[d] | CuBr$_2$ | *i*Pr$_2$NH (6.0) | dioxane | 73 | 16 |
| 8 | CuBr$_2$ | Cy$_2$NH (7.2) | dioxane | 77 | 16 |
| 9 | CuBr$_2$ | Et$_3$N (7.2) | dioxane | 77 | 16 |
| 10 | CuBr$_2$ | DABCO (7.2) | dioxane | 51 | 17 |
| 11 | CuBr$_2$ | *n*BuNH$_2$ (7.2) | dioxane | 52 | 20 |
| 12 | CuBr$_2$ | 2,6-lutidine (7.2) | dioxane | 40 | 12 |
| 13 | CuBr$_2$ | *i*Pr$_2$NH (7.2) | toluene | 74 | 16 |
| 14 | CuBr$_2$ | *i*Pr$_2$NH (7.2) | DCE | 73 | 11 |
| 15[e] | CuBr$_2$ | *i*Pr$_2$NH (7.2) | DMF | 52 | 14 |
| 16 | CuBr$_2$ | *i*Pr$_2$NH (7.2) | IPA | 62 | 12 |
| 17 | Cu(OAc)$_2$ | *i*Pr$_2$NH (7.2) | dioxane | 76 | 19 |
| 18 | Cu(OTf)$_2$ | *i*Pr$_2$NH (7.2) | dioxane | 19 | 56 |
| 19 | CuCl | *i*Pr$_2$NH (7.2) | dioxane | 80 | 15 |
| 20 | CuI | *i*Pr$_2$NH (7.2) | dioxane | 72 | 22 |
| 21 | none | none | dioxane | – | 50 |

[a] Yields are estimated by $^1$H NMR spectra of the crude product obtained after short column chromatography, which consisted of **3b** and **4b**, with tetrachloroethane as the internal standard. [b] Isolated yields. [c] CuBr$_2$ (0.5 equiv) was used. [d] CuBr$_2$ (1.0 equiv) was used. [e] Reaction was performed at 100 °C.

The effect of an amine additive was next examined for the Cu-promoted reaction. The use of 1.2 equiv of *i*Pr$_2$NH led to an improvement in the chemical yield of **3b** (entry 2). The best result was obtained when 7.2 equiv of *i*Pr$_2$NH were used (entry 4). A decrease in the amount of Cu salt to 0.5 or 1.0 equiv led to a drop in the product yield (entries 6 and 7). Some primary to tertiary amines or an aromatic amine (entries 8–12) also allowed the preparation of the bicyclo[4.2.0]octadiene product **3b**, and Cy$_2$NH and Et$_3$N gave results comparable to *i*Pr$_2$NH (entries 8 and 9). With the combination of CuBr$_2$ and *i*Pr$_2$NH, we examined several other solvents, which were less effective than dioxane (entries 13–16). Other copper sources such as Cu(II) acetate and Cu(I) halides worked as effectively as

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(7) We have also observed the production of bicyclo[*n*.2.0] compounds (*n* = 5–7) in the reaction of 1,*n*-bis(sulfonylallene)s in the presence or absence of a Rh(I) complex. (a) Inagaki, F.; Narita, S.; Hasegawa, T.; Kitagaki, S.; Mukai, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 2007–2011. (b) Kawamura, T.; Inagaki, F.; Narita, S.; Takahashi, Y.; Hirata, S.; Kitagaki, S.; Mukai, C. *Chem.—Eur. J.* **2010**, *16*, 5173–5183. (c) Inagaki, F.; Kitagaki, S.; Mukai, C. *Synlett* **2011**, 594–614.

(8) Production of **4a** from **1a** in the gas phase and in solution has been reported. (a) Skattebøl, L.; Solomon, S. *J. Am. Chem. Soc.* **1965**, *87*, 4506–4513. (b) Roth, W. R.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 503–504. (c) Grimme, W.; Rother, H.-J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 505–506. (d) Becher, G.; Skattebøl, L. *Tetrahedron Lett.* **1979**, *20*, 1261–1264. (e) Roth, W. R.; Scholz, B. P.; Breuckmann, R.; Jelich, K.; Lennartz, H.-W. *Chem. Ber.* **1982**, *115*, 1934–1946.

(9) (a) Toda, F.; Tanaka, K.; Sano, I.; Isozaki, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1757–1758. (b) Inanaga, J.; Sugimoto, Y.; Hanamoto, T. *Tetrahedron Lett.* **1992**, *33*, 7035–7038. (c) Ezcurra, J. E.; Moore, H. W. *Tetrahedron Lett.* **1993**, *34*, 6177–6180. (d) Braverman, S.; Duar, Y. *J. Am. Chem. Soc.* **1990**, *112*, 5830–5837. (e) Höhn, J.; Weyerstahl, P. *Chem. Ber.* **1983**, *116*, 808–814. (f) Staab, H. A.; Draeger, B. *Chem. Ber.* **1972**, *105*, 2320–2333.

(10) (a) Kitagaki, S.; Okumura, Y.; Mukai, C. *Tetrahedron* **2006**, *62*, 10311–10320. (b) Kitagaki, S.; Okumura, Y.; Mukai, C. *Tetrahedron Lett.* **2006**, *47*, 1849–1852. (c) Kitagaki, S.; Katoh, K.; Ohdachi, K.; Takahashi, Y.; Shibata, D.; Mukai, C. *J. Org. Chem.* **2006**, *71*, 6908–6914.

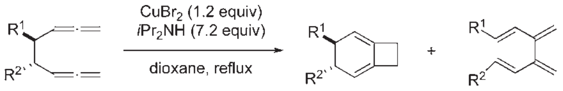
(11) Aubert, P.; Princet, B.; Pornet, J. *Synth. Commun.* **1997**, *27*, 2615–2625.

(12) For the metal-catalyzed [2 + 2] cycloaddition, see: Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49–92.

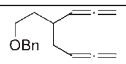
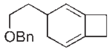
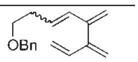
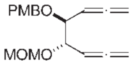
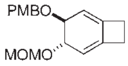
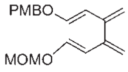
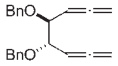
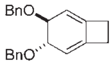
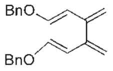
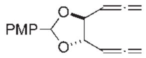
CuBr$_2$ (entries 17, 19, and 20). Cu(OTf)$_2$ was found to be much less effective than CuBr$_2$ (entry 18). A thermal reaction in dioxane with neither a Cu source nor amine gave the tetraene **4b** as the only isolated product (entry 21).[13]

Encouraged by this initial result, we sought to explore the generality of this process. A geminal substitution moiety in the tether (e.g., **1b**) generally tends to facilitate cyclization.[14] 1,4-Bisallene **1c** possessing a monoalkyl group in the tether still gave the corresponding cycloadduct **3c** in an acceptable yield with an extended reaction time (6 h) (Table 2, entry 1). 1,4-Bisallenes **1d** and **1e** with a vicinal dialkoxy substitution led to the smooth conversion into bicyclo[4.2.0] compounds (2.5–3 h, 63–69% yield: entries 2 and 3). The trans-bisallene functionality of the dioxolane derivative **1f** caused inactivity regarding the ring closure (entry 4).

**Table 2.** Effect of the Substituent in the Tether



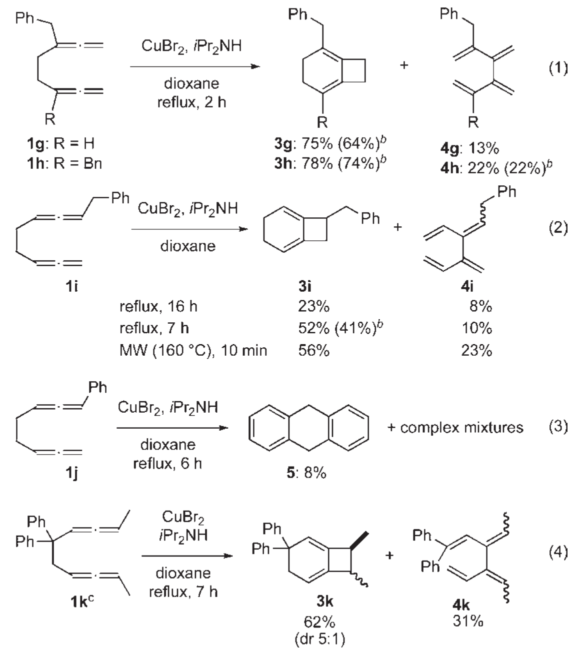
**1** **3** **4**

| entry | allene | time (h) | product (% yield)[a] | |
|---|---|---|---|---|
| 1 | <br>**1c** | 6 | <br>**3c** 61 (63) | <br>**4c** 9 |
| 2[b] | <br>**1d** | 3 | <br>**3d** (69) | <br>**4d** (14) |
| 3 | <br>**1e** | 2.5 | <br>**3e** 63 (63) | <br>**4e** 15 |
| 4 | <br>**1f** | 16 | no reaction | |

[a] Yields are estimated by $^1$H NMR data. Numbers in parentheses are isolated yields. [b] $i$Pr$_2$NH (10 equiv) was used.

Further studies to survey the substrate scope are shown in Scheme 2. Thus, the effect of the substituent on the allene moiety was examined. The reaction of 3-benzylocta-1,2,7,8-tetraene (**1g**) without any substituents in the alkyl tether was completed within 2 h to produce the cycloadduct **3g** in good yield (eq 1). 3,6-Dibenzyl derivative **1h** also gave the desired product **3h** in similar yield. Upon exposure of the 1-benzyl derivative **1i**, a regioisomer of **1g**, to the standard reaction conditions for 7 h, **3i** was obtained in 52% yield along with the tetraene **4i** (10%), and **1i** was recovered in 10% yield (eq 2). A prolonged reaction time (16 h) completely consumed the starting material, but the yield of **3i** decreased to 23%. These results must reflect the instability of the product **3i**, which might be in accordance with the low isolated yield (41%). Microwave irradiation conditions at 160 °C for 10 min slightly improved the chemical yield (56%). Reaction of 1-phenyl derivative **1j** resulted in the production of a complex mixture including dihydroanthracene **5**, which would be obtained by the participation of the phenyl group in the cyclization (eq 3). The installation of a methyl group on both allene moieties did not inhibit the cycloaddition. In this case, the bicyclo[4.2.0] compounds **3k** were obtained in 62% yield as a 5:1 mixture of diastereomers (eq 4).

**Scheme 2.** Effect of the Substituent on the Allene Moiety[a]



[a] Yields are estimated by $^1$H NMR data. [b] Isolated yields. [c] A mixture of diastereomers, the ratio of which is not determined.

The obtained results indicated that the presence of both a Cu salt and amine is critical for the preferential production of the [2 + 2] cycloadduct over that of tetraenes. Although it is premature to discuss the mechanistic details, the following interpretation that involves the initial formation of Cu(I) or a related complex as the active catalyst, followed by the process via the cupracyclopentane **6**,[1c,15] would be assumed (Scheme 3). More than 1 equiv of Cu salt would be needed to overcome the undesired thermal reaction leading to the formation of the tetraene or other byproducts. The amine might not only reduce Cu(II) to Cu(I)[16] and dissociate the polymeric structure of the complex[17] but also stabilize the active species, and/or make the oxidative addition more facile.

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(13) Only tetraene **4b** was detected on TLC also in the reaction of **1b** with $i$Pr$_2$NH (7.2 equiv) in heated dioxane.

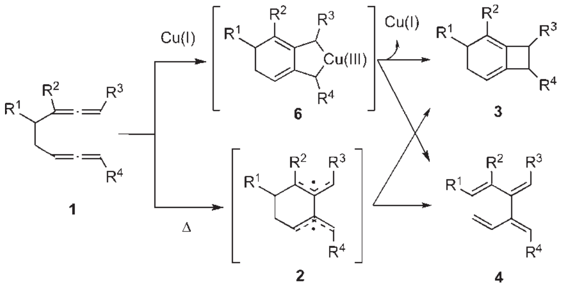
(14) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735–1766.

(15) For example, in the Ni-catalyzed intermolecular [2 + 2] cycloaddition of allenes and Fe-catalyzed intramolecular one of $\alpha,\omega$-dienes, the mechanism involving a reductive elimination of the corresponding metallacycle such as **6**, which consists of a C$_{sp^3}$–metal bond, has been presented. See: (a) Saito, S.; Hirayama, K.; Kabuto, C.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10776–10780. (b) Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13340–13341. For the mechanistic proposal involving a cupracyclopentene for the intramolecular [2 + 2] cycloaddition of allene-alkynes, see ref 3g.

(16) (a) Montaignac, B.; Vitale, M. R.; Ratovelomanana-Vidal, V.; Michelet, V. *Eur. J. Org. Chem.* **2011**, 3723–3727. (b) Paine, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1496–1502.

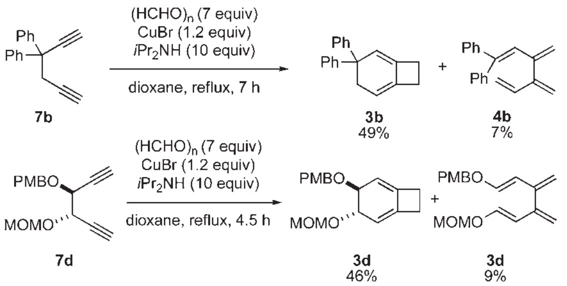
(17) Meldal, M.; Tornøe, C. W. *Chem. Rev.* **2008**, *108*, 2952–3015.

**Scheme 3.** Plausible Reaction Mechanism



The newly developed cycloaddition conditions nearly overlapped with those of the Crabbé homologation (conversion of alkynes to allenes).[18] We expected that the direct transformation of 1,5-diynes **7**, precursors of the bisallenes **1**, into the bicyclo[4.2.0]octadienes **3** could be realized. The preliminary results are shown in Scheme 4. Treatment of 3,3-diphenylhexa-1,5-diyne (**7b**) with CuBr (1.2 equiv), *i*Pr$_2$NH (10 equiv), and paraformaldehyde (7 equiv) in refluxing dioxane for 7 h afforded the desired cycloadduct **3b** in 49% yield along with tetraene **4b** in 7% yield. The dialkoxylated hexadiyne **7d** also gave the corresponding bicyclo compound **3d** in 46% yield.

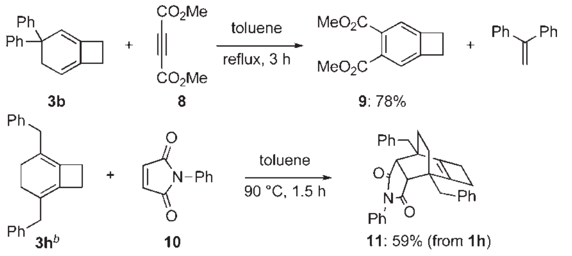
**Scheme 4.** One-Pot Reaction Producing **3** from **7**[a]



[a] Isolated yields are shown.

Finally, the diene reactivity in the [4 + 2] cycloaddition of thus obtained bicyclo[4.2.0]octa-1,5-dienes was investigated.[19] **3b** underwent [4 + 2] cycloaddition with dimethyl acetylenedicarboxylate (**8**), followed by retro-Diels–Alder reaction of the resulting cycloadduct to produce benzocyclobutene **9** (Scheme 5). Reaction with *N*-phenylmaleimide (**10**) did not proceed probably due to the steric hindrance of geminal phenyl groups in **3b**. On the other hand, **3h** readily reacted with **10** to produce the bridged polycyclic compound **11**.

**Scheme 5.** [4 + 2] Cycloaddition Reaction of **3b** and **3h**[a]



[a] Isolated yields are shown. [b] A mixture with **4h** (**3h**:**4h** = 78:22) was used.

In conclusion, we have shown that 1,4-bisallenes, which are well-known to be susceptible to [3,3] sigmatropic rearrangement under thermal conditions, consistently underwent [2 + 2] cycloaddition in the presence of a Cu salt/amine combination. This is the first successful example of the selective synthesis of bicyclo[4.2.0]octadienes from 1,4-bisallenes. We have also demonstrated that this process can be applied to the tandem Crabbé homologation and [2 + 2] cycloaddition of 1,5-hexadiynes. Further studies on the scope of this novel process and the synthetic use of the cycloadducts are currently underway.

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**Supporting Information Available.** Preparation and characterization data for compounds **1**, **3**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.