Cyclobutanes

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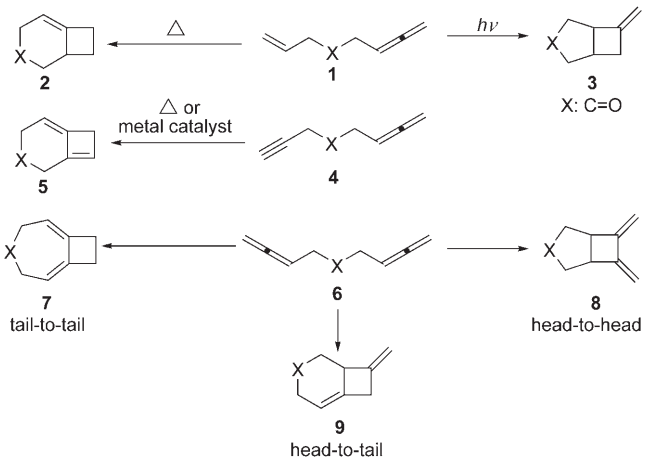
Controllable [2+2] Cycloadditions of 1,5-Bisallenyl-Substituted Compounds**

*Xuefeng Jiang, Xin Cheng, and Shengming Ma**

Cyclobutanes[1] are key structural units frequently found in biologically important compounds[2] and may be easily formed from the [2+2] cycloaddition of two C=C bonds. The [2+2] cycloaddition reaction using an allene as one or both of the partners has attracted much attention[3] because there is at least one extra carbon–carbon double bond ready for further elaboration. Reactions of allenenes **1** activated thermally[4] and photochemically[5] have been reported to afford distal adducts[4] **2** and proximal adducts[5] **3**, respectively, as a result of the regioselectivity of the reactions (Scheme 1). [2+2] Cycloadditions of allenynes **4** have been realized by heating,[4d] or from the catalytic action of transition-metal complexes.[6] However, to the best of our knowledge, reports of [2+2] cycloaddition reactions between two allenes are limited.[7,8] In this reaction the control of regioselectivity (head-to-head, tail-to-tail, head-to-tail) would be a formidable challenge[3b] (Scheme 1). Herein we report our recent observations of regiocontrollable [2+2] cycloadditions of 1,5-bisallenyl-substituted compounds.



Scheme 1. Intramolecular [2+2] cycloadditions of allenenes, allenynes, and bisallenes.

During our study of the cyclization of bisallenes,[9] we observed a facile regioselective [2+2] cycloaddition reaction of 1,5-bisallenyl compound **6**, which solely afforded the bicyclo[5.2.0] products **7** in moderate to good yields on heating in the absence of the *trans*-[RhCl(CO)(PPh_3)$_2$] complex, thereby differing from the formation of head-to-head products as reported by Skattebøl and Solomon.[7a] This thermal [2+2] cycloaddition reaction of bisallenes is very sensitive to the concentrations of the reagents in the reaction system. After screening the reaction conditions, we found that the best yields of bicyclo[5.2.0] products were obtained from reactions that were heated to reflux with a 0.04 M solution of the substrate in xylene. Bisallenes substituted at the allene moiety gave better results, possibly because the diradical intermediates would be stabilized by these substituents.[4a,b] Furthermore, it was observed that yields were much improved with a bulkier X group (Table 1). This result can be explained by the fact that a bulky X group may bring the two allene functionalities closer. The general structures of **7** were confirmed from the X-ray crystal structure of **7e** (Figure 1).[10]

Conversely, unsaturated carbon–carbon bonds may undergo cyclometalation with many transition metals,[11] such as Rh, Ru, Pd, Ir, Pt, Fe, Co, and Ni. As a result of the ring strain in four-membered cycles, the reductive elimination of metallacyclopentanes and metallacyclopentenes is the key step in affording the four-membered carbocyclic ring.[7h,i] It is noteworthy that the reductive elimination of metallacyclopentanes and metallacyclopentenes has been observed in a limited number of catalytic reactions.[12] After some screening of reaction conditions, we found that the reaction catalyzed by [$Pd(PPh_3)_4$]/K_2CO_3/$n$$Bu_4NI$ provides an exclusive pathway to the bicyclo[3.2.0] product **8a** from 1,5-bisallenyl compound **6a**. In the course of optimizing the Pd^0-catalyzed [2+2] cycloaddition of bisallenes, we noted the following: 1) no reaction was observed in the absence of K_2CO_3 and $n$$Bu_4NI$ (entry 1, Table 2); 2) on adding only four equivalents of K_2CO_3, the reaction afforded trace amounts of bicyclo[3.2.0] product **8a** as determined by ^{1}H NMR analysis of the crude reaction mixture (entry 2, Table 2); and 3) the reaction failed on using $n$$Bu_4NI$ alone (entry 3, Table 2). After much experimentation, we determined the optimal conditions (entry 4, Table 2). The I^{-1} species in $n$$Bu_4NI$ may act as a ligand facilitating the reductive elimination process.[13] The structure and stereochemistry of **8a** was confirmed by X-ray crystal-structure analysis (Figure 2).[14]

With these optimized conditions in hand, the generality of the Pd^0-catalyzed [2+2] cycloaddition of 1,5-bisallenyl compounds was explored (Table 3). However, compounds **6e**–**6k** with substituents on the proximal side did not give the expected bicyclo[3.2.0] products **8e**–**k** probably because of steric reasons. The formation of other regioisomers was not observed. Polymerization of the starting material may be partially responsible for the relatively low yields.

Furthermore, when X is the chiral L-valine ester, compound **8m** was formed in greater than 99% *ee* (Table 3), which indicates that the reaction proceeded without racemization of the α-amino acid ester. We attempted many

[*] X. Jiang, X. Cheng, Prof. Dr. S. Ma
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
354 Fenglin Lu, Shanghai 200032 (P.R. China)
Fax: (+86) 21-6416-7510
E-mail: masm@mail.sioc.ac.cn

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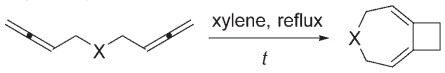
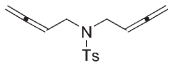
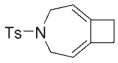
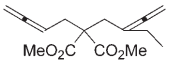
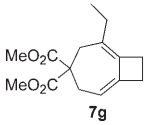
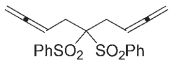
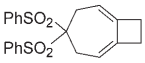
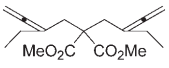
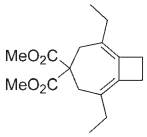
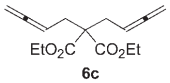
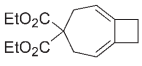
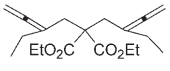
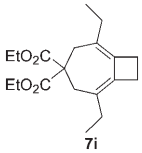
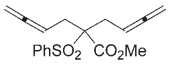
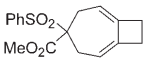
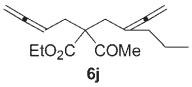
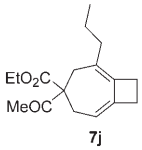
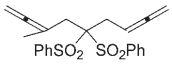
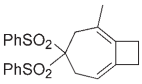
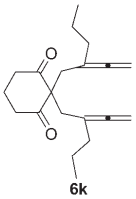
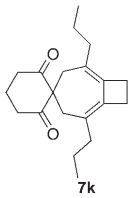
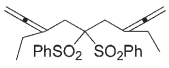
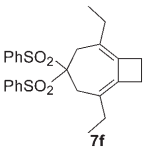
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Table 1: Thermal [2+2] cycloaddition of 1,5-bisallenyl compounds.[a]



6 **7**

Bisallene	*t* [h]	Bicyclo[5.2.0]	Yield[b] [%]	Bisallene	*t* [h]	Bicyclo[5.2.0]	Yield[b] [%]
 **6a**	24	 **7a**	43	 **6g**	10	 **7g**	56
 **6b**	3	 **7b**	61	 **6h**	24	 **7h**	70
 **6c**	46	 **7c**	38	 **6i**	6	 **7i**	69
 **6d**	8	 **7d**	61	 **6j**	5	 **7j**	70
 **6e**	1.5	 **7e**	69	 **6k**	0.5	 **7k**	78
 **6f**	1	 **7f**	74				

[a] Reactions were carried out in xylene (0.04 M), heated to reflux. [b] Yield of isolated products. Ts = toluene-4-sulfonic acid.

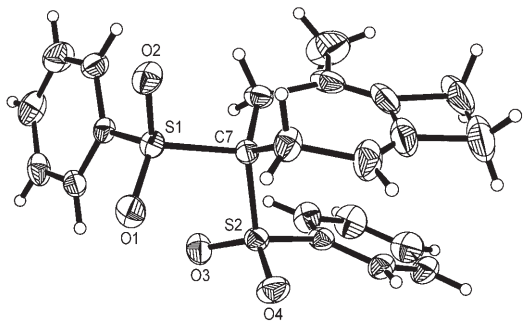
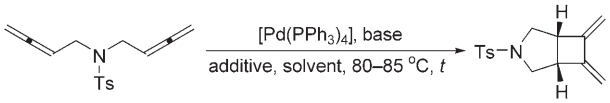


Figure 1. ORTEP representation of **7e** with thermal ellipsoids at the 30% probability level.

reactions to determine the absolute structure of **8m**, and it was found that the methyl ester analogue of **8m** (that is, **8n**)

Table 2: Pd^0-catalyzed [2+2] cycloaddition of 1,5-bisallenyl compounds under different conditions.



6a **8a**

Entry	$[Pd(PPh_3)_4]$ [mol%]	Base	Additive	Solvent	*t* [h]	Yield of **8a**[a] [%]
1	10	–[b]	–[b]	toluene	8	n.r.
2	10	K_2CO_3 (4 equiv)	–[b]	xylene	4	trace
3	10	–[b]	nBu_4NI (2 equiv)	xylene	10	n.r.
4	**5**	**K_2CO_3 (4 equiv)**	**nBu_4NI (2 equiv)**	**toluene**	**4**	**59**

[a] Yield of isolated product. [b] Without additive. n.r. = no reaction.

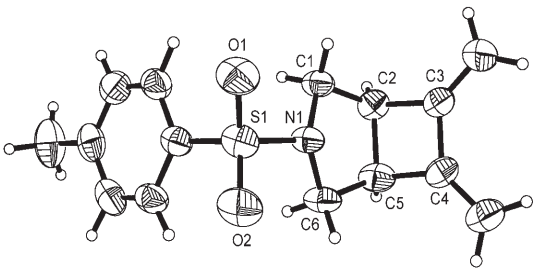
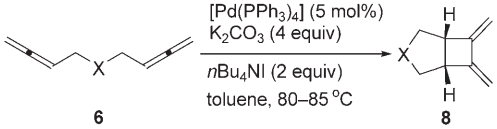
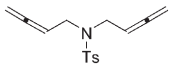
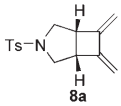
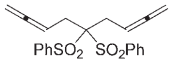
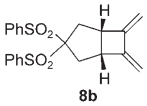
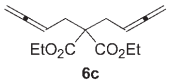
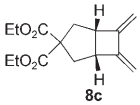
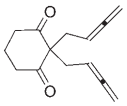
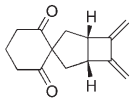
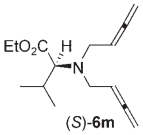
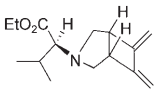


Figure 2. ORTEP representation of **8a** with thermal ellipsoids at the 30% probability level.

Table 3: Pd^0-catalyzed [2+2] cycloaddition of 1,5-bisallenyl compounds.



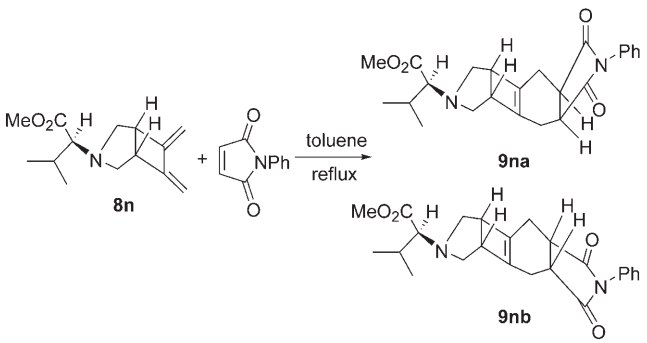
Bisallene	t [h]	Bicyclo[3.2.0]	Yield[a] [%]
 **6a**	4	 **8a**	59
 **6b**	4	 **8b**	62
 **6c**	19	 **8c**	45
 **6l**	8	 **8l**	54
 (*S*)-**6m**	5[b]	 **8m** (>99% ee)	66

[a] Yield of isolated products. [b] 10 mol% of $[Pd(PPh_3)_4]$ was used.

could react with *N*-phenylmaleimide to afford a solid tetracyclic compound **9na** (Scheme 2). The X-ray crystal structure of **9na**[15] led to the assignment of the absolute structures of **8m**, **8n**, and **9na** (Figure 3).

A plausible working model for the highly diastereoselective Pd^0-catalyzed [2+2] cycloaddition of 1,5-bisallenyl compound (*S*)-**6m** is depicted in Scheme 3. The coordination between the Pd atom and the lone pair of electrons of the N atom in the intermediate **10**, along with the requirement of the Pd atom to be distant from the bulkier CO_2Et group, leads to the exclusive formation of **8m**. The inversion of the nitrogen center may be very difficult in this case because of the presence of the bicyclic skeleton.

In summary, we have realized two different [2+2] cycloaddition pathways of 1,5-bisallenyl compounds that result in the formation of two types of bicyclic products **7** and **8** with a single four-membered ring. As a result of the challenge often



Scheme 2. Diels–Alder reaction of **8n** with *N*-phenylmaleimide.

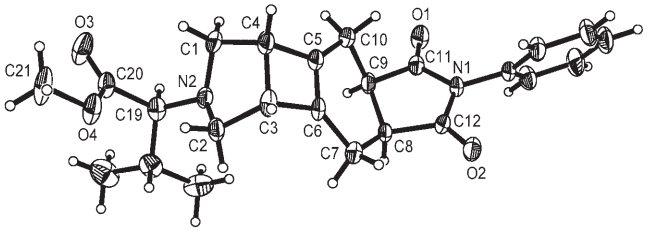
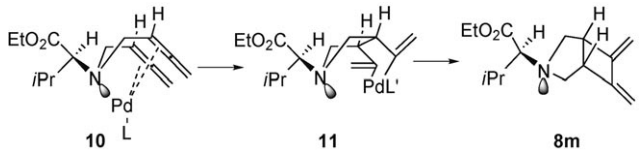


Figure 3. ORTEP representation of **9na** with thermal ellipsoids at the 30% probability level.



Scheme 3. Proposed working model for the highly diastereoselective formation of **8m**.

encountered in the synthesis of four-membered rings and their biological importance, these reactions may be powerful tools in organic synthesis and medicinal chemistry. Further studies, including the determination of the mechanism of thermal [2+2] cycloadditions of 1,5-bisallenyl compounds and the role of K_2CO_3 and nBu_4NI on the reductive elimination, are being pursued.

Experimental Section

General procedure I: A solution of bisallene **6a** (145 mg, 0.53 mmol) in dry xylene (12 mL) was heated at reflux under Ar for 24 h. After the reaction was complete by TLC (petroleum ether/ethyl acetate 5:1), rotary evaporation followed by flash chromatography on silica gel (petroleum ether/diethyl ether 20:1) afforded 62 mg (43%) of the product **7a**: liquid; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.68$ (d, $J =$ 8.1 Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 5.22 (s, 2H), 4.12 (d, $J =$ 2.7 Hz, 4H), 2.39 (s, 3H), 2.28 ppm (s, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 143.2$, 142.7, 137.9, 128.8, 127.7, 119.6, 50.7, 26.0, 21.4 ppm; MS (ESI): m/z (%) 274 ($[M-H]^+$, 100), 275 (M^+, 45), 277 ($[M+Na-H]^+$, 40); IR (neat): $\tilde{\nu} = 2926$, 1710, 1674, 1598, 1495, 1448, 1338, 1161 cm^{-1}; HR-MS (ESI) calcd for $C_{15}H_{16}NO_2S$: $[M-H]^+$ 274.0896; found 274.0890.

General procedure II: K_2CO_3 (281 mg, 2.04 mmol, 4 equiv) and nBu$_4$NI (369 mg, 1 mmol, 2 equiv)were added to a stirred solution of bisallene **6a** (140 mg, 0.51 mmol) and [Pd(PPh$_3$)$_4$] (27 mg, 0.023 mmol, 5 mol%) in dry toluene (5 mL). The reaction mixture was heated at 80–85 °C for 4 h. After the reaction was complete by TLC (petroleum ether/ethyl acetate 5:1), rotary evaporation followed by flash chromatography on silica gel (petroleum ether/diethyl ether 20:1) afforded 82 mg (59%) of the product **8a**: solid; m.p. 77–79 °C (petroleum ether, ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.68 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 5.21 (s, 2H), 4.79 (s, 2H), 3.62 (d, $J = 9.9$ Hz, 2H), 3.30 (d, $J = 4.5$ Hz, 2H), 2.72 (dd, $J =$ 9.9, 4.5 Hz, 2H), 2.42 ppm (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta =$ 149.0, 143.5, 132.1, 129.4, 128.0, 105.5, 53.3, 44.6, 21.5 ppm; MS (EI): m/z (%) 275 ([M]$^+$, 4.41); 91 (100); IR (neat): 2923, 2851, 1459, 1344, 1167 cm^{-1}.

Diels–Alder reaction of [3.2.0]bicyclic compounds with *N*-phenylmaleimide: A solution of **8n** (13 mg, 0.055 mmol) and *N*-phenylmaleimide (19 mg, 0.11 mmol, 2 equiv) in dry toluene (2 mL) was heated at reflux under Ar for 8 h to afford 24 mg (100%) of the product **9n** (**9na**/**9nb** 100:3, determined by ^{1}H NMR analysis); $[\alpha]_D^{20} =$ −20.6 ($c = 1.00$ in $CHCl_3$): solid; m.p. 123–124 °C (petroleum ether/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$–7.41 (m, 2H), 7.41–7.32 (m, 1H), 7.28 (d, $J = 7.8$ Hz, 2H), 3.67 (s, 3H), 3.30–3.22 (m, 2H), 3.22–3.10 (m, 2H), 2.95 (d, $J = 10.5$ Hz, 1H), 2.80–2.68 (m, 2H), 2.58–2.30 (m, 4H), 2.18–2.04 (m, 2H), 2.10–1.85 (m, 1H), 0.91 (d, $J =$ 6.9 Hz, 3H), 0.87 ppm (d, $J = 6.9$ Hz, 3H); the following data are discernible for the minor isomer **9nb**: $\delta = 3.65$ (s), 0.79 (d, $J = 6.6$ Hz), 0.76 ppm (d, $J = 6.6$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 178.88$, 178.85, 172.5, 138.4, 132.0, 129.1, 128.4, 126.3, 70.0, 50.5, 50.3, 46.6, 46.0, 44.3, 37.8, 37.7, 28.0, 20.7, 20.5, 19.6, 19.2 ppm; MS (ESI): m/z (%) 409 ([M+H]$^+$, 100), 441 ([M+Na]$^+$, 30); IR (neat): $\tilde{\nu} = 2924$, 2854, 1714, 1500, 1457, 1379, 1171, 1150 cm^{-1}; HR-MS (MALDI/2,5-dihydroxybenzoic acid matrix) calcd for $C_{24}H_{29}N_2O_4$ [M+H]$^+$: 409.2122; found: 409.2129.

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[15] Crystal data for compound **9na**: $C_{24}H_{28}N_2O_4$, $M_r = 408.48$, monoclinic, space group $P2(1)$, $a = 10.7399$ (18), $b = 5.7808$ (9), $c = 17.346(3)$ Å, $\alpha = 90$, $\beta = 97.128(3)$, $\gamma = 90°$, $V = 1068.6(3)$ Å^3, $T = 293$ (2) K, $Z = 2$, final R indices $[I > 2\sigma(I)]$, $R1 = 0.0543$, $wR2 = 0.1196$, R indices (all data), $R1 = 0.0675$, $wR2 = 0.1245$, reflections collected/unique: 6334/2563 (R(int) = 0.1458). CCDC-291779 (**7e**), CCDC-291780 (**8a**), CCDC-60887 (**9na**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

