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A New Route to Methyl (*R,E*)-(−)-Tetradeca-2,4,5-trienoate (Pheromone of *Acanthoscelides obtectus*) Utilizing a Palladium-Catalyzed Asymmetric Allene Formation Reaction

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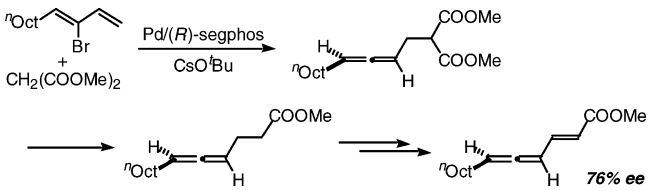
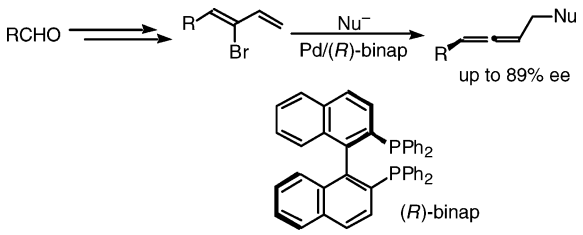


A formal total synthesis of the sex attractant of male dried bean beetle, methyl (*R,E*)-(−)-tetradeca-2,4,5-trienoate, was achieved by a new efficient route utilizing the Pd-catalyzed asymmetric allene synthesis reaction. It was found that the atropisomeric biaryl bisphosphine (*R*)-segphos showed better enantioselectivity than (*R*)-binap in the Pd-catalyzed reaction for preparing alkyl-substituted axially chiral allenes.

Recently, we have developed a novel palladium-catalyzed reaction of preparing functionalized allenes from 1-hydrocarbyl-2-bromo-1,3-butadienes,[1] which were easily derived from the corresponding aldehydes in high-yields.[1a] The Pd-catalyzed reaction has been extended into an asymmetric counterpart using a Pd/(*R*)-binap catalyst, and enantiomerically enriched axially chiral allenes were obtained with up to 89% ee (Scheme 1).[2] The reaction is a rare example of transition-metal-catalyzed asymmetric synthesis of axially chiral allenes.[3,4] In this paper, we report a formal total synthesis of methyl

SCHEME 1



(*R,E*)-tetradeca-2,4,5-trienoate ((*R*)-**1**), which is a naturally occurring allene[5] and a sex pheromone of male dried bean beetle,[6−8] by utilizing the asymmetric allene synthesis protocol. Among the known synthetic methods of the nonracemic pheromone,[8] our method is the first example of inducing the allenic axial chirality in (*R*)-**1** by a catalytic asymmetric reaction. It has been known that the pheromone extracted from the insect is optically active but not enantiomerically pure with ca. 79−81% ee.[6a,8b,9] Our asymmetric reaction gives certain axially chiral allenes with fairly high enantiomeric excess; however, the enantioselectivity still has room for further improvement. Indeed, while investigating its application to asymmetric synthesis of the pheromone, we had encountered the necessity to enhance the enantioselec-

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(9) The maximum optical rotation value for (*R*)-(−)-**1** reported so far is −162 (in hexane) by Mori and co-workers.[8b] They evaluated the enantiopurity of their sample as "not higher than 92%" based on the optical purity of the starting compound they employed for the synthesis of the pheromone. However, judging from our data (ee's and $[\alpha]_D$ values) for (*R*)-**1** as well as for (*R*)-**4** of which ee values were determined by the chiral HPLC technique, the compounds ((*R*)-**1** and (*R*)-**4**) reported in ref 8 appeared to be nearly enantiomerically pure. Assuming that the Mori's sample was enantiomerically pure, the natural pheromone (*R*)-**1** could be estimated to be 79% ee. On the other hand, the optical purity of the natural pheromone was calculated to be 81% by comparison with the sample prepared in this study.

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SCHEME 2

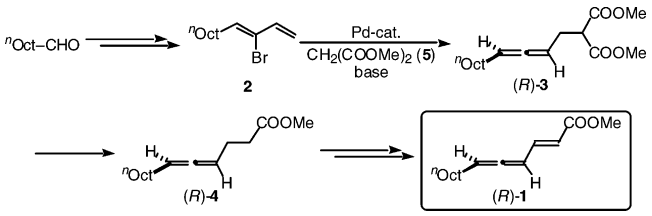
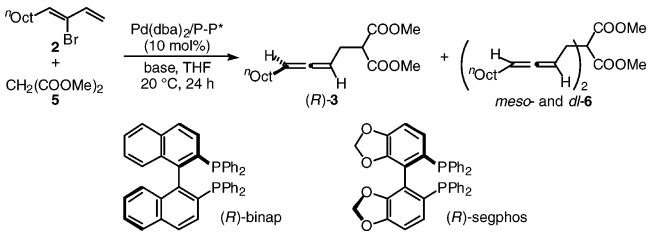


TABLE 1. Pd-Catalyzed Asymmetric Reaction of 2 with 5



			equiv to **2**		recovery or yield[a] (%)			ee of **3**[b]
entry	P−P*	base	**5**	base	**2**	**3**	**6**	(%)
1	(*R*)-binap	NaH	1.2	1.2		48	44	39
2	(*R*)-binap	CsO^{t}Bu	1.2	1.2		61	24	49
3	(*R*)-segphos	CsO^{t}Bu	1.2	1.2		47	36	77
4	(*R*)-segphos	CsO^{t}Bu	5.0	5.0		83	18	67
5	(*R*)-segphos	CsO^{t}Bu	5.0	1.0	26	71	2	77[c]

[a] Isolated yield by silica gel chromatography. [b] Determined by HPLC analysis with chiral stationary phase column (Daicel Chiralcel OD-H, hexane/^{i}PrOH = 500/1). [c] $[\alpha]_D = -45.8$ ($c = 1.08$, hexane).

tivity of the reaction for obtaining (*R*)-**1** of reasonable optical purity. It was found that the problem could be solved by the use of (*R*)-segphos[10] as a chiral supporting ligand in place of (*R*)-binap.[2b] In this paper, the scope and limitation of the Pd/(*R*)-segphos catalyst in the allene preparation will be described as well.

Strategy for Asymmetric Synthesis of the Pheromone. Our synthetic plan for methyl (*R,E*)-tetradeca-2,4,5-trienoate ((*R*)-**1**) is outlined in Scheme 2. Starting from 3-bromo-1,3-dodecadiene (**2**),[2a] which is easily derived from commercially available nonanal (see the Supporting Information for details), the axially chiral allene (*R*)-**3**[4c] would be prepared in an optically active form by the Pd-catalyzed asymmetric reaction using dimethyl malonate (**5**) as a pronucleophile. Removing one of the two methoxycarbonyl groups in (*R*)-**3** would afford (*R*)-methyl tetradeca-4,5-dienoate ((*R*)-**4**), which had been demonstrated as the key intermediate to (*R*)-**1**.[7e,8a−b]

Catalytic Asymmetric Synthesis of (*R*)-3. Transformation of the bromodiene **2** into (*R*)-**3** was examined under various conditions, and the results are summarized in Table 1. When the asymmetric reaction was carried out in THF with an equimolar mixture of the pronucleophile **5** and NaH (1.2 equiv to **2**) in the presence of the palladium catalyst (10 mol %) generated from Pd(dba)$_2$ and (*R*)-binap (entry 1),[2a] we encountered two problems: one was the low enantioselectivity of the reaction (39% ee), and the other was the low chemical yield of (*R*)-**3** (48%). The low chemical yield of **3** could be partly ascribed to the formation of bisallene species *meso*- and *dl*-**6**, which were obtained in 44% yield. Because the alkyl-substituted malonate **3** is more reactive than unsubstituted malonate **5** toward the palladium-catalyzed reaction, the initially formed **3** was deprotonated and reacted with **2** as a nucleophile giving **6**.[1] Use of CsO^{t}Bu as a base in place of NaH improved the yield of **3** as well as the enantioselectivity (entry 2). We have reported recently that (*R*)-segphos is superior to (*R*)-binap in terms of enantioselectivity in the Pd-catalyzed preparation of axially chiral (allenylmethyl)silanes, which are closely related to the present study.[2b] Thus, application of (*R*)-segphos to the present reaction was examined.[11] It was found that a palladium/(*R*)-segphos catalyst showed much higher enantioselectivity and (*R*)-**3** was obtained in 77% ee, although the **3/6** selectivity was poorer (entry 3). With 5 equiv of the nucleophile, the formation of **6** was reduced to 18%, but the enantiopurity of (*R*)-**3** was lowered to 67% ee (entry 4). A reaction using 5 equiv of **5** in the presence of a stoichiometric amount of CsO^{t}Bu (with respect to **2**) gave (*R*)-**3** of 77% ee in 71% yield (entry 5). Under these conditions, the formation of **6** was nearly suppressed. The starting substrate **2** was recovered in 26% yield, and thus the yield of (*R*)-**3** based on the consumed **2** was calculated to be as high as 96%. After these examinations, it was decided that (*R*)-**3** obtained under the optimized conditions of entry 5 (77% ee) was suitable for the following steps.

Application of (*R*)-Segphos to the Pd-Catalyzed Allene Preparation. The advantages of (*R*)-segphos over (*R*)-binap are recognized in the reaction in Table 1 as well as in the preparation of axially chiral (allenylmethyl)silanes that was reported previously.[2b] With these observations, the scope and limitation of the use of (*R*)-segphos were explored for the allene preparation reactions with other 2-bromo-1,3-diene substrates using the combination of HC(NHAc)(COOEt)$_2$ and CsO^{t}Bu as a nucleophile, of which applications to the asymmetric allene synthesis were thoroughly studied[2a] (Table 2). Unlike the above-mentioned examples, (*R*)-segphos showed lower performance than (*R*)-binap for the reactions with a phenyl-substituted diene **7** (entries 1 and 2). The Pd/(*R*)-segphos catalyst gave the allene **9** in lower yield with lower ee. Contrary to these, the superiority of (*R*)-segphos was observed for the preparation of allenes from the alkyl-substituted dienes **8** and **2**. The Pd/(*R*)-segphos showed better enantioselectivity than the Pd/(*R*)-binap (entries 3 vs 4 and 7 vs 8); however, its catalytic activity was lower at 20 °C and the allenes **10** and **11** were obtained in 6% and 12% yields, respectively (entries 4 and 8). By running the reactions at higher temperatures in THF, the low activity of the Pd/(*R*)-segphos catalyst was improved (entries 5 and 9). The allene **10** obtained at 60 °C in THF showed slightly lower ee (89% ee) than the product from entry 4 (93% ee at 20 °C). Interestingly, for the reactions of **2** using the Pd/(*R*)-segphos, the better

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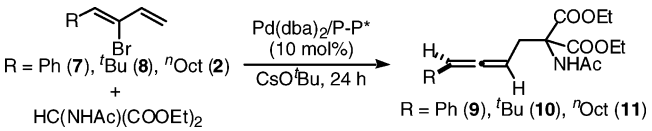
(11) Whereas use of a bidentate triarylphosphine ligand is essential in the Pd-catalyzed allene preparation,[1a] axially chiral biaryl phosphines are rationalized choices as chiral ligands for the present study.[2a] Other axially chiral biaryl phosphines examined so far are (*R*)-H$_8$-binap and (*R*)-binap's with modified PAr$_2$ groups (Ar = −C$_6$H$_2$-3,5-Me$_2$-4-OMe and *p*-tol); however, none of them showed better enantioselectivity than (*R*)-segphos for the reaction of **8** with HC(NHAc)(COOEt)$_2$ (Ogasawara, M.; Nagano, T.; Hayashi, T. Unpublished results).

TABLE 2. (*R*)-Binap vs (*R*)-Segphos in the Pd-Catalyzed Asymmetric Synthesis of Allenes from Bromodienes



entry	R in diene	P−P*	solvent	*T* (°C)	yield[a] (%)	ee[b] (%)
1[c]	Ph (**7**)	(*R*)-binap	CH_2Cl_2	20	75 (**9**)	89
2	Ph (**7**)	(*R*)-segphos	CH_2Cl_2	20	60 (**9**)	83
3[c]	^{t}Bu (**8**)	(*R*)-binap	CH_2Cl_2	20	74 (**10**)	75
4	^{t}Bu (**8**)	(*R*)-segphos	CH_2Cl_2	20	6 (**10**)	93
5	^{t}Bu (**8**)	(*R*)-segphos	THF	60	87 (**10**)	89
6	^{t}Bu (**8**)	(*R*)-binap	THF	60	92 (**10**)	67
7[c]	^{n}Oct (**2**)	(*R*)-binap	CH_2Cl_2	20	73 (**11**)	54
8	^{n}Oct (**2**)	(*R*)-segphos	CH_2Cl_2	20	12 (**11**)	70
9	^{n}Oct (**2**)	(*R*)-segphos	THF	40	63 (**11**)	74

[a] Isolated yield by silica gel chromatography. [b] Determined by HPLC analysis with chiral stationary phase column (see ref 2a). [c] Taken from ref 2a.

TABLE 3. Decarboxylation of (*R*)-3 Giving (*R*)-4

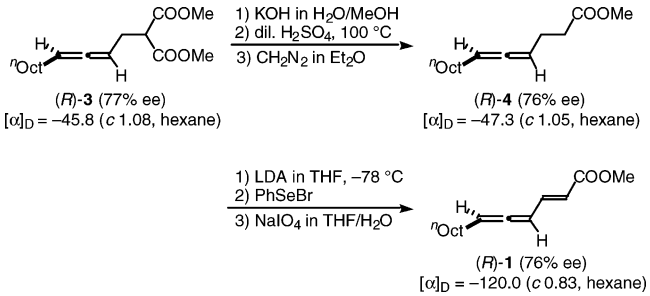
entry	conditions	yield[a] (%)	ee of **4**[b] (%)
1	LiI (5.5 equiv), NaCN (1.0 equiv) in DMF, 120 °C, 6 h	82	54
2	NaCl (0.5 equiv), H_2O (3.0 equiv) in DMSO, 130 °C, 8h	35	69
3	(1) KOH in H_2O/MeOH, 70 °C, 30 min (2) H_2SO_4 (cat.) in H_2O, 100 °C, 2 days (3) CH_2N_2 in Et_2O	60	76[c]

[a] Isolated yield by silica gel chromatography. [b] Determined by HPLC analysis with chiral stationary phase column (Daicel Chiralcel OD-H, hexane/^{i}PrOH = 500/1). [c] $[\alpha]_D = -47.3$ ($c = 1.05$, hexane).

enantioselectivity of 74% ee was observed at 40 °C in THF (entry 9) compared to the reaction at 20 °C in dichloromethane (70% ee, entry 8).

Decarboxylation of (*R*)-3. Using (*R*)-**3** of 77% ee, decarboxylation giving (*R*)-**4** was examined (Table 3).[12] Direct removal of one of the ester groups in (*R*)-**3** was achieved by treatment with LiI and NaCN in DMF at 120 °C (entry 1).[13] However, the decarboxylation proceeded with partial racemization of the allenic axial chirality,[14] and (*R*)-**4**, which was obtained in 82% yield, was found to have 54% ee. A reaction of (*R*)-**3** with NaCl in aqueous DMSO at 130 °C gave (*R*)-**4** of 69% ee in 35% yield (entry 2).[15] The racemization could be practically suppressed under the conditions of entry 3. That is a three-step process of methanolic hydrolysis followed by acidic decarboxylation at 100 °C and a diazomethane treatment. The overall yield of the process is 60%, and the product was obtained without appreciable loss of enantiopurity (76% ee).

SCHEME 3



Absolute Configurations of the Allenic Products from the Pd-Catalyzed Asymmetric Reaction. The obtained (*R*)-**4** was converted to the pheromone (*R*)-**1** according to the reported method.[7e,8a,b,16] The chiral HPLC analysis revealed that optical purity of the axially chiral allenes was retained during the transformation of (*R*)-**4** into (*R*)-**1**. Consequently, the asymmetric total synthesis of the sex pheromone of male dried bean beetle was completed by the new efficient route in practically the comparable optical purity as in the natural sample.

In the previous reports,[2] the absolute configurations of the axially chiral allenic products were deduced by the Lowe−Brewster rule.[17] Since the relation between the absolute configuration of the pheromone and its sign of optical rotation has been known (the (*R*)-enantiomer exhibits levorotatory),[8a] we had an opportunity to test the validity of the Lowe−Brewster rule in the Pd-catalyzed asymmetric reaction. As summarized in Scheme 3, the allenic products **1**, **3**, and **4** were all levorotatory, and thus their absolute configurations were deduced to be (*R*) by the Lowe−Brewster rule. This stereochemical conclusion for the synthetic **1** showed good agreement with the reported data for the naturally occurring (*R*)-(−)-**1**. During the transformations in Scheme 3, the allenic stereochemistry had been retained. Accordingly, it can be concluded that the Lowe−Brewster rule has drawn the correct absolute configurations for **3** and **4** as well.

In summary, we have developed a novel and efficient method for the preparation of the sex attractant of male dried bean beetle, methyl (*R,E*)-tetradeca-2,4,5-trienoate, utilizing the palladium-catalyzed asymmetric allene synthesis as the key reaction. The unique axial chirality in the pheromone was induced by the transition-metal-catalyzed asymmetric reaction and the pheromone was obtained in 76% ee, which is practically the comparable optical purity as in the sample extracted from the natural source. During this study, the better performances of (*R*)-segphos over (*R*)-binap in the Pd-catalyzed reaction, especially for the preparation of the alkyl-substituted axially chiral allenes, were recognized.

(12) For reviews on decarboxylation, see: (a) McMurry, J. *Org. React.* **1976**, *24*, 187. (b) Krapcho, A. P. *Synthesis* **1982**, 805. (c) Krapcho, A. P. *Synthesis* **1982**, 893.

(13) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.

(14) Thermal racemization of axially chiral allenes was reported and the racemization barriers in 1,3-dialkylallenes were estimated to be about 46 kcal/mol. However, the reaction temperatures in Table 3 are relatively low and a mechanism of the racemization at the decarboxylation of (*R*)-**3** is still uncertain. See: (a) Maitland, P.; Mills, W. H. *J. Chem. Soc.* **1936**, 987. (b) Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974**, *107*, 48.

(15) (a) Krapcho, A. P.; Lovey, A. J. *Tetrahedron Lett.* **1973**, *14*, 957. (b) Krapcho, A. P.; Jahngen, Jr., E. G. E.; Lovey, A. J. *Tetrahedron Lett.* **1974**, *15*, 1091.

(16) For preparation of **4**, see also: (a) Fujisawa, T.; Iida, S.; Sato, T. *Tetrahedron Lett.* **1984**, *25*, 4007 (in an optically active form). (b) Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 5237 (in a racemic form).

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Experimental Section

Palladium-Catalyzed Asymmetric Synthesis of Allenes. The reactions were conducted according to a reported procedure.[2a] The reaction conditions and the results are described in Tables 1 and 2. A typical procedure is given for the reaction of entry 1 in Table 1: A mixture of $Pd(dba)_2$ (29 mg, 50 μmol), (*R*)-binap (34 mg, 55 μmol), and (*Z*)-3-bromo-1,3-dodecadiene[2a] (**2**, 123 mg, 0.502 mmol) was dissolved in THF (5 mL), and the solution was added to a mixture of $CH_2(COOMe)_2$ (**5**, 80.0 mg, 0.605 mmol) and NaH (15 mg, 0.62 mmol) in THF (2 mL) by cannula transfer under nitrogen. The mixture was stirred at 20 °C for 24 h and then filtered through a short pad of silica gel to remove precipitated inorganic salts. The silica gel pad was washed with small amount of Et_2O three times, and the combined solution was evaporated to dryness under reduced pressure. The yellow residue was chromatographed on silica gel (hexane/Et_2O = 3/1) to give the monoallene **3** (71.4 mg, 48% yield) and the bisallene **6** (as a mixture of *meso*- and *dl*-isomers. 102 mg, 44%). The characterization data of **3** and **6** are listed below. The allenes **9**−**11** were characterized by comparison of their spectroscopic data with those reported previously.[2a]

Dimethyl 2-(2,3-Dodecadienyl)propane-1,3-dioate (3). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 7.1 Hz, 3H), 1.26−1.33 (m, 10H), 1.34−1.41 (m, 2H), 1.93 (dd, J = 3.1 and 6.7 Hz, 1H), 1.96 (dd, J = 3.1 and 6.9 Hz, 1H), 2.56−2.60 (m, 2H), 3.51 (t, J = 7.6 Hz, 1H), 3.739 (s, 3H), 3.741 (s, 3H), 5.08−5.17 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.1, 22.7, 28.1, 28.9, 29.1, 29.2, 29.3, 29.5, 31.9, 51.3, 52.5, 52.6, 87.4, 93.1, 169.4, 169.5, 204.0. Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.79; H, 9.27.

***meso*- and *dl*-Dimethyl 2-Bis(2,3-dodecadienyl)propane-1,3-dioate (*meso*- and *dl*-6).** ^{1}H NMR ($CDCl_3$): δ 0.88 (apparent t, J = 7.1 Hz, 6H), 1.26−1.39 (m, 24H), 1.93−1.98 (m, 4H), 2.63−2.65 (m, 4H), 3.71 (s, 6H), 4.86−4.92 (m, 2H), 5.03−5.08 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.1, 22.7, 28.8, 28.9, 29.16, 29.17, 29.26, 29.28, 29.31, 29.4, 31.9, 32.48, 32.49, 52.33, 52.36, 52.40, 58.0, 58.1, 84.6, 84.7, 91.01, 91.03, 171.094, 171.096, 171.100, 205.76, 205.81. Anal. Calcd for $C_{29}H_{48}O_4$: C, 75.61; H, 10.50. Found: C, 75.36; H, 10.62.

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Supporting Information Available: Experimental details for preparation of **2**, ^{1}H and ^{13}C NMR spectra of 1,1-dibromo-1-decene, **2**−**4**, and **6**, and ^{1}H NMR spectra for the reaction products which were reported previously (**1**, **9**−**11**). This material is available free of charge via the Internet at http://pubs.acs.org.

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