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Stereoselective cyclopropanation of 3-aryl-2-phosphonoacrylates induced by the (−)-8-phenylmenthyl group as a chiral auxiliary

Ryukichi Takagi, Minoru Nakamura, Miki Hashizume, Satoshi Kojima and Katsuo Ohkata*

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

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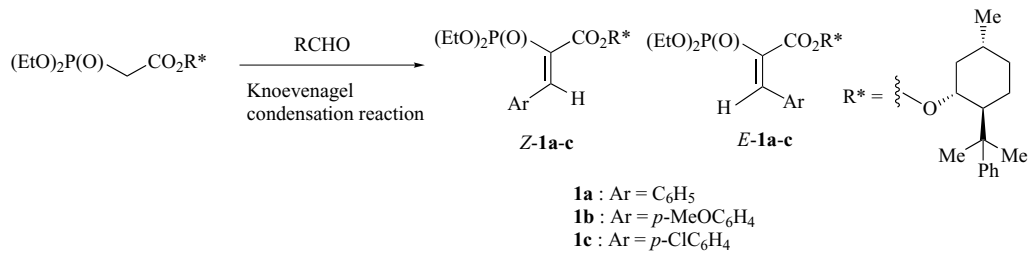
Abstract—The cyclopropanation of (−)-8-phenylmenthyl (*E*)-3-aryl-2-phosphonoacrylates with dimethyloxosulfonium methylide and diazomethane afforded the corresponding *trans* cyclopropane derivatives with high diastereoselectivity as the major diastereomer. The high selectivity is understandable in terms of the π–π interaction between the phenyl ring of the chiral auxiliary and the acrylate moiety.

Many phosphonate derivatives have been applied to the areas of agricultural chemistry, owing to their biological activity.[1] Much effort has been directed toward the synthesis of 1-aminocyclopropanecarboxylic acid derivatives[2] because of their biological activity[3] and the potential use in conformationally restricted peptides.[4] The synthesis of cyclopropane phosphonic acid derivatives has widely been investigated.[5]

Recently, we have investigated the asymmetric induction in the formation of cyclic compounds by means of the (−)-8-phenylmenthyl group as a chiral auxiliary.[6] Various types of asymmetric reactions using the (−)-8-phenylmenthyl group as a chiral auxiliary have been investigated and the reaction proceeded with considerably high stereoselectivity.[7,8] The high stereoselectivity has been attributed to the differentiation of the π-faces induced by the (−)-8-phenylmenthyl group. In this paper, we describe the π-differentiational cyclopropanation of 3-aryl-2-diethylphosphonoacrylates by means of the (−)-8-phenylmenthyl group.

(*E*)-, (*Z*)-3-Aryl-2-phosphonoacrylates **1a–c** were prepared by the titanium mediated Knoevenagel condensation of (−)-8-phenylmenthyl diethylphosphonoacetate with the corresponding aryl aldehydes with high stereoselectivity (Scheme 1).[9] The condensation reaction of the diethylphosphonoacetate with aryl aldehydes in the presence of *N*-methylmorpholine (NMM)/$TiCl_4$ gave Knoevenagel products **1a–c** having the thermodynamically more stable (*E*)-geometry.[9b] The thermodynamically less stable (*Z*)-isomers *Z*-**1a–c** were obtained by the reaction of the diethylphosphoate with aryl aldehydes in the presence of $ClTi(OiPr)_3/Et_3N$ at low temperature (−78°C).[9a,10]



Scheme 1. *Reagents and conditions*: For *E*-**1a–c**: $TiCl_4$ (2 equiv.), NMM (10 equiv.), THF. For *Z*-**1a–c**: $Ti(OiPr)_3Cl$ (2 equiv.), Et_3N (10 equiv.), THF.

Keywords: activated cyclopropane; 8-phenylmenthyl; diastereoselective.

* Corresponding author. Tel.: +81-824-24-7432; fax: +81-824-0747; e-mail: ohkata@sci.hiroshima-u.ac.jp

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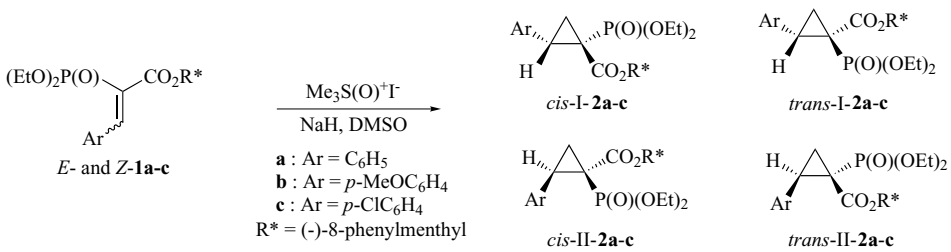
The cyclopropanation of **1a–c** with dimethyloxosulfonium methylide was examined (Scheme 2). All four diastereomers of **2a–c** were separated by HPLC, respectively. The relative configuration of the diastereomers was assigned by the coupling constant ($^3J_{CP}$) between the *ipso*-carbon of the aryl group and the phosphorus. Table 1 shows the results of the cyclopropanation reaction of **1a–c** with dimethyloxosulfonium methylide. The reaction of *E*-**1a–c** at 25°C afforded preferentially the *trans* isomers (Table 1, entries 1–3). The diastereoselectivity in the cyclopropanation was moderate (40–49% de) for the *cis* isomers **2a–c** and considerably high (80–86% de) for the *trans* isomers **2a–c**. The cyclopropanation of *Z*-**1a–c** in DMSO at 25°C gave mixtures of *cis* and *trans* cyclopropanation derivatives **2a–c** (Table 1, entries 4–6). The diastereoselectivity in the reactions were from low to fair (17–58% de).

Next, the cyclopropanation reaction of **1a–c** with excess diazomethane was examined (Scheme 3). Treatment of **1a–c** in Et_2O at 0–25°C with diazomethane afforded a mixture of Δ^1-pyrazoline derivatives **3a–c** (Table 2). The diastereomers of the pyrazolines **3a–c** could not be separated. However, the relative configuration of the pyrazolines could be determined by the coupling constant ($^3J_{CP}$) in ^{13}C NMR spectra between the *ipso*-carbon of the aryl ring and the phosphorus. The 1,3-dipolar cycloaddition reaction of *E*-**1a–c** with dia-

Table 2. The formation of pyrazolines by the reaction of **1a–c** with CH_2N_2

Entry	Substrate	Product	*trans*:*cis*[a]	% de[a]	
				trans	*cis*
1	*E*-**1a**	**3a**	1:–	84	–
2	*E*-**1b**	**3b**	1:–	85	–
3	*E*-**1c**	**3c**	10:1	80	43
4	*Z*-**1a**	**3a**	1:28	>90	25
5	*Z*-**1b**	**3b**	1:1.2	76	40
6	*Z*-**1c**	**3c**	1:2.8	80	56

[a] The ratios were determined by integral values of ^{31}P NMR.

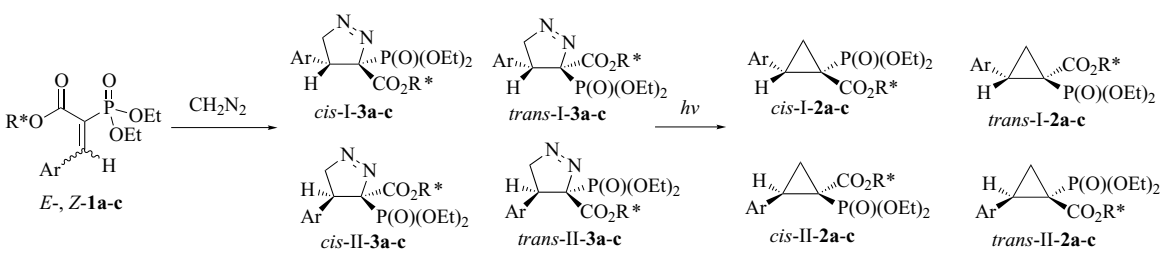


Scheme 2.

Table 1. The cyclopropanation of **1a–c** with dimethyloxosulfonium methylide

Entry	Substrate	Product	Yield (%)	*trans*:*cis*	% de[a]	
					trans	*cis*
1	*E*-**1a**	**2a**	69	7.8:1	86	46
2	*E*-**1b**	**2b**	96	1.7:1	83	49
3	*E*-**1c**	**2c**	93	1.8:1	80	40
4	*Z*-**1a**	**2a**	91	1:1.3	35	17
5	*Z*-**1b**	**2b**	97	1:1.1	35	20
6	*Z*-**1c**	**2c**	73	1.1:1	58	21

[a] The ratios were determined by integral values of the cyclopropyl proton in ^1H NMR.



Scheme 3.

Table 3. The cyclopropanation of **1a**–**c** with CH_2N_2 via pyrazolines

Entry	Substrate	Product	Yield (%)[a]	*trans*:*cis*[b]	% de	
					trans	*cis*
1	*E*-**1a**	**2a**	59	25:1	87	0
2	*E*-**1b**	**2b**	62	15:1	87	0
3	*E*-**1c**	**2c**	32	6:1	93	29
4	*Z*-**1a**	**2a**	28	1:2.5	66	50
5	*Z*-**1b**	**2b**	41	1.1:1	88	45
6	*Z*-**1c**	**2c**	48	1:2	83	46

[a] The yields were calculated from **1a**–**c**.
[b] The ratios were determined by integral values of ^{1}H NMR.

zomethane proceeded with high stereoselectivity and the *trans* pyrazoline derivatives *trans*-**3a**–**c** were preferentially obtained as the major diastereomer (Table 2, entries 1–3). The reaction of *Z*-**1a**–**c** with diazomethane gave the *cis* pyrazolines *cis*-**3a**–**c** as the major diastereomers (Table 2, entries 4–6). The diastereoselectivity of the *cis* pyrazolines **3a**–**c** was low.

The photolysis of the pyrazolines **3a**–**c** which were obtained by the reaction of **1a**–**c** with diazomethane gave cyclopropane derivatives **2a**–**c**.[11] Table 3 shows the results of the cyclopropanation via the pyrazolines. The *trans* cyclopropane derivatives **2a**–**c** were preferentially obtained with high diastereoselectivity in the cyclopropanation of *E*-**1a**–**c** via pyrazolines (Table 3, entries 1–3). The cyclopropanation of *Z*-**1a**–**c** via pyrazolines gave mixtures of *cis*- and *trans*-diastereomers of which ratios were ca. 1:1 (Table 3, entries 4–6). The diastereomeric ratios of the *cis* diastereomers were very low and those of the *trans* diastereomers were high.

trans-II-**2b** turned out to be crystalline and was subjected to X-ray structural analysis (Fig. 1). The absolute stereochemistry was determined to be (1*S*,2*R*) as shown in Fig. 1. On the basis of this observation, the absolute stereochemistry of the major products (*trans*-II and *cis*-I) was presumed to be as shown in Scheme 4.

The high diastereoselectivity in the reaction of *E*-**1a**–**c** with both oxosulfonium methylide and diazomethane is understandable in terms of π–π interaction between the phenyl ring of the chiral auxiliary and the acrylate moiety (Scheme 4).[12] In this conformation, it is considered that the phenyl group of the chiral auxiliary is suitably positioned to block the depicted back face of the acrylate moiety and induce the reagents (dimethyloxosulfonium methylide and diazomethane) to approach from the *Re*-face. The reagents attack *Z*-**1a**–**c** from both the *Re*- and the *Si*-face of the acrylate moiety and the cyclopropanation of *Z*-**1a**–**c** afforded cyclopropane derivatives with low diastereoselectivity.

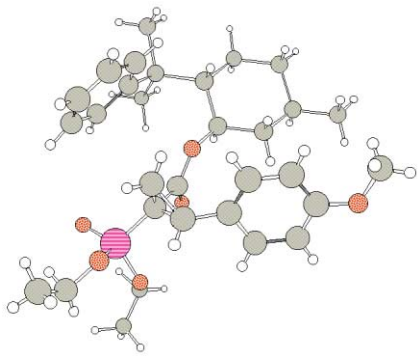


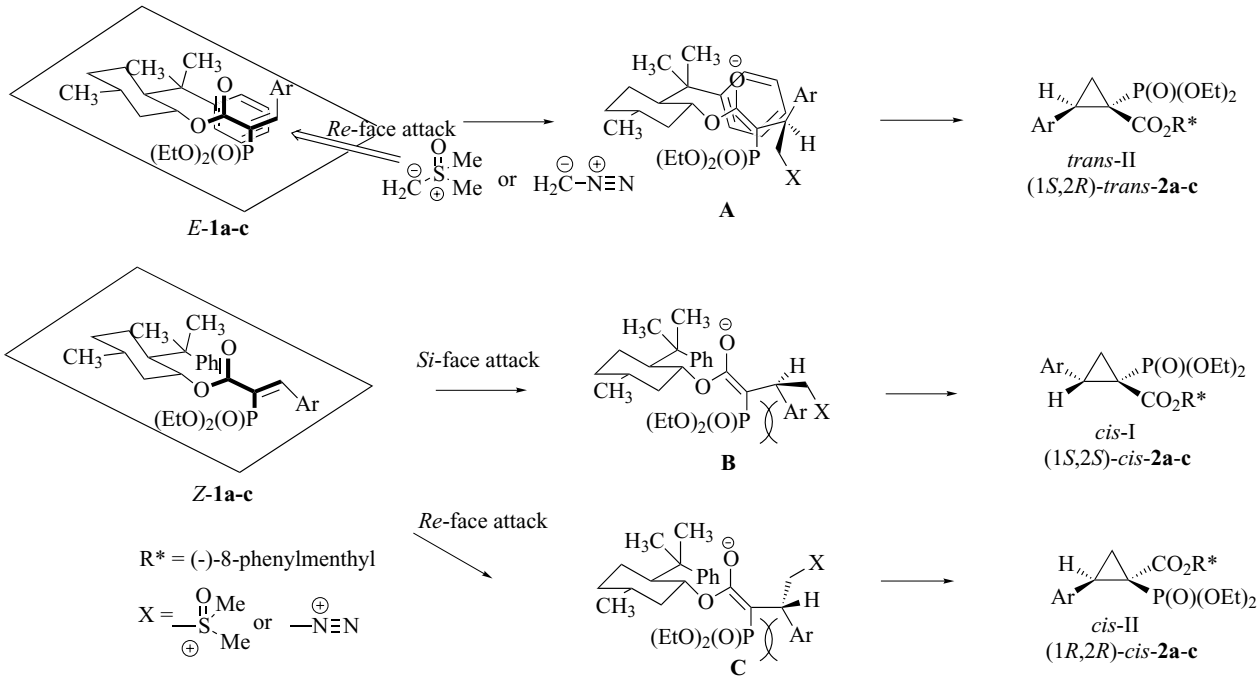
Figure 1. Ball–stick drawing of the X-ray structure of *trans*-II-**2b**.

In the cyclopropanation using both dimethyloxosulfonium methylide and diazomethane, the geometric ratios (*cis*/*trans*) of cyclopropanation derivatives **2a**–**c**[13] generated by the reaction with *E*-**1a**–**c** were higher than that of *Z*-**1a**–**c**. This indicates that the *trans* isomers were obtain in order to avoid the repulsion between the aryl ring and the phosphonate moiety in the intermediates **B** and **C**.

In conclusion, we have shown that the cyclopropanation reaction of (*E*)-3-aryl-2-phosphonoacrylates using the (−)-8-phenylmenthyl group as a chiral auxiliary gives the *trans* cyclopropane derivatives with high diastereoselectivity. The high diastereoselectivity can be attributed to the high π-face differentiation of the acrylate moiety by the face-to-face interaction with the phenyl ring of the chiral auxiliary.

Acknowledgements

NMR measurements were carried out on JEOL GSX-270 and LA-500 instruments, and HRMS measurements on a JEOL SX-102A spectrometer at the Instrument Center for Chemical Analysis, Hiroshima University.



Scheme 4.

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10. Treatment of benzaldehyde with (–)-8-phenylmenthyl diethylphosphonoacetate at 0°C gave a mixture of *E*- and *Z*-**1a** (*E*/*Z*=ca. 1:1).
11. Photolysis of the pyrazolines was conducted as below: A solution of the pyrazolines **3a**–**c** in CH_2Cl_2 was purged with N_2 in a quartz flask. The solution was irradiated with low-pressure mercury lamp at 25°C.
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13. NMR spectra data: *cis*-I-**2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75–0.90 (m, 2H), 0.87 (d, $J=6.4$ Hz, 3H), 0.97–1.08 (m, 1H), 1.11 (t, $J=7.1$ Hz, 3H), 1.12 (t, $J=7.0$ Hz, 3H), 1.33 (s, 3H), 1.43 (m, 1H), 1.46 (s, 3H), 1.52–1.62 (m, 3H), 1.90–2.00 (m, 3H), 2.74(q, $J=8.9$ Hz, 1H), 3.65–3.78 (m, 3H), 3.85–3.93 (m, 1H), 5.00 (td, $J=4.6$, 10.8 Hz, 1H), 7.18–7.34 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.2 (d, $^3J_{CP}=5.3$ Hz), 16.3 (d, $^3J_{CP}=3.8$ Hz), 17.1 (d, $^2J_{CP}=2.0$ Hz), 21.7 (×2), 25.0, 27.0, 29.0, 29.1 (d, $^1J_{CP}=197.7$ Hz), 31.2 (×2), 33.4 (d, $^2J_{CP}=2.0$ Hz), 34.4, 40.6, 41.7, 50.5, 61.6 (d, $^2J_{CP}=5.9$ Hz), 62.6 (d, $^2J_{CP}=5.9$ Hz), 75.8, 125.4, 125.6, 127.3, 127.7 (×2), 128.1 (×2), 130.0, 134.7 (d, $^3J_{CP}=4.5$ Hz), 150.8, 169.1 (d, $^2J_{CP}=8.6$ Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.5; HRMS (EI) calcd for $C_{30}H_{31}O_5P$ M^+: 512.2602. Found: 512.2684.
cis-II-**2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75–0.90 (m, 1H), 0.88 (d, $J=6.6$ Hz, 3H), 0.98–1.12 (m, 1H), 1.08 (t, $J=7.1$ Hz, 3H), 1.09 (t, $J=7.0$ Hz, 3H), 1.24–1.28 (m, 1H), 1.27 (s, 3H), 1.38 (s, 3H), 1.41–1.48 (m, 2H), 1.53–1.62 (m, 2H), 1.62–1.67 (m, 1H), 1.92–1.98 (m, 1H), 2.00–2.08 (m, 1H), 2.63 (q, $J=8.2$ Hz, 1H), 3.60–3.70 (m, 1H), 3.78–3.92 (m, 3H), 5.00 (td, $J=4.6$, 10.7 Hz, 1H), 7.40–7.80 (m, 1H), 7.19–7.34 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.1 (d, $^3J_{CP}=3.7$ Hz), 16.2 (d, $^3J_{CP}=1.8$ Hz), 17.9 (d, $^2J_{CP}=2.1$ Hz), 21.8, 25.4, 27.1, 28.3, 28.9 (d, $^1J_{CP}=198.0$ Hz), 31.4 (×2), 31.8 (d, $^2J_{CP}=3.9$ Hz), 34.4, 40.2, 41.8 (×2), 49.9, 61.7 (d, $^2J_{CP}=5.6$ Hz), 62.1 (d, $^2J_{CP}=6.9$ Hz), 76.4, 125.4, 125.5. 127.0, 127.7 (×2), 128.1, 130.0 (×2), 135.3 (d, $^3J_{CP}=6.4$ Hz), 150.8, 169.2 (d, $^2J_{CP}=9.6$ Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.2; HRMS (EI) calcd for $C_{30}H_{31}O_5P$ M^+: 512.2602. Found: 512.2645.
trans-I-**2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.37 (q, $J=$ 11.9 Hz, 1H), 0.47–0.60 (m, 1H), 0.58 (d, $J=6.6$ Hz, 3H), 0.64–0.77 (m, 2H), 1.00–1.50 (m, 2H), 1.23 (s, 3H), 1.34 (t, $J=7.0$ Hz, 3H), 1.34 (s, 3H), 1.49 (t, $J=7.1$ Hz, 3H), 1.68–1.75 (m, 1H), 1.76–1.82 (m, 1H), 1.82–1.89 (m, 1H), 2.19–2.25 (m, 1H), 3.10–3.17 (m, 1H), 4.15–4.24 (m, 2H), 4.29–4.36 (m, 2H), 4.65 (dt, $J=4.5$, 10.5 Hz, 1H), 7.06–7.41 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9 (d, $^2J_{CP}=2.4$ Hz), 16.2 (d, $^3J_{CP}=7.1$ Hz), 16.6 (d, $^3J_{CP}=7.2$ Hz), 21.4, 22.7, 27.4, 29.3 (d, $^1J_{CP}=184.7$ Hz), 30.8, 31.0, 31.5, 34.1, 40.5, 41.3, 50.1, 62.3 (d, $^2J_{CP}=4.5$ Hz), 62.4 (d, $^2J_{CP}=3.6$ Hz), 76.8, 125.3, 125.9 (×2), 127.9 (×2), 128.1 (×2), 128.4, 129.4 (×2), 133.8 (d, $^3J_{CP}=1.8$ Hz), 150.1, 166.0 (d, $^2J_{CP}=6.3$ Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.4; HRMS (EI) calcd for $C_{30}H_{31}O_5P$ M^+: 512.2602. Found: 512.2709.
trans-II-**2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ –0.04 (q, $J=13.1$ Hz, 1H), 0.55–0.64 (m, 2H), 0.62 (d, $J=6.8$ Hz, 3H), 0.78–0.88 (m, 2H), 1.00 (s, 3H), 1.19 (s, 3H), 1.35–1.45 (m, 3H), 1.39 (t, $J=7.1$ Hz, 3H), 1.44 (t, $J=7.0$ Hz, 3H), 1.52–1.58 (m, 1H), 1.70–1.76 (m, 1H), 2.98 (ddd, $J=8.4$, 8.4, 17.0 Hz, 1H), 4.24 (dq, $J=7.2$, 14.5 Hz, 2H), 4.31 (dq, $J=7.2$, 14.5 Hz, 2H), 4.53 (td, $J=4.1$, 10.8 Hz, 1H), 7.15–7.32 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.6 (d, $^2J_{CP}=1.9$ Hz), 16.5 (d, $^3J_{CP}=6.7$ Hz), 16.6 (d, $^3J_{CP}=6.7$ Hz), 21.4 (×2), 26.0, 26.7, 26.9, 28.8 (d, $^1J_{CP}=$ 191.0 Hz), 30.9 (d, $^2J_{CP}=17.2$ Hz), 34.3, 39.7, 40.0, 50.1, 62.5 (d, $^2J_{CP}=5.5$ Hz), 62.7 (d, $^2J_{CP}=6.5$ Hz), 75.7, 125.2, 125.5 (×2), 127.4, 128.0 (×2), 128.2 (×2), 129.5 (×2), 134.6 (d, $^3J_{CP}=1.8$ Hz), 151.4, 166.1 (d, $^2J_{CP}=8.6$ Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 24.1; HRMS (EI) calcd for $C_{30}H_{31}O_5P$ M^+: 512.2692. Found: 512.2698.