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Palladium(II)–Catalyzed 1,3-Dipolar Cycloaddition of Nitrones with Enol Ethers

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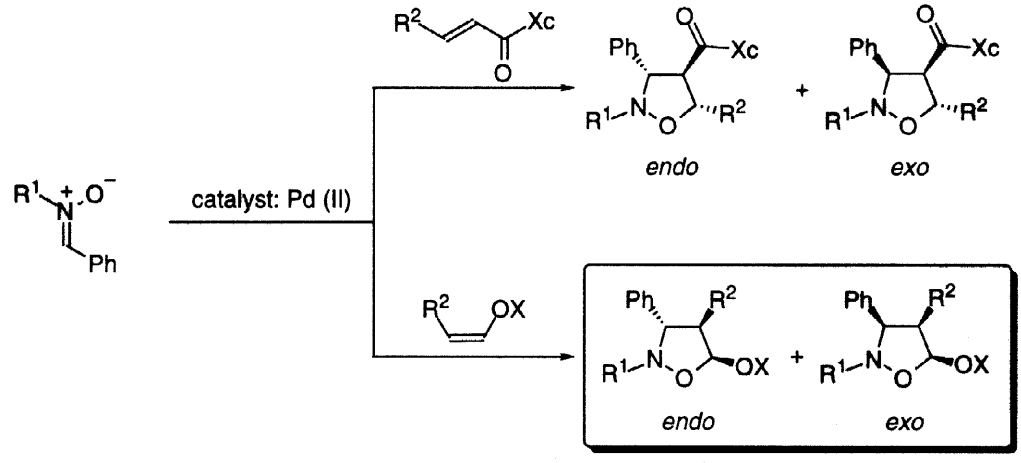
Abstract: The 1,3-dipolar cycloadditions of enol ethers as electron-rich olefins with *C*-phenyl-*N*-alkyl nitrones proceeded smoothly in the presence of easy handling palladium(II) catalysts under mild conditions to give isoxazolidines in good yield.

INTRODUCTION

1,3-Dipolar cycloaddition reactions are one of the most useful methods for the synthesis of five-membered heterocyclic compounds.[1] In particular, isoxazolidines which are obtained by the reaction of nitrones with olefins, can be converted into γ-aminoalcohols as precursors for biologically active compounds such as alkaloids and β-lactam antibiotics.[2]

Nitrones are comparatively stable 1,3-dipoles, in other words, they tend to be less reactive than other 1,3-dipoles. For this reason, 1,3-dipolar cycloaddition of nitrones with olefins has often been performed under relatively drastic reaction conditions. Especially, in order to obtain oxazolidines from electron-rich olefins such as alkyl vinyl ethers, and vinyl esters with nitrones, the reaction must be performed under high pressure or high temperature.[3] DeShong *et al.* and Chiacchio *et al.* carried out the reaction of nitrone **1a** and ethyl vinyl ether (**2**) under high pressure and temperature (sealed tube at 80 °C or under 2,000 bar) to obtain the isoxazolidine **3** in 61–83% yields.[3] Recently, Seerden *et al.*[4] reported that the reaction described above could be catalyzed by chiral oxazaborolidine or ZnI_2 to proceed smoothly at room temperature giving isoxazolidine **3** in 64% yield



(1)

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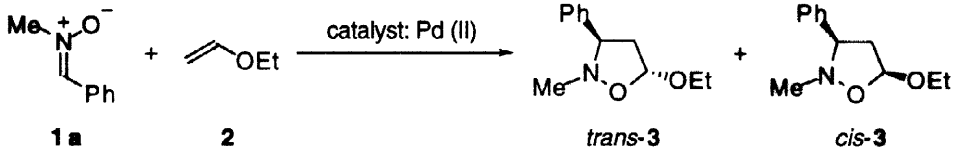
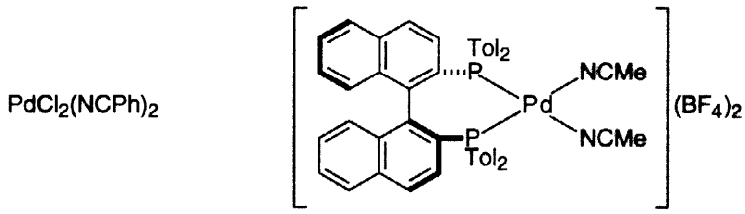
under atmospheric pressure and in 84% yield under high pressure (2,000 bar).[4c] However, these Lewis acids are difficult to handle because they are easily decomposed with a small amount of water.

In contrast, late transition metal complexes can be used in moisture and are handled simply. We reported that the asymmetric 1,3-dipolar cycloaddition between electron-deficient olefins such as 3-crotonoyl-1,3-oxazolidin-2-one with *C*-phenyl-*N*-alkyl nitrones was catalyzed by optically active palladium(II) complexes.[5] From further investigation of this catalytic system, we have found that palladium(II) complexes accelerate the 1,3-dipolar cycloaddition of enol ethers as electron-rich olefins with *C*-phenyl-*N*-alkyl nitrones and wish to describe the details here.

RESULTS AND DISCUSSION



1a **2** *trans*-**3** *cis*-**3** (2)



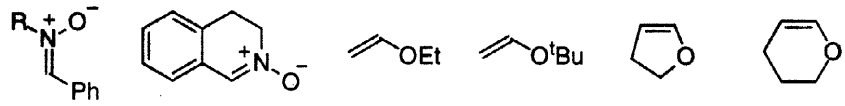
4 **5**

Table 1. Palladium(II) Complex–Catalyzed 1,3-Dipolar Cycloaddition of the Nitrone **1a** with Ethyl Vinyl Ether (**2**)[a]

entry	catalyst	cat.: mol%	solvent	temp.	yield: %[b,c]	*trans/cis*[c]
1	none	–	$CHCl_3$	reflux	trace	–
2	**4**	10	CH_2Cl_2	reflux	32	50/50
3	**4**	10	$CHCl_3$	reflux	60	50/50
4	**4**	10	THF	reflux	23	50/50
5	**4**	10	MeCN	reflux	trace	–
6	**4**	10	CH_2Cl_2[d]	r. t.	74	50/50
7	**4**	10	$CHCl_3$[d]	reflux	quant.	50/50
8	**4**	5	$CHCl_3$[d]	reflux	86	50/50
9	**4**	1	$CHCl_3$[d]	reflux	71	50/50
10	**5**	10	$CHCl_3$[d]	reflux	quant.	53/47

[a] Reaction conditions: Ethyl vinyl ether (10.0 mmol), nitrone **1a** (1.0 mmol) and catalyst were dissolved in the solvent (5 mL), and then the resulting mixture was stirred for 24 h. [b] Based on nitrone **1a**. [c] Determined by ^1H NMR spectroscopy of the reaction mixture. [d] 2 mL of solvent.

We have investigated the reaction conditions in the 1,3-dipolar cycloaddition of the nitrone **1a** and ethyl vinyl ether (**2**) catalyzed by bis(benzonitrile)palladium dichloride (**4**) which showed the highest catalytic activity among the complexes used. The results are listed in Table 1. The nitrone **1a** and 0.1 eq. of the catalyst **4** was dissolved in 5 mL of solvent, and then 10 eq. of ethyl vinyl ether (**2**) was added to this solution. At this moment, the solution turned dark-red from red-brown, and an exothermic reaction occurred. In refluxing chloroform, the nitrone **1a** nearly disappeared after 24 h, and the isoxazolidine **3** was obtained in 60% yield with 50:50 *trans/cis* ratio (entry 3), but the use of THF and acetonitrile lowered the yields (entries 4 and 5). When the volume of solvent was reduced from 5 mL to 2 mL, the reaction proceeded smoothly, and the isoxazolidine **3** was obtained in 74% yield in CH_2Cl_2 at room temperature and in quantitative yield in $CHCl_3$ under reflux. The use of 5 mol% catalyst resulted in 86% yield of **3** (entry 8), and that of 1 mol% gave **3** in 71% yield (entry 9) after 24 h. The use of the optically active palladium(II) catalyst **5**, which is effective for



1a : R = Me
1b : R = Bn

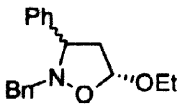
1c

2

6

7

8



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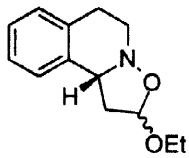

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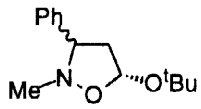

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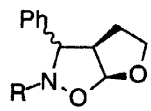
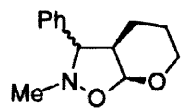


12 : R = Me
13 : R = Bn



14 : R = Me
15 : R = Bn

Table 2. Palladium(II) Complex–Catalyzed 1,3-Dipolar Cycloaddition of Nitrones with Enol Ethers[a]

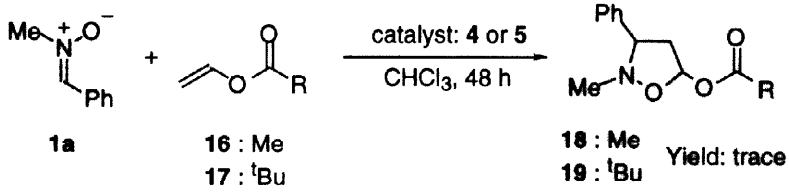
entry	nitrone	enol ether	catalyst	product	yield: %[b,c]	*trans/cis*[c]
1	**1a**	**2**	**4**	**3**	quant.	50/50
2	**1b**	**2**	**4**	**9**	71	68/32
3[d]	**1c**	**2**	**5**	**10**	82[e]	39/61
4	**1a**	**6**	**4**	**11**	71[e]	77/23
5	**1a**	**7**	**4**	**12**	80	9/91
6	**1b**	**7**	**4**	**13**	70 (55)[f]	16/84
7	**1b**	**7**	**5**	**13**	71	27/73
8	**1a**	**8**	**4**	**14**	–[g]	–
9	**1b**	**8**	**4**	**15**	–[g]	–

[a] Reaction conditions: Nitrone (1.0 mmol), enol ether (10.0 mmol) and catalyst (0.1 mmol) were dissolved in $CHCl_3$ (2 mL), and the resulting mixture was stirred for 24 h under reflux except for entry 3. [b] Based on nitrone. [c] Determined by ^1H NMR spectroscopy of the reaction mixture. [d] The reaction performed at room temperature. [e] Isolated yield. [f] Isolated yield of the *cis* isomer. [g] A complex mixture was obtained.

the asymmetric 1,3-dipolar cycloaddition of 3-crotonoyl-1,3-oxazolidin-2-ones with *C*-phenyl-*N*-alkyl nitrones[5], gave **3** in excellent yield, but the product was almost racemic. Unfortunately, the stereoselectivity (*trans*/*cis*) of the products under various conditions (Table 1) was not observed.

On the basis of the above results, 1,3-dipolar cycloaddition of some nitrones with several enol ethers catalyzed by palladium complex **4** or **5** was performed (Table 2). The result for the reaction of *N*-benzyl nitrone **1b** with **2** was similar to that of the nitrone **1a** with **2**, and the isoxazolidine **9** was obtained in 71% yield with moderate *trans*-selectivity. Seerden *et al.* reported that the reaction of cyclic *E*-nitrone **1c** with **2** catalyzed by 20 mol% chiral oxazaborolidine proceeded at room temperature under high pressure (2,000 bar) to give the isoxazolidine **10** in 65% yield with *trans*-selectivity.[4c] When chiral catalyst **5** was applied in this reaction, the isoxazolidine **10** was obtained in 82% isolated yield with *cis*-selectivity as racemic form at room temperature. The product **11** from bulky *tert*-butyl vinyl ether (**6**) was obtained in 71% isolated yield with *trans*-selectivity. Cyclic *Z*-enol ether **7** gave the isoxazolidine in good yield and with *cis*-selectivity (entries 5–7), and employing chiral catalyst **5** in the reaction of **1b** and **7** resulted in racemic **13** in 71% yield (entry 7). On the other hand, various products were obtained from the 6-membered ring substrate **8** (entries 8 and 9).

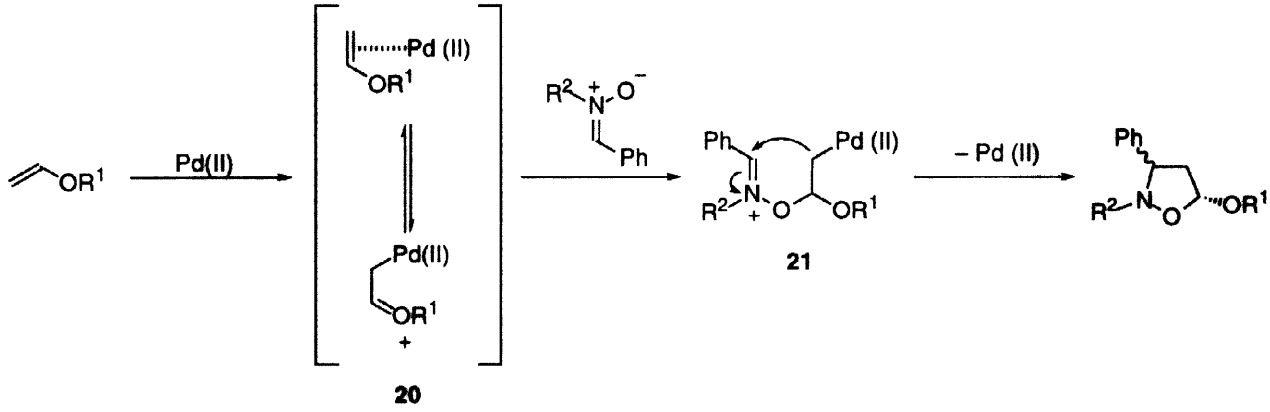
Chiacchio *et al.* reported that the reaction of the nitrone **1a** with excess vinyl acetate (**16**) at 80 °C without solvent in a sealed tube gave isoxazolidine **18** in 43% yield.[3c] We have utilized enol esters such as vinyl acetate (**16**) and vinyl pivalate (**17**) as olefins for the 1,3-dipolar cycloaddition with **1a**. However, these reactions in the presence of **4** in $CHCl_3$ under reflux resulted in only a trace amount of the products **18** and **19**, respectively (eq. 3). It is considered that the low reactivity of vinyl esters depends on the lower electron density on the carbon-carbon double bonds of the vinyl esters than that of vinyl ethers, and the activation of vinyl esters by the complex **4** is not sufficient for the 1,3-dipolar cycloaddition reaction.



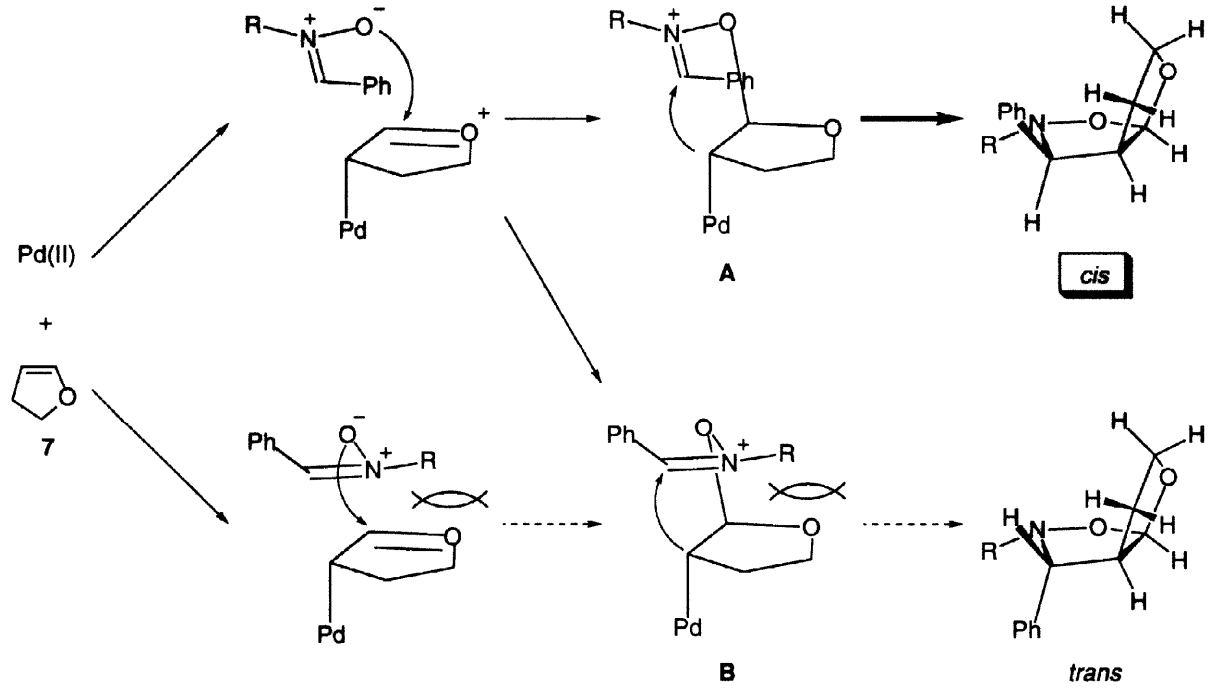
1a **16** : Me, **17** : ^{t}Bu **18** : Me, **19** : ^{t}Bu (3)

The mechanistic aspects are very difficult to clarify. In the reaction of 3-crotonoyl-1,3-oxazolidin-2-ones with nitrones, we have already proposed that a palladium catalyst acts as a Lewis acid toward olefinic substrates. On the other hand, Seerden *et al.* reported that Lewis acid catalysts such as ZnI_2 and oxazaborolidine act to lower the LUMO energy of a nitrone, and the lowered LUMO of the nitrone reacts more easily with the HOMO of the vinyl ether.[4c] In our case, a cationic palladium(II) catalyst could play a similar role as a Lewis acid but can be considered to undergo a different action as well, i.e., our palladium complex activates vinyl ethers, and then the activated intermediate reacts with nitrones. The result of the separate experiment showed that the reaction of ethyl vinyl ether (**2**) and the palladium complex **4** was strongly exothermic to yield polymeric materials. Even in the presence of nitrone **1a**, an exothermic reaction occurred when **2** was added to the mixture of **1a** and palladium complex **4** or **5** in $CHCl_3$ (vide infra).

Consequently, we wish to propose the reaction mechanism (Scheme 1) which was based on the palladium-catalyzed Heck reaction of enol ethers.[6] The enol ether coordinates to palladium(II) and generates the intermediate **20**. As a result, the activated α-carbon of the enol ether is attacked by the oxygen atom of nitrone, and then the β-carbon of the enol ether combines with the α-carbon of the nitrone via stepwise cyclization. At the same time, the palladium species is eliminated and then regenerated. The *cis*-selectivity of the reaction of nitrones and 2,3-dihydrofuran (**7**) is considered in Scheme 2. The transition state **A** gives a *cis*-isomer, while a *trans*-isomer is formed from the transition state **B**. Steric hindrance exists between the *N*-substituent of the nitrone and the dimethylene moiety of the rigid five-membered ring of metalated intermediate **21** in transition state **B** and not in transition state **A**. As a result, the *cis*-isomer is preferentially formed from the favorable transition state **A**.



Scheme 1. Plausible reaction mechanism of nitrones with vinyl ethers by palladium(II) catalyst.



Scheme 2. Possible mechanism forming *cis*- and *trans*-isomers.

CONCLUSIONS

The 1,3-dipolar cycloaddition of nitrones with enol ethers was catalyzed by cationic palladium(II) complex to give isoxazolidine derivatives in good yields. This reaction is the first example of the 1,3-dipolar cycloaddition of nitrones with electron-rich olefins such as vinyl ethers by promoted a late transition metal catalyst. Especially, the reaction conditions are mild, and a small amount of catalyst (1 mol%) can be used. Also, the palladium(II) complex was found to catalyze the 1,3-dipolar cycloaddition of nitrones with olefins regardless of their electron demands such as electron-deficient and electron-rich. Further investigation of this catalytic system is currently in progress.

Acknowledgment: We are grateful to Dr. Takayuki Yamashita for his helpful discussions and support during the course of this study and graduate students Mitsuru Kawazome and Noriteru Maeda for their kind

assistance. We also thank undergraduate project students Akiko Fujii and Daisuke Kobayashi. This work was partially supported by a grant to RCAST at Doshisha University from the Ministry of Education, Japan.

EXPERIMENTAL SECTION

General. The NMR (400 MHz for ^{1}H and 160 MHz for ^{31}P) spectra were recorded on a JEOL JNM A-400 spectrometer with TMS as an internal standard for ^{1}H and H_3PO_4 as an external standard for ^{31}P. IR spectra were measured with a Shimadzu IR-408 spectrometer. Fast atom bombardment (high resolution FAB$^+$) mass spectra were recorded on a JEOL JMS-700 instrument using *m*-nitrobenzyl alcohol as a matrix and PEG-200 as a calibration standard. Melting points were determined with a Yanako MODEL MP and were not corrected. Solvents were dried using standard procedures[7] and distilled under Ar. Nitrones **1a**[8] and **1b**[9] were prepared according to the literature procedures, and the other chemicals were used as supplied without further purification. Silica gel column chromatography was performed by Nacalai Tesque Silica gel 60.

Preparation of Bis(acetonitrile)((*S*)-TolBINAP)palladium Di(tetrafluoroborate) (5). Into a solution of (*S*)-TolBINAP–palladium dichloride[10, 11] (2.56 g, 3.0 mmol) in acetonitrile (60 mL) was added silver tetrafluoroborate (1.23 g, 6.3 mmol) under argon atmosphere, and the solution was stirred at room temperature. After the mixture was stirred for 30 min, the resulting mixture was filtered and concentrated to ca. 5 mL, and then this solution was added slowly into ether (50 mL). The light yellow precipitate was filtered and dried *in vacuo*. This complex was used without further purification. Yield **5**: 2.30 g (63%); mp 123.0 °C (dec.); ^{1}H NMR δ 2.05 (s, 6H), 2.41 (s, 6H), 3.25 (br, 6H), 6.70 (d, J = 8.4 Hz, 4H), 7.17–7.73 (m, 24H); ^{31}P NMR δ 32.52 (s); IR (KBr) 2950, 2250, 1610, 1430, 1300, 1050, 970, 740, 690 cm^{-1}.

General Procedure for Palladium(II)-Catalyzed 1,3-Dipolar Cycloaddition of Nitrones 1 with Enol Ether. In a 50–mL three-necked reaction vessel equipped with a condenser and a magnetic stirring bar were placed nitrone (1.0 mmol) and **4** (38 mg, 0.1 mmol) under argon atmosphere. To this were added $CHCl_3$ (2 mL) and enol ether (10.0 mmol). The resulting mixture was stirred under reflux for 24 h. After the solution was concentrated *in vacuo*, the product was afforded by silica gel column chromatography. The yields of the products were determined by ^{1}H NMR spectroscopy using an integral ratio between the signal of anthracene (δ 8.43 (s, 2H)) as an internal standard and the acetal protons of the isoxazolidines (see below). Spectral and analytical data of the isoxazolidines are listed below.

5-Ethoxy-2-methyl-3-phenylisoxazolidine (*cis*-3 and *trans*-3). These products were identified by comparisons of their ^{1}H NMR signals with those in the literature.[3] The enantiomeric excesses were determined by HPLC analysis using a chiral column (Daicel Chiralcel OJ–R; mobile phase, methanol : water = 70 : 30; detector, UV 220 nm; flow rate, 0.5 mL /min; racemic *cis*-**3**: t_R = 13.4 and 23.0 min; racemic *trans*-**3**: t_R = 33.8 and 54.1 min). The *cis*/*trans* ratio was determined by ^{1}H NMR spectroscopy using the integral ratio of each *N*-Me proton (*cis*-**3**: δ 2.55 (s, 3H), *trans*-**3**: δ 2.78 (s, 3H)) of the isoxazolidine **3**.

2-Benzyl-5-ethoxy-3-phenylisoxazolidine (*cis*-9 and *trans*-9). These products were identified by comparisons of their ^{1}H NMR signals with those in the literature.[4c] The *cis*/*trans* ratio was determined by ^{1}H NMR spectroscopy using the integral ratio of each 4-H proton (*cis*-**9**: δ 2.84–2.91 (m, 1H), *trans*-**9**: δ 2.63 (dd, J = 12.4, 6.4 Hz, 1H)) of the isoxazolidine **9**.

2-Ethoxy-1,5,6,10b-tetrahydro-2*H*-isoxazolo[3,2-a]isoquinoline (*cis*-10 and *trans*-10). These products were identified by comparisons of their ^{1}H NMR signals with those in the literature.[4c] The enantiomeric excesses were determined by HPLC analysis using a chiral column (Daicel Chiralcel OD–H; mobile phase, hexane : 2-propanol = 95 : 5; detector, UV 220 nm; flow rate, 0.5 mL /min; racemic *cis*-**10**: t_R = 23.7 and 24.8 min; racemic *trans*-**10**: t_R = 21.0 and 56.2 min). The *cis*/*trans* ratio was determined by ^{1}H NMR spectroscopy using the integral ratio of each acetal proton (*cis*-**10**: δ 5.38 (dd, J = 6.6 3.8 Hz, 1H), *trans*-**10**: δ 5.28 (d, J = 5.6 Hz, 1H)) of the isoxazolidine **10**.

5-*tert*-Butoxy-2-methyl-3-phenylisoxazolidine (11).[12] The *cis*- and *trans*-**11** were separated by silica gel column chromatography (eluent, n-hexane : ethyl acetate = 5 : 1). *cis*-**11**: Yellow oil; ^{1}H NMR

($CDCl_3$) δ 1.30 (s, 9H, O^{t}Bu), 2.30–2.37 (m, 1H, 4-H), 2.55 (s, 3H, *N*-Me), 2.81–2.88 (m, 1H, 4-H), 3.31–3.43 (m, 1H, 3-H), 5.47 (dd, J = 6.8, 4.0 Hz, 1H, 5-H), 7.26–7.43 (m, 5H, Ph); IR (NaCl) 2950, 1450, 1385, 1360, 1250, 1185, 1070, 990, 900, 760, 700 cm^{-1}; HRMS (FAB^+) calcd. for $C_{14}H_{22}NO_2$ $(M+H)^+$ 236.1649, found 236.1659. *trans*-**11**: Yellow oil; ^1H NMR ($CDCl_3$) δ 1.29 (s, 9H, O^{t}Bu), 2.47 (dd, J = 7.6, 3.0 Hz, 2H, 4-H), 2.79 (s, 3H, *N*-Me), 4.01 (t, J = 7.6 Hz, 1H, 3-H), 5.49 (t, J = 3.0 Hz, 1H, 5-H), 7.24–7.39 (m, 5H, Ph); IR (NaCl) 2950, 1450, 1390, 1360, 1250, 1190, 1130, 1070, 1025, 950, 900, 750, 700 cm^{-1}; HRMS (FAB^+) calcd. for $C_{14}H_{22}NO_2$ $(M+H)^+$ 236.1649, found 236.1660. The *cis*/*trans* ratio was determined by ^1H NMR spectroscopy using the integral ratio of each *N*-Me proton of the isoxazolidine **11**.

2-Methyl-3-phenyl-1,7-dioxa-2-aza-bicyclo[3.3.0]octane (*cis*-12 and *trans*-12).[13] The *cis*- and *trans*-**12** were separated by silica gel column chromatography (eluent, n-hexane : ethyl acetate = 5 : 1). *cis*-**12**: Colorless crystals; mp 68.8–69.2 °C; ^1H NMR ($CDCl_3$) δ 1.57–1.66 (m, 2H, 5-H), 2.64 (s, 3H, *N*-Me), 3.25–3.29 (m, 1H, 4-H), 3.71 (d, J = 7.6 Hz, 1H, 3-H), 3.91 (dt, J = 2.0, 8.0 Hz, 1H, 6-H), 4.07–4.13 (m, 1H, 6-H), 5.79 (d, J = 5.6 Hz, 1H, 8-H), 7.24–7.39 (m, 5H, 3-Ph); IR (KBr) 2940, 1490, 1445, 1350, 1205, 1070, 995, 945, 880, 800, 750, 705 cm^{-1}; HRMS (FAB^+) calcd. for $C_{12}H_{15}NO_2$ $(M)^+$ 205.1102, found 205.1082. *trans*-**12**: Colorless crystals; mp 71.0–85.0 °C; ^1H NMR ($CDCl_3$) δ 1.65–2.03 (m, 2H, 5-H), 2.54 (s, 3H, *N*-Me), 3.12–3.13 (m, 2H, 4-H and 6-H), 4.09–4.11 (m, 2H, 3-H and 6-H), 5.88 (d, J = 6.4 Hz, 1H, 8-H), 7.33–7.36 (m, 5H, 3-Ph); HRMS (FAB^+) calcd. for $C_{12}H_{15}NO_2$ $(M)^+$ 205.1102, found 205.1096. The *cis*/*trans* ratio was determined by ^1H NMR spectroscopy using the integral ratio of each acetal (8-H) proton of the isoxazolidine **12**.

***cis-cis*-2-Benzyl-3-phenyl-1,7-dioxa-2-azabicyclo[3.3.0]octane (*cis*-13).**[14] The *cis*-isomer was separated by silica gel column chromatography (eluent, n-hexane : ethyl acetate = 5 : 1). Colorless needles (recrystallization from ethanol); mp 139.0–146.0 °C; ^1H NMR ($CDCl_3$) δ 1.59–1.71 (m, 2H, 5-H), 3.23–3.78 (m, 1H, 4-H), 3.63 (d, J = 15.0 Hz, 1H, *N*-C$\underline{H}_2$Ph), 3.92–3.97 (m, 1H, 6-H), 3.97 (d, J = 7.2 Hz, 1H, 3-H), 4.16 (d, J = 15.0 Hz, 1H, *N*-C$\underline{H}_2$Ph), 4.16–4.22 (m, 1H, 6-H), 5.80 (d, J = 5.2 Hz, 1H, 8-H), 7.22–7.40 (m, 10H, 3-Ph and *N*-$CH_2\underline{Ph}$); IR (KBr) 2840, 1485, 1440, 1310, 1150, 1070, 1020, 960, 930, 750, 730, 705 cm^{-1}; HRMS (FAB^+) calcd. for $C_{18}H_{20}NO_2$ $(M+H)^+$ 282.1493, found 282.1483. The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralcel OJ–R; mobile phase, acetonitrile : water = 30 : 70; detector, UV 220 nm; flow rate, 0.5 mL /min., t_R = 47.8 and 63.1 min.). *trans*-**13** could not be isolated in pure form, but the crude materials showed a reasonable pattern in ^1H NMR spectroscopy. Especially, the signal of 8-H appeared at 5.86 ppm. This signal was used for determining the yield and selectivity of the product.

REFERENCES AND NOTES

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11. TolBINAP = 2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl.
12. Identification of the stereoisomers was performed on the basis of ^{1}H NMR spectroscopy by comparison of their chemical shifts of **11** with those of *cis*-**3** and *trans*-**3**.
13. Identification of the stereoisomer (*cis*-**12**) was performed on the basis of ^{1}H NMR spectroscopy by the coupling constant of 3-H and 4-H. Calculated coupling constants between 3-H and 4-H for *trans*-**12** (2.9 Hz) and *cis*-**12** (8.3 Hz) were determined with the Karplus rule[15] using dihedral angles (*trans*-**12**: 108.1 °, *cis*-**12**: 23.3 °) of molecular models by MOPAC PM3 calculation in CAChe Program (CAChe Scientific, Inc., Sony/Techtronics Corp.). The observed coupling constant between 3-H and 4-H of the major isomer was 7.6 Hz, and this major isomer was determined to be the *cis*-isomer. On the other hand, the coupling constant between 3-H and 4-H of the minor isomer could not be observed because of the complex and broad signals of 3-H and 4-H.
14. Identification of the stereoisomer was performed on the basis of ^{1}H NMR spectroscopy by the coupling constant of 3-H and 4-H. Calculated coupling constants between 3-H and 4-H for *trans*-**13** (3.3 Hz) and *cis*-**13** (8.2 Hz) were determined with the Karplus rule[15] using dihedral angles (*trans*-**13**: 110.8 °, *cis*-**13**: 23.8 °) of molecular models by MOPAC PM3 calculation. The observed coupling constant between 3-H and 4-H of the isolatable isomer was 7.2 Hz, which showed this isomer to be *cis*-**13**.
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