(6.19 g, 94%), and **11c** (6.05 g, 84%) were obtained.

[2-[1',1'-Bis(ethoxycarbonyl)-5'-oxopentyl]cyclobutyl]triphenylphosphonium perchlorate (11a): mp 165–169 °C; IR (KBr) 2950, 1720, 1585, 1485, 1435, 1100–1060, 745, 720, 690 cm^{-1}; ^1H NMR δ 1.12 (t, J = 6.96 Hz, 3 H, CH_3), 1.41 (t, J = 7.14 Hz, 3 H, CH_3), 1.50–3.25 (m, 11 H, CH_2 and CH), 3.72 (q, J = 7.14 Hz, 2 H, OCH_2), 4.47 (q, J = 6.96 Hz, 2 H, OCH_2), 4.16–5.00 (br, 1 H, CH), 7.30–8.25 (m, 15 H, phenyl H), 9.68 (s, 1 H, CHO).

[2-[1',1'-Bis(ethoxycarbonyl)-5'-oxohexyl]cyclobutyl]triphenylphosphonium perchlorate (11b): mp 149–152 °C; IR (KBr) 2950, 2900, 1740, 1720, 1585, 1485, 1440, 1100–1070, 750, 720, 690 cm^{-1}; ^1H NMR δ 1.12 (t, J = 7.18 Hz, 3 H, CH_3), 1.41 (t, J = 7.18 Hz, 3 H, CH_3), 1.50–3.30 (m, 11 H, CH_2 and CH), 2.09 (s, 3 H, CH_3), 3.73 (q, J = 7.18 Hz, 2 H, OCH_2), 4.49 (q, J = 7.18 Hz, 2 H, OCH_2), 4.20–5.00 (br, 1 H, CH), 7.36–8.10 (m, 15 H, phenyl H).

[2-[1',1'-Bis(ethoxycarbonyl)-4'-benzoylbutyl]cyclobutyl]triphenylphosphonium perchlorate (11c): mp 138–143 °C; IR (KBr) 2950, 2900, 1740, 1720, 1680, 1590, 1485, 1440, 1110–1070, 755, 720, 690 cm^{-1}; ^1H NMR δ 1.02 (t, J = 6.96 Hz, 3 H, CH_3), 1.38 (t, J = 6.96 Hz, 3 H, CH_3), 1.50–3.25 (m, 11 H, CH_2 and CH), 3.72 (q, J = 6.96 Hz, 2 H, OCH_2), 4.50 (q, J = 6.96 Hz, 2 H, OCH_2), 4.10–5.00 (br 1 H, CH), 7.20–8.25 (m, 20 H, phenyl H).

General Procedure for the Synthesis of 12a–c and/or 13b,c. To a solution of the salt **11a–c** (1.0 mmol) in dry DMF (10 mL) was added NaH (60% in oil, 44 mg, 1.1 mmol). The solution was heated at 130 °C for 4 h with stirring. After similar workup, the residue was chromatographed on preparative TLC (silica gel, Wakogel B-5F, benzene) to give samples **12a–c** and/or **13b,c**.

6,6-Bis(ethoxycarbonyl)-*trans*-bicyclo[5.2.0]non-2-ene (12a): yield 56 mg, 21%; IR (neat) 2950, 1720 cm^{-1}; ^1H NMR δ 1.24 (t, J = 7.03 Hz, 3 H, CH_3), 1.26 (t, J = 7.03 Hz, 3 H, CH_3), 1.00–3.00 (m, 10 H, CH_2 and CH), 3.90–4.50 (m, 4 H, OCH_2), 5.60–5.92 (m, 2 H, olefinic H); HRMS m/z calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1508.

6,6-Bis(ethoxycarbonyl)-2-methyl-*trans*-bicyclo[5.2.0]non-2-ene (12b): yield 60 mg, 11%; IR (neat) 2950, 1720 cm^{-1}; ^1H NMR δ 1.25 (t, J = 7.03 Hz, 6 H, CH_3), 1.74 (d, J = 1.32 Hz, 3 H, CH_3), 1.50–3.00 (m, 10 H, CH_2 and CH), 4.14 (q, J = 7.03 Hz, 4 H, OCH_2), 5.42 (br, 1 H, olefinic H); HRMS m/z calcd for $C_{16}H_{24}O_4$ 280.1675, found 280.1688.

6,6-Bis(ethoxycarbonyl)-2-methyl-*cis*-bicyclo[5.2.0]non-2-ene (13b): yield 93 mg, 17%; IR (neat) 2880, 1720 cm^{-1}; ^1H NMR δ 1.25 (t, J = 7.03 Hz, 6 H, CH_3), 1.62 (d, J = 1.47 Hz, 3 H, CH_3), 1.44–2.80 (m, 10 H, CH_2 and CH), 4.14 (q, J = 7.03 Hz, 4 H, OCH_2), 5.59 (br, 1 H, olefinic H); HRMS m/z calcd for $C_{16}H_{24}O_4$ 280.1675, found 280.1661.

6,6-Bis(ethoxycarbonyl)-2-phenyl-*trans*-bicyclo[5.2.0]non-2-ene (12c): yield 39 mg, 11%; IR (neat) 2900, 1720, 1595, 760, 695 cm^{-1}; ^1H NMR δ 1.22 (t, J = 7.03 Hz, 3 H, CH_3), 1.26 (t, J = 7.03 Hz, 3 H, CH_3), 1.44–2.90 (m, 10 H, CH_2 and CH), 4.15 (q, J = 7.03 Hz, 2 H, OCH_2), 4.18 (q, J = 7.03 Hz, 2 H, OCH_2), 6.07 (t, J = 3.66 Hz, 1 H, olefinic H), 6.90–7.38 (m, 5 H, phenyl H); HRMS m/z calcd for $C_{21}H_{26}O_4$ 342.1831, found 342.1794.

6,6-Bis(ethoxycarbonyl)-2-phenyl-*cis*-bicyclo[5.2.0]non-2-ene (13c): yield 77 mg, 22%; IR (neat) 2900, 1715, 1590, 750, 695 cm^{-1}; ^1H NMR δ 1.08 (t, J = 7.03 Hz, 3 H, CH_3), 1.19 (t, J = 6.89 Hz, 3 H, CH_3), 1.48–2.96 (m, 10 H, CH_2 and CH), 4.07 (q, J = 7.03 Hz, 2 H, OCH_2), 4.15 (q, J = 6.98 Hz, 2 H, OCH_2), 5.85 (t, J = 3.66 Hz, 1 H, olefinic H), 6.80–7.30 (m, 5 H, phenyl H); HRMS m/z calcd for $C_{21}H_{26}O_4$ 342.1831, found 342.1829.

Hydrogenation of 12c and 13c. Hydrogenation of **12c** (48 mg, 0.14 mmol) and **13c** (90 mg, 0.26 mmol) in ethanol (20 mL) over PtO_2 (10 mg) at 1–2 atm of hydrogen pressure for 7 h afforded **14** (30 mg, 62%) and **15** (51 mg, 56%), respectively.

2,2-Bis(ethoxycarbonyl)-6-phenyl-*trans*-bicyclo[5.2.0]nonane (14): IR (neat) 2900, 2830, 1715, 1595, 745, 695 cm^{-1}; ^1H NMR δ 1.07 (t, J = 7.03 Hz, 3 H, CH_3), 1.27 (t, J = 7.03 Hz, 3 H, CH_3), 1.00–3.00 (m, 13 H, CH_2 and CH), 3.68–4.40 (m, 4 H, OCH_2), 6.80–7.40 (m, 5 H, phenyl H); HRMS m/z calcd for $C_{21}H_{28}O_4$ 344.1987, found 344.2007.

2,2-Bis(ethoxycarbonyl)-6-phenyl-*cis*-bicyclo[5.2.0]nonane (15): IR (neat) 2900, 2830, 1715, 1595, 750, 695 cm^{-1}; ^1H NMR δ 1.14 (t, J = 7.03 Hz, 3 H, CH_3), 1.37 (t, J = 7.03 Hz, 3 H, CH_3), 1.00–3.00 (m, 13 H, CH_2 and CH), 3.80–4.52 (m, 4 H, OCH_2), 7.00–7.58 (m, 5 H, phenyl H); HRMS m/z calcd for $C_{21}H_{28}O_4$ 344.1987, found 344.2015.

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Registry No. 1, 86046-73-3; **3a**, 118418-37-4; **3b**, 118418-46-5; **3c**, 118418-47-6; **4a**, 118418-38-5; **4b**, 118418-48-7; **4c**, 118418-49-8; **5**, 4761-26-6; **6**, 7796-23-8; **7**, 118418-40-9; **8**, 118418-41-0; **9**, 118418-42-1; **10a**, 118418-43-2; **10b**, 101417-29-2; **10c**, 118418-58-9; **11a**, 118457-88-8; **11b**, 118418-51-2; **11c**, 118418-53-4; **12a**, 118418-44-3; **12b**, 118418-54-5; **12c**, 118418-55-6; **13b**, 118418-56-7; **13c**, 118418-57-8; **14**, 118418-45-4; **15**, 118490-60-1; diethyl (formylmethyl)malonate, 23193-16-0; diethyl (2-oxopropyl)malonate, 23193-18-2; diethyl (benzoylmethyl)malonate, 94011-49-1.

Supplementary Material Available: Table I giving ^{13}C NMR data of compounds **3a–c**, **4a–c**, **8**, **9**, **12a–c**, **13b,c**, **14**, and **15** (2 pages). Ordering information is given on any current masthead page.

Palladium(0)-Catalyzed Reaction of Methyl γ,δ-Epoxysorbate with Nitrogen Nucleophiles

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The reaction of nucleophiles and (π-allyl)palladium complexes bearing functional groups is useful for the synthesis of complex organic molecules.[1] Many regioselective nucleophilic reactions toward (π-allyl)palladium complexes having one functional group at an allylic carbon atom have been reported.[1,2] On the other hand, examples of the reaction involving (π-allyl)palladium complexes having two different functional groups at both allylic carbon atoms are limited. A hydroxyalkyl[3] or alkoxycarbonyl[4] functional group is known to direct carbon or nitrogen nucleophiles to attack regioselectively the allylic carbon atom distal to the functional group. As to competition of these two functional groups in the control of regioselectivity, the palladium(0)-catalyzed reaction of methyl γ,δ-epoxysorbate (**1**) with carbon nucleophiles has recently been reported.[3b,c] In this reaction, the directing effect of the hydroxyalkyl group generated from the oxirane ring dominates over that of the alkoxycarbonyl group: carbon–carbon bond formation takes place regioselectively

(1) See, for example: (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980. (b) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1982; Vol. 8, p 799.

(2) (a) Collins, D. J.; Jackson, W. R.; Timms, R. N. *Tetrahedron Lett.* **1976**, 495. (b) Tsuji, J.; Ueno, H.; Kobayashi, Y.; Okumoto, H. *Tetrahedron Lett.* **1981** *22*, 2573. (c) Dunkerton, L. V.; Serino, A. J. *J. Org. Chem.* **1982**, *47*, 2812. (d) Genêt, J.-P.; Balabane, M.; Charbonnier, F. *Tetrahedron Lett.* **1982**, *23*, 5027. (e) Guibe, F.; Grierson, D. S.; Husson, H.-P. *Tetrahedron Lett.* **1982**, *23*, 5055. For the hydroxyalkyl and alkoxycarbonyl functional groups, see ref 3 and 4.

(3) For the carbon nucleophile, see: (a) Genêt, J. P.; Ficini, P. J. *Tetrahedron Lett.* **1980**, *21*, 3183. (b) Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575. (c) Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969. (d) Tsuda, T.; Tokai, M.; Ishida, T.; Saegusa, T. *J. Org. Chem.* **1986**, *51*, 5216. For the nitrogen nucleophile, see: (e) Genêt, J. P.; Balabane, M.; Bäckvall, J. E.; Nyström, J. E. *Tetrahedron Lett.* **1983**, *27*, 2745.

(4) For the carbon nucleophile, see: (a) Jackson, W. R.; Strauss, J. U. G. *Tetrahedron Lett.* **1975**, 2591 and ref 2b. For the nitrogen nucleophile, see: (b) Tanikaga, R.; Takeuchi, J.; Takyu, M.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1987**, 386.

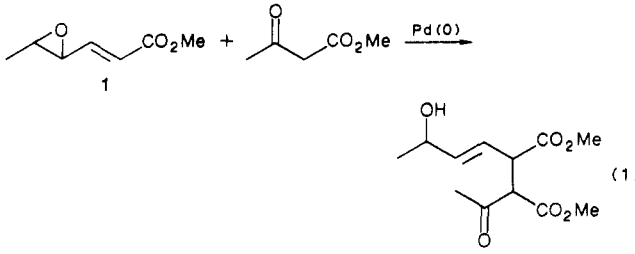
0022-3263/89/1954-0977$01.50/0

Table I. Palladium(0)-Catalyzed Reaction of Methyl γ,δ-Epoxysorbate (1) and Phthalimide (2a) (eq 3)[a]

ligand (L)	solvent	time, h	products % 4a[b]	products % 5 + 6[c]
$P(OPr^i)_3$	THF	1.5	93	trace
	DMSO	7	76	nd[d]
	DMF	0.5	90	10
	C_6H_6–THF[e]	5	92	4
$P(OCH_2)_3CEt$	THF	6	85	5
$P(c\text{-}C_6H_{11})_3$		0.5	81	nd[d]
PEt_3		1.5	83	15
PPh_3		24	79	nd[d]
dppf[f]		1	89	nd[d]
dppb[g]		0.25	nd	77

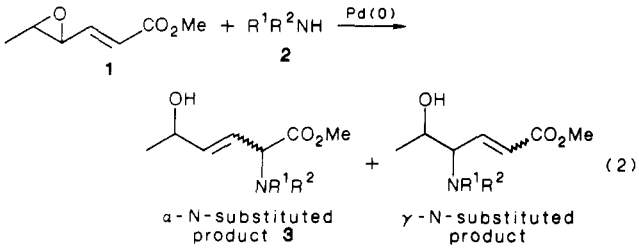
[a] 1, 1.00 mmol; 1:2a:$Pd(dba)_3$·$CHCl_3$:L = 1:1:0.025:0.2; solvent, 4 mL; temperature, room temperature. [b] Isolated yield by PLC. [c] GC yield. [d] Not determined. [e] C_6H_6 (4 mL)–THF (7 mL). [f] Dppf; 1,1′-bis(diphenylphosphino)ferrocene. [g] Dppb; 1,4-bis(diphenylphosphino)butane.

at the allylic carbon atom distal to the hydroxyalkyl group (for example, eq 1).



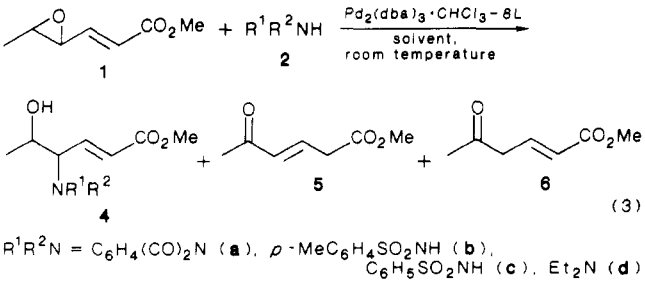
(1)

We have studied the palladium(0)-catalyzed C–N coupling reaction of 1 with nitrogen nucleophiles 2 to examine the influence of the nucleophile upon the competitive regiocontrol by hydroxyalkyl and alkoxycarbonyl groups (eq 2).



(2)

When 1 was reacted with phthalimide (2a) in THF at room temperature in the presence of a palladium(0) catalyst generated from $Pd_2(dba)_3$·$CHCl_3$ and $P(OPr^i)_3$, methyl (*E*)-5-hydroxy-4-phthalimido-2-hexenoate (4a), i.e., the γ-N-substituted product, was obtained regiospecifically in an excellent yield (eq 3, Table I). The *E* isomer was



(3)

produced stereospecifically. The *E* configuration of the double bond was determined on the basis of the vicinal coupling constant of the olefinic protons J = 15.8 Hz. Byproducts resulting from isomerization of 1, i.e., methyl (*E*)-5-oxo-3-hexenoate (5) and methyl (*E*)-5-oxo-2-hexenoate (6), were produced in trace amounts. Without the palladium(0) catalyst no reaction took place. Solvent polarity did not influence the regioselectivity of the reaction. Various phosphorus ligands could be used for the C–N coupling reaction except dppb. They changed the reaction rate but did not alter the regioselectivity of the reaction. The formation of 4a may reasonably be assumed to proceed by the reaction path depicted in Scheme I.[3b-d]

Scheme I

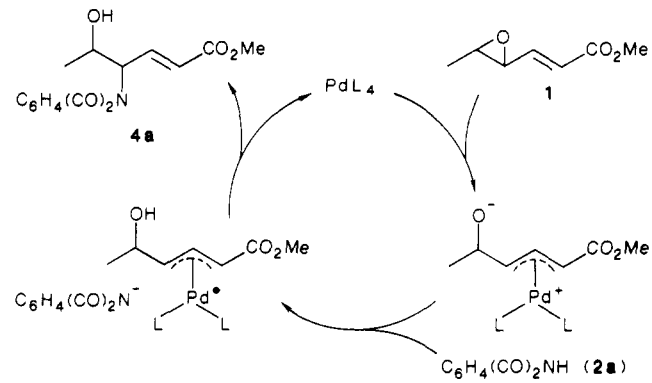


Table II. Palladium(0)-Catalyzed Reaction of Methyl γ,δ-Epoxysorbate (1) and Nitrogen Nucleophiles (2) (eq 3)[a]

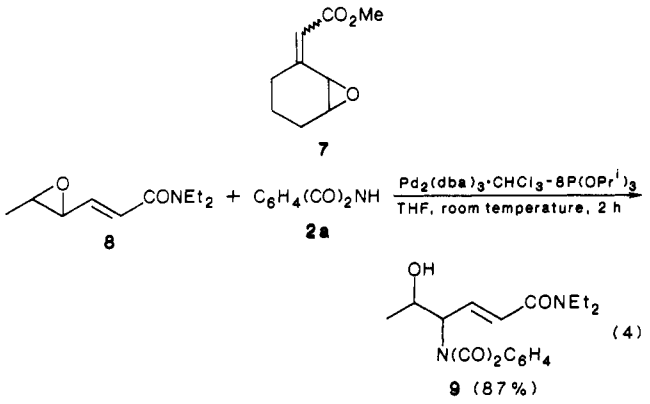
R^1R^2NH (2)	time, h	products % 4[b]	products % 5 + 6[c]
$C_6H_4(CO)_2NH$ (2a)	1.5	4a, 93	trace
$p\text{-}MeC_6H_4SO_2NH_2$ (2b)	1	4b, 58	9
$C_6H_5SO_2NH_2$ (2c)	2	4c, 58	nd[d]
Et_2NH (2d)	48	4d, 19	39
EtO_2CNH_2 (2e)	4	4e, 0	26[e]
MeCONHMe (2f)	2	4f, 0	39[e]

[a] 1, 1.00 mmol; 1:2:$Pd_2(dba)_3$·$CHCl_3$:$P(OPr^i)_3$ = 1:1:0.025:0.2; solvent, THF, 4 mL; temperature, room temperature. [b] Isolated yield by PLC. [c] GC yield. [d] Not determined. [e] Nitrogen nucleophile 2 remained unreacted.

The C–N coupling reaction was found to be dependent upon the structure of the nitrogen nucleophile (eq 3, Table II). *p*-Toluenesulfonamide (2b) and benzenesulfonamide (2c), in the same way as 2a, produced the γ-N-substituted products 4b and 4c in good yields. In these reactions, the corresponding α-N-substituted products 3 were not detected. The reaction of 1 with diethylamine (2d) proceeded slowly to produce the corresponding γ-N-substituted product 4d in a low yield. On the contrary, no C–N coupling product was obtained in the reaction using ethyl carbamate (2e) or *N*-methylacetamide (2f); the nitrogen nucleophile remained unreacted, and the isomerization products 5 and 6 were produced. Thus, the nitrogen nucleophile with a highly acidic hydrogen appears to be required for success of the catalytic C–N coupling reaction illustrated in Scheme I. It is noteworthy that the nitrogen nucleophile exhibits regioselectivity opposite to the carbon nucleophile[3b,c] (vide ante) in the reaction toward the (π-allyl)palladium complex having hydroxyalkyl and alkoxycarbonyl groups at both allylic carbon atoms, respectively. Explanation of the observed regiocontrol by these two functional groups in the present reaction and related previous works,[3,4] however, requires a detailed mechanistic study.

Methyl (7-oxabicyclo[4.1.0]hept-2-ylidene)acetate (7), the γ,δ-epoxy-α,β-unsaturated carboxylate having a cyclohexene monoxide moiety, did not produce a C–N coupling product in the reaction with 2a; 7 was consumed, but 2a remained unreacted. To examine the influence of the carbonyl functionality upon the regioselectivity of the C–N coupling reaction, the reaction of *N*,*N*-diethyl-γ,δ-epoxy-

sorbamide (8) with **2a** was carried out: the γ-N-substituted product **9** was produced in a high yield (eq 4).



The products **4a–c** and **9** may be a precursor of α,β-unsaturated γ-amino acids, and the present reaction may have relevance to the α,β-unsaturated α-amino acid synthesis, which has actively been studied recently.[5]

Experimental Section

IR spectra were determined on a Hitachi 260-50 grating spectrophotometer. ^{1}H NMR spectra (400 MHz) were recorded in $CDCl_3$ on a JEOL JNM-JX-400 instrument unless otherwise stated. ^{1}H NMR spectra (60 MHz) were recorded in $CDCl_3$ on a Hitachi R-20B instrument. ^{13}C NMR spectra (100 MHz) were obtained in $CDCl_3$ on a JEOL JNM-JX-400 instrument. All chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Coupling constants (*J*) are reported in hertz. Mass spectra were obtained on a JEOL DX-300 instrument. Elemental analyses were performed by the Microanalytical Center of Kyoto University. Gas chromatographic analyses (GC) were made on a Shimadzu 4CPT instrument. GC quantitative analyses of reaction products were made with internal standards with calibration based upon authentic samples employing a 20% silicone DC 550 on Celite 545 column or 20% polyethylene glycol (PEG) 20M on Celite 545 column. Preparative layer chromatography (PLC) was performed on silica gel plates (20 × 20 × 0.2 cm) prepared with Merck silica gel 60PF-254. Preparative medium-pressure liquid chromatography (MPLC) was carried out by using a prepacked silica gel column (CPS-223L-1) supplied by Kusano Kagaku Co. Melting points were determined on a Yanaco MP melting point apparatus and are uncorrected.

Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under nitrogen. Benzene, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) were distilled from CaH_2 under nitrogen. Methyl γ,δ-epoxysorbate (**1**) and *N,N*-diethyl-γ,δ-epoxysorbamide (**8**) were prepared in 1,2-dichloroethane by the reaction of *m*-chloroperbenzoic acid with methyl sorbate and *N,N*-diethylsorbamide, respectively. Methyl (7-oxabicyclo[4.1.0]hept-2-ylidene)acetate (**7**) was prepared according to the published method.[6] Phthalimide (**2a**), *p*-toluenesulfonamide (**2b**), benzenesulfonamide (**2c**), ethyl carbamate (**2e**), and *N*-methylacetamide (**2f**) were commercial reagents and were used without further purification. Diethylamine (**2d**) was distilled from $LiAlH_4$ under nitrogen. $Pd_2(dba)_3{\cdot}CHCl_3$ was prepared by the reported procedure.[7] Phosphorus ligands were commercial reagents and were used without further purification except $P(OPr^i)_3$ and trimethylolpropane phosphite ($P(OCH_2)_3CEt$), which were distilled under nitrogen after drying over $CaSO_4$(Drierite).

Palladium(0)-Catalyzed Reaction of Methyl γ,δ-Epoxysorbate (1) and Phthalimide (2a). The reaction was carried out under nitrogen. To a stirred THF (4 mL) solution containing $Pd_2(dba)_3{\cdot}CHCl_3$ (0.0259 g, 0.0250 mmol), $P(OPr^i)_3$ (0.0493 mL, 0.200 mmol), and **2a** (0.147 g, 1.00 mmol) was added **1** (0.134 mL, 1.00 mmol) at room temperature. GC analysis of the mixture after 1.5 h showed that **1** disappeared and isomerization products, methyl (*E*)-5-oxo-3-hexenoate (**5**) and methyl (*E*)-5-oxo-2-hexenoate (**6**), were formed in trace amounts. The reaction mixture was concentrated under vacuum to give a residue. PLC (benzene–ethyl acetate, 5:1 V/V) of the residue produced methyl (*E*)-5-hydroxy-4-phthalimido-2-hexenoate (**4a**) (0.269 g, 93%), which was recrystallized from benzene–*n*-hexane to give a white solid: mp 99–100 °C; IR (KBr, cm^{-1}) 3475, 1775, 1720, 1700, 1655, 1180, 725; ^{1}H NMR δ 1.26 (d, *J* = 6.4, 3 H), 3.00 (d, *J* = 8.7, 1 H), 3.72 (s, 3 H), 4.44 (ddq, *J* = 8.7, 6.7, 6.4, 1 H), 4.86 (dd, *J* = 6.8, 6.7, 1 H), 5.94 (d, *J* = 15.8, 1 H), 7.19 (dd, *J* = 15.8, 6.8, 1 H), 7.74–7.91 (m, 4 H); ^{13}C NMR δ 20.9, 51.8, 58.8, 67.0, 123.7, 124.2, 131.7, 134.4, 141.9, 166.1, 168.5. Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.27; H, 5.22; N, 4.81.

Products **5** and **6** were prepared by palladium(0)-catalyzed isomerization reaction of **1** without **2a**. Attempts to isolate **5** and **6** by PLC failed. The mixture of **5** and **6** was isolated by preparative GC: IR (neat, cm^{-1}) 1730, 1680, 1640, 1270, 1160, 990; MS, *m/e* (relative intensity) 142 (M^+, 1.3), 127 (32), 111 (23), 110 (54), 100 (100), 99 (54), 95 (25), 69 (22), 58 (24). HRMS value of the M^+ peak was not obtained owing to its low intensity, and analytically pure sample was not prepared by preparative GC. Analysis of ^{1}H and ^{13}C NMR spectra of the mixture of **5** and **6**, partly by using a 2D measurement, gave the value of **5**/**6** = 1.25 and the following data. Isomer **5**: ^{1}H NMR δ 2.29 (s, 3 H), 3.29 (d, *J* = 7.1, 2 H), 3.74 (s, 3 H), 6.15 (d, *J* = 16.1, 1 H), 6.86 (dt, *J* = 16.1, 7.1, 1 H); ^{13}C NMR δ 26.9, 37.4, 52.2, 134.1, 138.4, 170.3, 198.0. Isomer **6**: ^{1}H NMR δ 2.21 (s, 3 H), 3.36 (d, *J* = 7.3, 2 H), 3.75 (s, 3 H), 5.91 (d, *J* = 15.8, 1 H), 7.04 (dt, *J* = 15.7, 7.3, 1 H); ^{13}C NMR δ 29.9, 46.5, 51.6, 124.6, 140.0, 166.2, 204.1.

C–N coupling products **4b** and **4c** were obtained similarly to **4a** and were identified as follows. Product **4b** (PLC, hexane–acetone, 3:2 v/v: IR (neat, cm^{-1}) 3500, 3270, 1710, 1660, 1600, 1335, 1160, 920, 820; ^{1}H NMR (60 MHz) δ 1.12 (d, *J* = 5.9, 3 H), 2.39 (s, 3 H), 2.77 (br s, 1 H), 3.65 (s, 3 H), 3.5–4.0 (m, 2 H), 5.41 (br s, 1 H), 5.73 (d, *J* = 15.7, 1 H), 6.70 (dd, *J* = 15.7, 6.2, 1 H), 7.0–8.0 (m, 4 H). Product **4b** isolated by PLC was further purified by MPLC (hexane–ethyl acetate, 1:2 v/v) to give a white solid: mp 107–108 °C. Anal. Calcd for $C_{14}H_{19}O_5SN$: C, 53.66; H, 6.11; N, 4.47; S, 10.23. Found: C, 53.62; H, 6.23; N, 4.25; S, 10.26. Product **4c** (PLC, benzene–ethyl acetate, 3:1 v/v): IR (neat, cm^{-1}) 3500, 3275, 1720, 1660, 1325, 1160, 980, 920, 730; ^{1}H NMR (60 MHz) δ 1.12 (d, *J* = 5.9, 3 H), 3.0–3.4 (br s, 1 H), 3.65 (s, 3 H), 3.7–4.0 (m, 2 H), 5.75 (d, *J* = 16, 1 H), 5.99 (br s, 1 H), 6.73 (dd, *J* = 17, 6.3, 1 H), 7.2–8.2 (m, 5 H). Product **4c** isolated by PLC was further purified by MPLC (hexane–ethyl acetate, 1:2 v/v) to give white needles: mp 91–92 °C. Anal. Calcd for $C_{13}H_{17}O_5SN$: C, 52.16; H, 5.72; N, 4.68; S, 10.71. Found: C, 52.02; H, 5.84; N, 4.74; S, 10.48. Product **4d** (PLC, benzene–ethyl acetate, 3:1 v/v): IR (neat, cm^{-1}) 3375, 1720, 1650, 1620, 1250, 1000; ^{1}H NMR (60 MHz) δ 1.06 (t, *J* = 5.8, 6 H), 1.32 (d, *J* = 5.8, 3 H), 2.36 (q, *J* = 5.8, 2 H), 2.66 (q, *J* = 5.8, 2 H), 2.83 (t, *J* = 9.3, 1 H), 3.45 (br s, 1 H), 3.74 (s, 3 H), 4.2–4.9 (m, 1 H), 5.92 (d, *J* = 15.6, 1 H), 6.81 (dd, *J* = 15.6, 9.3, 1 H); MS, *m/e* (relative intensity) 170 (100), 142 (6), 110 (10), 88 (7), 71 (7). The M^+ peak was not observed in MS, and analytically pure sample was not obtained by PLC and MPLC (hexane–ethyl acetate, 1:1 v/v).

Palladium(0)-Catalyzed Reaction of *N,N*-Diethylsorbamide (8) and Phthalimide (2a). The reaction was carried out similarly to the reaction of **1** and **2a** by using **8** (1.00 mmol), **2a** (1.00 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.0250 mmol), $P(OPr^i)_3$ (0.200 mmol), and THF (4 mL). Product **9** (PLC, ether): IR (film, cm^{-1}) 3380, 1770, 1705, 1660, 1605, 965, 720; ^{1}H NMR δ 1.08–1.17 (m, 6 H), 1.27 (d, *J* = 6.4, 3 H), 3.26–3.42 (m, 5 H), 4.51 (m, 1 H), 4.78 (t, *J* = 7.9, 1 H), 6.43 (d, *J* = 15.2, 1 H), 7.07 (dd, *J* = 15.2, 8.1, 1 H), 7.71 (m, 2 H), 7.82 (m, 2 H). Anal. Calcd for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.34; H, 6.67; N, 8.56.

Registry No. 1, 51830-12-7; **2a**, 85-41-6; **2b**, 70-55-3; **2c**, 98-10-2; **2d**, 109-89-7; **5**, 118355-42-3; **6**, 104394-80-1; **7**, 118355-43-4; **8**, 50362-20-4; **9**, 118355-44-5; **11**, 52522-40-4; **12**, 118355-45-6; **13**, 118355-46-7; **14**, 118355-47-8; **15**, 118355-48-9.

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