5882 *Macromolecules* **2003,** *36,* 5882−5884

Palladium(0)-Catalyzed Polyaddition of Bifunctional Vinyloxirane with Nitrogen Nucleophiles. Synthesis of Polymers Containing an Allylamine Moiety in the Main Chain and Pendant Hydroxyl Groups

Toshio Koizumi,*,† Yuichiro Koma,† and Takeshi Endo‡

Department of Applied Chemistry, The National Defense Academy, Hashirimizu, Yokosuka 239-8686, Japan, and Department of Polymer Science and Engineering, Yamagata University, Yonezawa 992-8510, Japan

Received October 15, 2002
Revised Manuscript Received May 12, 2003

Introduction

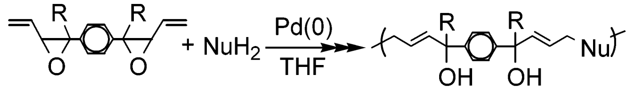
The palladium(0)-catalyzed reaction of vinyloxiranes with carbon nucleophiles such as active methylene compounds is a useful carbon−carbon bond formation reaction in organic synthesis.[1−5] However, no application of this reaction with vinyloxiranes for polymer synthesis via π-allylpalladium intermediates had been reported. We recently reported that the palladium(0)-catalyzed polyaddition of bifunctional vinyloxiranes [1,4-bis(2-vinylepoxyethyl)benzene (**1a**) and 1,4-bis(1-methyl-2-vinylepoxyethyl)benzene (**1b**)] with carbon nucleophiles such as acetylacetone and dimethyl malonate could afford new polymers (**2**) having an allyl alcohol moiety in the main chain accompanying carbon−oxygen bond cleavage of the oxirane ring, as shown in Scheme 1.[6−8] The stereochemistry of the obtained polymers was *E*-configuration. We also reported that **1a** and **1b** could react with phenols such as bisphenol A in the presence of Pd(0) catalyst to give the corresponding polymers having an allyl aryl ether moiety in the main chain and pendant hydroxyl groups.[9]

Although there are many reports on the Pd(0)-catalyzed reaction of vinyloxiranes with carbon nucleophiles, only a few studies on this reaction with nitrogen nucleophiles have been reported.[2,10,11] From the viewpoint of polymer synthesis, however, it is important to contemplate carbon−nitrogen bond formation by palladium-catalyzed reaction in order to obtain various functional polymers containing nitrogen atoms in the main chain. In this article, we describe the Pd(0)-catalyzed polyaddition of bifunctional vinyloxirane **1b** and nitrogen nucleophiles such as benzenesulfonamide and pyromellitic diimide to synthesize new polymers containing an allylamine moiety in the main chain and pendant hydroxyl groups.

Experimental Section

Measurement. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker-DMX 500 with $CDCl_3$ or dimethyl-d_6 sulfoxide (DMSO-d_6) as a solvent and Me_4Si as an internal standard. Gel permeation chromatography (GPC) was performed on a Shimadzu HPLC LC-6A system equipped with two columns (Shim-pack GPC-802 and GPC-804), and tetrahydrofuran (THF) was used as an eluent at 45 °C. The GPC was calibrated against standard polystyrene samples.

Scheme 1



1 **a**: R = H
b: R = Me
2
NuH$_2$ = active methylene compounds

Materials. Extra-pure grade reagents were used without further purification, unless otherwise stated. Bifunctional vinyloxirane **1b** was prepared by the method reported in our previous paper.[7] THF used as a solvent for polymerization was distilled from sodium/benzophenone ketyl under nitrogen prior to use.

Pd(0)-Catalyzed Reaction of 2-Methyl-2-phenyl-3-vinyloxirane (3) and Benzenesulfonamide (4): Model Reaction. To a solution of benzenesulfonamide (**4**) (0.159 g, 1.0 mmol) and $Pd(PPh_3)_4$ (0.116 g, 0.10 mmol) in THF (5 mL), a solution of vinyloxirane **3**[12] (0.325 g, 2.0 mmol) in THF (1 mL) was added. After being stirred for 6 h at room temperature under an Ar atmosphere, the reaction mixture was evapoporated to dryness. The residue was subjected to flash column chromatography on silica gel (hexane−ethyl acetate, 1:1) to give the desired 2:1 adduct **5** (0.348 g, 73%). IR (neat): 3480, 3059, 3030, 2978, 2930, 1489, 1560, 1333, 1160, 912, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.52 (CH_3, s, 3H), 1.54 (CH_3, s, 3H), 2.41 (OH, s, 1H), 2.44 (OH, s, 1H), 3.67−3.89 (CH_2, m, 4H), 5.44−5.51 ($-CH{=}C\mathbf{H}CH_2-$, m, 2H), 5.73 ($-CC\mathbf{H}{=}CH-$, d, $J = 15.7$ Hz, 2H), 7.22−7.34 (ArH, m, 10H), 7.45 (ArH, dd, $J = 7.7$ and 7.7 Hz, 2H), 7.51−7.57 (ArH, m, 1H), 7.77 (ArH, d, $J = 7.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 29.3 (CH_3), 49.2 (CH_2), 49.3 (CH_2), 74.1 (quat C), 122.7, 122.8, 125.0, 126.4, 127.1, 128.3, 129.1, 132.6, 132.7, 139.8, 141.4, 146.1, 146.2. HRMS: Calcd for $C_{28}H_{31}NO_4S$: 477.1974. Found: 477.1978.

Pd(0)-Catalyzed Polyaddition of Bifunctional Vinyloxirane 1b with Nitrogen Nucleophiles: A Typical Procedure. To a yellow solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (where dba is dibenzylideneacetone; 0.026 g, 0.025 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe; 0.040 g, 0.1 mmol) in THF (1 mL) a solution of benzenesulfonamide (**4**) (0.157 g, 1.0 mmol) in THF (1 mL) was added. To this a solution of bifunctional vinyloxirane **1b** (0.242 g, 1.0 mmol) in THF (1 mL) was added. The mixture was stirred at 60 °C for 6 h under an Ar atmosphere and poured into toluene (100 mL) to precipitate the polymer (run 4 in Table 1). The resulting polymer (**6b**) was filtered off, washed with toluene, and dried in vacuo (0.325 g, 81%), giving a gray solid. IR (KBr): 3448, 3059, 2974, 2925, 1331, 1157, 1090 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 1.39 (CH_3, s, 3H), 1.40 (CH_3, s, 3H), 3.75 ($-CH_2-$, d, $J = 5.6$ Hz, 4H), 5.26 (OH, s, 2H) 5.35−5.40 ($-CH{=}C\mathbf{H}CH_2-$, m, 2H), 5.76 ($-CC\mathbf{H}{=}CH-$, d, $J = 14.9$ Hz, 1H), 5.79 ($-CC\mathbf{H}{=}CH-$, d, $J = 15.0$ Hz, 1H), 7.27 (ArH, s, 4H), 7.51−7.56 (ArH, m, 2H), 7.63−7.68 (ArH, m, 1H), 7.80 (ArH, d, $J = 7.7$ Hz, 2H). ^{13}C NMR (DMSO-d_6) δ: 29.9 (CH_3), 30.0 (CH_3), 48.1 (CH_2), 72.8 (quat C), 120.5, 125.0, 127.2, 129.7, 133.1, 140.3, 143.2, 146.0.

8b, a pale gray solid. IR (KBr): 3427, 3103, 2976, 2927, 1529, 1350, 1159 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 1.40 (CH_3, s, 6H), 3.82 ($-CH_2-$, s, 4H), 5.26 (OH, s, 2H), 5.41−5.44 ($-CH{=}C\mathbf{H}CH_2-$, m, 2H), 5.81 ($-CC\mathbf{H}{=}CH-$, d, $J = 14.4$, 1H), 5.84 ($-CC\mathbf{H}{=}CH-$, d, $J = 14.4$, 1H), 7.27 (ArH, s, 4H), 8.06 (ArH, d, $J = 8.5$ Hz, 2H), 8.33 (ArH, d, $J = 8.4$ Hz, 2H). ^{13}C NMR (DMSO-d_6) δ: 29.9 (CH_3), 48.3 (CH_2), 72.8 (quat C), 120.2, 124.9, 125.0, 128.9, 143.4, 145.9, 146.0, 150.0.

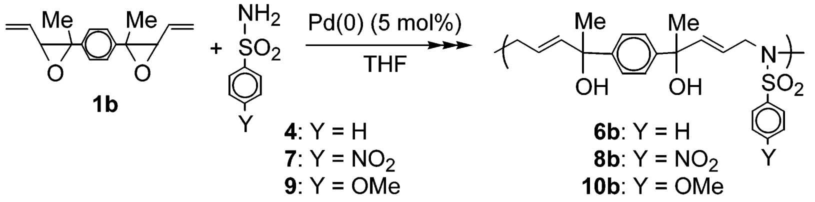
10b, a pale gray solid. IR (KBr): 3450, 2974, 2929, 1333, 1259, 1151, 1092 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 1.40 (CH_3, s, 3H), 1.41 (CH_3, s, 3H), 3.71 (CH_2, d, $J = 4.7$ Hz, 4H), 3.83 (OCH_3, s, 3H), 5.25 (OH, s, 2H), 5.38−5.43 ($-CH{=}C\mathbf{H}CH_2-$, m, 2H), 5.76 ($-CC\mathbf{H}{=}CH-$, d, $J = 15.1$ Hz, 1H), 5.79 ($-CC\mathbf{H}{=}CH-$, d, $J = 15.1$ Hz, 1H), 7.07 (ArH, d, $J = 8.6$ Hz, 2H), 7.28

---

† The National Defense Academy.
‡ Yamagata University.

10.1021/ma021591b CCC: $25.00

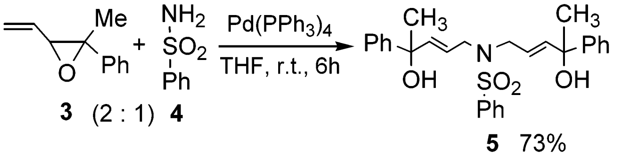
Table 1. Pd(0)-Catalyzed Polyaddition of 1b with Benzenesulfonamides



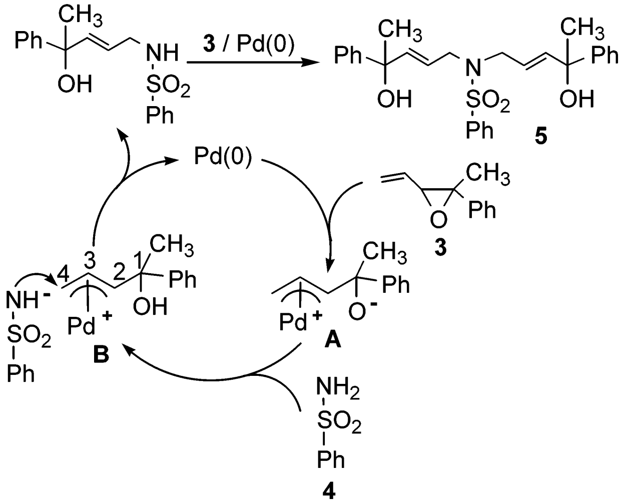
run	Pd(0)	$ArSO_2NH_2$	temp (°C)	time (h)	yield (%)[a]	M_n[b]	M_w/M_n[b]
1	$Pd(PPh_3)_4$	**4**	rt[c]	24	0		
2	$Pd(PPh_3)_4$	**4**	60	6	26	1030	1.45
3	$Pd_2(dba)_3$/dppe	**4**	rt[c]	24	87	3100	2.95
4	$Pd_2(dba)_3$/dppe	**4**	60	6	81	5100	7.81
5	$Pd(PPh_3)_4$	**7**	60	6	77	1800	1.95
6	$Pd_2(dba)_3$/dppe	**7**	60	6	85	5500	8.95
7	$Pd(PPh_3)_4$	**9**	60	6	0		
8	$Pd_2(dba)_3$/dppe	**9**	60	6	88	5800	3.25

[a] Insoluble in toluene. [b] Estimated by GPC (based on PSt). [c] Room temperature.

Scheme 2



Scheme 3



(ArH, s, 4H), 7.73 (ArH, d, $J = 8.6$ Hz, 2H). ^{13}C NMR (DMSO-d_6) δ: 29.9 (CH_3), 30.0 (CH_3), 48.1 (CH_2), 56.0 (OCH_3), 72.8 (quat C), 114.6, 114.8, 120.7, 124.9, 129.2, 130.9, 143.0, 146.1, 162.7.

12b, a white solid. IR (KBr): 3473, 3035, 2976, 2929, 1716, 1390, 1346, 1119, 1088, 968 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 1.44 (CH_3, s, 6H), 4.26 ($-CH_2-$, s, 4H), 5.33 (OH, s, 2H), 5.69−5.72 ($-CH{=}C\mathbf{H}CH_2-$, m, 2H), 5.94 ($-CC\mathbf{H}{=}CH-$, d, $J = 14.9$ Hz, 2H), 7.31 (ArH, s, 4H), 8.18 (ArH, s, 2H). ^{13}C NMR (DMSO-d_6) δ: 30.1 (CH_3), 40.6 (CH_2), 72.9 (quat C), 117.8, 120.2, 125.0, 137.3, 141.0, 146.2, 166.3.

Results and Discussion

The Pd(0)-catalyzed reaction of vinyloxirane **3** was first examined by use of benzenesulfonamide (**4**) as a nitrogen nucleophile. The reaction using 2 equiv of **3** to **4** was conducted at room temperature for 6 h in THF in the presence of $Pd(PPh_3)_4$ (5 mol % for **3**). The desired 2:1 adduct (**5**) was isolated in a good yield (73%) by flash column chromatography (Scheme 2). Tsuda et al.[2] reported that the Pd(0)-catalyzed reaction of methyl γ,δ-epoxysorbate with **4** gave a 1:1 adduct in a moderate yield (58%). However, they did not mention the formation of the 2:1 adduct. The Pd(0)-catalyzed reaction of **3** with **4** was also carried out in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$/dppe as a catalyst and gave 2:1 adduct **5** (99%), the yield of which was higher than that of **5** obtained by reaction with $Pd(PPh_3)_4$. A plausible reaction mechanism of the formation of **5** is shown in Scheme 3. π-Allylpalladium intermediate **A** generated by oxidative addition of Pd(0) to **3** abstracts a proton of **4**. Nucleophilic 1,4-attack of the generated anion on intermediate **B** affords a 1:1 adduct, which reacts with **3** to yield 2:1 adduct **5**. No detectable 1,2-adduct was formed. The structure of **5** was confirmed by NMR, IR, and elemental analysis. Figure 1a shows the ^{1}H NMR spectrum of **5** in DMSO-d_6. The methylene and vinyl protons were observed around 3.69−3.79 and 5.69−5.77 ppm, respectively. The IR spectrum of **5** showed the characteristic absorption based on the hydroxyl group (3480 cm^{-1}). The stereochemistry of **5** was confirmed as an *E*-configuration by the coupling constant of the vinyl proton (d); the *J* value was 15.7 Hz (see the Experimental Section). The *Z* isomer was not observed.

Table 1 shows the results of the Pd(0)-catalyzed polyaddition of **1b** with **4** in THF (runs 1−4). The formed polymers were isolated by pouring the reaction mixtures into toluene. In the polyaddition with $Pd(PPh_3)_4$ at room temperature, the desired polymer (**6b**) was not obtained (run 1). Polymer **6b** was afforded by polymerization at 60 °C, but the yield and M_n value were not high (run 2). In the Pd(0)-catalyzed reaction of vinyloxirane **3** with **4**, dppe was more effective than PPh_3. When dppe was employed as a ligand instead of PPh_3, **6b** was obtained in a good yield even at room temperature (run 3). **6b** with a higher M_n value was obtained by polymerization at 60 °C using dppe (run 4). Consequently, dppe was found to be more effective than PPh_3 for the polyaddition of **1b** and **4**. We have already reported a similar ligand effect for the Pd(0)-catalyzed polyaddition of **1b** and dimethyl malonate.[8] Tsuji et al. also found that dppe was more effective than PPh_3 for the Pd(0)-catalyzed reaction with weak nucleophiles.[13] Nitrogen nucleophile **4** seems to be a weak nucleophile in the Pd(0)-catalyzed polyaddition.

The structure of **6b** was determined on the basis of IR and NMR data. The proton signals of **6b** could be assigned as illustrated in Figure 1b. The methylene was observed around 4.50. The stereochemistry of **6b** was

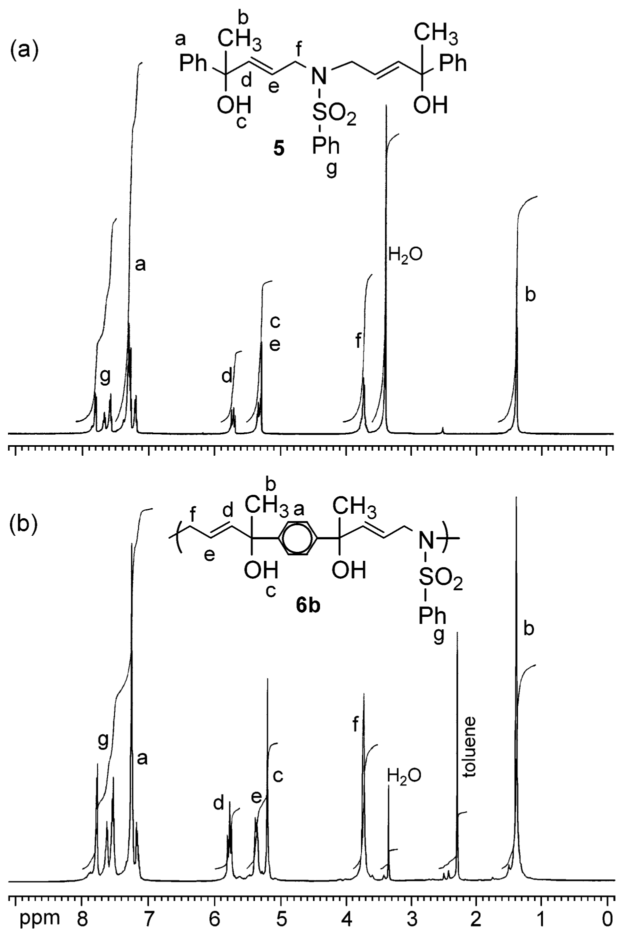


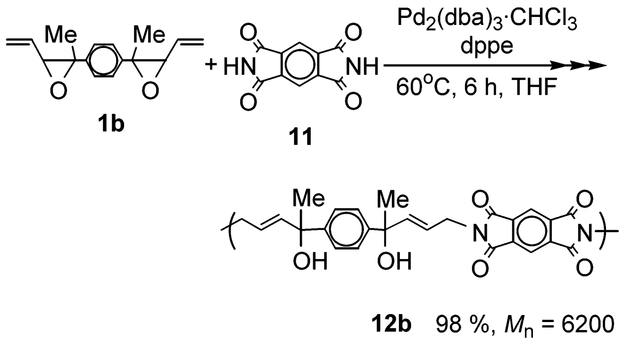
Figure 1. ^{1}H NMR spectra of **5** and polymer **6b** (DMSO-d_6, 500 MHz).

determined as an *E*-configuration by the coupling constant of the vinyl proton (**d**); the *J* value was 15.0 Hz. The clear signals based on the *Z* isomer were not observed. The IR spectrum of **6b** showed the characteristic absorptions based on the hydroxyl group around 3448 cm^{-1}. From these spectral data, we confirmed that the Pd(0)-catalyzed polyaddition of **1b** with **4** proceeded successfully and gave polymers **6b** with an allylamine moiety in the main chain and pendant hydroxyl groups.

Next, the Pd(0)-catalyzed polyaddition of **1b** with para-substituted benzenesulfonamides, *p*-nitrobenzenesulfonamide (**7**) and *p*-methoxybenzenesulfonamide (**9**), was examined at 60 °C in THF. The corresponding polymer (**8b**) was obtained in a good yield when the polyaddition of **1b** and **7** was conducted at 60 °C for 6 h in the presence of $Pd(PPh_3)_4$ (run 5). However, the M_n value was not high ($M_n = 1800$). On the other hand, the polyaddition with $Pd_2(dba)_3 \cdot CHCl_3$/dppe afforded polymer **8b** with a higher M_n value ($M_n = 5500$) in an 85% yield (run 6). These results indicate that dppe is more effective than PPh_3 for the polyaddition of **1b** and **7**, similar to that of **1b** and **4**. In the Pd(0)-catalyzed polyaddition of **1b** with **9**, the desired polymer **10b** could not be obtained by polymerization with $Pd(PPh_3)_4$, contrary to the polyaddition with **7** (runs 5 and 7). The polyaddition with dppe instead of PPh_3 could give polymer **10b** in an excellent yield ($M_n = 5800$, run 8).

The structures of polymers **8b** and **10b** were confirmed by IR and NMR spectra. The stereochemistry was *E*-configuration; the coupling constants of vinyl proton (−CC**H**=CH−) of **8b** and **10b** were 14.4 and 15.1 Hz, respectively. The IR spectra exhibit the characteristic absorptions due to the hydroxyl groups: 3427 cm^{-1} for **8b** and 3450 cm^{-1} for **10b**.

Scheme 4



Finally, we examined the Pd(0)-catalyzed polyaddition of **1b** with pyromellitic diimide (**11**). The polyaddition of **1b** with **11** was carried out at 60 °C in THF in the presence of $Pd(PPh_3)_4$, but the corresponding polymer (**12b**) could not be obtained. On the other hand, the polyaddition of **1b** and **11** using $Pd_2(dba)_3 \cdot CHCl_3$/dppe as a catalyst proceeded successfully, and the desired polymer **12b** ($M_n = 6200$) was obtained quantitatively (Scheme 4). The stereochemistry of **12b** was confirmed as an *E*-configuration by the coupling constant the vinyl proton; the *J* value was 14.9 Hz.

Conclusion

We found that the Pd(0)-catalyzed polyaddition of **1b** with **4**, **7**, **9**, and **11** proceeded successfully and gave new polymers with an allylamine moiety in the main chain and hydroxyl groups in the side groups. In the polyaddition, dppe was more effective than PPh_3. Polymers **6b**, **8b**, **10b**, and **12b** with high M_n values were obtained when the polyaddition was conducted at 60 °C in the presence of $Pd_2(dba)_3 \cdot CHCl_3$/dppe. The stereochemistry of polymers **6b**, **8b**, **10b**, and **12b** was *E*-configuration. All of the obtained polymers were soluble in organic solvents such as THF and DMSO.

References and Notes

(1) Tsuji, J. *Palladium Reagents and Catalysts, Innovations in Organic Synthesis*; John Wiley: New York, 1995; p 320.
(2) Tsuda, T.; Horii, Y.; Nakagawa, Y.; Ishida, T.; Saegusa, T. *J. Org. Chem.* **1989**, *54*, 977.
(3) Trost, B. M.; Luengo, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8239.
(4) Deardorff, D. R.; Myles, D. C.; MacFerrin, K. D. *Tetrahedron Lett.* **1985**, *26*, 5615.
(5) Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575.
(6) Koizumi, T.; Sakamoto, J.; Gondo, Y.; Endo, T. *Macromolecules* **2000**, *33*, 7235.
(7) Koizumi, T.; Sakamoto, J.; Gondo, Y.; Endo, T. *Macromolecules* **2002**, *35*, 2898.
(8) Koizumi, T.; Sakamoto, J.; Gondo, Y.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2487.
(9) Koizumi, T.; Imai, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 476.
(10) Peel, M. R.; Strenbach, D. D.; Johnson, M. R. *J. Org. Chem.* **1991**, *56*, 4990.
(11) Trost, B. M.; Kuo, G.-H.; Benneche, T. *J. Am. Chem. Soc.* **1988**, *110*, 621.
(12) Suga, K. Ph.D. Dissertation, Tokyo Institute of Technology, 1990.
(13) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523.

MA021591B