Polyaddition of Bifunctional Vinyloxirane with Carbon Nucleophiles via π-Allylpalladium Intermediate. Synthesis of New Polymers Bearing an Allyl Alcohol Moiety in the Main Chain

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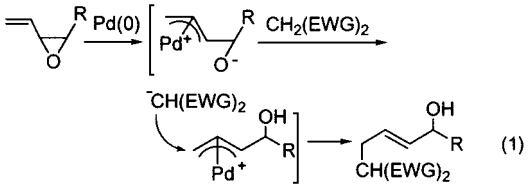
Received May 22, 2000
Revised Manuscript Received August 1, 2000

Palladium-catalyzed allylic alkylation reaction using soft carbon nucleophiles is a very useful carbon−carbon bond formation reaction in which a great variety of active methylene compounds can be used.[1] The ring-opening reaction of vinyloxirane derivatives, which are useful for synthesis of functionalized compounds, by organometallics has provided a valuable approach to allylic alcohols.[2] It is known that a Pd(0)-catalyzed reaction of vinyloxiranes with pronucleophiles (NuH) gives synthetically useful (*E*)-allylic alcohols via π-allylpalladium intermediates.[3] In this reaction, the nucleophilic attack takes place selectively under neutral conditions at the terminal carbon (eq 1).



(1)

EWG: Electron-Withdrawing Group

This Pd(0)-catalyzed reaction prompted us to explore the synthesis of new functional polymers. Polymers bearing hydroxy groups are important in coatings, adhesives, and polymeric reagents.[4] However, it is very difficult to synthesize a variety of polymers having hydroxy and other functional groups. There is a report of the preparation of such polymers reported by Nomura and Endo.[5]

In this paper, we describe the Pd(0)-catalyzed polyaddition of a bifunctional vinyloxirane with carbon nucleophiles such as active methylene compounds. The Pd(0)-catalyzed addition of vinyloxiranes with active methylene compounds affords 1:1 adducts in good yields (eq 1). Although the adducts still have one active hydrogen, the formation of 2:1 adducts has not been reported yet. Hence, the Pd(0)-catalyzed addition of 2-phenyl-3-vinyloxirane (**1**) with acetylacetone **2a** (pK_a 9)[6] was first examined as a model reaction. The Pd(0)-catalyzed addition using 2 equiv of **1** to **2a** was carried out at room temperature for 3 h in the presence of Pd-

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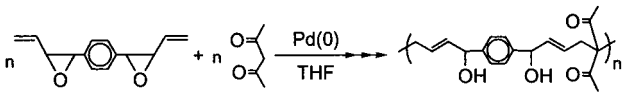
Table 1. Palladium(0)-Catalyzed Polyaddition of 4 with Acetylacetone 2a

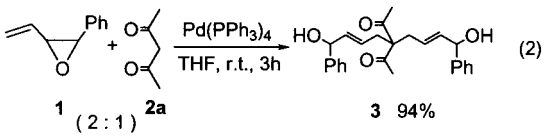


4 **2a** **5a**

run	Pd(0)[a]	temp	time (h)	yield (%)[b]	M_n[c] × 10^{-3}	M_w/M_n[c]
1	$Pd(PPh_3)_4$ (5)	0 °C	6	100	3.4	2.73
2	$Pd(PPh_3)_4$ (5)	r.t.	6	98	3.6	2.04
3	$Pd(PPh_3)_4$ (5)	reflux	6	100	3.3	2.17
4	$Pd(PPh_3)_4$ (1)	r.t.	6	0		
5	$Pd(PPh_3)_4$ (1)	r.t.	24	93	4.7	2.31
6	$Pd_2(dba)_3$/4dppe (5)	r.t.	24	100	3.4	2.49
7	$Pd_2(dba)_3$/4dppp (5)	r.t.	24	100	3.7	2.37
8	$Pd_2(dba)_3$/4dppb (5)	r.t.	24	79	3.5	3.03

[a] Numbers in parentheses: [Pd/**4**] × 100. [b] Insoluble in toluene. [c] Estimated by GPC (based on PSt).

$(PPh_3)_4$ (5 mol %). The desired 2:1 adduct **3** was isolated in 94% yield by flash column chromatography (eq 2).



1 (2 : 1) **2a** **3** 94% (2)

When 2 equiv of dimethyl malonate, **2c** (pK_a 13),[6] was employed as a carbon nucleophile under the same conditions, the corresponding 2:1 product was not isolated. In the reaction with **2c**, the corresponding 1:1 adduct was obtained in 45% yield. These results suggest that active methylene compounds with lower pK_a values are required to obtain 2:1 adducts in high yields. Thus, acetylacetone as a carbon nucleophile is a good candidate for the polyaddition of bifunctional vinyloxirane, 1,4-bis(2-vinylepoxyethyl)benzene (**4**).

Bifunctional vinyloxirane **4** was synthesized by the phase-transfer reaction of an allyldimethylsulfonium salt with terephthalaldehyde according to the method reported in our previous paper.[7] The Pd(0)-catalyzed polyaddition of **4** with **2a** was carried out in THF under various conditions.[8] The formed polymers were isolated by pouring the reaction mixtures into toluene. The results are summarized in Table 1. In the polyaddition using 5 mol % of $Pd(PPh_3)_4$ relative to **4**, the desired polymers (**5a**) were obtained quantitatively (runs 1−3). The reaction temperature did not affect the yield and average molecular weight (M_n) of **5a**. The polyaddition at room temperature for 6 h did not afford **5a** when 1 mol % of $Pd(PPh_3)_4$ was used (run 4), although prolonged polymerization time (24 h) did (93%, M_n 4700) (run 5). Next, the effect of the ligands, 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)propane (dppp), and 1,2-bis(diphenylphosphino)butane (dppb), on the polyaddition was examined. Although the polyaddition using dppb produced polymer **5a** with somewhat lower yield than those of the polymers obtained with dppe and dppp, all of the ligands produced polymers with molecular weights in the range of 3400−3700 (runs 6−8), which were very similar to the results using Pd-$(PPh_3)_4$. These results indicate that the polyaddition of **4** with **2a** did not depend on the kind of ligands employed.

10.1021/ma000881u CCC: $19.00
Published on Web 09/13/2000

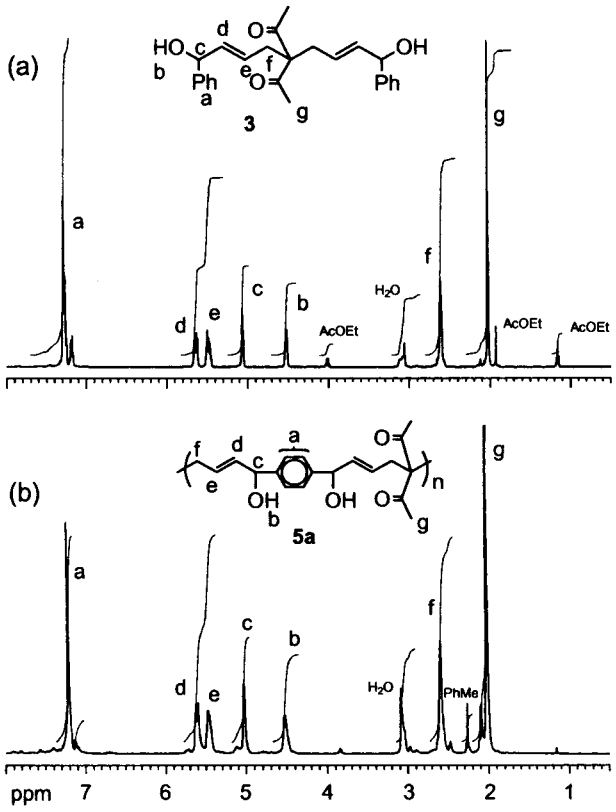


Figure 1. ^{1}H NMR spectra of **3** and polymer **5a** (acetone-d_6, 500 MHz).

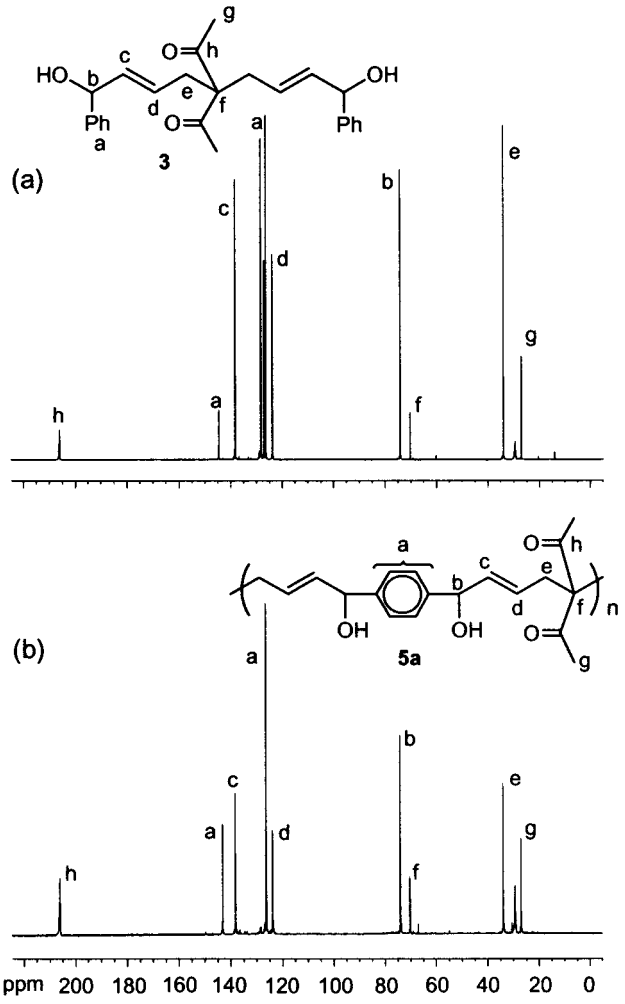
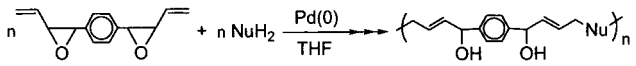


Figure 2. ^{13}C NMR spectra of **3** and polymer **5a** (acetone-d_6, 125 MHz).

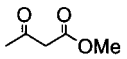
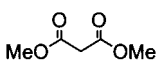
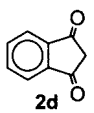
The structure of the polymers was confirmed by comparison with IR and NMR spectra of model compound **3**. All of the proton signals of **5a** could be assigned and were in good agreement with those of **3** as illustrated in Figure 1. Similarly, all of the carbon signals of **5a** could also be assigned and agreed well with those of **3** as shown in Figure 2. The stereochemistries of **3** and **5a** were confirmed as *E*-configuration by the coupling constant of the vinyl proton (**d** in Figure 1); the *J* values of **3** and **5a** were 15.1 and 14.5 Hz, respectively. The *Z*-isomers were observed neither in the ^{13}C NMR spectra nor in the ^{1}H NMR spectra of **3** and **5a**. These results demonstrate that the selectivity is exclusive as reported by Tsuji and Trost.[3] The IR spectra of both **3** and **5a** show the characteristic absorptions based on the hydroxy and carbonyl groups at 3400 and 1690 cm^{-1}, respectively. These spectral data confirm that the Pd(0)-catalyzed polyaddition of **4** with **2a** produced polymers having an allyl alcohol moiety in the main chain and carbonyl groups in the side group.

The Pd(0)-catalyzed polyaddition of **4** was carried out using other carbon nucleophiles. The results are shown in Table 2. The corresponding polymers (**5b**) were

Table 2. Palladium(0)-Catalyzed Polyaddition of 4 with Nucleophiles (NuH_2)[a]



4 **2** **5**

run	Pd(0)	NuH_2	yield (%)[b]	M_n[c] × 10^{-3}	M_w/M_n[c]
1	$Pd(PPh_3)_4$		87	4.2	2.03
2	$Pd_2(dba)_3$/4dppe		99	3.9	2.32
		2b			
3	$Pd(PPh_3)_4$		77	3.0	1.80
4	$Pd_2(dba)_3$/4dppe		47	1.7	1.70
		2c			
5	$Pd(PPh_3)_4$		87	9.2	1.96
6	$Pd_2(dba)_3$/4dppe		100	7.5	2.28
		2d			

[a] Conditions: Pd/**4** = 0.05, r.t., 24 h, THF. [b] Insoluble in toluene. [c] Estimated by GPC (based on PSt).

obtained in high yields by the polymerization of **4** with methyl acetoacetate (**2b**). $Pd(PPh_3)_4$ and $Pd_2(dba)_3$/dppe gave similar results (runs 1 and 2). The polyaddition of **4** with dimethyl malonate (**2c**) was carried out using $Pd(PPh_3)_4$ to obtain the expected polymer (M_n 3000) in 77% yield, whereas $Pd_2(dba)_3$/dppe produced polymer **5c** with low M_n in low yield (runs 3 and 4). $Pd_2(dba)_3$/dppe does not seem to be suitable for the polymerization with **2c**. In the addition of **1** with **2c**, the corresponding 2:1 adduct was not isolated from the reaction mixture as mentioned above. However, the polyaddition of **4** with **2c** gave polymer **5c** of which the structure was confirmed by IR and NMR. Polymerization of **4** using 1,3-indandione (**2d**) produced the polymers with higher values of M_n (runs 5 and 6). Thus, we found that the Pd(0)-catalyzed polyaddition of **4** with **2** proceeded successfully to give new polymers having an allyl alcohol moiety in the main chain.

This is the first example of palladium-catalyzed polyaddition of bifunctional vinyloxirane with carbon nucleophiles. Further studies on this new polyaddition of bifunctional vinyloxirane derivatives with various nucleophiles (active methylene compounds, phenols, amines, and so on) are now in progress.

References and Notes

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(8) A typical procedure: To a solution of **2a** (0.201 g, 2 mmol) and $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol) in THF (4 mL), a solution of **4** (0.428 g, 2 mmol) in THF (2 mL) was added. The mixture was stirred at room temperature for 24 h under argon and poured into toluene (100 mL) to precipitate polymer (Table 1, run 5). The resulting polymer **5a** was filtered, washed with toluene, and dried in vacuo (0.582 g, 93%). ^{1}H NMR (acetone-d_6): δ 2.01 (s, 6H), 2.47 (s, 4H), 4.51 (s, 2H), 5.02 (s, 2H), 5.4−5.5 (m, 2H), 5.61 (d, J = 14.5, 2H), 7.21 (s, 4H). ^{13}C NMR (acetone-d_6): δ 26.99, 33.43, 70.11, 73.81, 123.81, 126.06, 138.18, 143.05, 206.00. IR (KBr): 3400, 3010, 2920, 2860, 1690, 1420, 1360, 1170, 1090, 970 cm^{-1}.

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