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Novel Palladium-Catalyzed Polycondensation of Propargyl Carbonates and Bisphenols. Synthesis of Polyethers Having Exomethylene Groups

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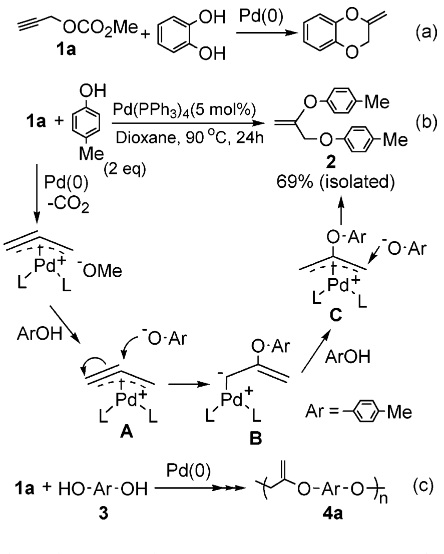
The palladium-catalyzed allylic substitution reaction of various allylic compounds and nucleophiles is well established and a remarkably useful reaction in organic synthesis.[1] The substitution reaction proceeds through π-allylpalladium intermediates. There are some applications of this reaction for polymer synthesis via η^3-allylpalladium complexes.[2−4] We also reported that the Pd(0)-catalyzed polyaddition of bifunctional vinyloxiranes and various nucleophiles afforded new unsaturated polymers having hydroxyl and other functional groups.[5] To our knowledge, however, the Pd(0)-catalyzed polycondensation of propargylic compounds and nucleophiles has not been reported so far. It is known that propargyl carbonates react with active methylene compounds to give dihydrofurans or furans in the presence of a Pd(0) catalyst.[6] More recently, Sinou reported that a Pd(0)-catalyzed condensation of propargyl carbonates with catechol as an oxygen nucleophile afforded 1,4-benzodioxins (Scheme 1a).[7] These reactions show that propargyl carbonates have two reaction sites for nucleophilic attack. In the course of our studies on the Pd(0)-catalyzed polyaddition of bifunctional vinyloxiranes and nucleophiles, we expected that propargyl carbonates could be polymerized with appropriate nucleophiles to give the corresponding polymers having exomethylene groups under palladium catalysis (Scheme 1c). We report here a new Pd(0)-catalyzed polycondensation of propargyl carbonates and bisphenols to give polyethers.

Scheme 1. Pd(0)-Catalyzed Condensation of 1a and Phenols



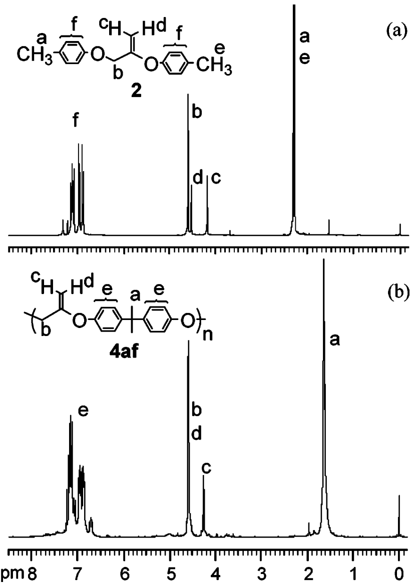


Figure 1. ^{1}H NMR spectra of model **2** and polymer **4af** ($CDCl_3$, 300 MHz).

The Pd(0)-catalyzed condensation of methyl propargyl carbonate (**1a**)[6c] was first examined using some heteroatom nucleophiles as a model reaction because there are few studies of the condensation of propargyl carbonates and heteroatom nucleophiles.[6a,7] The Pd(0)-catalyzed reaction using 2 equiv of nucleophiles to **1a** was carried out in dioxane at 90 °C for 24 h in the presence of $Pd(PPh_3)_4$ (5 mol % for **1a**). Morpholine, saccharin, phthalimide, *p*-toluic acid, and *p*-cresol were employed as nucleophiles. Among them, only *p*-cresol gave the desired 1:2 product **2** in 69% yield (Scheme 1b). Consequently, phenols were judged to be suitable nucleophiles for the reaction. A plausible mechanism is shown in Scheme 1b.[8b] η^3-Propargylpalladium intermediate **A**[8] generated by oxidative addition of Pd(0) to **1a** is attacked by the first *p*-cresol at the central carbon to produce intermediate **B**, which is then protonated to afford η^3-allylpalladium intermediate **C**. Intermediate **C** is attacked by a second *p*-cresol to give 1:2 product **2**. The ^{1}H NMR spectrum of **2** is shown in Figure 1a. The exomethylene protons were observed around 4.18 and 4.53 ppm.

On the basis of the results of the model reaction, we selected bisphenol analogues **3** such as bisphenol A (**3f**) and 4,4′-dihydroxydiphenyl ether (**3g**) as oxygen nucleophiles. The Pd(0)-catalyzed polycondensation with **1a** was carried out in dioxane at 90 °C for 24 h in the presence of $Pd(PPh_3)_4$ (Scheme 1c).[9] The results are summarized in Table 1. The polycondensation with hydroquinone (**3d**) and 4,4′-biphenol (**3e**) was not successful (runs 1 and 2). Although signals due to the desired products were observed in the ^{1}H NMR spectra of the reaction mixtures, methanol-insoluble polymers **4ad** and **4ae** were not obtained. The polycondensation of **1a** and **3f** gave the corresponding polyether **4af** in a moderate yield (run 3). The structure of **4af** was confirmed by comparison with IR and NMR spectra of model compound **2**. All of the proton signals of **4af** could

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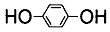
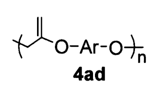
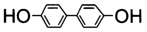
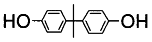
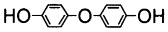
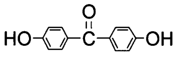
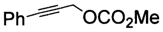
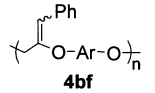
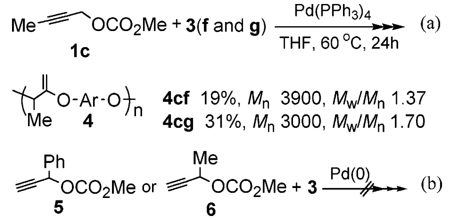
Table 1. Pd-Catalyzed Polycondensation of Propargyl Carbonates 1 and Bisphenols 3[a]

run	carbonate **1**	HO-Ar-OH **3**	polymer **4**	yield (%)[b]	M_n[c]	M_w / M_n[c]
1	 **1a**	 **3d**	 **4ad**	0		
2	**1a**	 **3e**	**4ae**	0		
3	**1a**	 **3f**	**4af**	53	3300	1.63
4	**1a**	 **3g**	**4ag**	77	2400	1.94
5[d]	**1a**	**3g**	**4ag**	100[e]	3700	2.16
6	**1a**	 **3h**	**4ah**	16	1400	1.36
7	 **1b**	**3f**	 **4bf**	68	2900	1.55
8	**1b**	**3g**	**4bg**	45	2200	1.44

[a] Conditions: **1a**, 1.0 mmol; **3**, 1.0 mmol; Pd(PPh$_3$)$_4$, 50 μmol (5.0 mol %); dioxane, 3.0 mL; 90 °C; 24 h. [b] Insoluble in methanol. [c] Estimated by GPC (based on PSt). [d] The polymerization with **3g** (0.5 equiv to **1a**) was carried out in THF at 60 °C for 24 h. [e] Based on **3g**.

be assigned and were in good agreement with those of **2**, as illustrated in Figure 1b. In the ^{13}C NMR spectra of **4af**, the exomethylene carbon and methylene carbon were also observed at 91.1 and 68.0 ppm, respectively. These spectral data support the structure of **4af**. **3g**, which has an ether linkage, was also polymerized with **1a** to give polyether **4ag** in a good yield (run 4). Interestingly, **4ag** with a higher M_n value (M_n = 3700) could be obtained when 0.5 equiv of **3g** to **1a** was used (run 5). This reason is not clear at this stage. Judging from the plausible mechanism (Scheme 1b), however, it is assumed that the polycondensation could proceed under stoichiometrically imbalanced conditions[10] because oligomeric products produced by reaction of **1a** and **3g** can act as HO−Ar−OH during polymerization, which is similar to the polycondensation reported by Nomura. In the polycondensation of **1a** and **3h**, the M_n value and yield of product **4ah** were low (run 6). Thus, the Pd(0)-catalyzed polycondensation of **1a** and **3** was found to be largely affected by the kinds of bisphenol analogues employed.

Scheme 2. Pd(0)-Catalyzed Polycondensation of Propargyl Carbonates and 3



Next, we tried the polycondensation by use of a substituted propargyl carbonate, methyl 3-phenyl-2-propynyl carbonate (**1b**). The desired polyether **4bf** could be obtained in a good yield by polymerization of **1b** and **3f** (M_n = 2900, run 7). The polycondensation of **1b** and **3g** also produced the corresponding polymer **4bg** (run 8). Polymers **4bf** and **4bg** had mainly Ph-substituted exomethylene groups.[11] Methyl-substituted propargyl carbonate **1c** could also be used (Scheme 2a). The Pd(0)-catalyzed polycondensation with **1c** was carried out at 60 °C for 24 h in THF instead of dioxane because complex mixtures were obtained by polymerization with **1c** and **3** in dioxane 90 °C for 24 h. When **3f** was employed as a nucleophile, the corresponding polymer **4cf** was obtained (M_n = 3900). The polycondensation of **1c** and **3g** also proceeded and gave the desired polymer **4cg**, the M_n value of which was 3000. Interestingly, the structures of **4cf** and **4cg** were different from those predicted from the results of the polycondensation with **1b**. These polymers had exomethylene groups similar to polymers **4a**. In the ^{1}H NMR spectra of polymer **4bf** and **4bg**, the methylene protons (−CH$_2$−O−) were observed around 4.50 and 4.54 ppm, respectively. Signals due to the methylene carbons of **4bf** and **4bg** appeared at 67.0 and 67.7 ppm, respectively, in the ^{13}C NMR spectra. On the other hand, in the ^{1}H NMR spectra of **4cf** and **4cg** signals due to the exomethylene protons (CH$_2$=C−) appeared around 4.0 and 4.4 ppm, respectively. In addition, the presence of the methine carbons of **4cf** and **4cg** was confirmed by ^{13}C NMR: 73.7 and 74.6 ppm, respectively. These results indicate that the second nucleophilic attack onto the η^3-allylpalladium intermediates generated from **1** depends on the kinds of substituents (Scheme 1b). Other bisphenols such as **3d** and **3h** were not successful for the polycondensation with **1b** and **1c**.

Finally, the Pd(0)-catalyzed polycondensation was attempted by using propargyl carbonates **5** and **6** (Scheme 2b). The polymerization of **5** and **3** was carried out under conditions where the Pd(0)-catalyzed polycondensation with **1** was able to produce the desired polyethers. Although the complete consumption of **5** was confirmed by ^{1}H NMR, the corresponding polymers were not formed, and a complex mixture was obtained. In addition, the polycondensation of **6** and **3** did not proceed, and **6** still remained in the reaction mixtures. Thus, **5** and **6** did not give the desired polymers. The reason is not obvious at present. The position of a substituent in the propargylic moiety seems to be an important factor for the successful Pd(0)-catalyzed polycondensation.

We found that the Pd(0)-catalyzed polycondensation of propargyl carbonates **1** and bisphenol analogues **3** proceeded successfully and gave novel polyethers. Further investigation including the optimization of conditions for this new polymerization is now in progress to obtain the higher polyethers from **1** and **3**.

Supporting Information Available: ^{1}H NMR spectra for all new polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Tsuji, J. In *Palladium Reagents and Catalysts, Innovations in Organic Synthesis*; John Wiley: New York, 1995; p 290. (b) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395.

(2) (a) Suzuki, M.; Lim, J.-C.; Oguni, M.; Eberhardt, A.; Saegusa, T. *Polym. J.* **1990**, *22*, 815. (b) Suzuki, M.; Ii, A.; Saegusa, T. *Macromolecules* **1992**, *25*, 7071. (c) Suzuki, M.; Sawada, S.; Yoshida, S.; Eberhardt, A.; Saegusa, T. *Macromolecules* **1993**, *26*, 4748.

(3) (a) Miyaki, N.; Tomita, I.; Kido, J.; Endo, T. *Macromolecules* **1997**, *30*, 4504. (b) Miyaki, N.; Tomita, I.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2097.

(4) (a) Nomura, N.; Tsurugi, K.; Okada, M. *J. Am. Chem. Soc.* **1999**, *121*, 7268. (b) Nomura, N.; Yoshida, N.; Tsurugi, K.; Aoi, K. *Macromolecules* **2003**, *36*, 3007.

(5) (a) Koizumi, T.; Sakamoto, J.; Gondo, Y.; Endo, T. *Macromolecules* **2002**, *35*, 2898. (b) Koizumi, T.; Sakamoto, J.; Gondo, Y.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2487. (c) Koizumi, T.; Imai, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 476. (d) Koizumi, T.; Koma, Y.; Endo, T. *Macromolecules* **2003**, *36*, 5882.

(6) (a) Tsuji, J.; Mandai, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2589. (b) Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196. (c) Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225.

(7) Labrosse, J.-R.; Lhoste, P.; Sinou, D. *J. Org. Chem.* **2001**, *66*, 6634.

(8) For η^3-propargylpalladium intermediates, see: (a) Su, C.-C.; Chen, J.-T.; Lee, G. H.; Wang. Y. *J. Am. Chem. Soc.* **1994**, *116*, 4999. (b) Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmeczy, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722. (c) Tsutsumi, K.; Ogoshi, S.; Nishiguchi, S.; Kurosawa, H. *J. Am. Chem. Soc.* **1998**, *120*, 1938.

(9) A typical procedure: To an orange solution of $Pd(PPh_3)_4$ (0.058 g, 0.05 mmol) in dioxane (2 mL) bisphenol A (**3f**; 0.228 g, 1.0 mmol) was added. To the mixture a solution of methyl propargyl carbonate (**1a**; 0.114 g, 1.0 mmol) in dioxane (1 mL) was added. After being stirred at 90 °C for 24 h under an Ar atmosphere, the reaction mixture was poured into methanol (100 mL) to precipitate the polymer (run 3 in Table 1). The resulting polymer was filtered off, washed with methanol, and dried in vacuo (0.142 g, 53%), giving polymer **4af**: IR (KBr): 3041, 2965, 2871, 1505, 1225, 1176, 832 cm^{-1}.

(10) Nomura reported the Pd-catalyzed polycondensation of allylic compounds and nucleophiles under stoichiometrically imbalanced conditions: (a) Nomura, N.; Tsurugi, K.; Okada, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1932. (b) Tsurugi, K.; Nomura, N.; Aoi, K. *Tetrahedron Lett.* **2002**, *43*, 469.

(11) Very small signals, probably due to a unit containing an exomethylene group, were also observed in the ^{1}H NMR spectra of **4bf** and **4bg**.

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