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A New Reduction Method of Poly(Phosphine Oxide) to Polyphosphine

Preparation of Poly[(P-Phenyl)Trimethylenephosphine]

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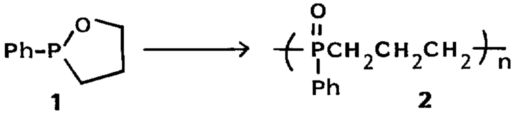
Summary

A clean reaction of the reduction of poly[(*P*-phenyl)trimethylenephosphine oxide] (**2**) to poly[(*P*-phenyl)trimethylenephosphine] (**3**) has been found, in which **2** was treated first with oxalyl chloride and then with diisobutylaluminum hydride. These two reactions were carried out in sequence in one-pot. The complete conversion was observed in both reactions, and the structure of the product **3** was clean. The same procedure was applied to diethylphenylphosphine oxide to produce the corresponding phosphine in an almost quantitative yield.

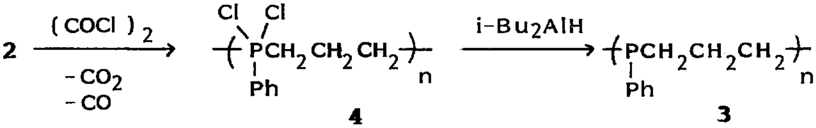
Introduction

Very recently we have reported a new cationic ring-opening polymerization of 2-phenyl-1,2-oxaphospholane, a five-membered "deoxophostone" (**1**) to give poly[(*P*-phenyl)trimethylenephosphine oxide] (**2**) (KOBAYASHI et al, 1981). The polymerization of **1** was a clean reaction involving no side reaction.



1 **2**

An attempt was made to reduce **2** with trichlorosilane-triethylamine system to poly[(*P*-phenyl)trimethylenephosphine] (**3**). The polymer thus obtained, however, contained a small amount of an unidentified unit (~15%) in addition to the desired phosphine unit (KOBAYASHI et al, 1981). The present paper reports a new reduction method of **2** to **3** consisting exclusively of the phosphine unit. The method is a one-pot reaction employing oxalyl chloride in the first-step of treatment and diisobutylaluminum hydride ($i\text{-}Bu_2AlH$) in the second-step. The first-step involves the formation of dichlorophosphorane type polymer (**4**).



$$2 \xrightarrow[-CO_2,\ -CO]{(COCl)_2} \left(\overset{Cl\ Cl}{\underset{Ph}{P}}CH_2CH_2CH_2\right)_n \xrightarrow{i\text{-}Bu_2AlH} \left(\underset{Ph}{P}CH_2CH_2CH_2\right)_n$$

4 **3**

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Results and Discussion

The trichlorosilane-triethylamine system is the most well-known reducing agent of phosphine oxides to phosphines (FRITZSCHE et al, 1965; NAUMANN et al, 1969). Since this system was found not suitable for the preparation of **3** from **2**, we have developed a new reduction method of phosphoryl group. To a dichloromethane solution of **2** (molecular weight=3500 by vapor pressure osmometry) oxalyl chloride was dropwise added at room temperature. Vigorous gas evolution was observed during the addition and simultaneously a paste-like material precipitated. At this point, the ^{31}P NMR of the supernatant liquid showed the disappearance of the signal at +39.8 ppm due to **2** and instead a new peak appeared at +85.0 ppm which is assignable to a dichlorophosphorane structure **4**. Without isolating **4** the mixture was cooled to -78°C and a CH_2Cl_2 solution of i-Bu_2AlH was added slowly. Then, the mixture was allowed to warm up to room temperature. The ^{31}P NMR of the mixture showed a single peak at -26.8 ppm which was ascribed to a phosphine structure **3**. After work-up procedures a pale yellow paste-like material of **3** was obtained in 75% yield (molecular weight of **3**=4100). The molecular weight increase from **2** to **3** was probably due to the loss of the lower molecular weight part of **3** during work-up procedures.

The data supporting the structure **3** were additionally obtained: ^{1}H NMR ($CDCl_3$); δ0.7-2.1(broad, 6H) and δ6.6-7.7 (broad, 5H). IR($CHCl_3$ solution); no ν(P=O) band. The ^{13}C NMR spectra ($CDCl_3$) of **3** and a model compound of 1,3-bis(diphenylphosphino)propane look very similar (Figure 1).

3 was soluble in CH_2Cl_2 or $CHCl_3$ but insoluble in hexane or diethyl ether and was readily oxidized by air in solution.

Thus, the present method provides a new one-pot reduction of a phosphoryl group. Both steps using oxalyl chloride and i-Bu_2AlH are quantitative under mild reaction conditions. We attempted the reduction of diethylphenylphosphine oxide as a model compound of polymer **2** under similar reaction conditions as that of **2**. Diethylphenylphosphine oxide (^{31}P NMR; +43.4 ppm) gave a dichlorophosphorane (+98.9 ppm, single peak) and the phosphorane was reduced with i-Bu_2AlH to give quantitatively diethylphenylphosphine (-19.2 ppm) without any side reaction products. On the other hand, the reduction of diethylphenylphosphine oxide with the trichlorosilane-triethylamine system under analogous reaction conditions as the previous reduction conditions of **2** yielded diethylphenylphosphine and a small amount of an unidentified product (+32.0 ppm). The formation of such a side reaction product is undesirable in the case of polymer, in which the separation of the undesirable unit in the polymer chain is impossible.

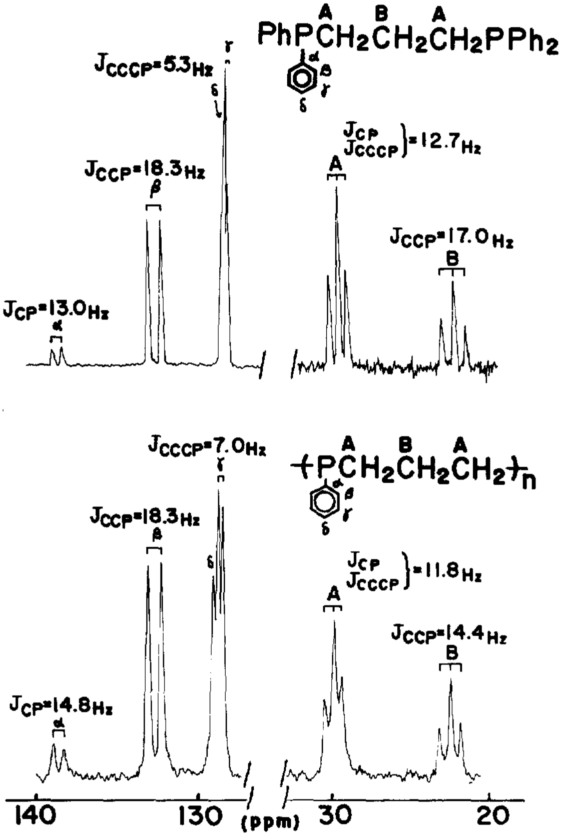

Figure 1. Expanded $^{13}C\{^1H\}$ FT-NMR spectra (22.6 MHz, $CDCl_3$ with TMS) of 1,3-bis(diphenylphosphino)propane (upper) and polyphosphine(**3**) (lower).

Experimental

Materials. Polymer **2** was prepared by the cationic ring-opening polymerization of **1** according to the procedure reported previously (KOBAYASHI et al, 1981). Solvents of CH_2Cl_2 and $CHCl_3$ were dried over P_2O_5 and purified by distillation under nitrogen. A commercial reagent of oxalyl chloride was purified by distillation under nitrogen. Commercial diisobutylaluminum hydride (20 wt % solution in hexane, Ventron Corp.) was used without further purification. 1,3-Bis(diphenylphosphino)propane was prepared according to the reported procedure (YOSHIDA et al, 1967). The chemical shift data in Figure 1 are as follows: $^{13}C\{^1H\}NMR(CDCl_3)$; 22.3(t), 29.5(t), 128.3(d), 128.4(s), 132.6 (d), and 138.5 ppm(d).

*Reduction of **2**.* All procedures were carried out under nitrogen. Into a 0.8 ml CH_2Cl_2 solution containing 69.2 mg of poly(phosphine oxide)**2**(0.42 mmol of the P=O group) oxalyl chloride(0.044 ml, 0.5 mmol) was slowly added at room temperature. During the addition, vigorous evolution of gas (probably CO_2 and CO) was observed and a paste-like material precipitated. Then, a CH_2Cl_2 solution of i-Bu_2AlH(0.178 g, 1.25 mmol) was added to the mixture cooled at -78°C. The mixture was allowed to warm up gradually to room temperature and after overnight it became homogeneous. Then, 1.5 ml of oxygen-free 30% NaOH(aq) was slowly added to the mixture with ice-cooling. After 2 ml of water was further added to the mixture the CH_2Cl_2 layer was separated. The aqueous layer was extracted once more with 1 ml of CH_2Cl_2. The combined CH_2Cl_2 layer was washed with 2 ml of water, separated, dried over $MgSO_4$, and concentrated to ca. 1 ml. This solution was poured into 20 ml of n-hexane (degased, oxygen-free), a precipitated material was separated and 46 mg of polymer **3** was obtained after drying in vacuo (75% yield). The chemical shift data of **3** in Figure 1 are as follows: $^{13}C\{^1H\}$NMR($CDCl_3$); 22.3(t), 29.7 (t), 128.3(d), 128.7(s), 132.3(d), and 138.3 ppm(d).

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