

Cationic Ring-Opening Polymerization of 2-Phenyl-1,2-oxaphospholane (Deoxophostone)

Synthesis of Poly(phosphine oxide) and Polyphosphine

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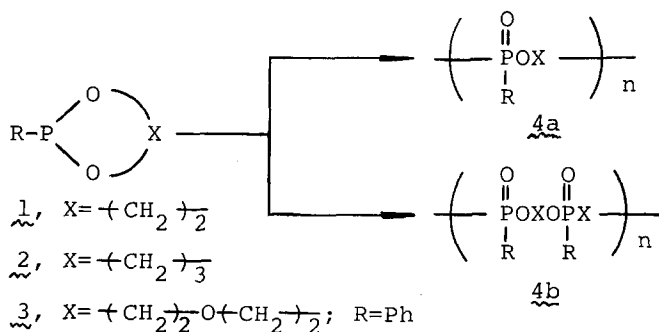
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Summary

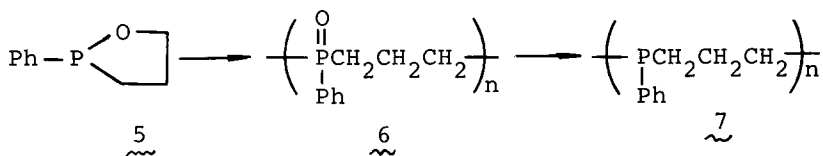
The ring-opening polymerization of deoxophostone (5), a five-membered cyclic phosphinite, has been studied. Some cationic initiators gave polymer whereas anionic and radical initiators as well as metal chloride (Lewis acid) catalysts did not yield polymer. The polymer consisted of a phosphine oxide repeating unit (6). The polymerization proceeded via the Arbuzov-type reaction. The reduction of polymer 6 with a $\text{HSiCl}_3/\text{Et}_3\text{N}$ system gave polyphosphine 7.

Introduction

Cationic ring-opening polymerizations of cyclic phosphorus(III) compounds have been reported on 1,3,2-dioxaphospholanes (1) (PETROV et al, 1962; MUKAIYAMA et al, 1964; SHIMIDZU et al, 1965 and 1966; HARWOOD and PATEL, 1968; VOGT and AHMAD, 1977), on 1,3,2-dioxaphosphorinanes (2) (PETROV et al, 1960; HARWOOD and PATEL, 1968; SINGH, 3, 1979), and very recently on an eight-membered monomer of phosphocane (3) (KOBAYASHI et al, 1981). These polymerizations proceeded via the Arbuzov type reaction involving cyclic phosphonium intermediates to produce polyphosphinates or polyphosphonates (4a). During the polymerization, however, side reactions took place to form an isomerized repeating



unit (4b). Sometimes the amount of the isomerized unit is higher than that of the "normal" unit (4a) (HARWOOD and PATEL, 1968; VOGT and AHMAD, 1977). It should be noted also that the isomerization was negligible in the benzyl chloride initiated polymerization of monomer 3 (KOBAYASHI et al, 1981). The present paper reports the cationic ring-opening polymerization of 2-phenyl-1,2-oxaphospholane, a five-membered cyclic phosphinite ("deoxophostone", 5) to yield poly(phosphine oxide) (6) and the reduction of 6 to polyphosphine (7). The polymerization of monomer (5) did not cause the isomerization and gave polymer 6 which consisted exclusively of phosphine oxide unit.



Results and Discussion

Polymerization of 5 was examined with cationic (No 1-10) anionic (No 11 and 12), and radical (No 13) initiators (TABLE 1). Only cationic initiators gave polymers (No 1-8). Chlorine containing Lewis acids (TiCl_4 and SnCl_4) did not yield polymer. With anionic and radical initiators monomer 5 remained unchanged under the reaction conditions.

Polymer (sample No 2) was a white powdery material (very hygroscopic) soluble in organic solvents like CHCl_3 , CH_2Cl_2 , DMSO, EtOH, CH_3OH , and water, hardly soluble in DMF, CH_3CN , PhCN, CH_3NO_2 and PhNO_2 but insoluble in organic solvents such as C_6H_6 , PhCH_3 and PhCl . The molecular weight of the polymer was 3860 determined by vapor pressure osmometry.

The structure of poly(phosphine oxide) 6 was established on the basis of the following data with the polymer sample No 6. The ^1H NMR spectrum (CDCl_3 with TMS) showed a broad signal at δ 1.4-2.3 due to three methylene protons (6H) and a broad multiplet at δ 7.1-7.9 due to aromatic protons (5H). The ^1H -decoupled ^{31}P NMR spectrum of the polymer in CHCl_3 showed only single peak at +39.8 ppm (lower magnetic field from 80% H_3PO_4 external standard), which was reasonably assigned to a phosphine oxide structure. Figure 1 shows expanded ^{13}C NMR spectra of the polymer (lower) and of diethylphenylphosphine oxide (upper) as an authentic sample of the polymer. The signal assignments are given in the figure. Both spectra show a similar signal pattern although the chemical shift of aliphatic carbons is, of course, somewhat

TABLE 1
 Polymerization of Deoxophostone (5)^a

No	Initiator (molar % for <u>5</u>)	Solvent	Temp. (°C)	Time (hr)	Polymer	
					Yield (%)	mol. wt. ^b
1	MeOTf (2.0)	CH ₂ Cl ₂	60	26	73	3440
2	MeOTf (2.0)	CHCl ₃	60	26	90	3860
3	MeI (2.0)	CHCl ₃	60	106	85	2800
4	PhCH ₂ Br (2.0)	CHCl ₃	80	87	64	1700
5	BF ₃ ·OEt ₂ (3.0)	PhCN	130	40	56	3300
6	BF ₃ ·OEt ₂ (3.0)	CH ₂ Cl ₂	60	46	73	3470
7	BF ₃ ·OEt ₂ (3.0)	none	60	41	56	3150
8	Et ₃ O ⁺ BF ₄ ⁻ (1.2)	CHCl ₃	60	25	50	2320
9	TiCl ₄ (2.0)	CHCl ₃	80	87	0	
10	SnCl ₄ (2.0)	CHCl ₃	80	87	0	
11	BuLi (3.0)	PhCN	130	36	0	
12	MeMgI (3.0)	diglyme	130	42	0	
13	AIBN (3.0)	PhCN	80	35	0	

a 5 = 1.0 mmol in 0.5 ml of solvent.

b Determined by vapor pressure osmometry in CHCl₃ at 35°C.

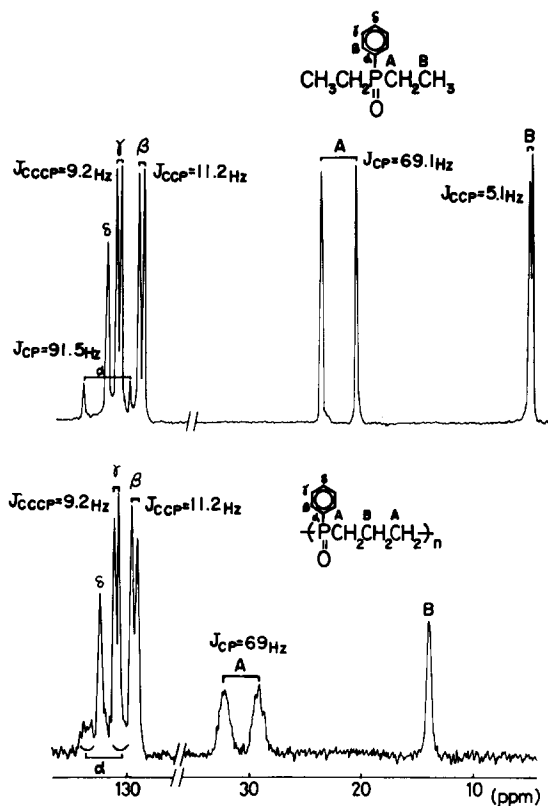


Figure 1. Expanded $^{13}\text{C}\{^1\text{H}\}$ FT-NMR spectra (22.6 MHz, CDCl_3 with TMS) of diethylphenylphosphine oxide (upper) and the polymer (lower).

different. It should be noted that the doublet-like signal of the polymer at +31.0 ppm due to PCH_2 has the coupling constant $J_{\text{CP}} = 69 \text{ Hz}$ which is very close to that of PCH_2 of the authentic sample. The same coupling constants were observed with β - and γ -carbons of the phenyl ring. The signal-broadening of the methylene and also the phenyl carbon atoms α to the phosphorus is probably due to the variety of the molecular weight. In the IR spectrum of the polymer (CHCl_3 solution) characteristic bands at 1440 cm^{-1} ($\nu_{\text{P-Ph}}$) and at 1170 cm^{-1} ($\nu_{\text{P=O}}$) were observed. Anal. Calcd for $[\text{C}_9\text{H}_{11}\text{OP} \cdot (\text{H}_2\text{O})_{0.65}]_n$: C, 60.77; H, 6.97; P, 17.41. Found: C, 61.58; H, 7.23; P, 16.45.

All the above data are taken to support the polymer

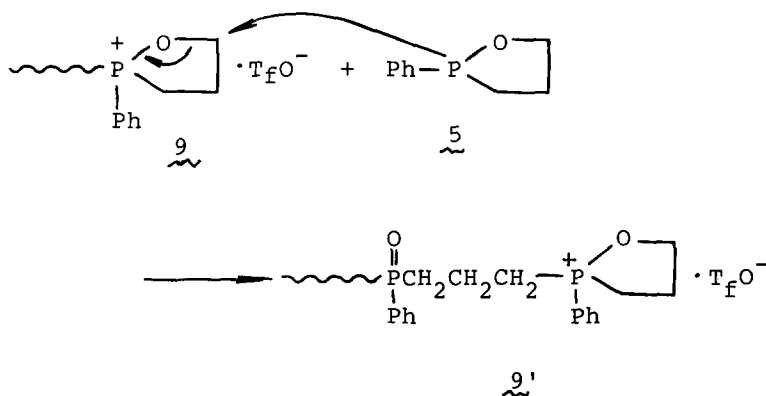
structure as poly(phosphine oxide) 6. Thus, the polymerization of deoxophostone 5 did not involve side reactions to yield, for example, an isomerized unit.

The polymerization scheme, therefore, is given with MeOTf catalyst as follows. The initiation step is a very fast process to form a cyclic phosphonium

Initiation



Propagation



species 8. The propagation is a nucleophilic attack of monomer 5 onto the propagating cyclic phosphonium species 9 via the Arbuzov type reaction to produce a unit of P-phenyl trimethylenephosphine oxide 9'. The present polymerization provides the first instance in the cationic ring-opening polymerization of cyclic phosphorus(III) compounds where the polymer of a clear-cut structure has been obtained.

The polymer 6 was subjected to the reduction with the HSiCl₃-Et₃N system analogously to the reported procedures for the reduction of phosphine oxides (FITZSCHE et al, 1965; NAUMANN et al, 1969). The structure of the reduced polymer was determined as polyphosphine 7 based on the spectroscopic data. The ³¹P NMR spectrum of the reduced polymer showed two signals; a signal at -26.5 ppm assignable to phosphine unit 7 and a small peak at +27.7 ppm whose structural

assignment has not been made yet. Therefore, the reduced polymer contained the phosphine unit 7 and a small portion of an unidentified unit (~15%). The optimization of the reduction conditions is the future problem. The polymer 7 is a pale-brown powdery material soluble in organic solvents such as CHCl_3 and CH_2Cl_2 . 7 was oxidized in solution under air.

Experimental.

Materials. Monomer (5) was prepared according to the reported procedure (GRAYSON and FARLEY, 1967); bp, 66-69°C (0.6 mm Hg); ^{31}P NMR (CDCl_3), +109 ppm; ^1H NMR, δ 1.4-2.5 (m, 4H), 3.6-4.3 (m, 2H), and 7.0-7.3 (m, 5H); IR, 1435 cm^{-1} ($\delta_{\text{P-Ph}}$) and 1170 cm^{-1} ($\nu_{\text{P-O-alkyl}}$).

Solvents of CH_2Cl_2 , CHCl_3 , PhCN, and diglyme were purified by distillation under nitrogen. Initiators were prepared or purified according to the ordinary procedures before use. A commercial reagent of HSiCl_3 was used without further purification.

Polymerization. A typical run was given as follows. A mixture of monomer 5 (1.0 mmol) and MeOTf initiator (0.02 mmol) was placed in 0.5 ml of CHCl_3 under nitrogen and kept at 60°C for 26 hr in a sealed tube. Then, the tube was opened and the reaction mixture was poured into a large amount of diethyl ether to precipitate the polymeric materials. This re-precipitation procedure was repeated twice. The polymer was separated and dried in vacuo to give 0.15 g (90% yield) of 6.

Reduction of Polymer. In a sealed tube a polymer sample 6 (0.2 mmol), HSiCl_3 and Et_3N (1.0 mmol each) were placed in 1.0 ml of CH_2Cl_2 and kept at 70°C for 36 hr. The system was heterogeneous during the reaction. The mixture was treated with 30% NaOH aqueous solution for 1 hr with stirring at room temperature. The CH_2Cl_2 layer was separated and the CH_2Cl_2 soluble portion was extracted twice from the aqueous part. The CH_2Cl_2 layer was dried on MgSO_4 , concentrated, and poured into diethyl ether to precipitate the polymeric material, which was obtained as a pale-brown powdery polymer 7 (85% yield after drying in vacuo). All the above procedures were carried out under nitrogen.

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Received and accepted February 12, 1981.