

NOTES

Synthesis and Polymerization of New Spirophosphoranes Having Five- and Six-Membered Rings

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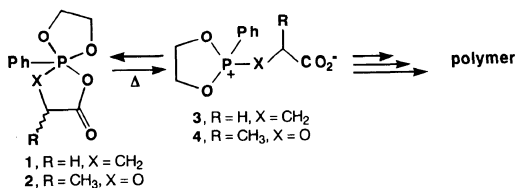
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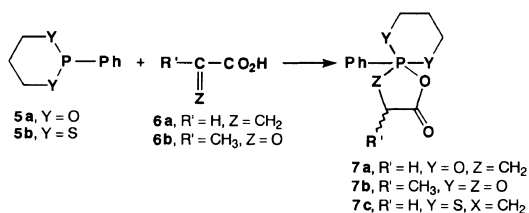
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Synthesis and polymerization of spiro-compounds have been extensively studied because some of these monomers and resulting polymers exhibit unique properties during polymerization. For instance, spiroortho-carbonate is a useful monomer which shows expansion in volume on polymerization.¹

On the other hand, various pentavalent spirophosphoranes have been synthesized because of interesting structures and polymerizabilities in the fields of organic phosphorus chemistry and polymer chemistry.^{2,3} We have already reported that the reaction of 2-phenyl-1,3,2-dioxaphospholane (five-membered cyclic phosponite) with acrylic acid or pyruvic acid gave the pentavalent spirophosphoranes **1** and **2**, respectively, having two five-membered rings.^{4,5} **1** and **2** can be isolated at a lower temperature. These compounds were in equilibrium with the zwitterions **3** and **4** upon heating, which led to the polymers by the Arbuzov-type reaction.^{6,7}



Spirophosphoranes possessing two different rings were prepared before,⁸ however, these were not used as a polymerization monomer. The present paper describes synthesis and polymerization of novel pentavalent spirophosphoranes **7a—c** having five- and six-membered rings, which were prepared by the reaction of six-membered cyclic phosponites **5a, b** with acrylic acid (**6a**) and pyruvic acid (**6b**).



EXPERIMENTAL

Materials

Six-membered cyclic phosponites **5a, b** were prepared according to the literatures.^{9,10} Acrylic acid (**6a**) and pyruvic acid (**6b**) were commercial reagents and were purified by distillation under reduced pressure. Solvents, diethyl ether, chloroform, and benzonitrile were purified in a usual manner under argon.

Preparation of 2-Oxo-5-phenyl-1,6,10-trioxa-5-phosphaspiro[4.5]decane 7a

Into 10 ml of diethyl ether containing 1.82 g (10 mmol) of 2-phenyl-1,3,2-dioxaphosphorinane (**5a**) was added 0.72 g (10 mmol) of **6a** in 10 ml of diethyl ether at room temperature under argon, and then the mixture was allowed to react at room temperature overnight. The resulting precipitate was separated by decantation, washed with a small amount of diethyl ether, and dried *in vacuo* to give 0.856 g (38% yield) of **7a**. IR (Neat): 1717 cm^{-1} ($\nu_{\text{C=O}}$), 1043 cm^{-1} ($\nu_{\text{P=O}}$). Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{O}_4(\text{H}_2\text{O})_{0.5}$: C, 54.75%; H, 6.08%. Found: C, 53.93%; H, 5.28%.

Preparation of 2-Oxo-3-methyl-5-phenyl-1,4,6,10-tetraoxa-5-phosphaspiro[4.5]decane 7b

Under argon **5a** (0.91 g, 3 mmol) and **6b** (0.44 g, 3 mmol) were mixed in diethyl ether (15 ml) at -78°C and allowed at -20°C for 4 days to precipitate the product. The precipitate was isolated by decantation and dried *in vacuo* to give 0.462 g (57% yield) of **7b**. IR (KBr): 1734 cm^{-1} ($\nu_{\text{C=O}}$), 1037 cm^{-1} ($\nu_{\text{P=O}}$). Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{O}_5\text{P}$: C, 53.33%; H, 5.56%. Found: C, 54.60%; H, 5.93%.

Preparation of 2-Oxo-5-phenyl-1-oxa-6,10-dithia-5-phosphaspiro[4.5]decane 7c

A mixture of 2-phenyl-1,3,2-dithiaphosphorinane **5b** (2.14 g, 10 mmol) and **6a** (0.72 g, 10 mmol) was allowed to react in 10 ml of diethyl ether at room temperature under argon for five days. The precipitate was isolated by decantation and the crude product was purified by recrystallization from chloroform. The resulting white crystalline material was separated by filtration and dried *in vacuo* to give 0.372 g (13% yield) of **7c**. IR (KBr): 1715 cm^{-1} ($\nu_{\text{C=O}}$), 1091 cm^{-1} ($\nu_{\text{P=O}}$). Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2\text{S}_2\text{P}$: C, 50.35%; H, 5.24%. Found: C, 50.47%; H, 5.48%.

Thermal Polymerization of Spirophosphoranes 7a-c

A typical example was as follows (entry 2 in Table II). **7a** (0.254 g, 1.0 mmol) was heated at 130°C in a sealed tube under argon. After 12 h, the product was dissolved in chloroform and the solution was poured into a large amount of diethyl ether to precipitate the polymeric material. The material was separated by decantation and dried *in vacuo* to give 0.216 g of the polymer (85% yield).

Measurements

^1H and ^{31}P NMR spectra were recorded on a 60 MHz JEOL FX-60Q spectrometer and 36.4 MHz JEOL FX-90Q NMR spectrometer, respectively. Gel permeation chromatographic (GPC) analysis was performed by using a Hitachi 655A apparatus with RI detectors under the following condition: Gelpack GL-A130 and A120 columns with chloroform eluent at a flow rate of 1.0 ml min^{-1} .

RESULTS AND DISCUSSION

Synthesis of Spirophosphoranes 7a-c

Reactions of a cyclic phosphorus compound (**5**) with acrylic or pyruvic acid (**6**) were carried out in diethyl ether to precipitate the spirophosphoranes **7a-c**. The yields of these compounds, however, were not so high, because **7a-c** were partly soluble in diethyl ether of the reaction solvent. All products precipitated were white crystalline materials. Their melting point (mp) and NMR data are listed in Table I. The ^1H NMR data of the reaction products support for the structures of spirophosphoranes **7a-c**. The chemical shifts of **7a-c** in the ^{31}P NMR spectra (H_3PO_4 external) are in accord with those of the phosphorane structures having a spiro-ring system.²

The reaction of **5b** with **6b** was attempted, however, formation of a spirophosphorane was not observed by ^{31}P NMR analysis of reaction mixture even at lower temperature like -20°C .

New Spirophosphorane

Table I. Synthesis of spirophosphoranes **7a–c**

Substrates	Products	Yield ^a	mp	¹ H NMR and ³¹ P NMR (CDCl ₃)
		%	°C	
5a + 6a	7a	38	93–94	¹ H NMR δ 1.76 (m, C–CH ₂ –C, 2H), 2.56 (br, P–CH ₂ CH ₂ –C, 4H), 3.92 (br, O–CH ₂ , 4H), 7.42 (m, P–C ₆ H ₅), ³¹ P NMR δ –13.0
5a + 6b	7b	57	95–98	¹ H NMR δ 1.51 (d, CH ₃ , 3H, J _{HCC} = 6 Hz), 2.10 (m, C–CH ₂ –C, 2H), 4.09 (m, O–CH ₂ , 4H), 4.68 (m, CH, 1H), 7.38 (m, P–C ₆ H ₅ , 5H), ³¹ P NMR δ –35.1
5b + 6a	7c	13	209–212	¹ H NMR δ 1.60–3.40 (m, CH ₂ , 10H), 7.20–8.20 (m, P–C ₆ H ₅ , 5H), ³¹ P NMR δ –20.2

^a Isolated yield.

Table II. Thermal polymerization of spirophosphoranes **7a–c**^a

Entry	Monomer	Solv	Temp/°C	Time/h	Yield/% ^b	M _c ^c
1 ^d	7a	PhCN	150	19	62	< 1000
2	7a		130	12	85	1500
3	7a		150	100		2400 ^e
4	7b		100	19	24	2100
5 ^d	7c	CDCl ₃	150	87	0	
6	7c		150	24	0	
7	7c		220	100	Decomp.	

^a 1 mmol of monomer was heated under argon.

^b Diethyl ether-insoluble part.

^c Determined by GPC with chloroform at 40°C.

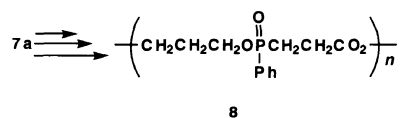
^d 0.5 mmol of monomer in 0.7 ml of solvent.

^e Without precipitation.

Thermal Polymerization of Spirophosphoranes **7a–c**

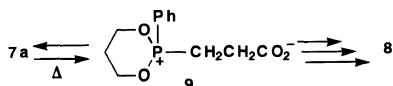
Thermal polymerization of the spirophosphorane **7a** was carried out upon heating above melting point of **7a**. Polymerization results are given in Table II. When the thermal polymerization of **7a** was carried out at a higher temperature like 150°C, the molecular weight of the polymer became up to 2400 (entry 3). In case of the solution polymerization in PhCN, however, the molecular weight was low (entry 1). The structure of the product polymer was determined by ¹H and ³¹P NMR spectroscopies; ¹H NMR (CDCl₃) δ 1.90 (br, C–CH₂–C, 2H), 2.33 (br, P–CH₂CH₂–C, 4H), 4.06 (br, O–CH₂, 4H), 7.52 (br, P–C₆H₅, 5H); ³¹P NMR (CDCl₃) δ +43.4. All these data

can be taken to support the polymer structure of **8**.

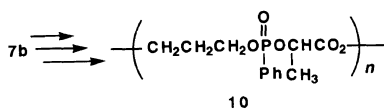


The thermal polymerization of **7a** probably involves a zwitterion intermediate **9**, which is in equilibrium with **7a** with heating above melting point of **7a**. The polymerization proceeds through the Arbuzov-type ring-opening reaction of phosphonium ring by the attack of carboxylate group of another zwitterion to yield polymer **8**. The ³¹P NMR spectrum of the polymerization system *in situ* showed a small peak at δ +58.7 ascribable to

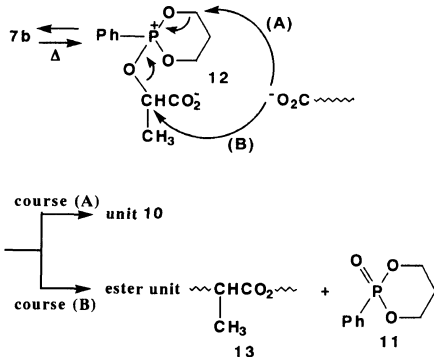
zwitterion species like **9** in addition to the main signal due to the polymer.



Thermal polymerization of **7b** also took place upon heating. The structure of the product polymer after precipitation from diethyl ether was determined as **10** by ^1H and ^{31}P NMR spectroscopies; ^1H NMR (CDCl_3) δ 1.52 (br, CH_3 , 3H), 2.10 (br, $\text{C}-\text{CH}_2-\text{C}$, 2H), 4.27 (br, $\text{O}-\text{CH}_2$, 4H), 5.20 (br, CH , 1H), 7.53 (br, $\text{P}-\text{C}_6\text{H}_5$, 5H); ^{31}P NMR (CDCl_3) δ +19.3.



However, ^{31}P NMR of the product before precipitation showed two peaks at δ +19.3 and +15.2. The former is ascribed to polymer **10** and the latter is due to 2-phenyl-2-oxo-1,3,2-dioxaphosphorinane (**11**). In addition, a very small signal at δ +60.2 was also observed, which is assignable to zwitterion species such as **12**. In order to explain the formation of **11** besides **10**, the following mechanism was proposed. The first step is the formation of the zwitterion **12** upon heating. The attack *via* course (A) gives polymer unit **10**, and **11** is produced by the attack *via* course (B) together with the generation of poly(α -ester) **13**.



From integration ratio of the two peaks in the ^{31}P NMR spectrum of the product, the ratio between the unit **10** (m) and the ester unit **13** (n) was determined as 2:3. The polymer composed from only the unit **10** was isolated by precipitation from diethyl ether; oligomeric products having units **10** and **13** ($M_n=400$) were soluble in diethyl ether.

Thermal polymerization of **7c** at 150°C in CDCl_3 or bulk did not take place; **7c** was recovered unchanged (entries 5 and 6). This may be because of so high melting point of **7c** ($209\text{--}212^\circ\text{C}$). Even at a higher temperature like 220°C (entry 7), the polymerization of **7c** was not observed. The ^{31}P NMR spectrum of the reaction mixture showed several peaks at around δ 0~+50 due to unidentified structures, indicating the decomposition of **7c**.

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