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The Ring-opening Polymerization of Cyclic Aminophosphinites

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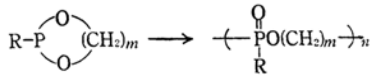
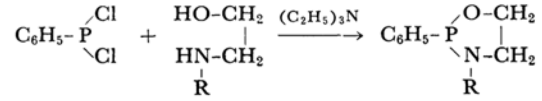
A further study of 1, 3-addition-type ring-opening polymerization has been attempted by using cyclic *N*-phenyl- and *N*-methylethyleneamino phenylphosphinites as monomers, each of those has a nitrogen atom in place of one of the two oxygen atoms in the ring structure of a cyclic phosphonite. They were prepared from phenylphosphonous dichloride and *N*-phenyl- and *N*-methylaminoethanols. The ring-opening 1, 3-addition reaction of the *N*-phenyl derivative with benzyl bromide, as a model experiment for the polymerization, has been found to proceed smoothly, giving the desired adduct, which in turn gave benzylphenylphosphinic acid and *N*, *N'*-diphenylpiperadine on hydrolysis. These cyclic aminophosphinites were then polymerized to give the expected poly(aminophosphine oxide)s in the presence of Arbusov reaction-type reagents or in the absence of a catalyst at elevated temperatures.

A previous paper[1] has shown that the 1, 3-addition-type ring-opening polymerization of cyclic phosphonites affords polyphosphinates in the manner shown in the following equation:



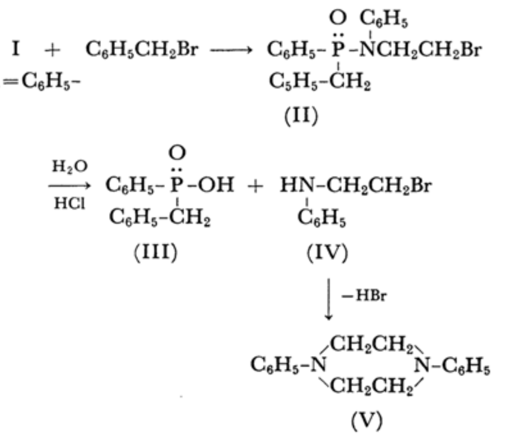
This paper will report as a further study of this type of polymerization of cyclic aminophosphinites, which are, structurally, cyclic amides of phosphonous acid.

Cyclic *N*-phenyl- and *N*-methylethyleneamino phenylphosphinites (3-substituted 2-phenyl-1, 3, 2-oxazaphospholidine) (I) were prepared from phenylphosphonous dichloride and the corresponding *N*-substituted aminoethanols by using triethyl amine as the condensing agent:



(I)

In order to confirm the possibility of the ring opening polymerization, the reaction of *N*-phenylethyleneamino phenylphosphinite with benzyl bromide was carried out. When they were refluxed in toluene, an undistillable, oily substance resulted. The hydrolysis of this substance in concentrated hydrochloric acid at the refluxing temperature gave benzyl-phenylphosphinic acid (III) in a yield of 78% as the precipitate. When the filtrate was neutralized with an aqueous sodium hydroxide solution after the filtration of III, *N*, *N'*-diphenylpiperadine (V) was obtained in a 17% yield. The piperadine might be formed by the condensation of 2 mol of the *N*-β-bromoethylaniline (IV) initially produced. The isolation of these two products, III and V, shows that the undistillable, oily substance is evidently *N*-β-bromoethylanilino-benzyl-phenylphosphine oxide (II), which appears to be formed by the Arbusov reaction,[2] the 1, 3-addition-type ring-opening reaction, as expected:



The results suggest that the cyclic aminophosphinites would afford poly(aminophosphine oxide)s by the 1, 3-addition-type ring-opening polymerization when they are polymerized in the presence of an Arbusov-reaction-type reagent, such as alkyl halide. Analogous to the case of the cyclic phosphonite, no noticeable polymerization occurred at room temperature when the cyclic aminophosphinites were treated with methyl iodide; however,

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[1] T. Mukaiyama, T. Fujisawa, Y. Tamura and Y. Yokota, *J. Org. Chem.*, **29**, 2572 (1964).

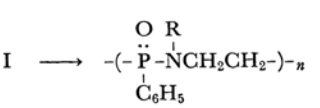
[2] M. Grayson and E. J. Griffith, "Topics in Phosphorus Chemistry," Vol. I, Interscience Pub., New York, N. Y. (1964), p. 57.

TABLE 1. RING OPENING POLYMERIZATION OF CYCLIC AMINOPHOSPHINITES

R	Catalyst	Reaction		Yield %	Mp (Decomp. p.)	$\eta_{inh}^{30°C}$*	Analysis N, %
		Time, hr	Temp. °C				
C_6H_5-	CH_3I	25	100	64	72—78(275)	0.04	Found 5.93 Calcd. 5.76
C_6H_5-	$(CH_3)_2SO_4$	25	150	50	56—65(292)	0.03	Found 5.67
C_6H_5-	None	25	180	85	63 (284)	0.03	Found 6.03
CH_3-	CH_3I	25	150	88	68 (265)	0.04	Found 7.16 Calcd. 7.73
CH_3-	None	25	180	80	55 (250)	0.03	Found 6.99
CH_3-	$BF_3O(C_2H_5)_2$	10	150	85	62 (258)	0.03	Found 7.61

* $\eta_{inh}^{30°C}$ = Inherent viscosities were measured in chloroform for phenyl derivative and in dimethylformamide for methyl derivative.

oily polymers resulted when they were heated at 150°C. After volatile materials have been removed from the oily polymers, brittle, glass-like polymers were obtained. The structure of the polymers was confirmed to be poly(aminophosphine oxide)s (VI) by means of their infrared spectra, which showed a new absorption peak at 1260 cm⁻¹ attributable to phosphoryl stretching vibration.



$$\mathrm{I} \longrightarrow -(-\overset{\overset{O}{\cdot\cdot}}{\underset{C_6H_5}{P}}-\overset{R}{N}CH_2CH_2-)-_n$$

(VI)

Furthermore, it was established that the poly(aminophosphine oxide)s were also formed by heating the aminophosphinites at 150°C with such a cationic catalyst as boron trifluoride etherate, or at a more elevated temperature, 180°C, without such a catalyst. The conditions of the polymerization and the physical properties of these poly(aminophosphine oxide)s produced are shown in Table 1.

These polymers resemble the polyphosphinate obtained from the polymerization of the cyclic phosphonite previously reported in that the inherent viscosities of the polymers are relatively low and in that thay are flame-proof substances, which change to tacky materials when left exposed to the air.

Poly (*N*-phenylethyleneamino-phenylphosphine oxide) is soluble in chloroform and dimethylformamide, but poly(*N*-methylethyleneamino-phenylphosphine oxide) is soluble only in dimethylformamide. They are insoluble in other organic solvents and in water.

Experimental

Anilinoethanol. This compound was prepared from aniline and ethylene oxide following the procedure of Demole.³⁾

***N*-Methylaminoethanol.** This compound was prepared from methylamine and ethylene oxide following the procedure of Knorr and Matthes.⁴⁾

***N*-Phenylethyleneamino Phenylphosphinite (I).** —Into a solution of 6.9 g (0.05 mol) of anilinoethanol and 11.1 g (0.11 mol) of triethylamine in 30 m*l* of dry benzene, there was stirred, drop by drop, a solution of 9.0 g (0.05 mol) of phenylphosphonous dichloride in 20 m*l* of dry benzene under cooling in an ice-water bath. Then the reaction mixture was refluxed on a water bath for 1 hr, and the triethylamine hydrochloride which thus precipitated was filtered off. After the benzene had been removed from the filtrate, *N*-phenylethyleneamino phenylphosphinite was distilled off. This product was solidified at room temperature and recrystallized from ether; yield, 6.1 g (50%); bp 150—153°C/0.13 mmHg; mp 78—81°C.⁵⁾

Its infrared absorption bands are at 1600(ms), 1500(s), 1330(s), 1130(ms), 1090(m), 1020(ms), 950 (ms), 930(s), 750(s), 700(ms), and 680(ms) cm⁻¹.

N-Methylethyleneamino phenylphosphinite was prepared from *N*-methylaminoethanol and phenylphosphonous dichloride in the same way as *N*-phenylethyleneamino phenylphosphinite; yield, 41%; bp 80—87°C/ 0.5 mmHg.⁵⁾ Its infrared absorption bands are at 2950(ms), 2850(ms), 1440(ms), 1210(m), 1090(m), 1060(m), 1040(s), 980(s), 915(s), 750(s), and 700(s) cm⁻¹.

The Reaction of *N*-Phenylethyleneamino Phenylphosphinite with Benzyl Bromide. A solution of 3.6 g (0.015 mol) of *N*-phenylethyleneamino phenylphosphinite and 2.6 g (0.015 mol) of benzyl bromide in 10 m*l* of dry toluene was refluxed in an oil bath for 6 hr. After the toluene had then been removed, an undistillable, oily substance resulted (Found: N, 3.58%. Calcd for $C_{21}H_{21}BrNOP$: N, 3.38%). Then, a mixture of this substance and 20 m*l* of concentrated hydrochloric acid was refluxed in an oil bath for 5 hr. Benzyl-phenylphosphinic acid was precipitated on cooling; it was collected by filtration and recrystallized from ethanol; yield, 2.7 g (78%); mp 180—182°C.

Found: C, 65.10; H, 5.81; P, 14.0%. Calcd for $C_{13}H_{13}O_2P$: C, 67.24; H, 5.64; P, 13.3%.

Its infrared absorption bands are at 1600(m), 1450(m),

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3) E. Demole, *Ann.*, **173**, 127 (1874).

4) L. Knorr and H. Matthes, *Ber.*, **31**, 1069 (1898).

5) T. Mukaiyama and Y. Yokota, This Bulletin, **38**, 858 (1965).

1440(ms), 1250(m), 1140(s), 1070(ms), 960(s), 780(ms), and 700(ms) cm^{-1}.

After the filtrate had been neutralized with an aqueous solution of sodium hydroxide, a dark, oily substance was separated and extracted with chloroform. Then the extract was dried over calcium chloride, and the chloroform was removed. *N*, *N'*-Diphenylpiperadine was solidified and recrystallized from ethanol; yield, 0.3 g (17%); mp 156—160°C.

The Polymerization of *N*-Phenylethyleneamino Phenylphosphinite. One gram of *N*-phenylethyleneamino phenylphosphinite was polymerized by heating it with a catalytic amount of methyl iodide under nitrogen for 25 hr at 150°C. Poly(*N*-phenylethyleneamino-phenylphosphine oxide) was obtained after a volatile material had been removed from the resulting residue at 150°C at 0.1 mmHg. The infrared absorption bands are at 3050(m), 2950(m), 1600(s), 1500(s), 1440(ms), 1260(ms), 1230(s), 1200(s), 1120(s), 1030(m), 950(ms), 750(s), and 700(s) cm^{-1}. Its inherent viscosity was measured in chloroform. Other polymerizations of the aminophosphinite were carried out in the same manner as described above under the reaction conditions indicated in Table 1.

N-Methylethyleneamino phenylphosphinite was polymerized in the same way as the *N*-phenyl derivative. The *N*-methyl derivative was also polymerized by heating it at 150°C for 10 hr in the presence of boron trifluoride etherate; the resultant poly(*N*-methylethyleneamino-phenylphosphine oxide) has an inherent viscosity in dimethylformamide of 0.03.

Found: C, 59.21; H, 6.97; N, 7.61%. Calcd for $(C_9H_{12}NOP)_n$: C, 59.66; H, 6.68; N, 7.73%.
The infrared absorption bands of the polymer are at 2950(ms), 1440(ms), 1260(ms), 1220—1120 broad(s), 1020(ms), 940(ms), 900(m), 750(s), and 700(ms) cm^{-1}.

The catalysts, yields, physical properties, inherent viscosities, and results of the nitrogen analysis of the poly(aminophosphine oxide)s obtained are listed in Table 1.