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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

## Synthesis and Polymerization of Spiro Oxyphosphoranes

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**To cite this Article** Saegusa, Takeo and Kobayashi, Shiro(1979) 'Synthesis and Polymerization of Spiro Oxyphosphoranes', *Journal of Macromolecular Science, Part A*, 13: 3, 295 – 309

**To link to this Article:** DOI: 10.1080/00222337908068104

**URL:** <http://dx.doi.org/10.1080/00222337908068104>

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## Synthesis and Polymerization of Spiro Oxyphosphoranes

TAKEO SAEGUSA and SHIRO KOBAYASHI

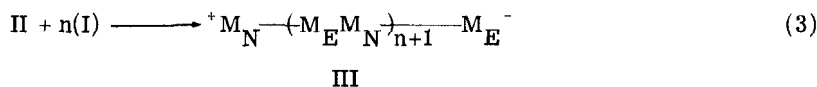
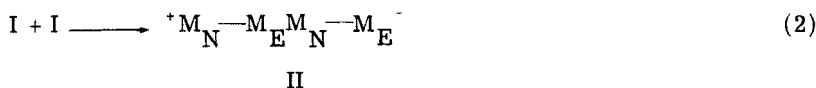
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### ABSTRACT

Novel methods of synthesis of spiro acyloxyphosphoranes are described emphasizing the significance of the first isolated instance of these new species. Then, the no-catalyst alternating copolymerizations of the combinations of cyclic phosphorus(III) compounds (serving as nucleophilic monomer,  $M_N$ ) with acrylic acid derivatives and with  $\alpha$ -keto acids (electrophilic monomer,  $M_E$ ) are mentioned. These copolymerizations proceed without added initiator. Spiro oxyphosphoranes play an important role in the copolymerization scheme in the equilibrium with the  $^+M_N - M_E^-$  zwitterion, the key intermediate of the copolymerization. Finally, new reactions of spiro acyloxyphosphoranes with nucleophiles, alcoholysis and aminolysis polymerizations are presented.

## INTRODUCTION

In recent years we have explored a new type of alternating copolymerization between a nucleophilic monomer ( $M_N$ ) and an electrophilic one ( $M_E$ ), which takes place, in most cases by heating, without added initiator [1-6]. In these copolymerizations the combination of  $M_N$  and  $M_E$  is the most important factor for the alternating copolymerization, i. e., a key intermediate is the zwitterion I which is formed from  $M_N$  and  $M_E$  and which takes part in both initiation [Eq. (2)] and propagation [Eq. (3)].



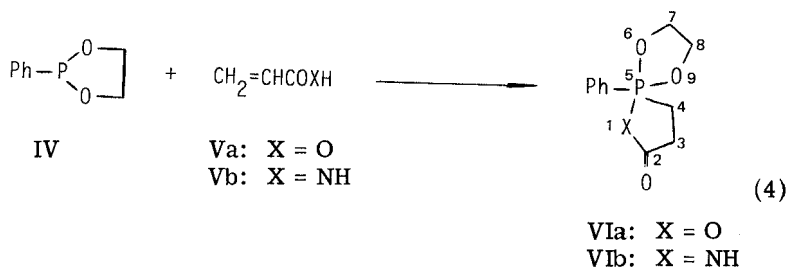
Several  $M_N$  monomers have successfully been adopted. They are cyclic imino ethers, 2-iminotetrahydrofuran, azetidene, Schiff base, 2-imino-1,3-dioxolane, and cyclic phosphorus compounds. During the course of our studies employing cyclic phosphorus compounds as  $M_N$  we have developed novel methods of synthesis of cyclic acyloxyphosphoranes, a new class of phosphorus compounds. This paper focuses on the syntheses of new oxyphosphoranes, mainly of cyclic acyloxyphosphoranes, and on the polymerizations involving these phosphoranes as intermediates or monomers. Thus, several new phosphorus-containing polymers were prepared.

## RESULTS AND DISCUSSION

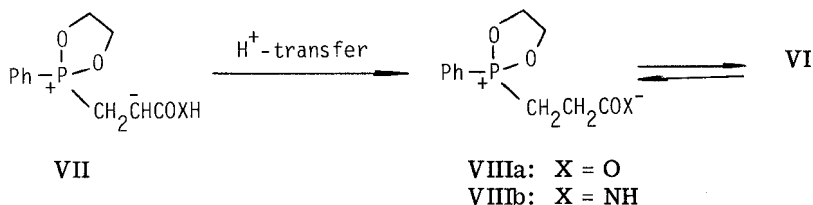
Synthesis of Spiro Oxyphosphoranes

An equimolar mixture of 2-phenyl-1,3,2-dioxaphospholane (IV) and acrylic acid (Va) was allowed to stand at 25°C for 15 hr in diethyl

ether to give needlelike crystals (mp 80°C) in a 92% isolated yield. The chemical structure of the crystalline product was established as 2-oxo-5-phenyl-1,6,9-trioxa-5-phosphaspiro[4,4]nonane (VIa). Similarly, the reaction of IV with Vb in acetonitrile at 50°C for 25 hr

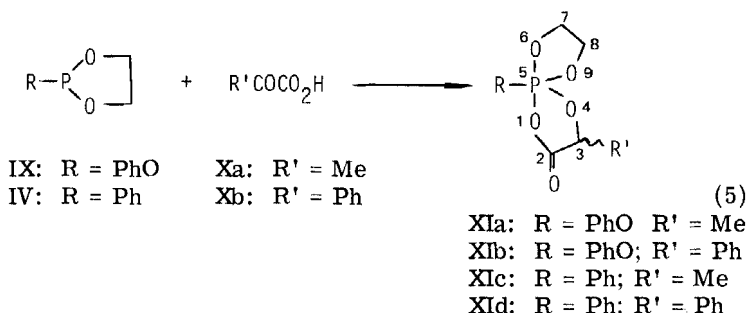


gave also a crystalline product (71% yield, mp 158°C) whose structure was shown to be VIb, a 1-aza derivative of VIa [7]. The reaction [Eq. (4)] is well explained in the following scheme; i. e., a phosphonium-carbanion intermediate (VII) is first formed and converted to a zwitterion (VIII) by hydrogen transfer, and then VIII becomes VI by cyclization.



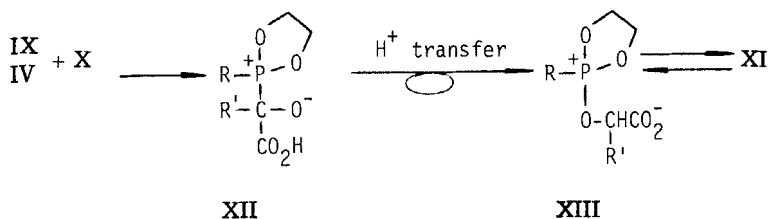
It is the first time pentacovalent cyclic acyloxy- and amido-phosphoranes, VIa and VIb, have been isolated. 5-Oxo-1,2-azaphospholidine in VIb is a new ring system which has not been known.

Another new group of spiro acyloxyphosphoranes were synthesized by the employment of  $\alpha$ -keto acids (X) such as pyruvic acid [Eq. (5)] [8]. A mixture of 2-phenoxy-1,3,2-dioxaphospholane (IX) and pyruvic acid (Xa) (3 mmole each) in 20 ml of diethyl ether was kept at room temperature for 15 hr and further at -20°C for 2 weeks to crystallize the product. The crystalline material (mp 87°C) was isolated in 31% yield (0.25 g). The structure of 2-oxo-3-methyl-5-phenoxy-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (XIa) has been established by  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR, IR, and elemental analysis data. A lower isolated yield of XIa was not due to the lower extent of reaction but due to the

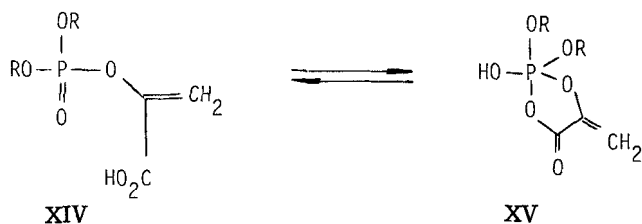


relative difficulty of crystallization process of pentaoxyphosphorane (XIa). Optimization of the crystallization of product would improve the yield. In similar ways, acyl penta- (XIb) and tetraoxyphosphoranes (XIc and XId) were isolated and characterized.

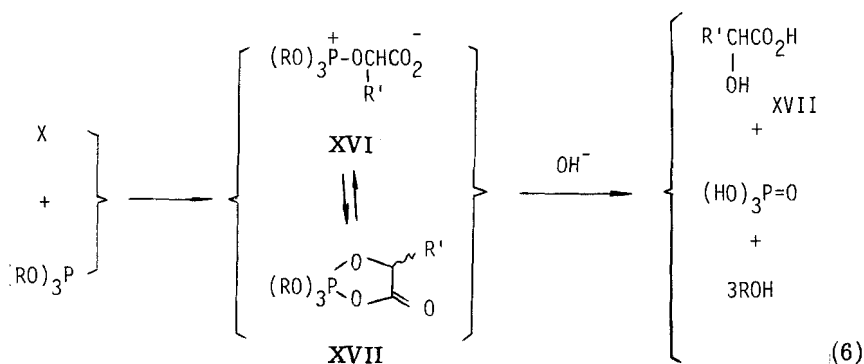
The reaction [ Eq. (5) ] of the synthesis of XI also involves a hydrogen-transfer process of  $\alpha$ -keto acid. It is not well understood at present whether the phosphorus of IX of IV attacks on the carbonyl oxygen or the carbonyl carbon atom. Probably the carbonyl carbon is the first reaction site to yield a phosphonium-oxy anion (XII). Then, XII rearranges with a hydrogen transfer process to a more stable phosphonium-carboxylate zwitterion (XIII) leading to spiro acyloxyphosphorane XI. The equilibrium between XI and XIII has actually been observed.



The chemistry of pentavalent phosphorus compounds is currently one of the most exciting fields of research [ 9-11 ]. These species are closely related to the biologically important phosphate ester reactions [ 10 ]. For example, a cyclic acylphosphorane (XV) is strongly implicated as an intermediate in the hydrolysis of phosphoenolpyruvate (XIV) [ 12, 13 ]. However, cyclic acyloxyphosphoranes, such as XV have not yet been isolated. New reactions [ Eqs. (4) and (5) ] presented in this paper, therefore, are quite significant, providing new methods for preparing spiro acyloxyphosphoranes, VIa and XI, which were not accessible by other methods.



One of application of phosphite- $\alpha$ -keto acid reactions [e. g., Eq. (5)] for syntheses was shown in the selective reduction of  $\alpha$ -keto acids to  $\alpha$ -hydroxy acids [14]. It has been found that cyclic and acyclic phosphites generally reduce  $\alpha$ -keto acids (X) to the corresponding  $\alpha$ -hydroxy acid. The reaction takes place at the oxygen atom of carbonyl group. The products of zwitterion type XVI and/or acyloxyphosphorane XVII hydrolyzed with 2 N NaOH solution at 50°C for 8 hr. The reduced



a, R' = CH<sub>3</sub>; b, R' = CH<sub>2</sub>CO<sub>2</sub>H; c, R' = (CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H; d, R' = Ph

products, XVIII from X, were isolated in a free or metal salt form. The results (Table 1) indicate that the reaction (6) is a quite versatile and selective reduction of X to XVIII by means of phosphites as reducing agents.

### Polymerization Involving Spiro Oxyphosphoranes

As described in the above, spiro oxyphosphoranes were produced by the reactions of cyclic phosphorous compounds, cyclic phosphonite IV and phosphite IX with acrylic acid, acrylamide and  $\alpha$ -keto acids.

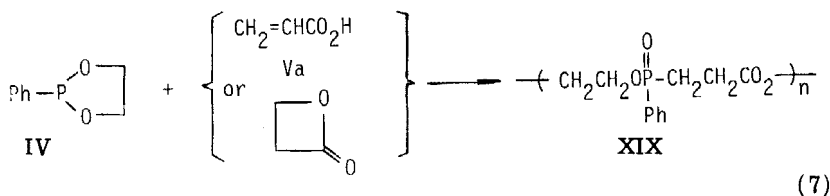
TABLE 1. Reduction of X to XVIII by Phosphite

Reaction	Yield of XVIII (%)	
	(EtO) <sub>3</sub> P	IX
Xa - XVIIIa	94	99
Xb - XVIIIb	-	78
Xc - XVIIIc	67	59
Xd - XVIIId	90	60

It was also found that spiro oxyphosphoranes play a very important role in the alternating co- and ter-polymerizations involving cyclic phosphorous compounds. These polymerizations are normally induced by heating. Furthermore, a new type of polymerization of spiro acyloxyphosphoranes was found, i. e., the polymerization by a stoichiometric amount of nucleophiles such as alcohol and amine.

### Thermally Induced Ionic Polymerization

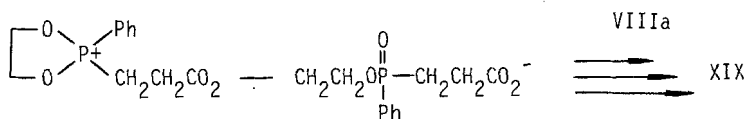
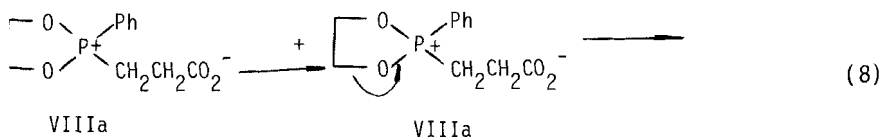
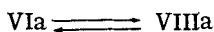
A mixture of cyclic phosphonite IV and acrylic acid Va was allowed to stand at a higher temperature, e. g., 140°C, in benzonitrile. The system became viscous. After 60 hr the usual work-up gave a resinous polymer in 46% yield. The molecular weight was 4370 by VPO measurement. The structure of the copolymer was established as polyphosphinate XIX in which IV and Va were incorporated in a 1:1 alternating arrangement [ 15].



In the copolymerization [ Eq. (7) ],  $\beta$ -propiolactone could be used instead of Va to give copolymer of the same structure XIX. A common intermediate of zwitterion VIIIa has been postulated in both cases with acrylic acid and with  $\beta$ -propiolactone.

VIIIa is probably in equilibrium with phosphorane VIa. The

equilibrium goes toward VIa at lower temperature. Under polymerization conditions of higher temperatures above 100°C, an equimolar mixture of IV and acrylic acid or  $\beta$ -propiolactone produced VIIa and VIa in situ, and the polymerization proceeded via VIIa.

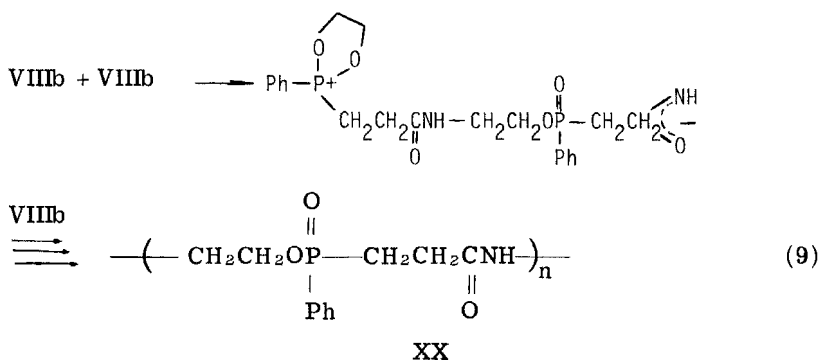
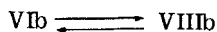


In the scheme (8), spiro oxyphosphorane VIa may be regarded as a monomer. Oxyphosphorane VIa was actually isolated and subjected to polymerization at higher temperatures (Table 2). Polymer XIX was produced quantitatively. Similarly, a pentavalent spiro oxyaza-phosphorane VIb isolated from acrylamide Vb and IV, was used as "monomer" (Table 2) [ 15] in relation to the copolymerization of IV and Vb. The structure of XX was established for the "homopolymer" of VIb, which was the same as the 1:1 alternating copolymer of IV (as  $M_N$ ) and Vb (as  $M_E$ ).

TABLE 2. Polymerization of Spiro Oxyphosphoranes VIa and VIb

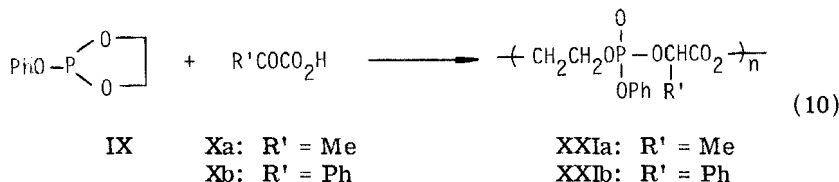
Monomer (2.0 mmole)	Solvent (ml)	Temp (°C)	Time (hr)	Mol. wt.	Softening point (°C)	Polymer structure
VIa	DMF (0.2)	150	9	650		XIX
VIa	.	150	6	2090	45-55	XIX
VIa	.	160	5	3430		XIX
VIb	DMF (0.2)	150	31	530		XX
VIb		150	3.5	1180	85-90	XX
VIb		160	3	1880		XX





In the scheme (9) the acid amide anion, an ambident anion, reacts at nitrogen as has been shown by the established structure of the product polymer.

The combination of IX ( $M_N$ ) and X ( $M_E$ ) gave copolymer at higher temperatures, e. g.,  $> 100^\circ\text{C}$ .



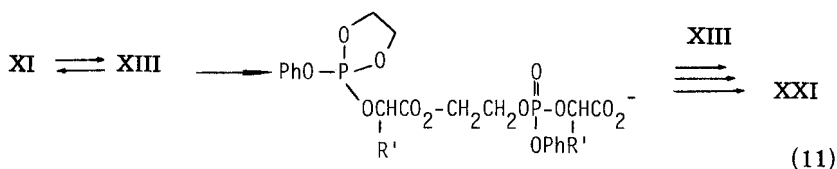
The structure of copolymer was that of 1:1 alternating arrangement (XXI). It is a type of polyphosphate [16]. Representative results of polymerization are shown in Table 3. In relation to the IX ( $M_N$ )-X ( $M_E$ ) copolymerization, the "homopolymerization" of XIa was examined. In the polymerization without solvent, polymer was obtained quantitatively (Table 3).

The homopolymerization is explained by the scheme (11). Phosphorane XI and zwitterion XIII are equilibrated with each other. Two moles of XIII gave dimeric zwitterion which grows to polymer XXI by its successive reaction with XIII.

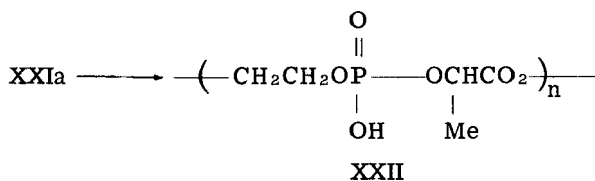
The product polymer XXI has a phosphoric acid triester structure. There are some biopolymers having polyphosphoric acid diesters.

TABLE 3. Alternating Copolymerization of IX ( $M_N$ ) with X ( $M_E$ )

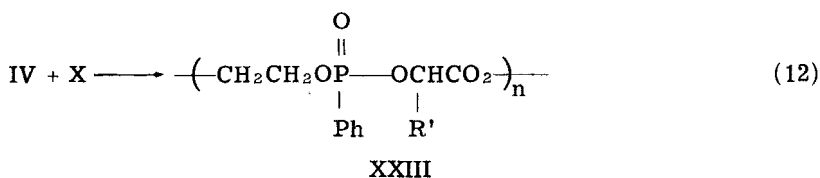
$M_E$	Solvent	Temp. ( $^{\circ}\text{C}$ )	Time (hr)	Copolymer yield (%)	Copolymer structure	Mol. wt.
Xa	PhCN	130	40	80	XXIa	3870
Xa	PhCH <sub>3</sub>	130	48	55	XXIa	7500
Xb	PhCN	130	21	41	XXIb	1610
Xb	PhCH <sub>3</sub>	130	21	57	XXIb	3740
XIa		120	24	100	XXIa	4100

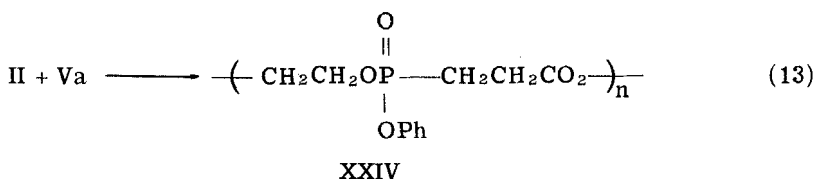


For the synthesis of a model, the conversion of XXI into diester XXII was attempted by hydrolysis and hydrogenolysis. Selective cleavage of phenoxy group of XXIa to XXII was realized by catalytic hydrogenation with platinum oxide.



In relation to copolymerizations of Eqs. (7) and (10), two alternative combinations of  $M_N$  and  $M_E$ , i. e., IV-X and IX-Va were examined. In both cases polyphosphonates XXIII and XXIV were produced [17].





Thus, with a variety of combinations, new synthetic methods of polyphosphate, polyphosphonate, and polyphosphinate [as shown in Eqs. (7)-(12)] have been explored.

Without added initiator, the cyclic phosphonite of IV was copolymerized with electron-deficient vinyl monomers such as methyl acrylate (SSVa), phenyl vinyl ketone (XXVb), methyl vinyl ketone (XXVc), and acrylonitrile (XXVd). Three  $M_E$  monomers, XXVa-SSVc, gave 1:1 alternating cooligomers XXVI-XXVIII [18]. The cooligomer from 1:1 feed of IV and XXVd, however, was not of the 1:1 composition.

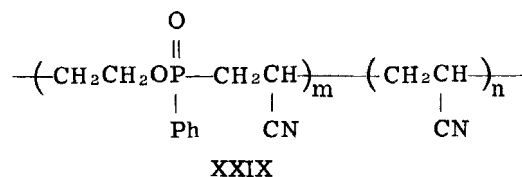
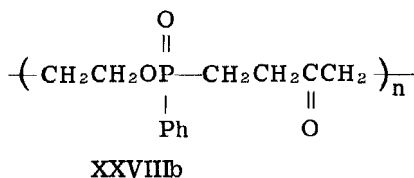
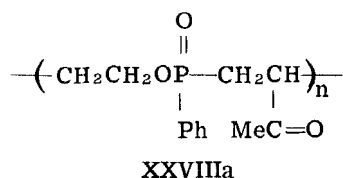
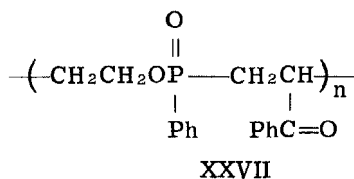
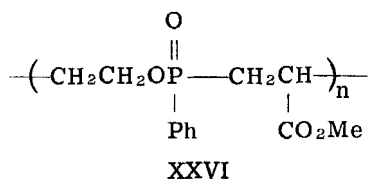
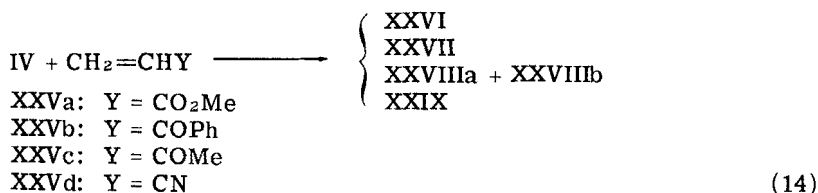
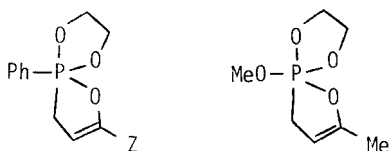


TABLE 4. Polymerization of Spiro Oxyphosphoranes, XXXa and XXXb

Phosphorane (20 mmole)	Solvent (DMF) (ml)	Temp. (°C)	Time (hr)	Polymer yield (%)	Mol. wt.	Polymer structure
XXXa	0.5	130	100	12	901	XXVI
XXXa	0.5	200	5	57	1430	XXVI
XXXa	0.5	130	70	62	1350	XXVI
XXXb	0.5	130	200	11	1200	XXVII

The units of XXVd were incorporated in excess as given by XXIX.

As to the 1:1 alternating copolymerizations of IV with XXVa-XXVc, corresponding adducts of spiro oxyphosphoranes were actually isolated. Spiro oxyphosphoranes XXXa (107-111°C 0.04 Torr) and XXXb (mp 131°C) were prepared and used as "monomer" for the synthesis of polyphosphinates (Table 4) [18]. In the XXVe system, an analogous spiro oxyphosphorane XXXI has already been reported [19].

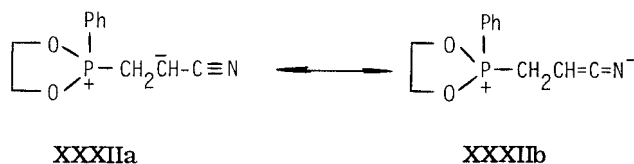


XXXa: Z = OMe

XXXI

XXXb: Z = Ph

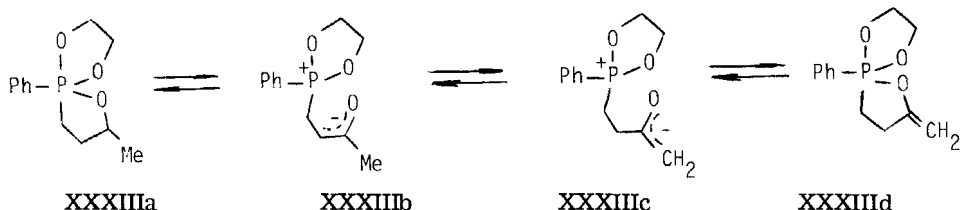
In the combination of IV and XXVd, the corresponding phosphorane was not obtained. This is probably due to the difficulty of cyclization of a zwitterion XXXIIa because the anionic part ( $-\text{CH}_2\text{CH}=\text{C}\equiv\text{N} \longleftrightarrow -\text{CH}_2-\text{CH}=\text{C}=\text{N}^-$ ) is linear.



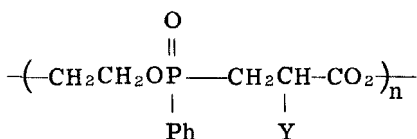
XXXIIa

XXXIIb

In the copolymerization of IV with methyl vinyl ketone, the production of two kinds of unit XXVIIIa and XXVIIIb is understood by assuming two kinds of zwitterions XXXIIIb and XXXIIIc.

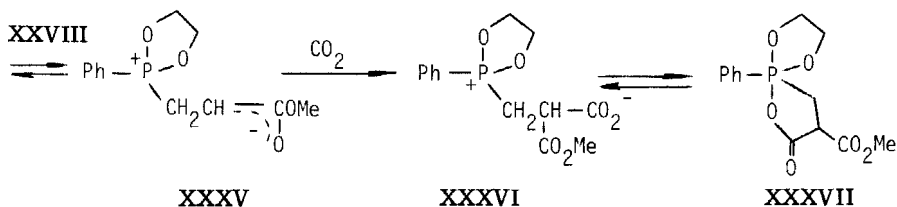


The above 1:1 alternating copolymerization was extended to the 1:1:1 alternating terpolymerization by utilizing specific reactivity of the intermediate zwitterion and phosphorane [20]. The combinations are IV-XXVa-CO<sub>2</sub>, and IV-XXVd-CO<sub>2</sub>, in which IV served as M<sub>N</sub>, XXVa and XXVd acted as the first M<sub>E</sub> component, and CO<sub>2</sub> behaved like a second M<sub>E</sub> monomer. Their terpolymer structures were XXXIVa and XXXIVb, respectively.



XXXIVa, Y = CO<sub>2</sub> Me

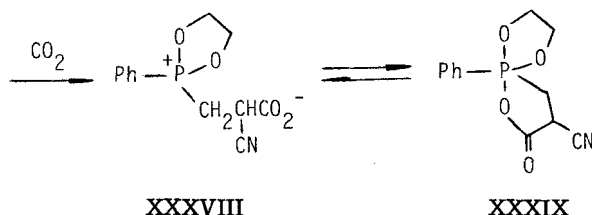
XXXIVb, Y = CN



In the combination of IV-XXVa-CO<sub>2</sub>, a zwitterion XXXV is first formed, which reacts with CO<sub>2</sub> to give the second zwitterion XXXVI.

A new species **XXXVI** is a zwitterion consisting of three monomeric components, which is responsible for the production of 1:1:1 alternating terpolymer **XXXIV**.

In the IV-**XXVd**-CO<sub>2</sub> combination **XXXIIa** reacts with CO<sub>2</sub>, yielding a ternary zwitterion **XXXVIII**, which leads to **XXXIVb**.

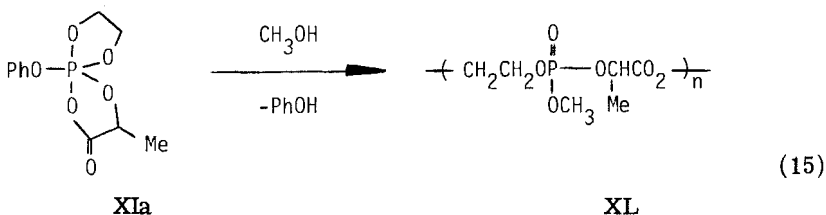


In both cases, the driving force from **XXXV** to **XXXVI** and from **XXXIIa** to **XXXVIII** may be attributed to the more increased stability of carboxylate form in **XXXVI** and **XXXVIII** than that of carbanion in **XXXV** and **XXXIIa**, respectively. It is also important that phosphoranes **XXXVII** and **XXXIX** contribute to producing **XXXVI** and **XXXVIII**.

#### Polymerization of Spiro Acyloxyphosphoranes by Stoichiometric Amount of Nucleophiles

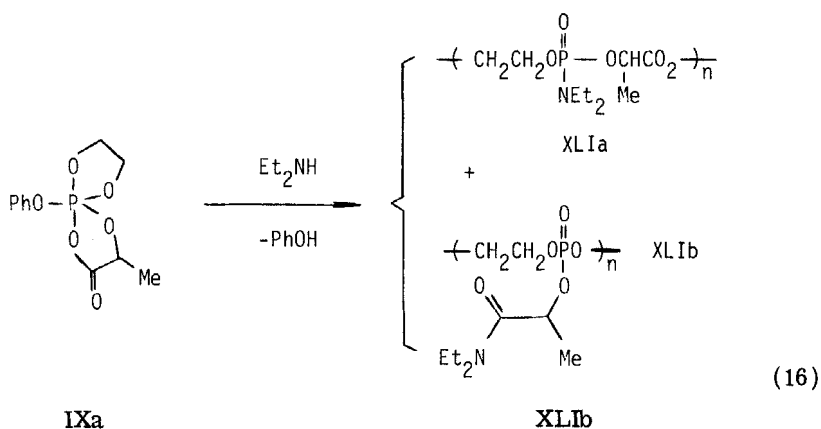
As already described, spiro acyloxyphosphoranes are quite reactive species toward various nucleophiles like alcohol and amine, yielding new polymers. Here two examples of new polymerizations are described.

When **XIa** was allowed to react with an equimolar amount of methanol in benzonitrile at 100-120°C for 2 days, a new type of polyphosphate triester **XL** was obtained (~40% yield). In the reaction shown in Eq. (15), phenoxy group was removed in the form of phenol and, instead, methanol was incorporated into the polymer

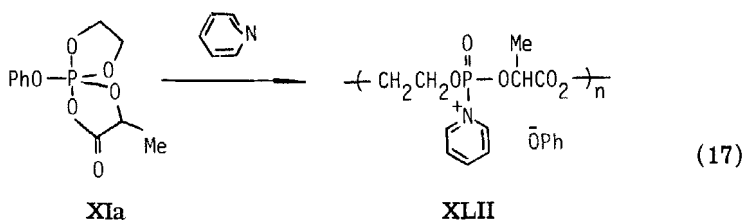


XL. Various primary and secondary alcohols have been successfully employed to afford corresponding polymers [21]. Thus, reaction (15) has the advantage that various type of polyphosphate triesters can be prepared from one spiro acyloxyphosphorane and various alcohols. It may be well expressed by the new terms "polyphosphorylation of alcohol" and "alcoholysis polymerization."

Another polymerization of spiro acyloxyphosphorane is that induced by amine [22]. An equimolar mixture of XIa and diethyl amine was kept at room temperature. Reaction took place and gave polymeric materials after usual work-up. The polymer was consisted of two structure units of XLIa and XLIb. In the reaction (16) phenol was



cleaved off and amine component was introduced into the polymer. A wide variety of amines, including primary and secondary amines, were found to be applicable for the above polymerization. Thus, it is called "aminolysis polymerization." The reaction leading to structures corresponding to XLIa and/or XLIb was dependent primarily upon the nature of the amine and phosphorane employed.



Pyridine also reacted with spiro acyloxyphosphorane. The reaction mode, however, was different from that of aliphatic amine. XIa and pyridine gave a new type of ionene polymer XLII [23].

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