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Copolymerization of 2-Phenoxy-1,3,2-Dioxaphosphorinanes with α-Keto Acids Involving Deoxygenation of the Keto Oxygen Atom: Deoxy-Copolymerization

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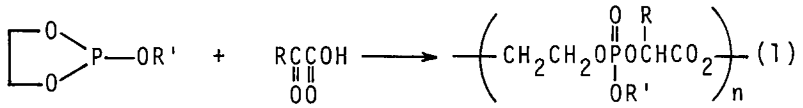
Dedicated to the 65th birthday of Professor G. Manecke

Summary

The copolymerization of 2-phenoxy-1,3,2-dioxaphosphorinanes (**4**) with α-keto acids (**2**) took place at room temperature without added catalyst to produce copolymers (**5**). The copolymer **5** is composed of phosphoric acid triester unit (**5α**) and of α-hydroxy-carboxylic acid ester unit (**5β**). Unit **5α** is an alternating unit of monomers **4** and **2** whereas unit **5β** is formed by deoxygenating **2** by **4**. **5** can be taken as copolymers of units **5α** and **5β**, the formation of the latter involving a deoxygenation process ("Deoxy-Copolymerization"). The ratio of **5β**/**5α** (m-value in **5**) increased in the order of unsubstituted (**4a**)-, 5,5-dimethyl (**4b**)-, and 5-t-butyl (**4c**)-phosphorinane systems. The reaction mechanism is also discussed.

Introduction

We have already reported a new alternating copolymerization of 2-alkoxy-1,3,2-dioxaphospholane, a five-membered cyclic phosphite (**1**) with α-keto acids (**2**) to produce poly(phosphoric acid triester)s (**3**) (SAEGUSA et al, 1977; KOBAYASHI et al, 1980). These copolymerizations occurred without added catalyst and proceeded



1a, R'=Ph
b, R'=R

2

3

through zwitterion intermediates (recent reviews, SAEGUSA and KOBAYASHI, 1979; KOBAYASHI and SAEGUSA, 1980). The present paper deals with copolymerizations of 2-phenoxy-1,3,2-dioxaphosphorinane, a six-membered cyclic phosphite, and its substituted derivatives (**4**) as nucleophilic monomers (M_N) with α-keto acids (**2**) as electrophilic ones (M_E). The reaction took place

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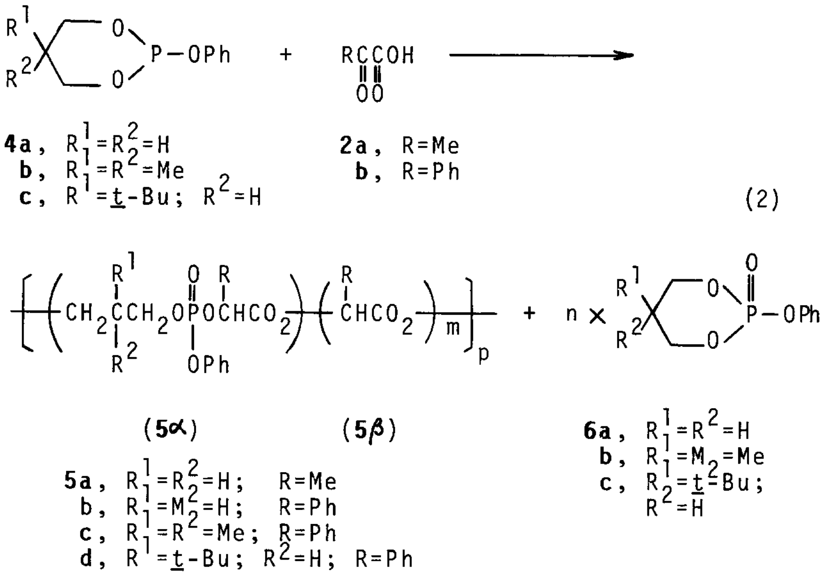
without added catalyst. But the product was not an alternating copolymer as shown in equation (1). It was consisted of phosphoric acid triester unit (5α) and of α-hydroxy-carboxylic acid ester unit (5β). The former unit is an alternating one derived from **4** and **2**, and the latter is a unit formed by the deoxygenation of **2** with **4** producing a cyclic phosphate (**6**) ("Deoxy-Copolymerization").



4a, $R^1=R^2=H$
b, $R^1=R^2=Me$
c, R^1=*t*-Bu; R^2=H

2a, R=Me
b, R=Ph

(2)

(**5α**) (**5β**)

5a, $R^1=R^2=H$; R=Me
b, $R^1=M^2=H$; R=Ph
c, $R^1=R^2=Me$; R=Ph
d, R^1=*t*-Bu; R^2=H; R=Ph

6a, $R^1=R^2=H$
b, $R^1=M^2=Me$
c, R^1=*t*-Bu; R^2=H

Experimental

Materials. Solvents of acetonitrile, diethyl ether, and *n*-hexane were purified by distillation under nitrogen. Pyruvic (**2a**) and phenylglyoxylic acids (**2b**) were obtained as proviously reported (SAEGUSA et al, 1977). 2-Phenoxy-1,3,2-dioxaphosphorinane (**4a**) was prepared by the reaction of triphenyl phosphite with 1,3-propanediol bp 72-74°C/0.25 mm (lit. 70-76°C/0.2 mm, AYRES and RYDON, 1957). The reaction of triphenyl phosphite with 2,2-dimethyl-1,3-propanediol gave phosphorinane **4b**, bp 84°C/0.3 mm (lit. 90-95°C/1 mm, CLOVIS and SULLIVAN, 1974). Similarly, 5-*t*-butyl-1,3,2-dioxaphosphorinane (**4c**) was obtained by the reaction of triphenyl phosphite with 2-*t*-butyl-1,3-propanediol, bp 87-92°C/0.06 mm.

Copolymerization. A typical run of the **4b**-**2b** system (No 5) was as follows. A mixture of **4b** and **2b** (3.0 mmol each) in 1.5 ml of acetonitrile was kept at 0°C in a sealed tube for 1 hr and then kept at 100°C for 22 hr. The tube was opened, and 2.0 ml of chloroform was added to the reaction mixture. The mixture was then poured into 50 ml of diethyl ether / n-hexane (1:4) mixed solvent to precipitate a polymeric material. This reprecipitation procedure was repeated five times to give 0.286 g (57% yield) of white powdery polymer **5c** after drying in vacuo. From the combined mixed solvent 0.452 g of cyclic phosphate **6b** was obtained by recrystallization from diethyl ether (62% yield), mp 132°C (lit. 133-135°C, McCONNELL and COOVER, 1959).

Results and Discussion

Copolymerization of 2-Phenoxy-1,3,2-dioxaphosphorinanes (**4**) with α-Keto Acids (**2**). The copolymerization of **4a** with **2a** at 80°C for 18 hr in CH_3CN gave copolymer (**5a**) in 48% yield. The polymer is a pale-yellow greece like material (MW=2190), which is soluble in polar solvent such as CH_3CN and $CHCl_3$ but insoluble in less polar solvents such as diethyl ether and n-hexane (No 1 in TABLE 1).

The polymer structure was determined as **5a** based on the following observations. The ^1H NMR spectrum of the polymer ($CDCl_3$) showed five signals, i.e., peak A at δ 1.3-1.8 (with TMS) is due to CH_3 protons, peak B at δ 1.9-2.4 is ascribed to CCH_2C protons, peak C at δ 3.9-4.7 is assigned to OCH_2 protons, peak D at δ 4.8 -5.3 is due to methine proton of OCHC, and peak E at δ 6.9-7.4 is assigned to phenyl protons. The integral ratio of these peaks was 6.0:2.0:4.0:2.0:5.0. If **4a** and **2a** produced alternating copolymer the ratio should be 3.0:2.0:4.0:1.0:5.0. The above observations, therefore, lead to the copolymer structure as **5a** in which m-value is 1.0. The IR spectrum of **5a** shows characteristic adsorptions at 1750 cm^{-1} ($\nu_{C=O}$), 1280 cm^{-1} ($\nu_{P=O}$), 1200 cm^{-1} (ν_{P-OPh}), and 1060-1000 cm^{-1} ($\nu_{P-O-alkyl}$). An elemental analysis datum of P=8.28 (found) lead to the value of m in **5a**=1.2, which is close to the value determined by ^1H NMR.

The following observations further support the polymer structure of **5a**. The ^{31}P NMR spectrum (δ in ppm with negative sign up-field from external 80% H_3PO_4) of the reaction mixture before the work-up showed two signals at -7.5 and -13.7 with almost equal intensity. After the work-up procedures the polymer sample showed only one peak at -7.5 ascribable to the phosphate unit in **5a**. From the precipitation solvent of diethyl ether / n-hexane (1:1) was obtained 160 mg of a solid product, which was identified as **6a** (25% yield), mp 73°C (lit. 76-77°C, AYRES and RYDON, 1957). The ^{31}P NMR of **6a** showed a signal at -13.7 (lit. -13, BLACKBURN et al, 1964). ^1H NMR data supported the structure of **6a**. IR data of **6a** are as follows: 1300 cm^{-1} ($\nu_{P=O}$), 1210 cm^{-1} (ν_{P-OPh}), and 1040 cm^{-1}

TABLE 1

Copolymerization of Phosphorinanes (**4**) with α-keto Acids (2)[a]

No	Phospho-rinane	α-keto acid	Reaction			Polymer			
			Solvent	Temp.	Time (hr)	Yield(%)	MW[b]	Structure	m-value[c]
1	**4a**	2a	CH_3CN	80°C	18	48	2190	5a	1.0
2	**4a**	2a	Et_2O[d]	r.t.	24	29	850	**5a**	0.3
3	**4a**	2b	CH_3CN	80°C	18	80	2490	**5b**	2.0
4	4a	2b	Et_2O[d]	r.t.	24	28	810	**5b**	0.6
5	**4b**	2b	CH_3CN	100°C	22	57	2450	5c	6.0
6	**4b**	**2b**	CH_3CN	r.t.	240	41	1430	5c	6.6
7	**4c**	2b	CH_3CN	100°C	27	30	1480	**5d**	7.3

[a] **4**=**2**=3.0 mmol each in 1.5 ml of solvent under nitrogen.
[b] Determined by vapor pressure osmometry in $CHCl_3$ at 35°C.
[c] The value of m in structure 5 was obtained by the ^1H NMR analysis.
[d] Precipitation of polymer occurred during the reaction.

(ν P-O-alkyl).

All the above findings indicate that the copolymerization of **4a** with **2a** gave copolymer **5a** composed of two kinds of unit, an alternating unit of phosphate triester **5**α and α-hydroxy-carboxylic acid ester unit **5**β, in almost equal amounts. During the reaction **4a** behaved as a comonomer as well as a deoxygenating agent from **2a** to produce unit **5**β and a cyclic phosphate **6a**, an oxidation product of **4a**.

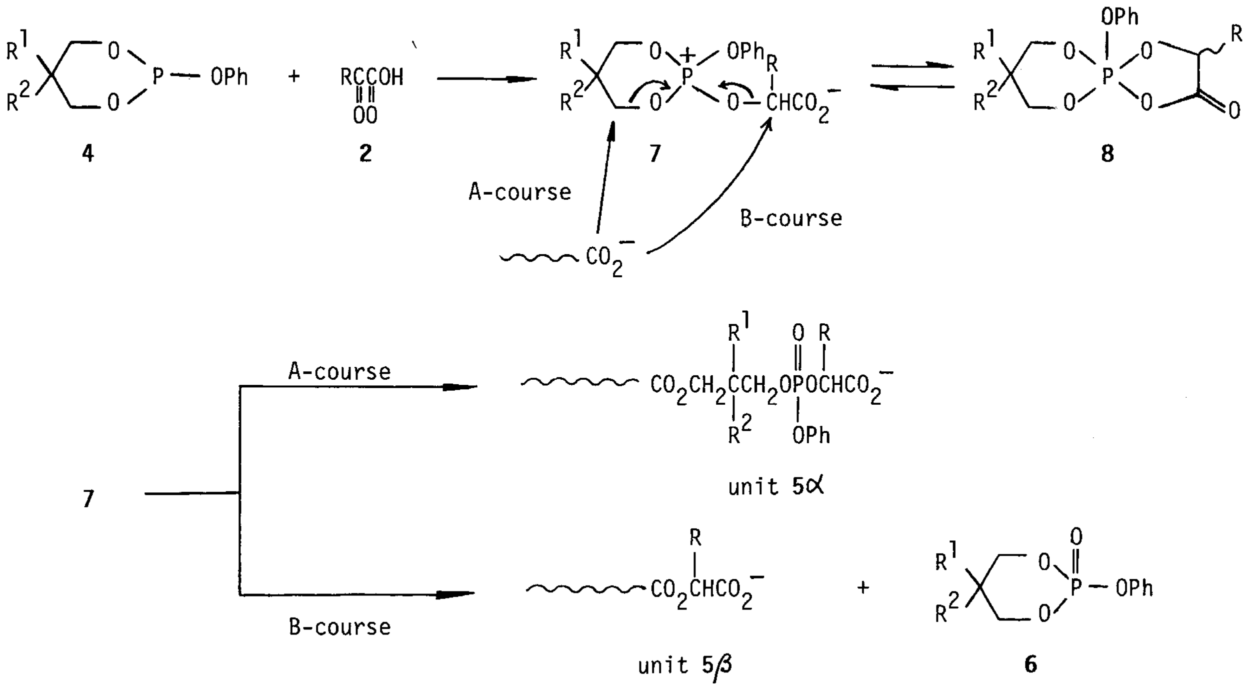
It is to be noted that the copolymerization of **4a** with **2a** took place even at room temperature (No 2 in TABLE 1). The copolymerization using five-membered cyclic phosphites (**1**) required higher temperatures, e.g., above 100°C. The present copolymerization using six-membered cyclic phosphites (**4**), therefore, is much higher in reactivity than that of equation (1).

The copolymerization of **4a** with **2b** was carried out under the similar reaction conditions as No 1 in TABLE 1 and the product copolymer was examined as above (No 3 in TABLE 1). This combination produced copolymer **5b** containing α-ester unit (**5**β) more than that of **5a**, i.e., m in **5b** is 2.0. The reaction of the combination took place at room temperature in diethyl ether and gave copolymer **5b** in which m is 0.6 (No 4 in TABLE 1).

Thus, the above two combinations of **4a**-**2a** and **4a**-**2b** did not produce alternating copolymers but gave copolymers containing a deoxygenated unit of **5**β in addition to an alternating unit **5**α. These results suggest that the structure of phosphorinane (**4**) and α-keto acid (**2**) may affect the reaction course to give **5**α unit and/or **5**β unit. Therefore, substituted phosphorinanes, 5,5-dimethyl-(**4b**) and 5-*t*-butyl-(**4c**) derivatives, were employed.

The copolymerization of **4b** with **2b** produced copolymer **5c** which contained a larger amount of **5**β unit, i.e., m in **5c** was 6.0 at 100°C (No 5) and 6.6 at room temperature (No 6 in TABLE 1). The content of **5**β increased with the copolymerization of **4c** and **2b**; m in polymer **5d** being 7.3 (No 7 in TABLE 1). In both combinations, **6b** and **6c**, oxidation products of **4b** and **4c**, respectively, were produced.

Copolymerization Mechanism. At present the copolymerization course is considered as follows. The first step in the reaction of **4** with **2** is the formation of a zwitterion **7** which is present probably in equilibrium with spiro acyloxyphosphorane **8**. There are two courses of the attack of a nucleophile onto **7**. The attack of the carboxylate anion onto the ring-methylene carbon (A-course) produces the phosphoric acid triester unit **5**α (an alternating unit) via the Arbuzov type reaction with ring-opening. On the other hand, the attack of the carboxylate onto the exo methine carbon (B-course) yields carboxylic acid α-ester unit **5**β and


4
2
7
8
A-course
B-course
7
A-course
B-course
unit 5α
unit 5β
6

cyclic phosphate **6**. B-course involves the deoxygenation of the keto oxygen atom of **2** with **4**. Introduction of two methyl groups or t-butyl group at 5-position of **4** makes B-course favorable for the attack of the carboxylate since A-course becomes more unfavorable due to the steric hindrance as well as the less ring-opening reactivity caused by these substituents in **7**. Concerning the effect of R of **2a** and **2b**, phenyl group facilitates to take B-course in **7** than methyl group because the exo methine carbon, onto which the nucleophile attacks, is situated at the benzyl position.

The present study suggests that poly(α –ester)s composed exclusively of unit **5β** can be prepared by controlling the reaction course, i.e., the selective reaction via B-course with the suppression of A-course.

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