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Deoxy-Polymerization of Phenylglyoxylic Acid Using a Cyclic Phosphite as Deoxygenating Agent

A New Synthesis of Poly(α-Ester)

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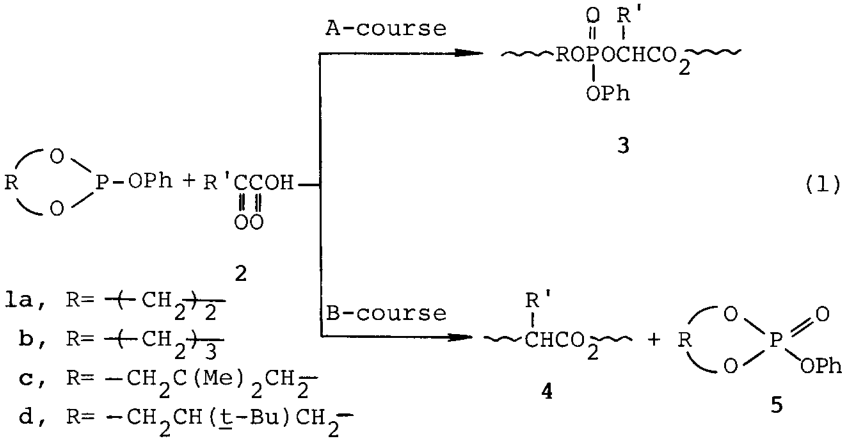
Summary

The reaction of phenylglyoxylic acid (**6**), an α-keto acid, with 2-phenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (**7**) produced poly(benzylidene carboxylate) (**8**), a poly(α -ester), and a cyclic phosphate (**9**). This reaction (2) provides a new method of preparation of poly(α -ester)s. In the reaction, the keto oxygen atom of **6** was deoxygenated by **7** to give polymer **8** (Deoxy-Polymerization). The structure of the polymer end group was elucidated, and the reaction mechanism has been presented.

Introduction

Copolymerizations of cyclic phosphites (**1**) with α -keto acids (**2**) have been reported in our recent papers. A five-membered cyclic phosphite (**1a**) gave poly(phosphoric aicd triester) **3**, an alternating



copolymer of **1a** and **2** via A-course (SAEGUSA et al, 1977). On the other hand, six-membered cyclic phosphites (**1b**, **1c**, and **1d**) produced copolymers composed of two kinds of units (A- and B-course in Scheme (1)), an

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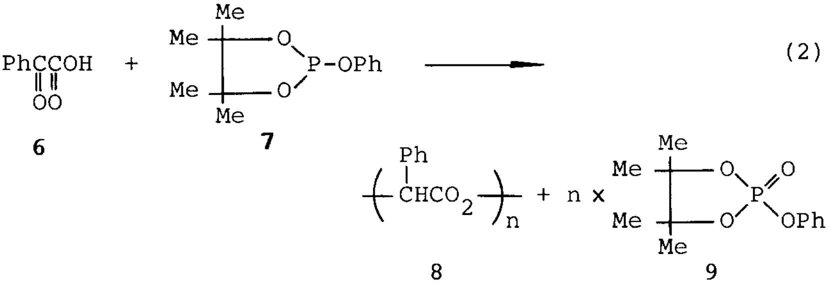
alternating unit **3** and an α-hydroxy-carboxylic acid ester unit **4**. The production of the latter unit involves the removal of oxygen atom (deoxygenation) of **2** by **1** (Deoxy-Copolymerization) (KOBAYASHI et al, 1980). It has been suggested that in an extreme case where the reaction proceeds exclusively via B-course it will lead to the production of poly(α -ester) shown by unit **4**. The presnet paper reports such a reaction which proceeds without added catalyst and provides a new method to give a poly(α -ester).

Results and Discusssion

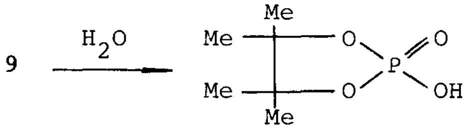
The reaction of this paper is shown by equation (2). The combination of phenylglyoxylic acid (**6**) and 2-phenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (**7**) produced poly(benzylidene carboxylate) (**8**), a poly-(α -ester), and a cyclic phosphate (**9**). During the polymerization the keto oxygen atom of **6** is removed (deoxygenated) by **7** (Deoxy-Polymerization). Polymer **8** is, therefore, a reduction product, whereas **9** is an oxidation product.



(2)

The reaction of **6** with **7** at 100°C for 30 hr in acetonitrile gave a white powdery polymer **8** (75% yield), which was soluble in DMF, acetonitrile, chloroform, and benzene but insoluble in diethyl ether, n-hexane, and water (No 1 in TABLE 1). The structure of the polymer was established as **8** mainly by ^{1}H NMR and IR spectroscopies, elemental analysis, and by the examination of the by-products. The ^{1}H NMR spectrum ($CDCl_3$ with TMS) of the polymer, which had been isolated by repeated precipitation, showed three signals; a very small peak (A) at δ 1.3-1.5 due to methyl protons from **7**, a peak (B) at δ 5.8-6.2 ascribed to methine proton, and a large peak (C) at δ 6.7-7.5 assigned to phenyl protons. Peak A is ascribed to the component derived from **7**, which is present at the end of polymer molecule. From the integral ratio of peaks A, B, and C, the unit ratio of component **7** and **8** was obtained as 1:59. Since the molecular weight of the polymer was 2380, the average degree of polymerization was 17.8. This means that one molecule derived from **7** is present at the polymer end of every 3.3 polymer molecules. The IR spectrum of the polymer showed a characteristic band at 1760 cm^{-1} of $\nu_{C=O}$, whereas a band due to $\nu_{P=O}$ was hardly detectable. Anal. Calcd for $(C_8H_6O_2)_n$: C, 71.63; H, 4.50. Found: C, 70.92; H, 4.78.

From the combined precipitant solvent an oxidation product **9** was isolated in a form of **10**. It was necessary to repeat the precipitation procedure several times for the complete removal of **9** from the polymer **8**. During the work-up procedure, **9** was hydrolyzed to **10** (70% yield), mp. 185-186°C (lit. 186-187°C, MODRO and SOKOLOWSKI, 1967), ^{31}P NMR +14.3 ppm (down-field for positive sign from H_3PO_4 standard).



10

The formation of species **9** was actually confirmed in situ by ^{31}P NMR of the reaction mixture i.e., a signal at +6.5 ppm was clearly observed.

TABLE 1

Deoxy-Polymerization of Phenylglyoxylic Acid (**6**) with **7** to Poly(α-ester) (**8**)

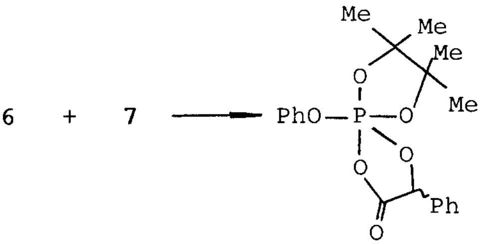
No	Solvent (ml)	Temp. (°C)	Time (hr)	Polymer **8** yield (%)	Mol. Wt.[c]
1[a]	3.0	100	30	75	2380
2[a]	3.0	60	30	48	2040
3[a]	5.0	100	24	28	1770
4[b]	2.0	100	30	39	3160

a **6** = **7** = 5.0 mmol in acetonitrile solvent.

b Spiro acyloxyphosphorane **11** (3.0 mmol) was used.

c Determined by vapor pressure osmometry in $CHCl_3$ at 35°C.

At lower temperatures, e.g., -20°C, **6** and **7** gave a 1 : 1 reaction product of a white crystalline material, whose structure was determined as spiro acyloxyphosphorane **11**. The compound **11** is considered as an

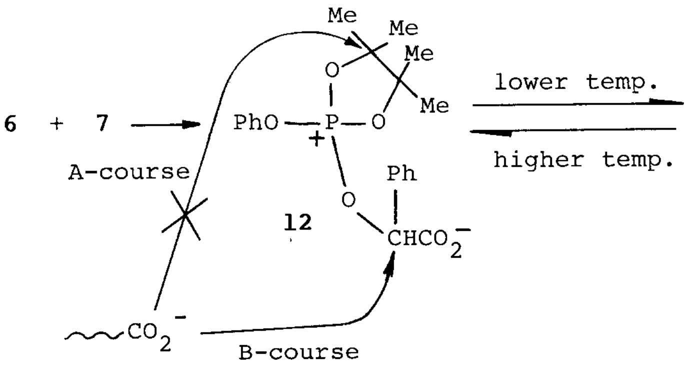


11

important species for the present reaction (2), and therefore, an isolated sample of 11 was used as the starting compound (monomer) (No 4 in TABLE 1). Then, the polymer **8** was obtained as in the cases of the 1 : 1 reaction of **6** with **7** (No 1-3 in TABLE 1).

Thus, the "Deoxy-Polymerization" of α-keto acids provides a new method of the preparation of poly(α-ester)s, which is compared with another ones, e.g., the ring-opening polymerization of anhydrosulphites of α-hydroxy-carboxylic acids (BALLARD and TIGHE, 1967) and of intermediate α-lactones (WHELAND and BARTLETT, 1970).

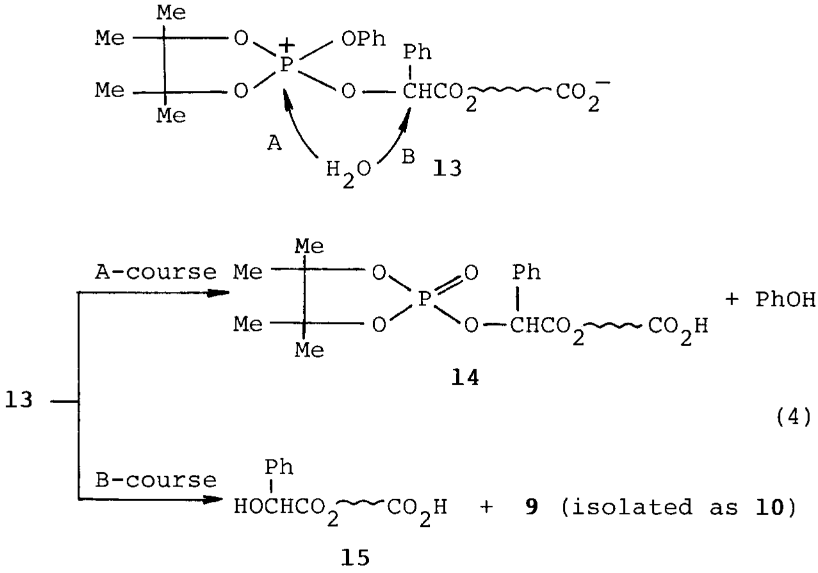
Reaction Mechanism. The Deoxy-Polymerization is best explained by the following scheme of reactions (3). The reaction of **6** with **7** affords at first a



(3)

zwitterion **12** which is equilibrated with spiro acyloxyphosphorane **11**. At higher temperature 12 becomes increased in concentration and enters into reaction. (recent reviews, SAEGUSA and KOBAYASHI, 1979. KOBAYASHI and SAEGUSA, 1980). The attack of the nucleophile of the carboxylate onto the ring-carbon atom in **12** (A-course) is sterically hindered by two methyl groups at each carbon atom. Therefore, the carboxylate attacks exclusively the exo methine carbon (B-course) to produce α-hydroxy-carboxylic acid ester unit **8**. B-course is further facilitated since the exo methine carbon, onto which the carboxylate attacks, is located at the benzyl position. The third conceivable course of the attack onto the phosphorus atom is sterically unfavorable due to four methyl groups.

Concerning the structure of end group derived from 7, the polymer sample No 1 was subjected to ^{31}P NMR analysis. With 64 times scans only one signal was observed at +14.6 ppm, which is close to the chemical shift of **10**, and hence, it was assigned to the structure of type **14**. The formation of **14** is explained as follows (Scheme (4)). Before the work-up the polymer is present as a macro-zwitterion form **13**. During the work-up procedures 13 is deactivated by the reaction



(4)

with water. The attack of water onto the phosphorus atom in 13 leads to the production of 14. If water takes B-course, polymer 15 and 9 are to be formed. Therefore, polymer **8** is a mixture of **14** and 15, e.g., the polymer sample No 1 is consisted of **14** and 15 in a ratio of 1.0 : 2.3 as already mentioned above.

Experimental

Materials. Solvents of chloroform, acetonitrile, diethyl ether, and *n*-hexane, were purified by distillation under nitrogen. Phenylglyoxylic acid (**6**) was obtained as previously reported (SAEGUSA et al., 1977).

2-Phenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (7) was prepared as followes. First, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was obtained by the reaction of phosphorus trichloride with pinacol in benzene in the presence of triethylamine, bp 83°C/17 mm (lit. 77-78°C/12 mm, ZWIERZAK, 1967). Then, this chloro compound was subjected to the reaction with phenol in benzene in the presence of triethylamine to give **7**, bp 85°C/0.2 mm (lit. 88-90°C/2 mm, FONTAL and GOLDWHITE, 1966).

Polymerization. In a sealed tube **6** and **7** (5.0 mmol of each) were dissolved in 3.0 ml of acetonitrile at 0°C under nitrogen. Then, the mixture was heated at 100°C for 30 hr (No 1 in TABLE 1). The tube was opened, and the reaction mixture was poured into about 100 ml of a mixed solvent of diethyl ether/*n*-hexane (4 : 6). The precipitated polymer was isolated by decantation and dried *in vacuo*. The reprecipitation procedure was further repeated five times using chloroform as a good solvent and a mixed solvent of diethyl ether/*n*-hexane (1 : 9) as a poor solvent (precipitating solvent). The polymer was obtained as a white powdery material.

Preparation of Spiro Acyloxyphosphorane (**11**). A mixture of **6** and **7** (3.0 mmol of each) was placed in 16 ml of a mixed solvent of diethyl ether/*n*-hexane (10 : 6) and kept -20°C for 7 days. During the reaction a white crystalline material precipitated, which was separated and dried *in vacuo* to give **11** in 53% yield; mp. 142-143°C. ^{31}P NMR (CH_3CN); -45.5 and -46.0 ppm. ^1H NMR ($CDCl_3$); a large peak at δ 0.8-1.7 due to four methyl protons (12H), two doublet at δ 5.4 (J_{POCH}=12 Hz) and at δ 5.5 (J_{POCH}=16 Hz) with almost equal intensity due to methine proton (1H), the two doublets being to the cis and trans isomers of the acyloxy-ring (KOBAYASHI et al, 1981), and a signal at δ 6.8-7.7 due to phenyl protons (10H).

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