Thermal Polymerization of Spiroacyloxyphosphoranes and the Related Cooligomerization between Cyclic Phosphorus(III) Compounds and α-Hydroxy Acids

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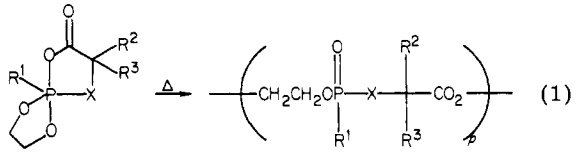
ABSTRACT: This paper is concerned with the ring-opening polymerization of spiroacyloxyphosphoranes **1** which were prepared by the condensation between cyclic phosphorus(III) compounds and α-hydroxy acids in the presence of diphenyl disulfide as a dehydrogenating agent (oxidant). On heating, **1** was polymerized. The product polymers consisted of phosphate or phosphonate units in the main chain. In addition, two "in situ" oligomerizations were observed. When a reaction mixture producing **1** was allowed to stand at room temperature without isolation of **1** for a long time, e.g., 3 days, oligomers of **3** were produced along with benzenethiol. The second in situ oligomerization was observed with benzilic acid as the α-hydroxy acid component. The corresponding spirophosphorane could not be isolated in the second case because of a lack of stability, and only an oligomer was obtained. A reaction scheme involving a zwitterion intermediate is suggested for the thermal polymerization and for the in situ oligomerization.

Previously,[2-7] we reported the preparation and polymerization of several spiroacyloxyphosphoranes having general formulas **1** and **2**.[1-6] Thermal polymerization of

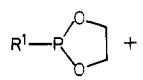


(1)

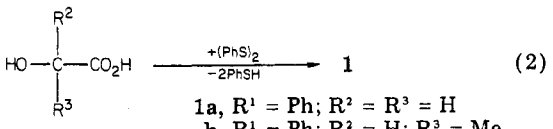
1, X = O
2, X = CH_2

3, X = O
4, X = CH_2

1 and **2** has been interpreted by the intermediacy of zwitterions which are formed by the heterolytic cleavage of the carboxy–phosphorus bond.[5,6] On the other hand, we have established recently[8] another facile method (eq 2) for obtaining spiroacyloxyphosphoranes, involving a condensation of an α-hydroxy acid with cyclic phosphorus compounds **5** in the presence of diphenyl disulfide as a dehydrogenating agent (oxidant). This method allowed



5a, R^1 = Ph
b, R^1 = OMe

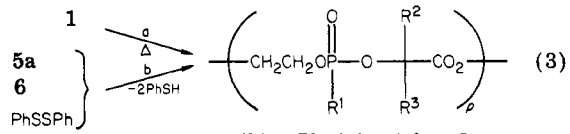


(2)

6a, $R^2 = R^3$ = H
b, R^2 = H; R^3 = Me
c, R^2 = H; R^3 = Ph
d, $R^2 = R^3$ = Me
e, $R^2 = R^3$ = Ph

1a, R^1 = Ph; $R^2 = R^3$ = H
b, R^1 = Ph; R^2 = H; R^3 = Me
c, R^1 = Ph; R^2 = H; R^3 = Ph
d, R^1 = Ph; $R^2 = R^3$ = Me
e, R^1 = OMe; $R^2 = R^3$ = H
f, $R^1 = R^2 = R^3$ = Ph

the syntheses of various homologues which were not accessible before. In the present paper we report (a) the thermal polymerizations of these new phosphoranes **1** and (b) the "in situ" oligomerization which occurred in the reaction mixture of three components producing **1** (eq 3). When the reaction mixture of the three components was allowed to stand at room temperature, the corresponding oligomer was formed together with benzenethiol. Sometimes the spiroacyloxyphosphorane was not stable enough and it was polymerized in the reaction cited above or as soon as it was formed. Thus, the cooligomer of **5** and **6** was produced directly by the aid of diphenyl disulfide. It



(3)

3a, R^1 = Ph; $R^2 = R^3$ = H
b, R^1 = Ph; R^2 = H; R^3 = Me
c, R^1 = Ph; R^2 = H; R^3 = Ph
d, R^1 = Ph; $R^2 = R^3$ = Me
e, R^1 = OMe; $R^2 = R^3$ = H
f, $R^1 = R^2 = R^3$ = Ph

is a new type of cooligomerization.

Experimental Section

Materials. The P(III) compounds [2-phenyl- (**5a**)[9] and 2-methoxy-1,3,2-dioxaphospholanes (**5b**)[10]] were prepared as previously reported. α-Hydroxy acids [glycolic (**6a**), lactic (**6b**), mandelic (**6c**), 2-hydroxy-2-methylpropionic (**6d**), and benzilic acids (**6e**)] were commercial reagents.

Preparation of 1. A typical preparation of **1**, which was carried out with complete exclusion of moisture, follows. Three millimoles of **5a** was allowed to react with a mixture of equimolar amounts of **6a** and diphenyl disulfide in diethyl ether (6 mL) at room temperature. After 2 h, both the solvent and benzenethiol (byproduct) were removed to dryness by evaporation under reduced pressure. The residue obtained was then recrystallized from a mixture of dichloromethane and diethyl ether to give white crystals of **1a**. The results and the characterizations of **1** are summarized in Table I.

Thermal Polymerization of 1a, 1d, and 1e. The following general procedure was performed and is similar to that already reported by us.[2,5-7] Acyloxyphosphorane (1.0 mmol) with or without solvent (1 mL) was placed, under nitrogen, in a sealed tube. After the sealed tube was kept at the desired temperature, 2 mL of chloroform was added to the system. Then the solution was poured into a large excess of a diethyl ether–*n*-hexane (1:1) mixed solvent to isolate the polymeric product. The polymer obtained was purified by repeated reprecipitation by the combination of chloroform (solvent) and diethyl ether–hexane (precipitant).

Cooligomerization of 5a with Benzilic Acid (6e). Compounds **5a** and **6e** (3 mmol of each) were added to diethyl ether (5 mL) containing an equimolar amount of diphenyl disulfide. At 0 °C and after 2 h, the reaction mixture deposited an oil polymeric material, which was isolated and purified as described above.

Results and Discussion

Thermal Polymerization of Spiroacyloxyphosphoranes. We have already reported[6] the polym-

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Table I
Syntheses of Various Acyloxyphosphoranes (Eq 2)

phospholane 5[a]	α-hydroxy acid 6[a]	spirophosphorane 1	mp, °C	% yield[b]
5a	6a	1a	128	77
5a	6b	1b	56	66
5a	6c	1c	108	66
5a	6d	1d	161	76
5b[c]	6a	1e	liquid	83

[a] [5] = [6] = [PhSSPh] = 3 mmol in 6 mL of diethyl ether. [b] After recrystallization from the solvent system diethyl ether/CH_2Cl_2. [c] The reaction was carried out in acetonitrile (4 mL) at 80 °C. The product **1e** was isolated on evaporation of both the solvent and the benzenethiol, which was not further purified: ^1H NMR ($CDCl_3$) δ 3.90 (d, J_{P-H} = 14.3 Hz, OCH_3, 3 H), 4.08 (d, J_{P-H} = 13.5 Hz, OCH_2CH_2O, 4 H), 4.25 (d, J_{P-H} = 14.0 Hz, OCH_2CO_2, 2 H); ^{31}P NMR ($CHCl_3$) δ −33.3. Anal. Calcd for $C_5H_9O_6P$: C, 30.63; H, 4.63; P, 15.80. Found (very hygroscopic): C, 30.18; H, 4.98; P, 15.47.

erization of **1b** and **1c**; these two compounds were prepared by a different method and involved the reaction of **5a** with pyruvic and phenylglyoxylic acids, respectively.[4] By the new synthetic method, **1a,d,e** could be prepared for the first time. Some typical results of the thermal polymerization of them are shown in Table II, where the data for **1b** and **1c** are also given for reference.

In all runs, the polymerization took place without added initiator to produce colorless waxy polymer. The bulk polymerizations of **1a** and **1d** gave higher yields and higher molecular weights in comparison with those of the solution polymerizations. Indeed, **1e** was polymerized under milder conditions in $CHCl_3$, since it gave an unknown insoluble substance when it was heated in bulk at 80 °C. The structures of these polymers, consisting of phosphonate or phosphate groups, were established by the following analytical data. **3a** (from **1a**): ^1H NMR ($CDCl_3$) δ 3.9–4.8 (m, OCH_2CH_2O, 4 H), 4.68 (d, J_{P-H} = 7.5 Hz, OCH_2CO_2, 2 H), 6.9–8.1 (m, aromatic H, 5 H); IR (neat) 1740 ($\nu_{C=O}$ of ester), 1220 ($\nu_{P=O}$), 1070 (ν_{P-O-C}) cm^{-1}, etc. Anal. Calcd for $[C_{10}H_{11}O_5P\cdot(H_2O)_{0.1}]_p$: C, 49.23; H, 4.63; P, 12.70. Found (hygroscopic): C, 49.00; H, 4.92; P, 12.43. **3d** (from **1d**): ^1H NMR ($CDCl_3$) δ 1.45 (s, $(CH_3)_2C<$, 6 H), 3.8–4.4 (m, OCH_2CH_2O, 4 H), 7.0–7.8 (m, aromatic H, 5 H); IR (KBr) 1743 ($\nu_{C=O}$ of ester), 1248 ($\nu_{P=O}$), 1110 (ν_{C-O}), 1030 (ν_{P-O-C}) cm^{-1}, etc. Anal. Calcd for $[C_{12}H_{15}O_5P\cdot(H_2O)_{0.6}]_p$: C, 51.29; H, 5.81; P, 11.02. Found (hygroscopic): C, 51.16; H, 5.72; P, 11.29. **3e**[11] (From **1e**): ^1H NMR ($CDCl_3$) δ 3.5–4.0 (broad, OCH_3, 3 H), 4.0–4.5 (broad, OCH_2CH_2O, 4 H), 4.5–4.9 (d, J_{P-H} = 10 Hz, OCH_2CO_2, 2 H); IR (neat) 1750 ($\nu_{C=O}$ of ester), 1250 ($\nu_{P=O}$), 1050 (ν_{P-O-C}) cm^{-1}, etc. Anal. Calcd for $[C_5H_9O_6P\cdot(H_2O)_{0.5}]_p$: C, 29.28; H, 4.91; P, 15.10. Found (hygroscopic): C, 29.02; H, 5.02; P, 15.25. The molecular weight of the polymer did not increase, even when the reaction was allowed to continue for a longer time. This may be due to the moisture in the samples of **1**, which are very hygroscopic.

Cooligomerization of 5a with α-Hydroxy Acids. As described in the Experimental Section, the three-component reaction of **5a**, **6e**, and PhSSPh in diethyl ether produced an oligomer having the formula of **3f** (R^1 = R^2 = R^3 = Ph) with 2 equiv mol of benzenethiol. The corresponding spirophosphorane **1f** (R^1 = R^2 = R^3 = Ph) could not be isolated. At 0 °C the oligomer yield reached 70% (MW = 880) after 2 h. **3f**: ^1H NMR ($CDCl_3$) δ 3.6–4.4 (broad, OCH_2CH_2O, 4 H), 6.3 (broad s, terminal OH and CO_2H, 1 H), 6.8–7.8 (m, aromatic H, 15 H); ^{31}P NMR ($CHCl_3$, 85% H_3PO_4 external standard) δ +13.8; IR (neat) 1730 ($\nu_{C=O}$ of ester), 1215 ($\nu_{P=O}$), 1020 (ν_{P-O-C}) cm^{-1}, etc. Anal. Calcd for $(C_{22}H_{19}O_5P\cdot H_2O)_p$: C, 64.08; H, 5.13; P, 7.51. Found (hygroscopic): C, 63.78; H, 5.22; P, 7.89. However, no reaction was observed in such solvents as acetonitrile, DMF, acetone, chloroform, and dichloromethane.

A similar "in situ" oligomerization was observed with the **1a** and **1d** systems when the ethereal reaction solutions were allowed to stand at room temperature for 3 days. Oligomers **6a** and **6d** were produced directly. The results are summarized in Table III. In every case, the molecular weight value corresponds to dimer or trimer of the unit structure of **3**. The ^1H NMR spectrum of the cooligomers showed a broad signal around δ 6.0–7.0, which may be ascribed to the one derived by the fast proton exchange of both OH and CO_2H groups. The signal disappeared completely with D_2O treatment. The degree of oligomerization calculated on the basis of the integral values agreed well with the observed one. This suggests that the oligomers carry the carboxyl and hydroxyl groups at the chain ends which are generated by the hydrolysis during the workup procedure (see reaction scheme). Conceivable benzenethiol terminal groups were not detected at all by NMR. The possibility of the production of cyclic oligomers cannot be ruled out, even though it has not been positively indicated.

In the cases of **6a** and **6d**, the phosphoranes **1a** and **1d** are intermediately formed, respectively, prior to their oligomerization. This was firmly established by direct ^{31}P NMR observation of the reaction system of **5a**, **6a**, and PhSSPh. The signal appearing at −22 ppm due to **1a** was the sole one after 3 h, which was gradually replaced by the signal at +17 ppm of the oligomer unit **3a**. After 3 days, [**1a**]/[**3a**] became 1.0/5.0. This ring-opening reaction of **1a** and **1d** may be caused by the catalysis of benzenethiol, as these phosphoranes themselves are very stable at room temperature. On the other hand, in the case of **6e**, the formation of the corresponding spirophosphorane was not detected at all during the course of cooligomerization as monitored by ^{31}P NMR spectroscopy. Two possibilities

Table II
Thermal Polymerizations of Acyloxyphosphoranes 1

phosphorane[a]	solvent[b]	temp, °C	time, h	polymer % yield	polymer structure	polymer mol wt[c]
1a	PhCN	130	10	45	3a	1370
1a		130	24	72	3a	2020
1d	PhCN	120	30	44	3d	2350
1d		130	30	74	3d	2860
1e	$CHCl_3$	70	60	71	3e	1610
1b[d]	PhCN	120	32	49	3b	1410
1c[d]	CH_3CN	120	30	37	3c	1870

[a] 1.0 mmol of each. [b] 1.0 mL. [c] Determined by vapor pressure osmometry in $CHCl_3$ (at 35 °C). [d] The data were reported previously.[6]

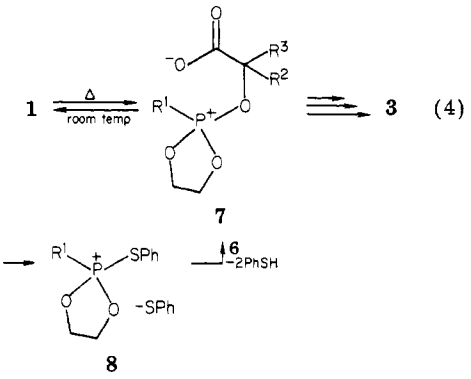
Table III
Cooligomerizations[a] of 5a with α-Hydroxy Acids by means of PhSSPh

α-hydroxy acid	time, days	% yield	polymer structure	mol wt[b]
6a	3	98	3a	710
6d	4	14	3d	770
6e	1	73	3f	1240

[a] 3 mmol of 5a, 6, and PhSSPh was used. The reaction was done at room temperature. [b] Determined by vapor pressure osmometry at 35 °C (chloroform).

may be assumed. First, the spirophosphorane from 6e was extremely reactive or, secondly, the cooligomerization proceeded via a different route without the intermediacy of the spirophosphorane.

Scheme of Polymerization. As in the case of other spiroacyloxyphosphoranes in a previous paper,[2,5,6] the thermal polymerization of 1 in the present study is schematized as follows:



First the heterolytic cleavage of the carboxy–phosphorus bond takes place to produce a zwitterion 7, and then propagation of 7 occurs through the opening of the phosphorus-containing ring by nucelophilic attack of carboxylate of another zwitterion.

For the formation of 1, a zwitterion 7 is considered as the intermediate which is produced by the exchange reaction between 6 and the first formed intermediate 8 from 5 and diphenyl disulfide.[8] At room temperature, the intramolecular cyclization of 7 is faster than its polymerization to 3. Thus, the related "in situ" cooligomerizations of 5a with 6a and with 6d are assumed to be the homooligomerizations of the corresponding acyloxyphosphoranes 1a and 1d, respectively, with benzenethiol catalyst. Elucidation of the detailed mechanism,[12] however, requires further studies. On the other hand, the cooligomerization of 5a, with 6e occurred directly without the formation of spiroacyloxyphosphorane. It may be ascribed to the bulkiness of two phenyl groups, which prevents the cyclization of the zwitterion 7 ($R^1 = R^2 = R^3 = Ph$).

References and Notes

(1) Shiga Prefectural Junior College, Hikone, Shiga 522, Japan; a visiting scholar at the laboratory of Professor Saegusa.
(2) (a) Saegusa, T. *Chem. Technol.* **1975**, *5*, 295. (b) *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 826.
(3) Saegusa, T.; Kobayashi, S.; Kimura, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 443.
(4) Saegusa, T.; Kobayashi, S.; Kimura, Y.; Yokoyama, T. *J. Am. Chem. Soc.* **1976**, *98*, 7843.
(5) Saegusa, T.; Kimura, Y.; Ishikawa, N.; Kobayashi, S. *Macromolecules* **1976**, *9*, 724.
(6) Saegusa, T.; Yokoyama, T.; Kimura, Y.; Kobayashi, S. *Macromolecules* **1977**, *10*, 791.
(7) Saegusa, T.; Yokoyama, T.; Kobayashi, S. *Polym. Bull.* **1978**, *1*, 55.
(8) Saegusa, T.; Miyamoto, M.; Kimura, Y., submitted to *J. Org. Chem.*
(9) Mukaiyama, T.; Fujisawa, T.; Tamura, Y.; Yokota, Y. *J. Org. Chem.* **1964**, *29*, 2572.
(10) Lucas, H. J.; Mitchell, F. W., Jr.; Scully, C. N. *J. Am. Chem. Soc.* **1950**, *72*, 5491.
(11) The phosphate structure was supported by the ^{31}P NMR spectroscopy: δ −0.8 (in $CHCl_3$, 85% H_3PO_4 external standard).
(12) How the oligomerization is controlled by benzenethiol has not yet been clarified. One possible explanation is that it may react with both the initiating and the propagating zwitterions as in eq 5. The product phosphorane can be readily hydrolyzed in the isolating stage to produce 3 having both carboxyl and hydroxyl terminals.