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Ring-opening copolymerization of 2,4-bisphenyl-1,3,2,4-dioxadiphosphetane-2,4-dioxide with oxetane via zwitterion intermediates

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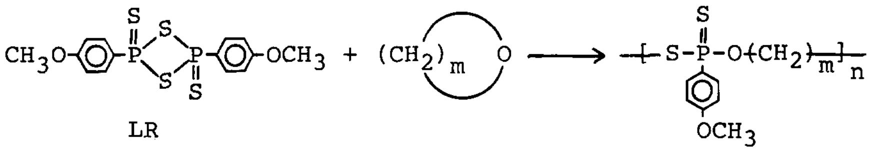
SUMMARY

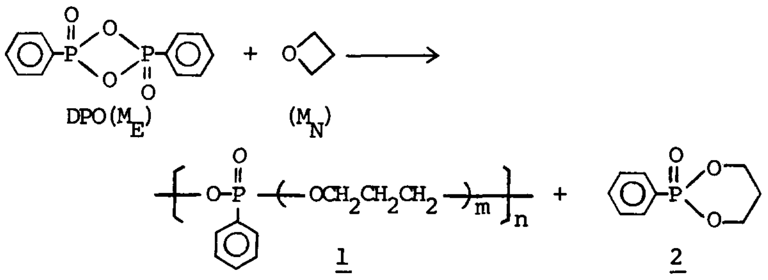
Copolymerization of 2,4-bisphenyl-1,3,2,4-dioxadiphosphetane-2,4-dioxide (DPO) with oxetane, a cyclic ether, was found to take place at 90 and 120°C without initiator. Copolymers obtained have a structure of phosphonate-ether units (1), which was determined by ^{31}P, ^{1}H and ^{13}C NMR, IR and elemental analysis. Oxetane was incorporated into 1 in a slight excess in all runs (m value in 1=1.5-2.1). A small amount ($<15\%$) of a by-product (2) was always formed. Other cyclic ethers such as ethylene oxide and propylene oxide did not afford copolymers but gave 1:1 addition products, 10 and 11, quantitatively. The copolymerization is reasonably explained by a mechanism in which DPO behaves as an electrophilic monomer and oxetane as a nucleophilic one. A pyrophosphonate species is considered to be a key intermediate to lead to copolymer 1 and the whole reaction course is discussed in detail.

INTRODUCTION

Our recent paper reported a new periodic 1/2:1 copolymerization of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (Lawesson's reagent, LR) with cyclic ethers (reaction i) which occured without initiator at room temperature (1). Product periodic copolymers consist of a half molecule of LR and a cyclic ether in an alternating arrangement. Thus, copolymerization (i) is one of no-catalyst alternating and periodic copolymerizations which have been developed mainly by us (2). The present paper describes a copolymerization of 2,4-bisphenyl-1,3,2,4-dioxadiphosphetane-2,4-dioxide (DPO) with oxetane (reaction ii).



(i)



(ii)

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phetane-2,4-dioxide (DPO) as an electrophilic monomer (M_E) with oxetane as a nucleophilic monomer (M_N) (reaction ii). DPO is considered as an O-analogue of LR, and hence, the present copolymerization is an extension study of reaction (i). The copolymerization (ii) takes place without catalyst at 90°C or 120°C to produce copolymer (1) and a by-product (2).

RESULTS AND DISCUSSION

Copolymerization

DPO was allowed to react with oxetane using a solvent in a sealed tube under nitrogen. The feed ratio was calculated on the basis that a half of DPO molecule is one monomer unit. The reaction took place without catalyst at or above 90°C. The work-up procedure of the reaction mixture was undertaken after the monomer DPO had been converted into copolymer 1 confirmed by ^{31}P NMR spectroscopy of the mixture. Colorless or pale brown paste-like polymeric materials were obtained in good yields (Table 1). All copolymers are readily soluble in $CHCl_3$. The structure of the copolymers was determined using ^{31}P NMR, ^1H NMR, ^{13}C NMR, IR and elemental analysis.

Table 1

Copolymerization of DPO with Oxetane[a]

No.	Feed ratio[b]	Solvent	Temp. (°C)	Time (hr)	Copolymer (1) m of 1	Mol.Wt.[c]	Yield(%) based on DPO[d]	oxetane[d]
1	1.5	C_6H_6	90	200	1.5	1300	70	70
2	2.0	C_6H_6	90	62	1.7	1700	76	64
3	2.0	C_6H_6	90	330	2.0	2300	71	71
4	4.0	C_6H_6	90	51	1.9	1600	71	34
5	4.0	C_6H_6	90	280	2.1	2200	58	30
6	2.0	C_6H_6	120	5	1.7	2000	59	50
7	2.0	$CHCl_3$	90	78	1.5	1800	60	54
8	2.0	CH_3CN	90	125	1.8	2000	60	54
9	2.0	C_6H_5CN	90	125	1.5	1900	64	48

a) Concentration of DPO=1.3-1.5 mol/l.
b) Oxetane/(DPO×2) (mol/mol).
c) Determined by vapor pressure osmometry in $CHCl_3$ at 40°C.
d) The yield was calculated on the basis of both monomers, DPO and oxetane.

^{31}P NMR spectrum ($CDCl_3$) of copolymer No.2 showed only one single peak at 19.4 ppm, which was reasonably assigned to a phosphonate structure (3). ^1H NMR spectrum ($CDCl_3$) exhibited four broad signals; δ 1.5-2.1 (CH_2C), 3.2-3.7 (CH_2OCH_2), 3.9-4.4 ($POCH_2$), and 7.2-8.1 (C_6H_5) (Figure 1).

From the integral ratio of the peaks due to POCH$_2$ and to CH$_2$OCH$_2$, the m value of copolymer 1 (No. 2) was obtained as 1.7. Anal. Calcd for (C$_{11.1}$ H$_{15.2}$ O$_{3.7}$ P)$_n$ (m=1.7): C, 55.77; H, 6.37; P, 13.14. Found: C, 54.47; H, 6.51; P, 12.06. ^{13}C NMR spectrum (CDCl$_3$) showed four signals; δ 30-32 (CCH$_2$C), 62-63 (OCH$_2$), 65.3 (d, POCH$_2$) and 127-133 (C$_6$H$_5$) (Figure 2). In the IR spectrum, a characteristic band at 1235cm^{-1} due to $\nu_{P=O}$ is observed. All these data strongly support the poly(phosphonate-ether) structure of copolymer 1.

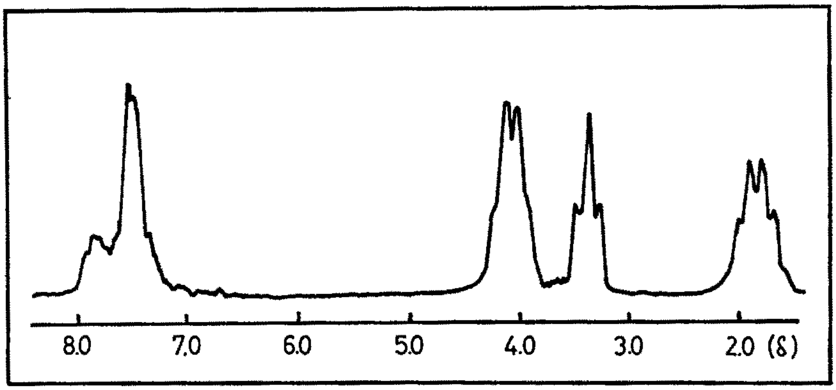


Figure 1. ^{1}H NMR spectrum (CDCl$_3$) of copolymer (1).

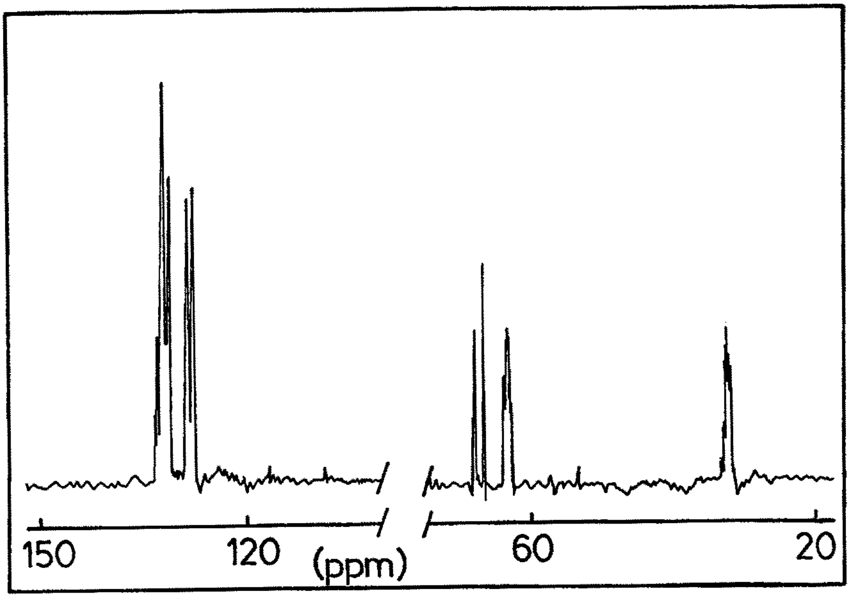


Figure 2. ^{13}C NMR spectrum (CDCl$_3$) of copolymer (1).

The molecular weight of copolymers was atmost 2300 under the various reaction conditions. Oxetane was usually incorporated into copolymer in 50-110% excess toward a half molecule of DPO. A large excess amount of oxetane for DPO (No.4 and 5) and/or prolonged reaction time (No.3 and 5) brought about the incorporation of oxetane into copolymer in a slightly increased amount. At any rate, the reaction of DPO with oxetane did not produce a periodic 1/2:1 copolymer under reaction conditions examined. This constitutes a sharp contrast to the copolymerization reaction (i), in which LR and a cyclic ether afforded always a 1/2:1 periodic copolymer regardless of the charged monomer ratio (1).

^{31}P NMR spectrum of the reaction mixture (No.2) before the work-up procedure showed two peaks at 19.4 and 14.8 ppm in a ratio 85%:15%. A product showing a ^{31}P NMR peak at +14.8 ppm was found in a supernatant layer of diethyl ether after reprecipitation procedure. The supernatnat was concentrated and the product was isolated by preparative thin layer chromatography. Its structure was determined as 2-phenyl-2-oxo-1,3,2-dioxaphosphorinane (2). For the structural determination an authentic sample of 2 was prepared. ^{31}P and ^{1}H NMR spectral data of the isolated product and of the authentic sample were completely identical. Thus, compound 2 was produced in 10-15% yields as a by-product in all copolymerization runs.

Copolymerization Mechanism

To shed light on the copolymerization mechanism, the reaction was monitored by ^{31}P NMR spectroscopy (Figure 3). During the copolymerization three peaks at 19.4, 14.8 and 9.7 ppm were observed. As noticed above two peaks at +19.4 and 14.8 ppm were due to the formation of copolymer 1 and a

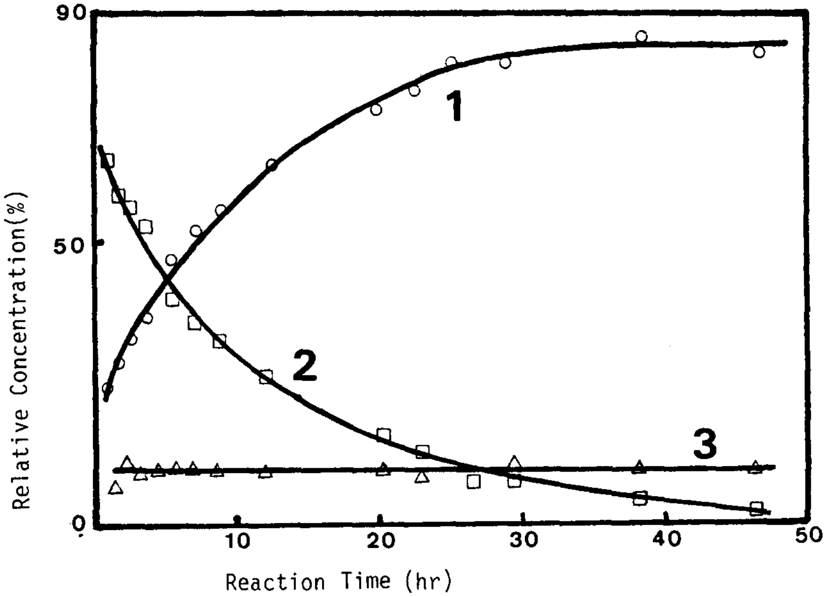
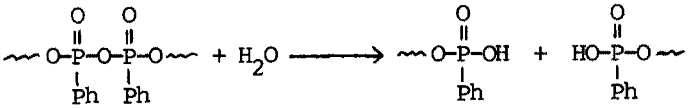


Figure 3. Time-conversion curves of the copolymerization of DPO with oxetane; the feed ratio of oxetane/(DPO×2)=4.0 in benzene at 90°C. Curves 1,2 and 3 denote peaks at 19.4, 9.7 and 14.8 ppm, respectively.

by-product 2, respectively. Apparently the increase of the peak at 19.4 ppm and the decrease of the peak at 9.7 ppm were complementary. Under similar reaction conditions as run No.4 and 5, the peak at 9.7 ppm disappeared within 50 hr. Product 2 was produced at only a very early stage of reaction, and hereafter, it's amount remained almost constant throughout the reaction.

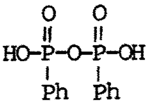
The structure of intermediate showing a ^{31}P NMR peak at 9.7 ppm was reasonably determined as a pyrophosphonate 3 on the basis of the following observations. When water was added to the reaction mixture at an early stage of reaction (∼2 hr), the only observable change was that the peak at 9.7 ppm disappeared immediately and instead a peak at 19.4 ppm increased. This implies that the rapid hydrolysis of species 3 produced species 4, a phosphonate structure.



$$\sim O-\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}-O\sim + H_2O \longrightarrow \sim O-\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}-OH + HO-\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}-O\sim$$

3 4 4

Furthermore, pyrophosphonate compounds 5 and 6 were prepared *in situ*. 5 and 6 showed peaks at 8.6 and 10.8 ppm in ^{31}P NMR spectrum, respectively. These chemical shift values are very close to 9.7 ppm.



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}-OH$$

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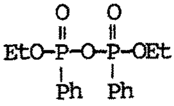


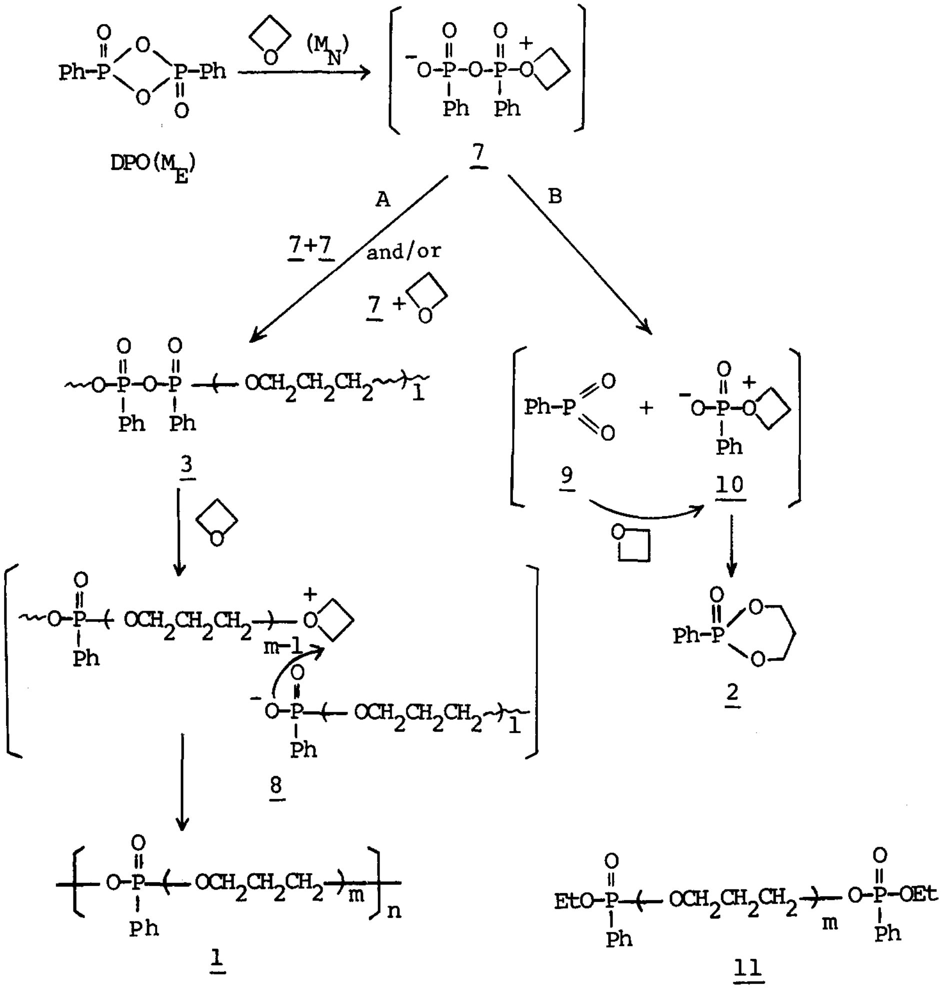
$$EtO-\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}-OEt$$

6

All the above observations led to that the intermediate species showing peak at 9.7 ppm has a pyrophosphonate structure 3.

Based on the results above the following scheme will explain the present copolymerization mechanism. First, the nucleophilic attack of oxetane (M_N) onto the phosphorus atom of DPO (M_E) is very rapid giving rise to zwitterion intermediate 7, which is unstable under the reaction conditions. Then, the consumption of 7 proceeds via two ways; route A leading to the formation of copolymer 1 and route B leading to the production of 2. Routes A and B are also very rapid and competitive to produce 3 and 2, respectively. Therefore, the rate ratio of routes A and B determines the production ratio of copolymer 1 and product 2. Once 2 is formed, 2 is no more involved in the polymerization.

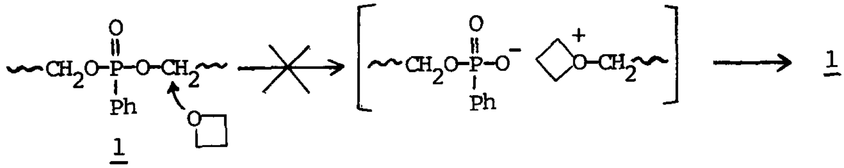
Route A involves the reactions between zwitterions 7 and/or between 7 and oxetane to produce oligomeric species 3 having pyrophosphonate unit(s). Subsequently, a pyrophosphonate group in 3 is able to induce the oligomerization of oxetane gradually via an oxonium intermediate 8 to lead eventually to copolymer 1. So, consumption of 3 and appearance of 1 are slow processes as seen in Figure 3.



To confirm the reaction of 3 with oxetane to lead to 1, the following model was undertaken. Compound 6 was prepared *in situ* in benzene as a model of 3. To this solution two equivalent of oxetane was added and kept at 90°C. The reaction was monitored by ^{31}P NMR. After 12 hr a new peak at 22.6 ppm reached 43% and after 50 hr at the same temperature the peak at 22.6 ppm was the only signal observed; peak at 10.8 ppm due to 6 completely disappeared. The peak at 22.6 ppm was ascribed to compound 11 of a phosphonate structure. These observations have been taken to support the conversion of 3 to copolymer 1.

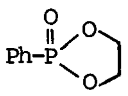
In turn, route B involves the conversion of 7 to a zwitterion 10, a precursor to lead to 2. From 7 to 10, metaphosphonate 9 (4) might be involved as a transient species, which reacts with oxetane to give 10 again.

Oxetane does not incorporate into copolymer chain 1. This was also confirmed by a model reaction; 11 a model compound of 1 was allowed to react with oxetane at 90°C for 30 hr in benzene, but no significant change was observed by ^{31}P NMR spectroscopy.



Reactions of DPO with Other Cyclic Ethers

Copolymerization of DPO with ethylene oxide was carried out but no polymeric material was obtained. Instead, the reaction produced 2-phenyl-2-oxo-1,3,2-dioxaphospholane (12), a 1/2:1 addition product, quantitatively at 40°C in $CHCl_3$ for 6 hr. A ^{31}P NMR signal of 12 appeared at 36.4 ppm (lit. 36 ppm (5)). In a similar manner the reaction of DPO with propylene oxide gave an addition product 13 (^{31}P NMR signal at 33.8 and 34.0 ppm), again no polymeric substance being produced.



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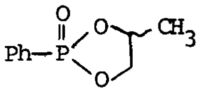

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EXPERIMENTAL PROCEDURES

Materials

All solvents were purified by distillation under nitrogen. Commercial reagents of phenylphosphonic acid, phenylphosphonic acid dichloride, oxetane and propylene oxide (Tokyo Kasei Co.) were purified before use. Ethylene oxide was supplied from Meisei Chem. Co. (Kyoto).

Preparation of 2,4-Bisphenyl-1,3,2,4-dioxadiphosphetane-2,4-dioxide (DPO)

DPO was obtained by the reaction of phenylphosphonic acid dichloride with phenylphosphonic acid as previously reported (6) and purified by recrystallization from benzene; mp 110-113°C (lit. 103-108°C (6)); ^{31}P NMR ($CHCl_3$) 2.1-2.3 ppm as several peaks.

Copolymerization of DPO with Oxetane

A typical run (No.1) was as follows. DPO (0.35g, 1.25 mmol) and oxetane (0.22g, 3.8mmol) were placed in a tube containing 0.4 ml of benzene under nitrogen. The tube was sealed and kept at 90°C for 200 hr. During the reaction the mixture became homogeneous. The tube was opened and 3.5 ml of $CHCl_3$ was added to the reaction mixture, which was subjected to ^{31}P NMR measurement to confirm the disappearance of DPO. Then, the mixture was poured into 30 ml of diethyl ether to precipitate polymeric materials. This reprecipitation procedure was repeated twice. After drying *in vacuo* 0.34g of paste-like materials 1 was obtained.

Preparation of 2-Phenyl-2-oxo-1,3,2-dioxaphosphorinane (2)

Phenylphosphonic acid dichloride (2.1 mmol) and triethylamine (2.5 mmol) were dissolved in 15 ml of benzene. Trimethylene glycol (2.1 mmol) was slowly added to this solution at 0°C. After separation of an ammonium salt by filtration, the filtrate was concentrated. Preparative thin layer chromatography (silica-gel) developed by acetone-ethyl acetate (3:1 v/v) gave 0.30g of slightly yellow crystalline 2: ^{31}P NMR ($CDCl_3$) 14.8 ppm. ^1H NMR ($CDCl_3$) δ 2.1 (quintet of d, 2H), 4.5 (m, 4H), 7.3-8.0 (m, 5H).

Isolation of 2 from Reaction Mixture

After the reprecipitation prodecure of the copolymerization mixture, the combined supernatant diethyl ether solution was concentrated and 2 was isolated by preparative thin layer chromatography. Spectral data of this compound was identical with those of the authentic sample (2).

Preparation of Diphenylpyrophosphonic Acid (5)

DPO (14 mg) was dissolved in $CHCl_3$ under nitrogen. A acetone solution (0.09 ml) containing 1.0 % water (volume) was added to the solution. 5 was formed in situ instantaneously (^{31}P NMR signal at 8.6 ppm). With further addition of water the peak disappeared and a new peak at +18.1 ppm ascribable to phenylphosphonic acid appeared.

Preparation of Diethyl Diphenylpyrophosphonate (6)

A benzene solution (8.2 ml) of ethyl alcohol (0.41 ml, 7.0 mmol) and triethylamine (1.15 ml, 8.2 mmol) was mixed with phenylphosphonic acid dichloride (^{31}P NMR; 34.5 ppm) (1.0 ml, 7.0 mmol) at 0°C under nitrogen. Instantaneously, ethyl phenylphosphonate chloride (^{31}P NMR; 26.4 ppm formed quantitatively in situ. After filtration the solution was concentrated to 30 ml and divided into two equal portions. Into one of these portions, 0.58 ml triethylamine (4.1 mmol) was mixed. Water (0.063 ml, 3.5 mmol) was added at 0°C and the system was kept at this temperature for 12 hr. Ethyl phenylphosphonate (^{31}P NMR; 8.9 ppm) was formed in situ quantitatively. This solution(A) was dried with anhydrous magnesium sulfate for 12 hr before use. After the addition of triethylamine (0.58 ml, 4.1 mmol), the other portion of ethyl phenylphosphonate chloride solution was cooled to 0°C. Solution A was added to this and allowed to react for 24 hr. After fitration, it was freeze-dried to give diphenylpyrophosphonic acid diethyl ester 6 quantitatively. ^{31}P NMR($CDCl_3$); 10.8 ppm. MS; m/e=354.

Measurements

^1H NMR spectra were recorded on a HITACHI R-20B(60 MHz) spectrometer. A HITACHI R-900 spectrometer was used to record ^{31}P NMR(36.43 MHz) and ^{13}C NMR(22.63 MHz) spectra. Molecular weight data were obtained using a CORONA 117 vapor pressure osmometer.

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