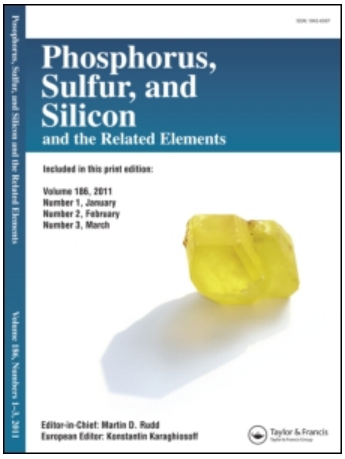


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XXXI. ALKALINE HYDROLYSIS OF 2-ALKYL-2-OXO-1,3,2-DIOXA-PHOSPHORINANE AND -PHOSPHEPANE

Chengye Yuan[a]; Shusen Li[a]; Xiugao Liao[a]
[a] Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, China

To cite this Article Yuan, Chengye , Li, Shusen and Liao, Xiugao(1988) 'STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XXXI. ALKALINE HYDROLYSIS OF 2-ALKYL-2-OXO-1,3,2-DIOXA-PHOSPHORINANE AND -PHOSPHEPANE', Phosphorus, Sulfur, and Silicon and the Related Elements, 37: 3, 205 — 212
To link to this Article: DOI: 10.1080/03086648808079039
URL: http://dx.doi.org/10.1080/03086648808079039

Phosphorus and Sulfur, 1988, Vol. 37, pp. 205–212
Reprints available directly from the publisher
Photocopying permitted by license only

STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XXXI. ALKALINE HYDROLYSIS OF 2-ALKYL-2-OXO-1,3,2-DIOXA-PHOSPHORINANE AND -PHOSPHEPANE

CHENGYE YUAN, SHUSEN LI and XIUGAO LIAO

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Linling Lu, Shanghai 200032, China

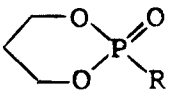
(Received December 10, 1987; in final form February 2, 1988)

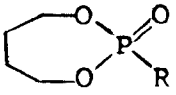
Alkaline hydrolysis of 2-alkyl-2-oxo-1,3,2-dioxaphosphorinane and -phosphepane was studied in aqueous dioxane. The rate constants were determined at various temperature and the activation parameter of the reaction were evaluated. The hydrolytic process is classified as a AE reaction. Quantitative structure-reactivity relationship was examined by multiple regression analysis involving the rate constants and the structural parameters of the exocyclic substituents on phosphorus. The difference between the hydrolytic behaviour of cyclic alkylphosphonates and carboxylates was also discussed.

INTRODUCTION

Structure-reactivity studies of the hydrolysis of cyclic phosphorus esters may contribute to the understanding of the chemistry and biochemistry of this class of compounds. The rate constants of alkaline hydrolysis and their relationship with structure of a series of phosphinic esters, including alkyl diethylphosphinates, alkyl diphenylphosphinates, as well as 2,2,3,4,4-pentamethyl-trimethylene phosphinates, were reported by Haake.[1,2] Nevertheless, the hydrolytic behaviours of cyclic phosphorus esters have been studied extensively during the past two decades in connection with Berry's pseudorotation theory.[3–8] Unfortunately, the influence of the nature of substituents on their hydrolytic behaviours has not been reported hetherto.

In this paper, the alkaline hydrolysis of 2-alkyl-2-oxo-1,3,2-dioxaphosphorinane (**1**) and 2-alkyl-2-oxo-1,3,2-phosphepane (**2**) (For convenience O,O-trimethylene and O,O-tetrabutylenealkylphosphonates were nomenclatured for **1** and **2** respectively in this paper) was studied in 50% dioxane–50% water (v/v) and the substituent effect on the rate constant (k) of hydrolysis was evaluated by regression analyses.





1 R = CH_3(**a**), C_2H_5(**b**), *n*-C_3H_7(**c**), iso-C_3H_7(**d**), *n*-C_4H_9(**e**), iso-C_4H_9(**f**), sec-C_4H_9(**g**), *n*-C_6H_{13}(**h**), cyc-C_6H_{11}(**i**), *n*-C_8H_{17}(**j**), *n*-$C_{12}H_{25}$(**k**).

2 R = C_2H_5(**a**), *n*-C_3H_7(**b**), iso-C_3H_7(**c**), *n*-C_4H_9(**d**), iso-C_4H_9(**e**), sec-C_5H_{11}(**f**), *n*-C_6H_{13}(**g**), *n*-C_8H_{17}(**h**).

For comparison, the hydrolytic behaviour of corresponding carboxylates was also examined.

RESULTS AND DISCUSSIONS

Both O,O-trimethylene alkylphosphonates (**1**) and O,O-tetrabutylene alkylphosphonates (**2**) are cyclic phosphonates with six- and seven-membered ester ring respectively. The hydrolysis was carried on in aqueous dioxane solution of sodium hydroxide. Reaction rate are found to be second order, i.e. $v = k$ [phosphonates] [OH^-] and the rate constant (k) were calculated by the least squares methods (Table I).

In the following k(**1**) and k(**2**) denote the rate constants of cyclic phosphonates **1** and **2** respectively. The experimental data in Table I demonstrated that the length of the unbranched alkyl substituent in the phosphonate has little influence on the rate constants of cyclic esters of the alkyl phosphonates under investigation. However, a substantial decrease of the rate was observed with increased branching of the exocyclic substituent. Thus, the rate constants of hydrolysis of compounds **1** and **2** decrease in the following sequential order Methyl ≫ Ethyl > *n*-Propyl > *n*-Butyl ~ *n*-Hexyl > *n*-Octyl > *n*-Dodecyl ~ iso-Butyl ≫ iso-Propyl > sec-Butyl > cyc-Hexyl. The order reveals the contribution of steric effect of exocyclic alkyl group in the hydrolyses of the cyclic phosphonates studied. For the quantitative structure-reactivity studies it was found that the Charton's ν parameter[9] did not fit the data. A rather poor correlation coefficient (0.813) of log k versus ν was calculated for a series of O,O-trimethylene alkylphosphonates.

TABLE I

Rate constants for alkaline hydrolysis of **1** and **2** at 302.7K and 363.2K respectively

Compd	R	k(l/mole . h)	log k	ν'	$\Delta\Delta E$	E_s^{c*}	σ^*
1a	CH_3	479	2.68	0.35	0.00	−1.24	0.00
1b	C_2H_5	60.1	1.78	0.38	0.33	−1.62	−0.100
1c	*n*-C_3H_7	45.7	1.66	0.42	0.30	−1.91	−0.115
1d	iso-C_3H_7	1.59	0.201	0.62	1.53	−2.31	−0.190
1e	*n*-C_4H_9	23.0	1.36	0.42	0.25	−1.94	−0.130
1f	iso-C_4H_9	16.8	1.23	0.55	0.50	−2.48	−0.125
1g	sec-C_4H_9	1.12	0.0492	0.66	1.91	−2.99	−0.210
1h	*n*-C_6H_{13}	23.7	1.38	(0.42)	0.23	−1.99	−0.160
1i	cyc-C_6H_{11}	0.700	−0.155				−0.150
1j	*n*-C_8H_{17}	19.5	1.29	(0.42)	0.23	−2.08	−0.160
1k	*n*-$C_{12}H_{25}$	14.2	1.15	(0.42)	0.24	(−2.18)	(−0.161)
2a	C_2H_{25}	71.8	1.86	0.38	0.21	−1.62	−0.100
2b	*n*-C_3H_7	46.8	1.67	0.42	0.21	−1.91	−0.115
2c	iso-C_3H_7	3.37	0.528	0.62	1.41	−2.31	−0.190
2d	*n*-C_4H_9	41.8	1.62	0.42	0.21	−1.94	−0.130
2e	iso-C_4H_9	16.1	1.21	0.55	0.61	−2.48	−0.125
2f	sec-C_5H_{11}	1.54	0.188	(0.66)	1.47	(−2.99)	−0.210
2g	*n*-C_6H_{13}	32.7	1.51	(0.42)	0.21	−1.99	−0.160
2h	*n*-C_8H_{17}	28.5	1.45	(0.42)	0.21	−2.08	−0.160

* Reference [13].

However, we found that $\log k$ correlates linearly with Charton's ν' coefficient, a steric parameter of alkyl group for pentacoordinated intermediate.[10]

$$\log k(\mathbf{1}) = -6.62\nu' + 4.35 \qquad r = 0.920 \quad n = 11 \tag{1}$$

$$\log k(\mathbf{2}) = -5.33\nu' + 3.84 \qquad r = 0.969, \quad n = 8 \tag{2}$$

where r = correlation coefficient, n = number of points. The correlation coefficient for compounds **1** and **2** are 0.920 and 0.969, respectively. The results of regression analysis are satisfactory. Recently, we found that the energy difference between the most stable conformation of the pentacoordinate transition state and the ground state phosphonates during basic hydrolysis, $\Delta\Delta E$, which was estimated from molecular mechanics calculation, seems to reflect the contribution of the primary steric effect in the process[11]. Our $\Delta\Delta E$ values used as steric parameters gave in fact better result in correlation analysis, for $\log k$ at least to certain extent, than Charton's ν'.

$$\log k(\mathbf{1}) = -0.826\Delta\Delta E - 0.928 \qquad r = 0.963, \quad n = 8 \tag{3}$$

$$\log k(\mathbf{2}) = -1.03, \Delta\Delta E - 0.886 \qquad r = 0.971, \quad n = 8 \tag{4}$$

Since $\Delta\Delta E$ was derived from the difference in steric energy between the phosphonate and the pentacoordinated transition state, it is reasonable to anticipate that the parameter is not specially sensitive to unbranched alkyl substituents. This is well demonstrated by the significant decrease in correlation coefficient with the increase of unbranched alkyl groups involved in regression analyses. In multiple regression studies, correlating $\log k$ with Taft's σ^* and E_s^c, a pair of commonly used parameters for polar and steric effect of substituent,[12] gave similar results.

$$\log k(\mathbf{1}) = 10.3\sigma^* + 0.542E_s^c + 3.83 \tag{5}$$

$$r = 0.932, \quad T_\rho = 1.59, \quad T_\delta = -2.73, \quad n = 11$$

$$\log k(\mathbf{2}) = 7.23\sigma^* + 0.744E_s^c + 3.95 \tag{6}$$

$$r = 0.953, \quad T_\rho = 2.52, \quad T_\delta = -2.27, \quad n = 8$$

Concerning the steric parameter E_s^c, derived from $E_s^c = Es + 0.306(N - 3)$, it is necessary to point out that, the substantial electronic contribution, either direct or hyperconjugative, in Taft Es was eliminated, at least to certain extent, by correction with number of α-hydrogen (N).[13] In case of substitution of E_s^c by $\Delta\Delta E$ the correlation coefficient was evidently improved.

$$\log k(\mathbf{1}) = 7.98\sigma^* - 0.536\Delta\Delta E + 2.65 \tag{7}$$

$$r = 0.982, \quad T_\rho = 4.06, \quad T_\delta - 4.88, \quad n = 11, \quad S_\rho = 1.96, \quad S_\delta = 0.11$$

$$\log k(\mathbf{2}) = 4.92\sigma^* - 0.765\Delta\Delta E + 2.66 \tag{8}$$

$$r = 0.990, \quad T_\rho = 4.92, \quad T_\delta - 7.05, \quad n = 8, \quad S_\rho = 1.59, \quad S_\delta = 0.11$$

It shows that $\Delta\Delta E$ gives better correlation than Taft's E_s^c as steric parameters. Meanwhile the coefficient for polar and steric terms as well as the T-test value in this multiple regression indicated that the rate constants of the alkaline hydrolysis of cyclic phosphonates **1** and **2** is influenced by both steric and polar effect of the exocyclic alkyl substituents on phosphorus. However, the weight of $\Delta\Delta E$ and σ^* on k value is varied depending on the nature of the substituents.

The similar substituent effect in the basic hydrolysis of O,O-tetrabutylene alkylphosphonates was revealed by the linear plot of $\log k(\mathbf{1})$ of compounds **1** against $\log k(\mathbf{2})$ of compounds **2** giving a correlation coefficient ($r = 0.981$) (Figure 1). It is therefore likely that the transition state in the alkaline hydrolysis of both cyclic phosphonates are similar.

A series of thermodynamic functions of alkaline hydrolysis of cyclic esters of alkylphosphonates was estimated based on rate constant measurements at various temperature. The activation parameters, $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$, thus obtained, are listed on Table II.

Since the activation enthalpy of compounds **2** (15.5–18.4 kcal/mole) was higher than that for compounds **1** (13–17.5 kcal/mole), the alkaline hydrolysis of O,O-trimethylene alkylphosphonates released larger cyclic ester ring strain energy than did the O,O-tetrabutylene alkylphosphonate, as the result of less

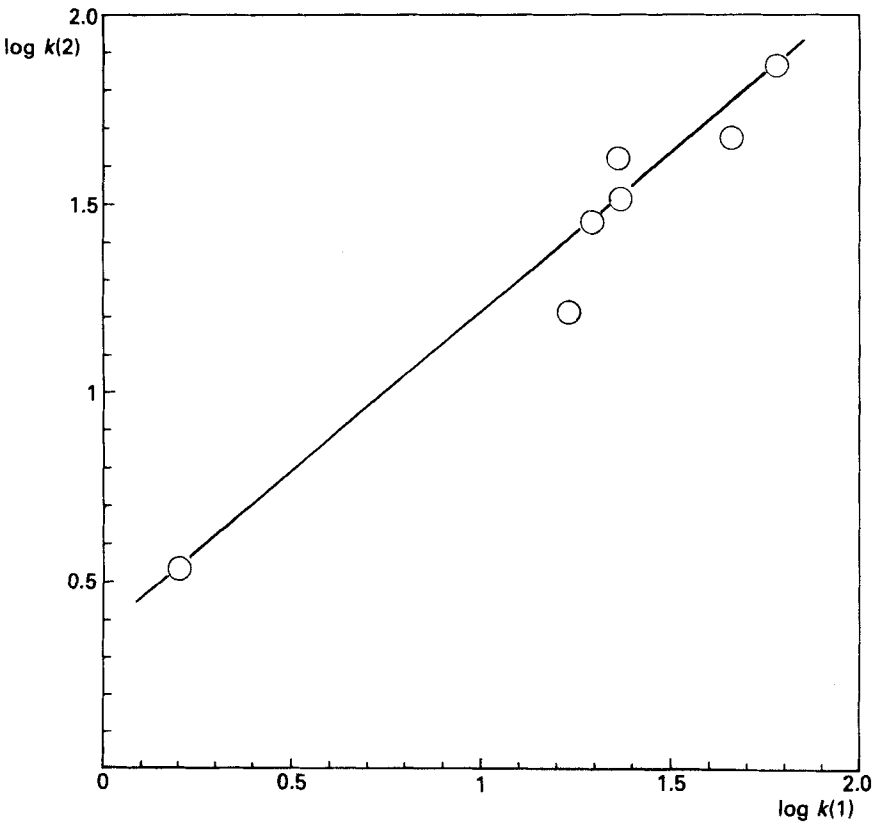


FIGURE 1 Plot of $\log k(\mathbf{1})$ versus $\log k(\mathbf{2})$.

TABLE II

Thermodynamic functions of alkaline hydrolysis of cyclic esters of alkylphosphonates

Phosphonates	$\Delta G^{\neq}$ (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (Gibbs)*
1a	30.0 ± 0.1	15.6 ± 0.02	−47.5 ± 0.2
1b	24.0 ± 0.3	13.2 ± 0.1	−35.6 ± 0.8
1c	24.8 ± 0.4	13.7 ± 0.2	−36.6 ± 0.6
1d	31.1 ± 0.1	17.9 ± 0.7	−43.6 ± 1.0
1e	23.5 ± 0.2	13.2 ± 0.1	−33.9 ± 0.4
1f	30.0 ± 0.6	16.6 ± 0.3	−44.2 ± 1.0
1g	30.0 ± 0.9	17.2 ± 0.5	−42.4 ± 1.5
1h	24.9 ± 0.2	13.9 ± 0.1	−36.3 ± 0.3
1j	30.7 ± 0.6	16.9 ± 0.3	−45.5 ± 0.7
1k	29.9 ± 0.3	16.6 ± 0.2	−43.9 ± 0.6
2a	28.8 ± 0.1	15.8 ● 0.1	−35.9 ± 0.2
2b	27.9 ± 1.0	15.5 ± 0.5	−34.0 ± 1.4
2d	33.7 ± 0.4	18.4 ± 0.2	−42.0 ± 0.7
2e	27.8 ± 0.1	15.8 ± 0.0	−32.9 ± 0.1
2g	31.8 ± 0.2	17.0 ± 0.1	−39.1 ± 0.4
2h	31.9 ± 0.5	17.7 ± 0.1	−39.1 ± 1.5

* $\Delta S^{\neq}$ values were determined between 20 and 50°C except for compound **1a** which was evaluated between 0 and 20°C for convenience of measurement.

steric hindrance conformation of the latter. In other words, the rate constants of alkaline hydrolysis of six-membered cyclic esters is greater than that of the seven-membered one.

The data in Table I show that the rate constants of O,O-trimethylene-alkylphosphonates are approximately ten times greater than the rates of the corresponding O,O-tetrabutylene-alkylphosphonate under similar conditions. It may be rationalized by the twist conformation of the seven membered ring ester moiety, which tends to release the steric hindrance on phosphorus atom.

As shown by the magnitude of the $\Delta S^{\neq}$ values (−33–48 Gibbs) the hydrolytic reaction is best classified as a bimolecular AE mechanism. Since the phorphorus compounds resemble to certain extent, compounds of carbon, and it is well established that alkaline hydrolysis of carboxylic ester and phosphoryl esters proceed by similar pathway, i.e. through nucleophilic attack of hydroxide ion on the C=O respecting P=O groups. However, the chemical environment of carbonyl carbon in carboxylate is different from the environment around phosphorus in phosphonates. It is therefore interesting to compare the influence of alkyl group on the hydrolytic behaviour of these two kinds of esters. Nevertheless, the different influence of alkyl group linked to P=O in phosphonate respecting C=O in carboxylate was observed by Haake [2] but a quantitative evaluation of the effect on the hydrolysis process has not been reported. A comparison of rate constants for alkaline hydrolysis of cyclic esters of alkylphosphonates and corresponding alkylcarboxylates are described in this paper (Table III).

As shown in Table III, the rate constants of alkaline hydrolysis of various alkyl carboxylates and corresponding alkylphosphonate are considerably lower. The ratio between ethyl and iso-propyl phosphonates **1** and **2** is 38, 21, but only 4 for

TABLE III

Rate constants of alkaline hydrolysis of cyclic esters alkylphosphonic acids and alkylcarboxylate

Esters	Solvent	Temp °C	k		$kC_2H_5/$ kiso-C_3H_7	Ref.
			R = C_2H_5,	iso-C_3H_7		
1	50%DX-H_2O	29.5	60.1	1.59	38	*
2	50%DX-H_2O	90.0	71.8	3.37	21	*
$RCO_2C_2H_5$	50%ACT-H_2O	35.0	4.06	1.03	4	14

* Data from this paper.
DX and ACT denote dioxane and acetone respectively.

the corresponding alkylcarboxylates. Experimental data demonstrated that the influence of the substituent effect for phosphonate was larger than that for carboxylate. It may be rationalized by the fact that the alkaline hydrolysis of a carboxylate involves the transformation from trigonal carbon to tetrahedral carbon, while the hydrolysis of cyclic ester of alkylphosphonate proceeded from tetrahedral to bipyramidal phosphorus. Therefore, since structural changes between ground state and transition state in the carboxylate hydrolysis are completely different from the phosphonate hydrolysis, the substituent effect might well be quite different too. It is thus, under effect might well be quite different too. It is thus understandable that structural parameter, as, σ^* and E_s^c which were derived from reaction of carboxylates are generally not suitable for QSAR study of organophosphorus compounds. As the result of Newman's steric six-number effect, which illustrates the number of atoms in the sixth position from the carbonyl oxygen of a carboxylate determines the steric effect,[15,16] the rate constant of alkaline hydrolysis of ethyl iso-pentyrate is much smaller than that for ethyl iso-butyrate. However, an opposite substituent steric effect was observed for the phosphorus ester, i.e., the k value of O,O-1,3-trimethylene and O,O-1.4-tetrabutylene iso-butylphosphonate is evidently greater than that for corresponding iso-propylphosphonates. It can be rationalized as follows: in the alkaline hydrolysis of alkylphosphonates, owing to the difference configuration of phosphonate, in the ground state and transition state the leaving group will be split off from the axial position, so Newman's steric six-number effect was eliminated completely.

EXPERIMENTAL

IR spectra were obtained on a Shimadzu 440 spectrometer. Sample was prepared in liquid film. ^1H NMR spectra were recorded on a Varian EM-360 L spectrometer, using carbon tetrachloride as solvent and TMS as external standard. ^{31}P NMR spectra were obtained on a JOEL FX-90Q spectrometer using $CDCL_3$ as solvent and 85% H_3PO_4 as external standard. Mass spectra were measured on a Finnigan 4021 apparatus. Titration was performed on a 636-Titroprocessor manufactured by Methohm Co, Switzerland.

Determination of Rate Constants

A 50% dioxane-water (v/v) solution containing known amount of ester and sodium hydroxide solution was prepared at room temperature and mixed thoroughly by shaking the flask in a Jubalo constant temperature bath (precision ±0.01°C). At appropriate time intervals, aliquots were removed and followed by addition of hydrochloric acid to retard the reaction. The excess acid was back titrated with standard sodium hydroxide solution, and the residual concentration of phosphorus esters calculated. The rate constants at various temperatures were obtained from both graphical analyses, and a calculation program utilizing the least squares method.

Synthesis of O,O-1,3-Trimethylene- and O,O-1,4-Tetramethylene Alkylphosphonates. The cyclic phosphonates with short unbranched alkyl substituents were synthesized by a method described by us.[17] The cyclic alkyl-phosphonates with more than six carbon atoms in the exocyclic alkyl group are synthesized by the following modification: To a stirred and heated (40–45°C) mixture of dioxane (100 ml) and triethylamine (10.1 g, 0.1 mol) are added concurrently, over a period of 2 h, from two dropping funnels containing separately the appropriate alkyl-phosphoryl dichloride (0.05 mol) in 50 ml dioxane, and the corresponding glycol (0.05 mol in 50 ml dioxane). The speed of addition is controlled so that the reaction temperature is kept under 65°C. The reaction proceeds with formation of triethylammonium chloride. After addition of phosphonyl dichloride and glycol, the mixture is heated to reflux for 1 h. Upon cooling to room temperature, the precipitate is removed and the filtrate is concentrated under reduced pressure. The remaining residue is purified by fractional distillation.

O,O-1,3-Trimethylene n-Hexylphosphonate (**1h**). b.p. 140–142°C/(0.1 torr), yield 70%, Anal. $C_9H_{19}O_3P$. Calc. C, 52.4; H, 9.29; P, 15.15; Found C, 52.57; H, 9.28; P, 15.02. IR, 1271 (P═O), 1059 (P—O—C), 725 cm^{-1} (P—C). ^1H NMR 3.80–4.70 (m, 4H, 2 × CH_2O), 0.74–2.25 (m, 15H, CH_3, 6 × CH_2) ppm. MS (m/z) 207(M + 1), 135(M − 71), 122(M − 84).

O,O-1,3-Trimethylene-n-Octylphosphonate (**1j**). b.p. 154–156°C/(0.01 torr), yield 47%, Anal. $C_{11}H_{23}O_3P$. Calc. C, 56.4; H, 9.61; P, 13.21. Found C, 56.34; H, 9.99; P, 12.90. IR, 1263 (P═O), 1053 (P—O—C), 720 cm^{-1} (P—C). ^1H NMR 3.7–4.40 (m, 4H, 2 × CH_2O)ppm, 0.75–2.1(m, 19H, CH_3, 8 × CH_2)ppm. MS (m/z) 235(M + 1), 135 (M − 100), 122(M − 113).

O,O-1,3-Trimethylene-n-Dodecylphosphonate (**1k**) b.p. 176–178°C/(0.01 torr), yield 50%, Anal. $C_{15}H_{31}O_3P$. Calc. C, 62.04; H, 10.76; P, 10.67. Found C, 61.37; H, 11.09; P, 11.06. IR, 1255 (P═O), 1064 (P—O—C), 723 cm^{-1} (P—C) ^1H NMR 3.95–4.75 (m, 4H, 2 × CH_2O) 0.74–2.15(27H, CH_3, 12 × CH_2, m)ppm. MS(m/z) 291(M + 1), 135(M − 155), 122(M − 168).

O,O-1,4-Tetramethylene-n-Hexylphosphonate (**2g**) b.p. 120–121°C(/0.02 torr), yield 47%, Anal. $C_{10}H_{21}O_3P$. Calc. C, 54.53; H, 9.61; P, 14.0. Found C, 53.96; H, 9.50; P, 13.64. IR 1251 (P═O), 1026 (P—O—C), 722 cm^{-1} (P—C). ^1H NMR 3.65–4.40 (m, 4H, 2 × CH_2O), 0.70–2.05 (m, 17H, CH_3, 7 × CH_2) ppm. MS (m/z) 221 (M + 1), 150 (M − 70), 136 (M − 84).

O,O-1,4-Tetramethylene-n-octylphosphonate (**2h**) b.p. 123–125°C/(0.01 torr), yield 50%, Anal. $C_{12}H_{25}O_3P$. Calc. C, 58.05; H, 10.15; P, 12.50. Found C, 57.83; H, 10.35; P, 12.46. IR, 1256 (P═O) 1026 (P—O—C), 720 cm^{-1} (P—C). ^1H NMR 3.70–4.40 (m, 4H, 2 × CH_2O), 0.75–2.10 (m, 21H, CH_3, 9 × CH_2) ppm. MS (m/z) 249 (M + 1), 150 (M − 98), 136 (M − 112).

Synthesis of Alkylphosphonyl Dichloride

The alkylphosphonyl dichloride bearing alkyl group with less than four carbon atoms were prepared by the methods[18,19]. The *n*-hexyl-, *n*-octyl- and *n*-dodecyl phosphonyl dichloride, important intermediates in the synthesis of cyclic esters of alkylphosphonates were prepared by dropwise addition of appropriate diethyl alkylphosphonate (0.20 mol) to phosphorus pentachloride (0.45 mol) and followed by reaction with vigorous stirring at 130–160°C for 4 hrs. Upon distillation under diminished pressure, corresponding alkylphosphonyl dichloride was obtained with higher yield.

n-Hexylphosphonyl dichloride, b.p. 98–100°C/(1.5 torr), yield 93%, $C_6H_{13}OCLP$, ^1H NMR (2.25–2.90 (m, 2H, CH_2), 1.10–2.20 (m, 8H, 4 × CH_2), 0.70–1.10 (t, 3H, CH_3) ppm.

n-Octylphosphonyl dichloride. b.p. 110–113°C/(0.1 torr), yield 83%, $C_8H_{17}OCLP$, 1H NMR 2.23–2.84 (m, 2H, CH_2), 1.06–2.10 (m, 12H, 6 × CH_2), 0.73–1.06 (t, 3H, CH_3) ppm.

n-Dodecylphosphonyl dichloride. b.p. 148–151°C/(0.1 torr), yield 91%, $C_{12}H_{25}OCLP$, ^1H NMR 2.22–2.82 (m, 2H, CH_2), 1.06–2.15 (m, 20H, 10 × CH_2), 0.73–1.06(t, 3H, CH_3) ppm.

REFERENCES

1. R. D. Cook, C. E. Diebert, P. C. Turley, P. Haake, *J. Am. Chem. Soc.*, **94,** 9260–1 (1972).
2. R. D. Cook, C. E. Diebert, W. Schwarz, P. C. Turley and P. Haake, *J. Am. Chem. Soc.*, **95,** 8088 (1973).
3. J. Kumamoto, J. R. Cox. Jr, and F. H. Westheimer, *J. Am. Chem. Soc.*, **78,** 4858 (1956).
4. F. Covitz and F. H. Westheimer, *J. Am. Chem. Soc.* **85,** 1773 (1963).
5. P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.* **83,** 1102 (1961).
6. F. Covitz, Ph.D. Thesis Harvard University 1965, Dissertation Abstr, 27 22918 (1967).
7. E. A. Dennis and F. H. Westheimer, *J. Am. Chem. Soc.*, **88,** 3432 (1966).
8. J. R. Cox, Jr, R. E. Wall and F. H. Westheimer, *Chem. Ind.*, (London) 929 (1959).

9. M. Charlton, *J. Am. Chem. Soc.*, **97,** 1552 (1975).
10. M. Charlton, *J. Am. Chem. Soc.*, **97,** 3694 (1975).
11. Chengye Yuan, Shusen Li, Xiugao Liao, (to be published).
12. S. H. Unger and C. Hansch, *Progress in Physical Organic Chemistry,* Vol. 12, p. 91. (Ed, R. W. Taft) J. Wiley and Sons Press 1976.
13. C. K. Hancock, and C. P. Falls, *J. Am. Chem. Soc.* **83,** 4214 (1961).
14. C. G. Davies and D. P. Evans, *J. Chem. Soc.*, 340 (1940).
15. M. S. Newman, *J. Am. Chem. Soc.*, **72,** 4783 (1950).
16. M. S. Newman, in *Steric Effects in Organic Chemistry,* M. S. Newman, ed. Wiley, New York, 1956, Chapter 4.
17. Chengye Yuan, Shusen Li, Zhini Cheng, *Synthesis* (to be published).
18. M. I. Kabachnik *et al., Dokl Akad Nauk, S.S.S.R.* **110,** 217 (1956).
19. A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

This Project Supported by National Natural Science Foundation of China.