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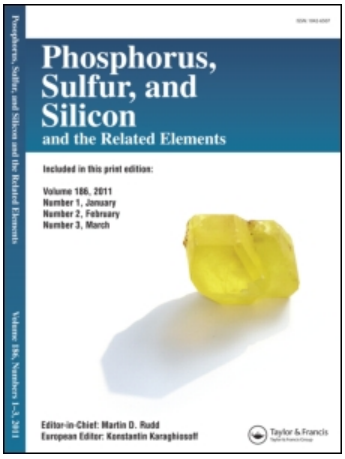

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IODINE INDUCED CYCLIZATION OF ORGANOPHOSPHORUS COMPOUNDS

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IODINE INDUCED CYCLIZATION OF ORGANOPHOSPHORUS COMPOUNDS

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The iodine induced cyclization reaction of unsaturated phosphates, phosphonates and phosphoamidates was studied. It was found that the nucleophilicity of the phosphoryl oxygen was affected by the substituent on phosphorus and the reactivity of the unsaturated center was perturbed by the neighboring atoms or groups. The P-31 NMR spectra and other spectroscopy techniques proved, the existence of the diiodo-compounds and the cyclic phosphonium ions as the reaction intermediates.

Key words: Electrophile induced cyclization; phosphoryl oxygen as nuclephilic center; structural effects on cyclization reaction.

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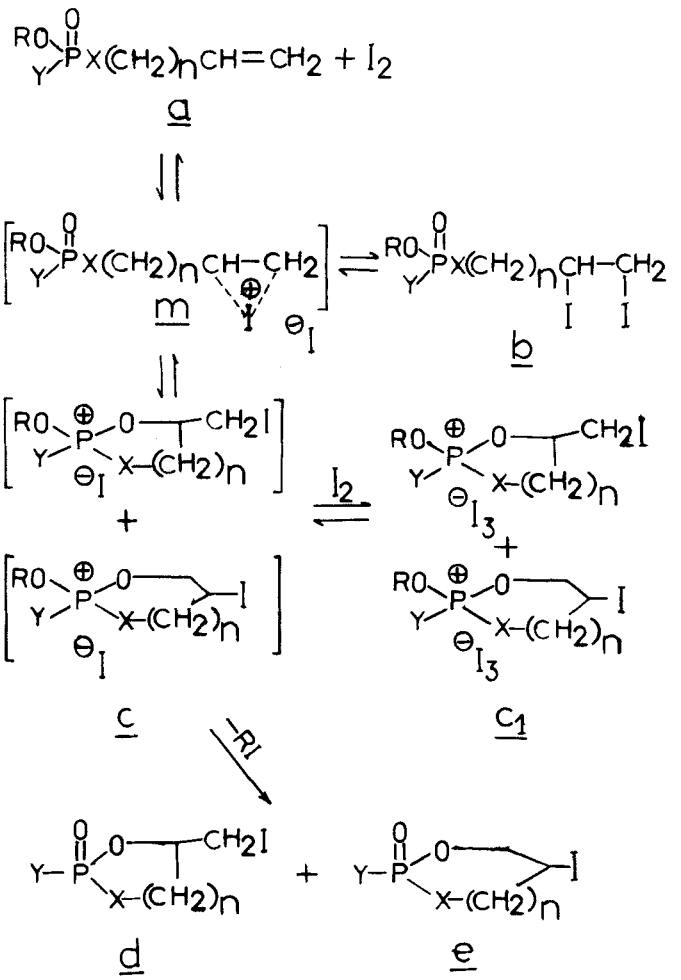
1. INTRODUCTION

The construction of a cyclic system by alkene cyclization reaction is a well established powerful strategy in organic synthesis. One of this kind of reactions is the electrophile induced cyclization reaction of unsaturated carboxylic acid, ester, anhydride, ether, amine, amide and organophosphorus compounds.[1,2] Although it had been applied extensively to organic synthesis and analysis, the investigation of its mechanism[3] and the effect of the molecular structure lagged behind, probably because there was no accessible technique to trace the complicated reaction mixture before. We had taken the advantage of the ^{31}P-NMR detection technique to study the mechanism on the iodine induced cyclization reaction of unsaturated phosphonates.[4] It was found that in chloroform there were two observable intermediates, the major one being 4,5-diiodo-pentenyl-phosphonate, which had never been proposed before, the other one could be the cyclic phosphonium ion. Both of them had been confirmed by the FAB-MS.[5]

The study of the iodine induced cyclization was now extended to include compounds with the general structure **a** (Scheme 1). The influence of the structural effects was determined by ^{31}P-NMR and other spectroscopic techniques.[6]

RESULTS AND DISCUSSION

Since the γ,δ-unsaturated phosphonate **1a** could be transformed after treatment with iodine, smoothly into the cyclic phosphonate **1d** in quite good isolated yield,[4]



SCHEME 1 Proposed mechanism for the cyclization reaction of **1a–9a** with iodine.

a series of analogues **2a–9a** were tested in order to understand the limits and scopes of this electrophile induced cyclization reaction. The structural effects on the cyclization were the results from three variables, namely, the methylene unites *n* and the hetero atom *X*, which separates the electrophilic and nucleophilic centers, and the substitute *Y*, which is directly bonded to the phosphorus atom. The results are discussed as follows, (Table I and Scheme 1).

Effects of n and X on the cyclization reaction

Table I shows that when the methylene unites are two ($n = 2$) and the substituted groups *Y* are ethoxy, no matter whether the *X* is CH_2 (**1a**), or oxygen atom (**6a**), the regio-selective six-membered ring products **1d**, and **6d** were formed after **1a** or **6a** were treated with two eq. of iodine in chloroform respectively. It seems that the thermodynamically favored six membered ring is the driving force for the reaction. But when the methylene unit is shortened to one ($n = 1$), the

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TABLE I

The iodine induced cyclization reaction of organophosphorus compounds **1a–9a**[a]

Compound	*Y*	*X*	*n*	equilibrated product iodine adduct	equilibrated product ring compound
1a	RO	CH_2	2		**1d**[b]
2a	EtO	CH_2	1		**2d, 2e**
3a	MeO	CH_2	0	**3b**	
4a	EtO	NCH_3	1		**4e**
5a	EtO	NH	1		**5e**[d]
6a	EtO	O	2		**6d**
7a	EtO	O	1	**7b**	
8a	Et_2N	O	1		**8d**
9a[c]	C_6H_5O	O	2	**9b**	

[a] Each of **1a–9a** was treated with two equivalent of iodine in chloroform.
[b] R = *n*Pr See ref. 4.
[c] **9a** is 0,0-diphenyl-*O*-3-butenylphosphate.
[d] **5e** (−1.4, −2.3 ppm) a pair of isomers.

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homologues **2a**, **4a**, **5a** and **7a** behaved completely differently; thus **2a** gave both six and five membered ring products **2d** and **2e**; **4a** and **5a** gave only the six membered ring compound **4e** and **5e**; while **7a** was converted into the diiodoadduct **7b**. Of course, when compared to $n = 2$, now for $n = 1$ the hetero atom X is closer to the bridged iodonium ion *m* (Scheme 1) hence its effect on the stability of *m* becomes apparent. Since the major factor which influences the stability of *m* is the electronic effect, and since the oxygen atom has the largest electronegativity 3.5 (nitrogen 3.0 and carbon 2.5), it was expected that 7*m* was the most unstable one and its life time might be too short to have the cyclization happen. Hence the equilibrium was shifted to the diiodo-adduct **7b**. While in 2*m*, X is CH_2 which has no such unfavorable electronic effect on the iodonium ion, therefore, both bridged carbons in 2*m* can be attacked by the phosphoryl oxygen. However, the ^{31}P-NMR spectra and the FAB-MS showed that when **5a** was treated with two eq. of iodine, **5e** was formed in 40% yield. It is a mixture of two stereoisomeric six membered phosphoamidates with the ^{31}P-NMR shift at −2.3 ppm and −1.4 ppm close to similar compound.[7] In this case the preferential attack on the terminal carbon could be rationalized by assuming that the electron donating resonance effect of the —*NH*— decreases the carbonium ion character on the β-carbon and minimizes its electrophilicity.

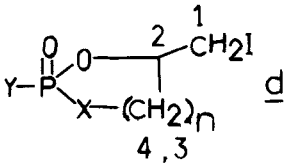
If the methylene unit between the phosphoryl group and the double bond was shortened further, $n = 0$, even for $X = CH_2$ as in **3a**, there was no cyclization at all. It seems that the phosphoryl group caused the destabilization effect on the iodonium ion 3*m*, hence only the diiodo-adduct **3b** was observed by the ^{13}C-NMR. (Tables I–II).

Effects of Y on the Cyclization Reaction

When the X and n were fixed, a changing of Y profoundly affected the cyclization reaction. For example, because of the existence of the oxygen atom in **7a**, the

TABLE II

^{13}C-NMR[a] and ^{31}P-NMR[b] shifts of **1d**, **2d**, **2e**, **4e**, **5e**, **6d**, **8d** and the ^{13}C-^{31}P coupling constants[c]



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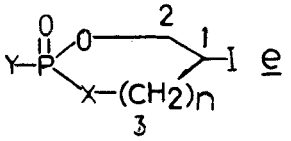

e

	C of								
	C_1	C_2	C_3	C_4	Y			X	^{31}P-NMR
1d	7.38 (7.33)	79.85 (7.33)	31.14 (6.10)	20.88 (8.54)	65.91 (6.10)	23.50 (6.10)	9.91	21.73 (129.39)	24.15
2d	7.5 (4.9)	77.1 (11.0)	29.8		62.5 (7.3)	16.6 (4.9)		20.5 (119.6)	46.0
2e	34.1 (7.3)	74.4 (7.3)	20.3 (5.9)		61.4 (5.9)	16.2 (5.9)		25.4 (130.4)	21.0
4e	35.49	73.46 (7.81)	58.38		62.99 (5.86)	15.95 (5.86)		16.60	3.7
5e	—	—	—	—	—	—	—	—	−1.4; −2.3
6d	6.1 (10.3)	78.0 (7.3)	30.7 (4.4)	66.7 (7.3)	62.7 (5.9)	15.4 (5.9)			−7.4
8d	3.8 (4.4)	76.0	69.5		39.8 (4.4)	13.9			26.3

[a] The ^{13}C-NMR spectra used the $CDCl_3$ as the internal reference at 76.9 ppm. All compounds were purified by column chromatography. Compound **5e** decomposed when column chromatographed.
[b] The ^{31}P-NMR spectra used the 85% H_3PO_4 as the external reference.
[c] Coupling constants in parenthesis are given in hertz.

cyclization reaction was inhibited, but this inhibition could be deleted if the *Y* in **7a** was replaced by a stronger electron donating group such as diethylamino group in **8a**, which after the same treatment gave the five membered ring compound **8d**. Inspection of the structure of molecule **8a** reveals that the group *Y* will directly affect the phosphoryl oxygen's nucleophilicity, and will not influence the iodonium ion *m*. Consequently, the unfavorable hetero atom effect was compensated by enhancing the nucleophilicity of the phosphoryl oxygen with a stronger electron donating group *Y*.

The assumption that the nucleophilicity affects the cyclization can also be deduced from another model compound **9a**. At beginning, it was designed for attempting to trap the phosphonium ion **9c**. Since **6a** gave cyclic six membered ring compound **6d** in 84% isolated yield, it was expected that **9a**, in which two phenoxy groups substituted for the ethoxy in **6a**, would be a good model for cyclization and the reaction in Scheme 1 should stop at the phosphonium ion stage, because dealkylation was prevented. However, **9a** did not give any cyclic product at all, the ^{31}P-NMR and the ^{13}C-NMR showed that the diiodo-adduct **9b** was the only end product. This unusual phenomenon might also be due to a decrease of the nucleophilicity of the phosphoryl oxygen, as a result of the weaker electron donating ability of the phenoxy group compared to the ethoxy group.[8]

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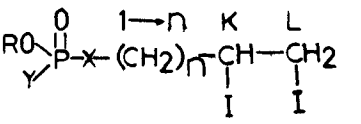
TABLE III

^{13}C-NMR and ^{31}P-NMR shifts of the iodine adducts **1b–9b**; and the ^{13}C-^{31}P coupling constants[a,b]

1b–9b 1b—9b



	^{13}C (ppm)						FAB-MS
	X	1		k	L	^{31}P	$(M+1)^+$
1b	24.7 (141.2)	22.4 (4.4)	39.7 (16.2)	31.4	13.2	31.4	489
2b	24.4 (139.7)	32.02 (2.94)		31.4 (19.11)	12.7	29.9	447
3b	35.6 (142.1)			17.6 (4.39)	15.8 (13.18)		
5b		48.4		32.8 (5.87)	9.5	7.7	448
6b		66.0 (5.86)	38.9 (7.32)	26.8	13.1	−1.50	463
7b		69.7 (4.4)		25.3 (8.79)	8.2	−1.83	449
8b		68.9		26.4 (2.21)	8.3	9.2	
9b		68.3 (5.9)	39.4 (7.3)	26.6	13.2	0.0	559

[a] Coupling constants in parenthesis given in Hertz.

[b] A 1.7 M solution of **1a–9a** in chloroform was treated with one eq of iodine at 21°C, after few min the C-13 NMR spectrum was taken with 2000 pulses and TMS as the reference.

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The existence of the diiodo-compound as the reaction intermediate or end product

As each of **1a–9a** was treated with iodine in chloroform, each of the diiodo-adduct **1b–9b** was observed by the ^{31}P-NMR and ^{13}C-NMR spectroscopy. Some of them were also detected and characterized by positive ion FAB-MS, (Table III). For the cases where the cyclization reaction occurred, the diiodo-adducts could be detected as intermediates by NMR. But in those cases where cyclization was suppressed by any unfavorable structural effects, the diiodocompounds were the end products, such as for **3b**, **7b** and **9b**.

The structural effects on the observation of the phosphonium ion

When each of **1a–9a** was treated with iodine, no matter whether the cyclization occurred or not, the first intermediate, diiodo-adduct, was detected by the ^{31}P-NMR spectra, (Table III). But only for **1a** and **2a** was the second intermediate, i.e. the phosphonium ion observed. It was reported that the concentration of the phosphonium ion was increased as the concentration of the iodine was enhanced.[4] For the substrate **2a** the same phenomenon occurred,

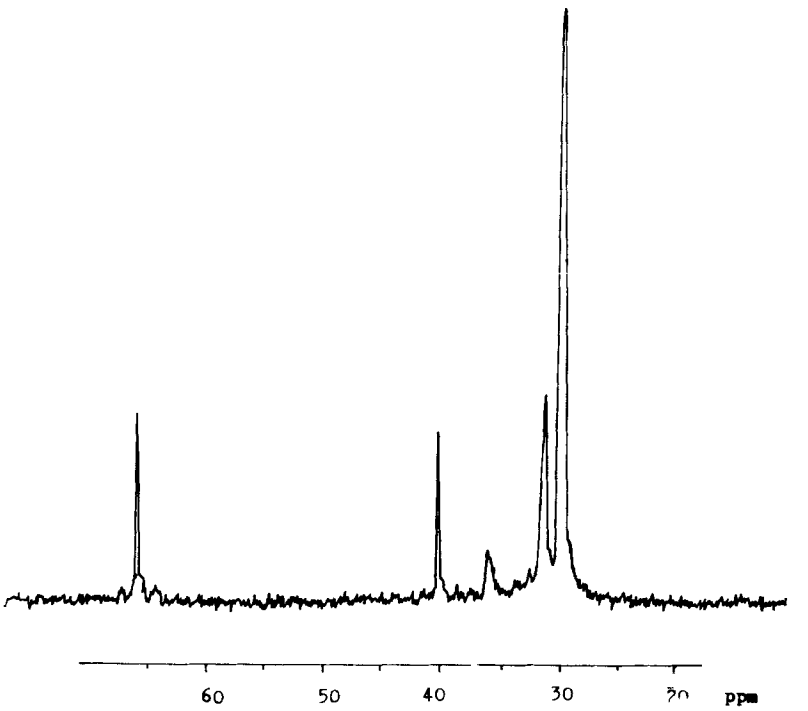

FIGURE 1 Formation of two phosphonium ions when **2a** is caused to react with two equiv. of iodine at RT for 6 hr, as determined by ^{31}P-NMR spectroscopy.

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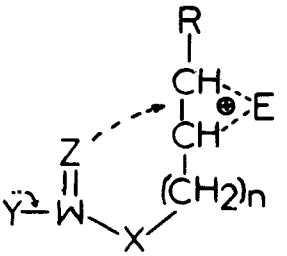
when it was treated with one eq. of iodine only traces of phosphonium ion could be detected by the ^{31}P-NMR. When two eq. of iodine were used, there were two distinctive peaks at +40.7 ppm and 66.6 ppm (Figure 1), which were assigned to the six and five membered ring phosphonium ion respectively. But for other cases, **4a**, **5a**, **6a**, and **8a**, although the cyclization succeeded, we were not able to detect the signal of the corresponding phosphonium ion. It seems that the stability of the positive phosphonium ion was severely disturbed by the adjacent hetero atom, oxygen or nitrogen atom, hence, their life times were too short to be observed by the NMR techniques.

CONCLUSION

Since the iodolactonization reaction is an intramolecular nucleophilic substitution reaction, which involves a charge affinity reversed double bond as the electrophilic center and a phosphoryl oxygen or a carbonyl oxygen as the nucleophilic center, any structural effect to perturb the reactivity of these two centers will eventually induce the intermediate to cyclize or not. It was found that an electron donating group *Y* would favor the cyclization, on the contrary, an electron withdrawing group might prevent the cyclization. The substitution effect on the rate of iodolactonization of unsaturated carboxylic acids was investigated



SCHEME 2 Structural effects on the electrophile induced cyclization reaction in which *W* could be any hetero atom or carbon.

before.[10] Also, the existence of the hetero atom and the methylene unites, which separate these two reaction centers, would play a crucial role in determining the stability of the iodonium ion, phosphonium ion, which will control the probability of cyclization. Some of these effects were investigated for the unsaturated carboxylic acids system.[11]

These conclusions might be generalized as in Scheme 2 which could be applied to other electrophile induced cyclization reaction, for W could be any hetero atom or carbon.

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EXPERIMENTS

Method: ^{1}H-NMR and ^{13}C-NMR spectra were taken on an EM-360 or JEOL FX-100 spectrometers, with TMS as the internal standard in $CDCl_3$. Positive ion FAB-MS were obtained on a KYKY ZhP-5 double focussing mass spectrometer (Scientific Instrument Factory, Beijing China) equipped with a standard KYKY fast atom gun. Elemental analyses were performed by the Analytical Laboratory, Institute of Chemistry, Academia Sinica, Beijing, China. The FT ^{31}P-NMR spectra were measured on a FT-80A spectrometer at 32.2 MHz with the probe temperature 37°C, by broad band decoupled technique with pulse angle 30°, acquisition time 0.5 sec, pulse delay 3 sec, with 85% H_3PO_4 as external reference. Compounds **2a**, **5a**, **7a** were prepared by the known methods.[12–15]

Synthesis of O,O-diethyl-N-methyl-N-(2-propenyl)-phosphoramidate, **4a**. To a suspended solution of sodium hydride (0.86 g, 0.035 mol) in 50 ml anhydrous THF at room temper., O,O-diethyl-*N*-methylphosphoramidate (5.70 g, 0.034 mol) was added. After the hydrogen evolution ceased, allylic bromide (4.50 g, 0.035 mol) in 8 ml THF was dropped in. The mixture was stirred for 10 hr, then diluted by 10 ml water. The organic layer was dried with $MgSO_4$. Then the solvent was evaporated and the residue distilled under reduced pressure. **4a** was obtained, 6.1 g (yield, 87%). bp. 121–122 C/2 mm Hg. ^{31}P-NMR: −0.40 ppm. ^{1}H-NMR: 1.27 (6 H, t), 2.50 (3 H, d), 3.50 (2 H, q), 3.90 (4 H, m), 4.87–5.33 (2 H, m), 5.40–6.07 (1 H, m). Anal. Calcd. for $C_8H_{18}NO_3P$: C, 46.33; H, 8.76; N, 6.76. Found: C, 45.86; H, 8.90; N, 7.10.

Synthesis of O,O-diethyl-O-3-butenylphosphate, **6a**. To a solution of 3-buten-1-ol (4.20 g, 0.060 mol) and triethylamine (6.1 g, 0.060 mol) in petroleum ether (60–90°C) 60 ml at 0°C, diethyl phosphochloridate (10.2 g, 0.60 mol) was dropwise added. Then the mixture was stirred at 0°C for 3 hr, and treated as above. Compound **6a** was isolated in 72% yield (9.0 g), bp. 104–106°C/1 mm. ^{31}P-NMR: −0.91 ppm. ^{1}H-NMR: at 1.32 (6 H, t), 2.41 (2 H, q), 4.10 (6 H, m), 4.87–5.30 (2 H, m), 5.47–6.17 (1 H, m). anal. Calcd. for $C_8H_{17}O_4P$: C, 46.15; H, 8.17. Found: C, 45.81; H, 8.21.

Synthesis of O-ethyl-O-2-propenyl-N-diethylphosphoramidate, **8a**. To a solution of ethyl dichlorophosphate (10.3 g, 0.064 mol) and allyl alcohol (3.7 g, 0.064 mol) in 50 ml CH_2Cl_2 at 0°C, triethyl amine (6.5 g, 0.065 mol) was added within 30 min. Then the mixture was stirred at 0°C for 3 hr and diethylamine (9.4 g, 0.13 mol) dropwise added. With stirring at RT overnight, the reaction mixture was filtered. The filtrate was washed with H_2O (10 ml × 3), dried with $MgSO_4$. Then the solvent was evaporated and the residue distilled under reduced pressure. Compound **8a** was obtained in 82%

yield, bp. 81–83°C/2 mm. ^{31}P-NMR: 10.47 ppm. ^{1}H-NMR: at 1.00 (6 H, t), 1.30 (3 H, t), 3.03 (4 H, m), 4.00 (2 H, q), 4.40 (2 H, t), 5.00–5.45 (2 H, m), 5.60–6.27 (1 H, m). anal. Calcd. for $C_9H_{2O}NO_3P$: C, 48.86; H, 9.05; N, 6.33. Found: C, 48.20; H, 9.04; N, 6.68.

Synthesis of O,O-diphenyl-O-3-butenylphosphate, **9a**. As described above, diphenyl phosphochloridate (4.6 g, 0.017 mol) was allowed to react with 3-buten-1-ol (1.2 g, 0.017 mol) in the presence of one eq. of triethylamine. The crude product was chromatographed on a silica-gel column, eluted with ethyl acetate. There was obtained a total of 3.8 g (74%) of **9a** as a colorless oil. ^{31}P-NMR: −11.4 ppm.

^{1}H-NMR: at 2.20–2.40 (2 H, m), 4.23 (2 H, q), 4.83–5.30 (2 H, m), 5.40–6.00 (1 H, m), 7.20 (10 H, s). anal. Calcd. for $C_{16}H_{17}O_4P$: C, 63.16; H, 5.59. Found: C, 62.94; H, 5.62.

Synthesis of 2-ethoxy-2-oxo-5-iodomethyl-1, 2-oxaphospholane, **2d**, *and 2-ethoxy-2-oxo-5-iodo-1, 2-oxaphosphorinane,* **2e**. A mixture of **2a** (1.0 g, 5.2 mmole) and iodine (2.6 g, 10.0 mmole) was dissolved in 3 ml $CHCl_3$.

After standing at 20°C for 60 hr. The solvent was evaporated and the residue passed through a silica-gel column.

A mixture of **2d**, ^{31}P-NMR shift at 46 ppm, and **2e** at 20.0 ppm, 0.85 g (57%) was obtained. Anal. Calcd. for $C_6H_{12}IO_3P$: C, 24.83; H, 4.13. Found: C, 24.87; H, 4.09. After rechromatography on a 260 mesh silica-gel column pure **2d** and **2e** was isolated. **2d**, ^{1}H-NMR: at 1.26 (3 H, t), 1.70–2.36 (4 H, m), 3.31 (2 H, m), 3.80–4.50 (3 H, m). **2e** ^{1}H-NMR: at 1.40 (3 H, t), 1.64–3.00 (4 H, m), 3.90–4.70 (5 H, m).

Synthesis of the 2-ethoxy-2-oxo-3-methyl-5-iodo-1,3,2-oxazaphosphorinane, **4e**, *and observation of* **5e**. Compound **4a** (1.50 g, 7.25 mmol) and iodine (3.68 g, 14.5 mmol) were mixed in 6.0 ml $CHCl_3$, then heated at 40°C for 12 hr. The solvent was removed. The residue was passed through an aluminum oxide column and eluted by $CHCl_3$ and $(CH_3)_2CO$ (10:1). There was obtained a total of 0.95 g (yield, 43%) of **4e** which was a yellow oil. ^{31}P-NMR: 3.7 ppm(s). ^{1}H-NMR: 1.33 (3 H, t), 2.67 (3 H, d), 3.05–3.53 (2 H, m), 3.77–4.50 (5 H, m). FAB-MS: $(M+1)^+ = 305$ (abundent 100).

For the synthesis of **5e**, (0.50 g, 2.6 mmol) **5a** was treated with two eq. of iodine at the same condition described above. The ^{31}P-NMR spectra showed two peaks (40%) at −1.4 ppm and −2.3 ppm which were assigned to two stereo-isomers of **5e**. FAB-MS of the reaction mixture showed the molecular ion peak of **5e** at $(M+1)^+ = 292$. However, attempts to isolate **5e** were not successful, probably it was decomposed on the column.

Synthesis of 2-ethoxy-2-oxo-4-iodomethyl-1,3,2-dioxaphosphorinane, **6d**. As described above, **6a** (0.80 g, 3.8 mmol) and iodine (2.0 g, 7.9 mmol) in 3.0 ml $CHCl_3$ gave **6d** (0.98 g, 84%). ^{1}H-NMR: 1.40 (3 H, t), 1.80–2.30 (2 H, m), 3.30 (2 H, d), 3.85–4.65 (5 H, m). ^{31}P-NMR: −7.4 ppm. Anal. Calcd. for $C_6H_{12}IO_4P$: C, 23.53; H, 3.92. Found: C, 24.01; H, 4.12.

Synthesis of 2-diethylamine-2-oxo-4-iodomethyl-1,3,2-dioxaphospholane, **8d**. A mixture of **8a** (0.70 g, 3.2 g, 3.2 mmol) and iodine (1.60 g, 6.3 mmol) in $CHCl_3$ (4.0 ml), was standing for 60 hr at 29°C. After the regular work up as described above a yellow oil 0.20 g (20%) was obtained. ^{1}H-NMR: at 1.14 (6 H, t), 3.08 (4 H, m), 3.35 (2 H, d), 4.08–4.62 (3 H, m). FAB-MS: $(M+1)^+ = 320$ (100), $(M-I+1)^+ = 193(20)$, $(M-CH_2I+1)^+ = 179(24)$, $(M-2XC_2H_5-I+1) = 135(49)$.

General procedure for observation and characterization of compounds **1b–9b** *by* ^{31}P-NMR. In a 0.5 cm ϕ NMR tube, each of compounds **1a–9a** was reacted with one eq. of iodine in $CDCl_3$. After 15 min, the ^{13}C-NMR spectrum was taken with 2000 pulse (1 hr and 10 min), the spectrum for each of **1b–9b** was obtained by substracting the known spectrum for each of **1a–9a** from the mixed one. (Table III). At the same time, their ^{31}P-NMR shifts were obtained. A typical ^{31}P-NMR spectrum of **2a** with iodine is showed in Figure 1.

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REFERENCES

1. M. D. Doyle and D. I. Davies, *Chem. Soc. Rev.*, 171, 1979.
2. P. A. Bartlett, *Tetrahedron*, **36,** 2, 1980.
3. R. T. Arnold, N. de M. Campos and K. L. Lindsay, *J. Am. Chem. Soc.*, 1953, **75,** 1044; L. do Amaral, S. C. Melo, *J. Org. Chem.*, **38,** 800, 1973.
4. Y. F. Zhao, S. J. Yan, and C. Zhai, *J. Org. Chem.*, **50,** 2136, 1985.
5. W. G. Chai, M. C. Ye, Y. Lin, Y. F. Zhao, *J. Org. Chem.*, **52,** 1617, 1987.
6. M. C. Ye, W. G. Chai, L. P. Li, Y. F. Zhao, *Tetrahedron Letters*, **28,** 2615, 1987.
7. P. O. Savignac, J. Chenault, M. Dreux, *J. Organometallic Chem.*, **66,** 63, 1974.
8. H. C. Brown in "Current Trends in Organic Synthesis", H. Nozaki ed., p. 247, 1983.
9. Y. F. Zhao, M. C. Ye, S. J. Yan, L. P. Li and C. Zhai, *Phosphorus and Sulfur*, **30,** 323, 1987.
10. M. Moura Campos, *An. Acad. Brasil Cienc.*, **27,** 405, 1955.
11. C. H. Cook *et al.*, *Arch. Pharmacol. Res.*, **6,** 45, 1983.
12. M. H. Bride, W. A. W. Cummings and W. Pickles, *J. Appl. Chem.*, **11,** 352, 1961.
13. V. Mark, C. Dungan, M. Crutchfield, J. Van Wazer, "Compilation of ^{31}P-NMR data", p. 333, 1967.
14. P. Savignac, A. Brgire, F. Mathey, *Synth. Commun.*, **9,** 487, 1979.
15. A. Zwierzak, *Organic Syntheses*, **11**, 921, 1982.

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