results in the rapid appearance of new carbonyl stretching bands in the infrared region. Rhodium carbonyl chloride dimer in *n*-heptane, has IR bands at 2103, 2084, 2075, 2032, and 2000 $cm^{-1}$. Exposure of the rhodium compound to an equivalent amount of zirconium *n*-propoxide results in the appearance of broad bands at 2068 and 1967 $cm^{-1}$. When a 10-fold excess of the zirconium alkoxide was used, only the two noted intense bands were observed. Analogous results were obtained with zirconium ethoxide or titanium *n*-butoxide in place of zirconium *n*-propoxide. Attempts to isolate these complexes in analytically pure form failed. Treatment of the generated complex with halide affords ester.

In conclusion, titanium and zirconium alkoxides are valuable reagents for converting halides to esters, using rhodium and/or palladium catalysts. The reaction is very sensitive to the nature of the alkoxy groups.

## Experimental Section

**General Methods.** All reactants (halides, titanium or zirconium alkoxides) were used as received. Chloro(1,5-hexadiene)-rhodium(I) dimer was prepared from rhodium chloride according to the procedure of Marko and co-workers.[5] Tetrakis(triphenylphosphine)palladium(0) was synthesized by standard methods.[6] Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer. Varian T-60, EM-360, and FT-80 instruments were used for recording NMR spectra. A VG 5050 Micromass spectrometer was used for mass spectral determinations.

**General Procedure for the Carbonylation Reaction of Benzylic Halides with Titanium and Zirconium Alkoxides.** A mixture of benzylic halide [2.0 mmol], metal alkoxide [2 mL—or an equimolar amount in *n*-heptane], and rhodium(I) catalyst [0.10–0.15 mmol] was heated overnight under a carbon monoxide atmosphere at 75 °C (bromide) or 100 °C (chloride). After cooling to room temperature, 1 M NaOH was added and the solution was extracted with ether or hexane. The organic extract was dried ($MgSO_4$) and concentrated and the pure ester was obtained by distillation and/or chromatography.

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**General Procedure for the Carbonylation Reaction of Non-Benzylic Bromides with $M(OR)_4$ [M = Ti, Zr].** Carbon monoxide was bubbled through a solution containing the bromide [2.0 mmol], metal alkoxide [2.0 mL], and tetrakis(triphenylphosphine)palladium [0.13 g, 0.11 mmol, M = Ti] or $Pd(PPh_3)_4$ [0.13 g, 0.11 mmol]/$[1,5\text{-HDRhCl}]_2$ [0.090 g, 0.20 mmol, M = Zr]. The reaction mixture was stirred overnight at 150 °C. Workup was effected in the same manner as that described for benzylic bromide.

**Acknowledgment.** We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council for support of this work.

**Registry No.** **2** (Ar = Ph, X = Br), 100-39-0; **2** (Ar = 2-$C_{10}H_7$, X = Br), 939-26-4; **2** (Ar = Ph, X = Cl), 100-44-7; **2** (Ar = *o*-$CH_3C_6H_4$, X = Cl), 552-45-4; **2** (Ar = *p*-$CH_3C_6H_4$, X = Cl), 104-82-5; **2** (Ar = *m*-$MeOC_6H_4$, X = Cl), 824-98-6; **2** (Ar = 1-$C_{10}H_7$, X = Cl), 86-52-2; **3** (M = Ti, R = $(CH_3)_2CH$), 546-68-9; **3** (M = Ti, R = *n*-$C_3H_7$), 3087-37-4; **3** (M = Zn, R = $C_2H_5$), 18267-08-8; **3** (M = Ti, R = *n*-$C_4H_9$), 5593-70-4; **3** (M = Zr, R = *n*-$C_3H_7$), 23519-77-9; **3** (M = Zr, R = $(CH_3)_2CH$), 2171-98-4; **3** (M = Zr, R = *n*-$C_4H_9$), 1071-76-7; **3** (M = Ti, R = $C_2H_5$), 3087-36-3; **4** (Ar = Ph, R = $(CH_3)_2CH$), 4861-85-2; **4** (Ar = Ph, R = *n*-$C_3H_7$), 4606-15-9; **4** (Ar = Ph, R = $C_2H_5$), 101-97-3; **4** (Ar = 2-$C_{10}H_7$, R = $(CH_3)_2CH$), 91759-48-7; **4** (Ar = 2-$C_{10}H_7$, R = *n*-$C_4H_9$), 2876-68-8; **4** (Ar = Ph, R = *n*-$C_4H_9$), 122-43-0; **4** (Ar = *o*-$CH_3C_6H_4$, R = *n*-$C_4H_9$), 96307-73-2; **4** (Ar = *o*-$CH_3C_6H_4$, R = $C_2H_5$), 40291-39-2; **4** (Ar = *o*-$CH_3C_6H_4$, R = *n*-$C_3H_7$), 96307-74-3; **4** (Ar = *p*-$CH_3C_6H_4$, R = $C_2H_5$), 14062-19-2; **4** (Ar = *p*-$CH_3C_6H_4$, R = *n*-$C_4H_9$), 93578-99-5; **4** (Ar = *m*-$CH_3OC_6H_4$, R = *n*-$C_4H_9$), 96307-75-4; **4** (Ar = *m*-$CH_3OC_6H_4$, R = *n*-$C_3H_7$), 96307-76-5; **4** (Ar = 1-$C_{10}H_7$, R = *n*-$C_4H_9$), 2876-75-7; **4** (Ar = 1-$C_{10}H_7$, R = $C_2H_5$), 2122-70-5; **4** (Ar = 1-$C_{10}H_7$, R = *n*-$C_3H_7$), 551-04-2; **4** (Ar = *m*-$CH_3C_6H_4$, R = $(CH_3)_2CH$), 6297-45-6; **4** (Ar = *m*-$CH_3C_6H_4$, R = *n*-$C_4H_9$), 6640-77-3; $(PhCH_2)_2CO$, 102-04-5; $PhCH_2O$-*n*-$C_3H_7$, 937-61-1; $PhCH_2O$-*n*-$C_4H_9$, 588-67-0; *o*-$CH_3C_6H_4CH_2O$-*n*-$C_3H_7$, 91967-69-0; $(p\text{-}CH_3C_6H_4CH_2)_2CO$, 70769-70-9; *m*-$CH_3OC_6H_4CH_2O$-*n*-$C_3H_7$, 96307-77-6; 1-$C_{10}H_7CH_2O$-*n*-$C_3H_7$, 92297-67-1; 1-$C_{10}H_7CH_2O$-*n*-$C_4H_9$, 96307-78-7; 1-$C_{10}H_7CH_3$, 90-12-0; $[1,5\text{-HDRhCl}]_2$, 32965-49-4; CO, 630-08-0; $Pd(PPh_3)_4$, 14221-01-3; 1-$C_{10}H_7C(O)O$-*n*-$C_4H_9$, 3007-95-2; 1-$C_{10}H_7C(O)O$-*n*-$C_3H_7$, 3007-96-3; PhCH=CHC(O)O-*n*-$C_4H_9$, 538-65-8; PhCH=CHC(O)O-*n*-$C_3H_7$, 7778-83-8; *n*-$C_8H_{17}C(O)O$-*n*-$C_4H_9$, 50623-57-9; *m*-$CH_3C_6H_4Br$, 591-17-3; 1-$C_{10}H_7Br$, 90-11-9; PhCH=CHBr, 103-64-0; *n*-$C_8H_{17}Br$, 111-83-1.

# Iodine-Induced Cyclization Reaction of *O,O*-Dialkyl 4-Pentenylphosphonates

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The stereoselective synthesis of *cis*-2-alkoxy-2-oxo-6-(iodomethyl)-1,2-oxaphosphorinanes is achieved by the treatment of *O,O*-dialkyl 4-pentenylphosphonates with iodine. The intermediates involved in iodine-induced cyclization reactions of δ-unsaturated phosphonates could be observed directly by $^{31}P$ NMR at 37 °C. The effects of the iodine concentration and solvents on the cyclization reaction were investigated. In chloroform, there were two intermediates, the major one being (4,5-diiodopentyl)phosphonate; the other one could be a cyclic alkyl trialkoxyphosphonium ion. In benzene and cyclohexane, in addition to these two intermediates, there was at least one more intermediate which could be either a tight ion pair or a pentacoordinate phosphorus compound.

2-Alkoxy-2-oxo-1,2-oxaphosphorinanes are useful as nonflammable hydraulic fluids, plasticizers, and fire retardants for plastics.[1-3] There are many methods[3-11] to synthesize these compounds, but these procedures require

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**Scheme I**

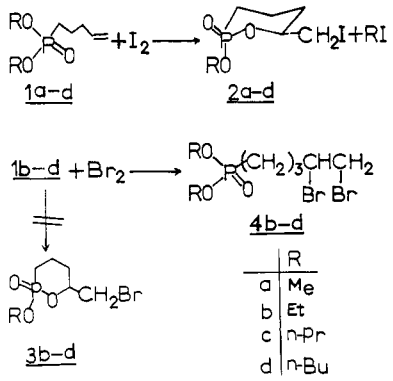



**Table I. Spectral Data of Compounds 2a–d and 4b–d**

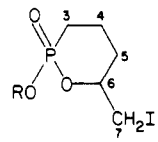
| compd[a] | $^{31}P$ | $^{1}H^{b}$ | IR, $cm^{-1}$ $\nu_{P=O}$ | IR, $cm^{-1}$ $\nu_{P-CH_2}$ | elemental anal. C, % | elemental anal. H, % | yield, % |
|---|---|---|---|---|---|---|---|
| **2a** | 25.41 | 3.30 | 1249 | 1296 | 24.99 | 4.03 | 39 |
| | | | 1239 | | (24.85 | 4.17)[c] | |
| **2b** | 23.91 | 3.30 | 1250 | 1296 | 27.97 | 4.92 | 56 |
| | | | 1240 | | (27.65 | 4.64)[c] | |
| **2c** | 24.15 | 3.30 | 1251 | 1296 | 30.94 | 5.46 | 60 |
| | | | 1240 | | (30.21 | 5.07)[c] | |
| **2d** | 24.13 | 3.30 | 1250 | 1296 | 32.23 | 5.41 | 63 |
| | | | 1240 | | (32.54 | 5.46)[c] | |
| **4b** | | | 1243 | | 29.97 | 5.30 | 72 |
| | | | | | (29.53 | 5.23)[c] | |
| **4c** | 30.39 | | 1243 | | 33.05 | 6.03 | 69 |
| | | | | | (33.52 | 5.88)[c] | |
| **4d** | 31.13 | | 1244 | | 36.74 | 6.39 | 68 |
| | | | | | (36.99 | 6.45)[c] | |

[a] All compounds have correct analyses within ±0.5% for C and H, except **2c** which has the C% within +0.7%. MS for **2c** has the $M^+$ 318 (0.2%). [b] $^1H$ NMR for the $CH_2I$. 85% $H_3PO_4$ as $^{31}P$ external reference. [c] Calculated values.

rather vigorous reaction conditions and often a mixture of stereoisomers is obtained.[5,6,12] We have investigated the iodine-induced cyclization of *O,O*-dialkyl 4-pentenylphosphonates as a mild method to yield the cis cyclic phosphonates **2a–d**.

The iodine-induced cyclization of unsaturated carboxylic acid was discovered at the beginning of this century.[13] Since then, the halolactonization reaction has been applied extensively to organic synthesis.[14,15] It was suggested that the intermediate involved was an oxonium species.[16,17] A cyclic tetraalkoxyphosphonium ion was proposed for the iodine-induced cyclization of a γ-unsaturated phosphate.[18] In this paper, we wish to report the direct observation of the intermediates for the iodine-induced cyclization of δ-unsaturated phosphonates.

**Table II. $^{13}C$ NMR[a] Shifts and the $^{13}C$–$^{31}P$ Coupling Constants[b] of 2a–d**




| compd | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | C of *R* |
|---|---|---|---|---|---|---|
| **2a** | 21.39 | 20.95 | 31.39 | 80.18 | 7.21 | 50.91 |
| | (129.40) | (7.33) | (6.10) | (7.32) | (8.55) | (7.33) |
| **2b** | 22.03 | 21.03 | 31.34 | 80.15 | 7.27 | 60.91, 16.43 |
| | (129.39) | (8.54) | (6.10) | (7.33) | (8.54) | (6.10), (4.89) |
| **2c** | 21.73 | 20.88 | 31.14 | 79.85 | 7.38 | 65.91, 23.50, 9.91 |
| | (129.39) | (8.54) | (6.10) | (7.33) | (7.33) | (6.10), (6.10) |
| **2d** | 21.68 | 20.83 | 31.09 | 80.77 | 7.36 | 64.09, 32.06, 18.62, 13.36 |
| | (129.39) | (7.32) | (6.10) | (6.11) | (8.55) | (7.33), (6.11) |

[a] The $^{13}C$ NMR used the $CDCl_3$ as internal reference at 76.88 ppm. [b] Coupling constants in parenthesis given in hertz.

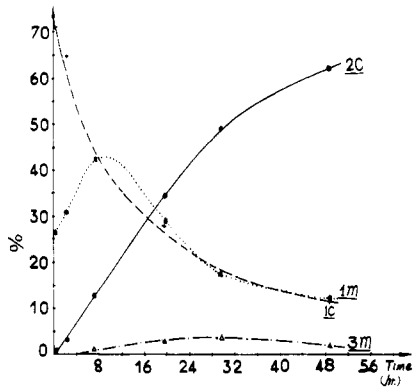



**Figure 1.** The percent contents of the reaction mixtures vs. time as **1c** is reacted with 1 equiv of iodine.

## Results and Discussion

The *O,O*-dimethyl 4-pentenylphosphonate **1a** was prepared by the Arbuzov reaction.[19] Compounds **1b–d** were synthesized by the Kosolapoff method.[20] Of these compounds, **1a,b,d** had been previously reported.[21] The cyclization reaction was referred to by Bartlett.[15] When 1.8 equiv of iodine was added to **1a–d** in chloroform, the cyclization products **2a–d** were obtained in good yields (Scheme I). Under the same conditions, but with bromine instead of iodine, the products isolated were *O,O*-dialkyl (4,5-dibromopentyl)phosphonates **4b–d**. After LC on a silica gel column, pure **2a–d** and **4b–d** were obtained. The structures were characterized by $^1H$, $^{31}P$, and $^{13}C$ NMR, IR, MS, and elemental analyses (Tables I and II).

For all of the four compounds **2a–d**, the chemical shifts of the iodomethyl group in the $^1H$ NMR was 3.30 ppm. Furthermore, these products had an IR absorption band at 1296 $cm^{-1}$ which is the characteristic peak for the cyclic $\nu_{P-CH_2}$ absorption in 1,2-oxaphosphorinanes.[22] For each of **2a–d**, there was only one $^{31}P$ NMR signal and one set of $^{13}C$ NMR signals (Tables I and II). This implies that there

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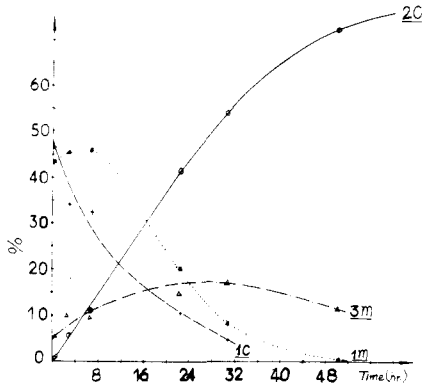


**Figure 2.** The percent contents of the reaction mixture vs. time as **1c** is reacted with 1.8 equiv of iodine.

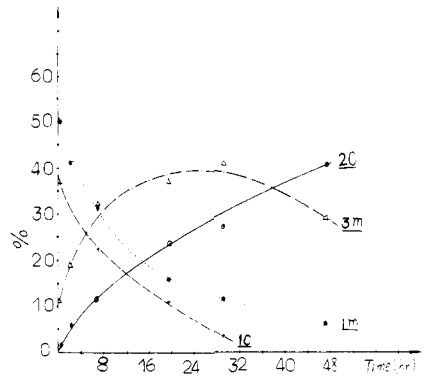


**Figure 3.** The percent contents of the reaction mixture vs. time as **1c** is reacted with 3.0 equiv of iodine.

is only one stereoisomer in each case.[23] From the literature,[22] *cis*-2-alkoxy-2-oxo-6-methyl-1,2-oxaphosphorinanes[24a] exhibit two P=O absorption bands at 1240 and 1255 $cm^{-1}$ for the two interconverting chair conformers, while the trans isomer spectrum had only one absorption for the P=O group near 1250 $cm^{-1}$. Since the IR spectrum for each of the **2a–d** had two absorption bands instead of one in that region, it suggests that each is the cis isomer, with the phosphoryl oxygen preferring the more stable equatorial position.[15,24] The thermodynamically controlled products are *cis*-**2a–d**.[25]

**Existence of Two Intermediates in Chloroform.** At 21 ± 1 °C, a solution of 1.3 M di-*n*-propyl 4-pentenylphosphonate (**1c**) in chloroform was allowed to react with 1.0 equiv, 1.8 equiv, and 3.0 equiv of $I_2$, respectively, sixteen min after adding the $I_2$, the $^{31}P$ NMR spectra were recorded. Then, at regular time intervals, a sequence of $^{31}P$ NMR spectra were obtained. In general, there were five peaks in each spectrum. The relative intensity of the four major peaks were plotted as %P vs. time (Figures 1, 2, and 3). The chemical shifts for these five peaks were 43.4, 32.7, 31.4, 28.0, and 24.7 ppm (from 85% $H_3PO_4$). In all of the three figures the peak intensity at 32.7 ppm (starting material **1c**) decreased as the reaction proceeded. The 24.7-ppm peak (cyclization product **2c**) increased from the beginning until the end of the reaction. For the peaks at 31.4 ppm and 43.4 ppm, the profiles were quite different (Figure 1); they increased up to 10 and 28 h, respectively, then started to decrease. Hence, they were considered as two observable intermediates in chloroform. The peak at 28.0 ppm increased from 0% to 16% for the 1.8 equiv of $I_2$ case and was assumed to be a side product which was not identified.

To deduce the mechanism, the first task was to elaborate which intermediate was formed at the beginning and which one was formed near the end of the reaction coordinate. In Figure 1, when the 31.4-ppm peak had reached 31% at 2 h and 20 min, the 43.4-ppm peak had not appeared yet. It was not until 7 h and 15 min had elapsed that the 43.4-ppm peak appeared with an intensity of 0.7%. Hence, the 31.4-ppm peak appeared before the 43.4-ppm one. This conclusion can also be derived from the difference between these two intermediates' profile in Figure 3. The 31.4-ppm peak had reached 50% at 17 min and then decreased to the end of the reaction, while the 43.4-ppm peak increased up to 28 h then started to decrease. This suggests that the 31.4-ppm intermediate was formed before the 43.4-ppm one.

**Table III. $^{13}C$ NMR Shifts of 1c, 1m, 5, and 6 and the $^{13}C$–$^{31}P$ Coupling Constants**[a]

$(\overset{8}{C}H_3\overset{7}{C}H_2\overset{6}{C}H_2O)_2\overset{}{P}(O)\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H{=}\overset{5}{C}H_2$

**1c**

$(\overset{8}{C}H_3\overset{7}{C}H_2\overset{6}{C}H_2O)_2\overset{}{P}(O)\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H\overset{5}{C}H_2$ (I, I)

**1m**

$\overset{5}{C}H_2{=}\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2Br$ **5**

$\overset{5}{C}H_2\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2Br$ (I, I) **6**

| compd | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ |
|---|---|---|---|---|---|---|---|---|
| **1c**[b] | 24.8 | 21.7 | 34.3 | 137.0 | 115.4 | 66.8 | 23.9 | 10.1 |
| | (140.4) | (4.9) | (17.1) | | | (7.3) | (6.1) | |
| **1c**[c] | 24.7 | 21.6 | 34.2 | 136.9 | 115.3 | 66.7 | 23.8 | 10.0 |
| | (141.2) | (4.4) | (16.2) | | | (5.9)[d] | (5.9)[e] | |
| **1m**[c] | 24.5 | 22.4 | 39.7 | 31.4 | 13.2 | 67.0 | 23.8 | 10.0 |
| | (142.0) | (4.4) | (16.2) | | | (5.9)[d] | (5.9)[e] | |
| **5** | 32.5 | 31.8 | 31.5 | 136.1 | 115.3 | | | |
| **6** | 32.5 | 31.6[f] | 37.2 | 31.4[f] | 13.9 | | | |

[a] Coupling constants in parenthesis given in hertz. [b] Without adding the iodine. [c] In the reaction mixture of **1c** and iodine. [d] Estimated values from a triplet (due to overlapping of two doublets). [e] The $C_7$ of **1c** and **1m** have the same chemical shift. [f] Estimated values.

Although the 43.4-ppm component was formed at the later stage of the reaction, it was not necessarily the precursor of the product. In Figure 1, at 2 h 20 min, the 43.4-ppm peak had not appeared, but the product had already formed (13%). The effect of the iodine concentration on the products' formation rate would also account for this fact. From Figures 1, 2, and 3, it is clear that the rate of disappearance of **1c** was parallel to the iodine concentration. But the product's formation rate was not so obvious. When the iodine concentration was 1.0 or 1.8 equiv, the products' formation rates were similar. However, when the iodine was increased to 3.0 equiv, the rate formation of the product decreased significantly. Therefore, at the higher concentration of iodine, the starting material was trapped as a stable intermediate, which could not be readily converted to the product.

**Characterization of Intermediates 1m and 3m.** Figure 2 shows that from 16 min to 8 h, the reaction mixture of **1c** and iodine consists of **1m** (45%), **1c** (47–32%). Each of **2c** and **3m** constitute less than 10%. Therefore, at the early stage of the reaction the $^{13}C$ NMR spectra of the reaction mixture were not too complicated.

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Table IV. $^{31}P$ NMR Shifts for the Dialkyl Alkylphosphonates and Their Phosphonium Ions

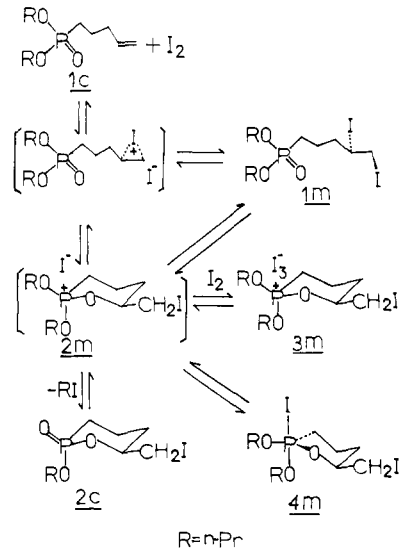
| | X = =O | X = OEt$^+$ $BF_4^-$ |
|---|---|---|
| $(i\text{-PrO})_2PXC_3H_7$ | 28.9 | 31.3 |
| $(EtO)_2PXC_3H_7$ | 31.0 | 35.2 |
| $(EtO)_2PXC_2H_5$ | 32.3 | 35.3 |
| 1c | 32.3 | 35.5, 46.9 |
| 2c | 24.2 | 32.9, 43.5 |

Indeed, Table III gives the $^{13}C$ NMR chemical shifts for neat **1c** and those for the mixture of **1c** and **1m**. These assignments are confirmed by model compound 4-bromo-1-pentene and its iodine addition product 1,2-diiodo-5-bromopentane, Table III. Furthermore, the structure of **1m** is also supported by its $^{31}P$ NMR chemical shift (31.4 ppm), close to that of (4,5-dibromopentyl)-phosphonate **4c** (30.4 ppm).

Trialkyl phosphates and dialkyl alkylphosphonates can be reacted with trialkyloxonium salts to yield the corresponding phosphonium salts.[26,27] Table IV shows that saturated dialkyl alkylphosphonates, after treatment with alkylation reagent, gave only one product. However, the unsaturated phosphonate **1c** produced two peaks after the same treatment, the second peak appearing at 46.9 ppm, which can be attributed to the reaction of the double bond. Similarly as the cyclic phosphonate **2c** was reacted with triethyloxonium tetrafluoroborate in the same manner, there were again two peaks formed at 32.9 ppm and 43.5 ppm. These facts suggest that the intermediate **3m** which has the shift at 43.4 ppm is probably a cyclic trialkoxyphosphonium ion, such as **2m** or **3m**. The highly charge-dispersed triiodide ion[28] in the intermediate **3m** is not as good a nucleophile as iodide. Therefore, **3m** might be expected to accumulate to observable concentration while **2m** might not. This assignment is consistent with the effect of increased iodine concentration. Based on the above information, the mechanism is believed to be as shown in Scheme II.

**Solvent Effect. There Is at Least One More Intermediate in Benzene.** The major difference between polar and nonpolar solvents is that the rate of disappearance of the starting material and the rate of the formation of the product **2c** are faster in nonpolar solvents. And at any specified time during the reaction, the concentration of the intermediate **1m** in the nonpolar solvents is always lower than that in the polar solvents. In nonpolar solvents such as benzene and cyclohexane, the reaction paths traced by the $^{31}P$ NMR were quite different from those in chloroform and acetonitrile. Table V shows that in benzene, 16 min after the iodine had been added, in addition to **1m** and **3m** intermediates, a new broad peak appeared at 32.9 ppm in 16%. Then at 2 h and 35 min, it had decreased to 6%, together with a second broad peak at 34.1 ppm in 6%. These two broad peaks still existed, with a total intensity of 2%, up to 70 h. In cyclohexane, these two broad peaks were also observed, and exhibited the same behavior. Since these two broad peaks had never showed up in chloroform, it is proposed that they are nonionic pentacoordinate phosphorus compounds **4m** (or a tight ion pair **2m** which would have greater stability in solvents of low dielectric constants). In the proposed compound **4m**, there must be a covalent P–I bond which is very weak. Also, the longer P–I bond length will result

Scheme II




in weaker shielding effect. Hence, as compared to **3m** compound **4m** is only upfield by 8–10 ppm, which is much less than that for the regular pentaoxyphosphorane.[29]

The solvent effect can be summarized in Table V. It shows that acetonitrile is the worst solvent, in which **2c** was produced in 60% accompanied with 36% side products and some equilibrated intermediates. In chloroform, although the rate for the formation of product is slowest, it gives the best yield and cleanest results. In benzene and cyclohexane, the yields are similar, and as good as in chloroform.

## Conclusion

The iodolactonization reaction has been applied to a variety of cyclic and acyclic unsaturated carboxylic acid, esters, and ethers for stereocontrol in organic synthesis. The general accepted mechanism of the reaction involves an iodonium intermediate which undergoes intramolecular nucleophilic attack by the oxygen atom on the carbonyl group or on the alkoxy group. However, due to the limitation of the instruments, these intermediates had not been observed yet. We have taken the advantage of $^{31}P$ NMR spectra for its simplicity and clearness to study the reaction mixtures of δ-unsaturated phosphonates and iodine. Together with the $^{13}C$ NMR technique, one of the intermediates has been proposed as the iodine addition product, which has never been proposed for the iodine-induced cyclization reaction. The second intermediate could be a cyclic alkyl trialkoxyphosphonium ion.

## Experimental Section

**Methods.** $^1H$ NMR spectra were taken on a Cameca-RMN 250-MHz spectrometer with $Me_4Si$ as the standard in $CDCl_3$. The $^{13}C$ NMR was done on a JEOL FX-100 spectrometer at 100 MHz. IR spectra were measured on the Shimadzu 430 spectrometer. An MS was taken on an AEI-50. HPLC was performed on the Shimadzu LC-2F. Elemental analyses were performed by the Analytical Laboratory, Institute of Chemistry, Academia Sinica, Beijing, China. The FT $^{31}P$ NMR spectra were performed on a FT-80A spectrometer at 32.2 MHz with the probe temperature 37 °C, by broad band decoupled technique with a pulse angle 30°, acquisition time of 0.5 s, and pulse delay of 3 s. For quantitative analysis the inverse gated decoupling technique was adopted and each spectrum was recorded in 400 scans with 85% $H_3PO_4$ as external reference.

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Table V. The Solvent Effect on the Iodine-Induced Cyclization of the δ-Unsaturated Phosphonate 1c

| solvent | time | relative amount of the reaction mixture | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1c | 1m | 3m | 2c | 4m | side products |
| $CH_3CN$, 1.4 M | 16 min | 29 | 21 | 43 | 5 | | 2 |
| | 71 h 26 min | | | 4 | 60 | | 36[a] |
| $CHCl_3$, 1.3 M | 16 min | 47 | 45 | 5 | 2 | | 1 |
| | 70 h 27 min | | | 6 | 76 | | 18[b] |
| benzene, 1.4 M | 16 min | 14 | 5 | 54 | 10 | 16[c] | 1 |
| | 69 h 24 min | | | 3 | 75 | 2[d] | 20[b] |
| cyclohexane, 1.4 M | 45 min | 14 | 10 | 33 | 14 | 25[d] | 4 |
| | 68 h 20 min | | | 8 | 74 | 1 | 17[b] |

[a] These side products were at 20, 23.8, 27, 29.7, 30.7, and 31.7 ppm. [b] The side product was at 28 ppm. [c] It was at 32.9 ppm. [d] There were two broad peaks at 33–35 ppm.

**Synthesis of Di-*n*-propyl 4-Pentenylphosphonate (1c).** Di-*n*-propyl phosphite (15.6 g, 0.094 mol) was slowly added to a refluxing solution of *n*-hexane (300 mL) containing 2.0 g (0.09 mol) of sodium. After all of the sodium had dissolved, 5-bromopentene (16.0 g, 0.107 mol) was added in 30 min. This solution was refluxed for 12 h and then cooled to 20 °C for 30 h. The NaBr precipitate was filtered. The filtrate was washed with water and dried. After the solvent was evaporated, the residue was distilled under reduced pressure. Compound **1c** was obtained in 76% yield: bp 104–106 °C (0.6 mm); IR 3080, 2980, 1641, 1235, 1067, 1043, and 995 $cm^{-1}$; $^1H$ NMR δ at 5.60–5.80 (1 H, m), 4.90–5.06 (2 H, m), 3.94 (4 H, m), 2.13 (2 H, m), 1.38–1.51 (8 H, m), 0.96 (6 H, t). Anal. Calcd for $C_{11}H_{23}O_3P$: C, 56.39; H, 9.89. Found: C, 56.22; H, 10.10.

**General Procedure for Synthesis of 2-Alkoxy-2-oxo-6-(iodomethyl)-1,2-oxaphosphorinanes (2a–d).** A mixture of **1a** (1.17 g, 6.57 mmol) and $I_2$ (3.0 g, 11.8 mmol) was dissolved in 3.5 mL of $CHCl_3$. After stirring for 10 min, the homogeneous solution was allowed to stand for 74 h at 10 °C. The solvent was removed and the residue was passed through a 60–100 mesh silica gel column, eluted with $CHCl_3$. The excess $I_2$ eluted first. After removing $CHCl_3$ from the following fractions, a viscous, yellow liquid (1.51 g) was obtained. This crude product was rechromatographed on a 260 mesh silica gel column, eluted with $CHCl_3$. Each fraction was analyzed by HPLC. There was obtained a total of 0.74 g of **2a** as a yellow solid: mp 86–87; $^1H$ NMR δ 4.08–4.22 (1 H, m), 3.76 (3 H, d), 3.30 (2 H, m), 2.26–1.32 (6 H, m).

**Synthesis of 2-Ethoxy-2-oxo-6-(iodomethyl)-1,2-oxaphosphorinane (2b).** When the same procedure as above was used, **1b** (1.10 g, 5.33 mmol) and $I_2$ (2.24 g, 9.6 mmol) in 3.0 mL of $CHCl_3$ gave **2b** (0.91 g, 56%): $^1H$ NMR δ 4.00–4.23 (3 H, m), 3.30 (2 H, m), 2.24–1.43 (6 H, m), 1.38 (3 H, t).

**Synthesis of 2-(*n*-Propyloxy)-2-oxo-6-(iodomethyl)-1,2-oxaphosphorinane (2c).** From **1c** (1.66 g, 7.08 mmol) and $I_2$ (3.24 g, 12.75 mmol) in 3.5 mL of $CHCl_3$, there was obtained **2c** as a yellow liquid (1.36 g, 60% yield): $^1H$ NMR δ 4.11–4.26 (1 H, m), 3.87–4.11 (2 H, m), 1.18–2.28 (8 H, m), 0.99 (3 H, t), 3.30 (2 H, m).

**Synthesis of 2-(*n*-Butyloxy)-2-oxo-6-(iodomethyl)-1,2-oxaphosphorinane (2d).** From **1d** (1.68 g, 6.29 mmol) and $I_2$ (2.87 g, 11.32 mmol) in 3.5 mL of $CHCl_3$, **2d** was isolated as yellow liquid (1.33 g, 63%): $^1H$ NMR δ 3.92–4.24 (3 H, m), 3.30 (2 H, m), 1.29–2.27 (10 H, m), 0.96 (3 H, t).

**Synthesis of Diethyl (4,5-Dibromopentyl)phosphonate (4b).** To a water-cooled solution of **1b** (0.82 g, 4.0 mmol) in 2.0 mL of $CHCl_3$ was slowly added 0.64 g (4.0 mmol) of $Br_2$. After standing at 15 °C for 18 h, the reaction mixture was evaporated to dryness. The residue (1.37 g) was passed through a 260 mesh silica gel column. Compound **4b**, a light yellow liquid (1.04 g, 72%), was obtained: IR 1240, 1030, 1060 $cm^{-1}$; $^1H$ NMR δ 3.98–4.20 (5 H, m), 3.78–3.88 (1 H, m), 3.52–3.66 (1 H, m), 1.62–2.36 (6 H, m), 1.34 (6 H, t).

**Synthesis of Di-*n*-propyl (4,5-Dibromopentyl)-phosphonate (4c).** A mixture of **1c** (0.70 g, 3.0 mmol) and $Br_2$ (0.48 g, 3.0 mmol) in 2.0 mL of $CHCl_3$ was stirred at 15 °C for 19 h. After regular workup as above, compound **4c** (0.81 g, 69%) was obtained as a light yellow liquid: IR 1242, 1067, 1025 $cm^{-1}$; $^1H$ NMR δ 4.05–4.20 (1 H, m), 3.88–4.05 (4 H, m), 3.79–3.88 (1 H, m), 3.53–3.64 (1 H, t), 1.50–2.34 (10 H, m), 0.96 (3 H, t).

**Synthesis of Di-*n*-butyl (4,5-Dibromopentyl)phosphonate (4d).** A mixture of **1d** (1.01 g, 3.85 mmol) and $Br_2$ (0.61 g, 3.8 mmol) in 2.5 mL of $CHCl_3$ was stirred at 15 °C for 18 h. On workup, there was obtained 1.12 g (68%) of **4d**: IR 1246, 1069, 1028 $cm^{-1}$; $^1H$ NMR δ 3.89–4.20 (5 H, m), 3.76–3.89 (1 H, m), 3.54–3.66 (1 H, t), 1.52–2.34 (10 H, m), 1.39 (4 H, m), 0.94 (6 H, t).

**Observation of Intermediates 1m and 3m.** In a 0.5-cm i.d. NMR tube, compound **1c** (0.0946 g, $4.04 \times 10^{-4}$ mol) was reacted with $I_2$ (0.185 g, $7.27 \times 10^{-4}$ mol, 1.8 equiv) in 0.3 mL of $CHCl_3$. To prevent the evaporation of the iodine and solvent, the NMR tube was well sealed by parafilm. The sample stood at 21 ± 1 °C for a specified time and its $^{31}P$ NMR was taken. Similarly, compound **1c** (0.0904 g, $3.86 \times 10^{-4}$ mol) was reacted with $I_2$ (0.294 g, $1.16 \times 10^{-4}$ mol, 3.0 equiv) in 0.3 mL of $CHCl_3$; **1c** (0.0940 g, $4.02 \times 10^{-4}$ mol) was reacted with $I_2$ (0.102 g, $4.00 \times 10^{-4}$ mol, 1.0 equiv) in 0.3 mL of $CHCl_3$.

**Solvent Effect.** As the general procedure described above, compound **1c** (0.101 g, $4.3 \times 10^{-4}$ mol) was reacted with $I_2$ (0.196 g, $7.76 \times 10^{-4}$ mol, 1.8 equiv) in 0.31 mL of $CH_3CN$; **1c** (0.100 g, $4.26 \times 10^{-4}$ mol) reacted with $I_2$ (0.195 g, $7.67 \times 10^{-4}$ mol, 1.8 equiv) in 0.3 mL of benzene; **1c** (0.098 g, $4.2 \times 10^{-4}$ mol) reacted with $I_2$ (0.192 g, $7.54 \times 10^{-4}$ mol, 1.8 equiv) in 0.3 mL of cyclohexane. In all of the solvents the iodine was well dissolved, except in the cyclohexane where some iodine crystal was left.

**Characterization of the Intermediate 1m by $^{13}C$ NMR Spectra.** At 27 °C, **1c** (0.27 g, $1.15 \times 10^{-3}$ mol) and $I_2$ (0.52 g, $2.0 \times 10^{-3}$ mol, 1.8 equiv) were dissolved in 1.0 mL of $CDCl_3$. After 15 min, the $^{13}C$ NMR spectra was taken with 2000 pulses (1 h and 10 min) and $Me_4Si$ as the reference. The results are shown in Table IV.

**Reaction of 4-Bromo-1-pentene (5) with Iodine.** At 27 °C, 4-bromo-1-pentene (**5**) (1.50 g, 0.0100 mol) and $I_2$ (5.21 g, 0.0205 mol, 2.0 equiv) were mixed with 1.5 mL of $CDCl_3$. After 4 h, the $^{13}C$ NMR spectrum of the clear solution was taken. The results are shown in Table III.

**Reaction of *O,O*-Dialkyl Alkylphosphonates with $Et_3O$–$BF_4$.** Three saturated alkylphosphonates, one unsaturated alkylphosphonate, **1c**, and one cyclic alkylphosphonate, **2c**, were reacted with 1 equiv of $Et_3O$–$BF_4$ (purchased from Aldrich) in $CH_2Cl_2$ at 21 ± 1 °C for 4 h. The $^{31}P$ NMR shifts of the starting materials and their reaction products are reported in Table IV.

**Registry No.** **1a**, 96152-22-6; **1b**, 77697-54-2; **1c**, 96152-09-9; **1d**, 96152-23-7; **1m**, 96152-17-9; **2a**, 96152-10-2; **2b**, 96152-11-3; **2c**, 96152-12-4; **2d**, 96152-13-5; **3m**, 96152-19-1; **4b**, 96152-14-6; **4c**, 96152-15-7; **4d**, 96152-16-8; **4m**, 96152-21-5; **5**, 1119-51-3; **6**, 96152-20-4; $(i\text{-PrO})_2P(O)C_3H_7$, 18812-55-0; $(EtO)_2P(O)C_3H_7$, 18812-51-6; $(EtO)_2P(O)C_2H_5$, 78-38-6; $(i\text{-PrO})_2P(OEt)C_3H_7^+BF_4^-$, 96152-25-9; $(EtO)_2P(OEt)C_3H_7^+BF_4^-$, 96152-27-1; $(EtO)_2P(OEt)C_2H_5^+BF_4^-$, 665-54-3; $(n\text{-PrO})_2P(OEt)CH_2CH_2CH_2CH{=}CH_2^+BF_4^-$, 96152-29-3; $(n\text{-PrO})\overline{P(OEt)O(CH_2)_3CHCH_2I}^+BF_4^-$, 96152-31-7; $CH_3CN$, 75-05-8; $CHCl_3$, 67-66-3; $I_2$, 7553-56-2; benzene, 71-43-2; cyclohexane, 110-82-7; di-*n*-propyl phosphite, 1809-21-8.