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# A two step synthesis of 2-oxo-2-vinyl 1,3,2-dioxaphospholanes and -dioxaphosphorinanes

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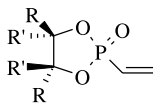
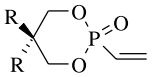
**Abstract**—The title compounds are prepared via a two step procedure involving a transesterification between a diol and diethyl phosphite followed by a palladium-catalyzed coupling of the so-obtained cyclic phosphite with vinyl bromide. Theoretical DFT calculations have been performed on phosphonate and phosphite anions models in order to estimate stereoelectronic effects in five-membered and six-membered ring compounds.



Vinylphosphonates are useful synthetic intermediates.[1] They have found applications in polymer chemistry,[2] as Michael acceptors,[3] in Diels–Alder reactions,[4] and they also display biological activities.[5] In this context, we became interested in the synthesis of cyclic vinyl phosphonates of type **A** (2-oxo-2-vinyl-1,3,2-dioxaphospholanes) and **B** (2-oxo-2-vinyl-1,3,2-dioxaphosphorinanes).



**A**



**B**

Although several synthetic approaches to vinyl phosphonates are known,[1] only two methods have been hitherto reported for the synthesis of our target molecules. Dioxaphospholanes **A** can be obtained in low yields (10–50%) by means of an Arbuzov-like reaction between a cyclic chlorophosphite and ethylene oxide or propylene oxide, followed by basic treatment of the resulting adduct.[6] On the other hand, several five- and six-membered cyclic vinyl phosphonates have been prepared by reacting vinyl phosphonic dichloride and a diol in the presence of triethylamine.[7] This method was used for the enantioselective synthesis of phosphonomycin.[8] The major drawback in this case is the synthesis of the starting dichloride which requires several steps.

*Keywords*: 2-oxo-2-vinyl 1,3,2-dioxaphospholanes; 2-oxo-2-vinyl 1,3,2-dioxaphosphorinanes; palladium; vinyl bromide; transesterification; DFT calculations.

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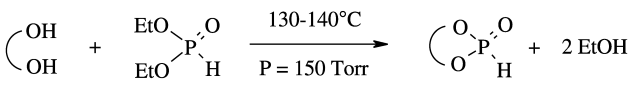
More recently, 2-oxo-2-vinyl-1,3,2-dioxaphospholanes derived from pinacol have been prepared by the rhodium-catalyzed hydrophosphonylation of acetylenes.[9] We decided to explore another approach based on the well documented coupling[10] of a dialkyl phosphite and a vinylic bromide catalyzed by palladium complexes.

Although the cyclic phosphites required for this coupling can be prepared through Zwierzak method[11] (i.e. reaction of phosphorus trichloride with a diol followed by hydrolysis) or directly from phosphonic acid,[12] we found that the transesterification procedure described by Ostwald[13] (Scheme 1) is equally convenient.

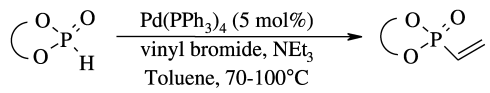



**I**

**Scheme 1.**

Thus, heating an equimolar mixture of diethyl phosphite and a diol under reduced pressure with concomitant distillation of ethanol led to the five- and six-membered cyclic phosphites with high purity and very good yields (72–96%). The reaction is easily monitored by the amount of ethanol produced. This procedure also allows an easy synthesis of chiral cyclic phosphites as exemplified by **Ib** and **Ic** from tartaric acid via 1,4-bis-methoxymethyl-2,3-butanediol[14] and 1,4-bis-benzyloxymethyl-2,3-butanediol,[15,16] respectively. These two compounds should find applications in asymmetric synthesis.[17]

The cyclic vinyl phosphonates were obtained from those




**I** **II**

**Scheme 2.**

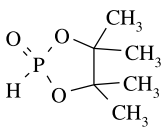
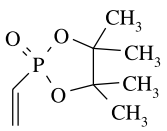
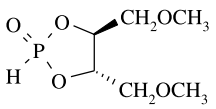
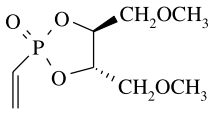
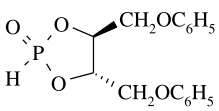
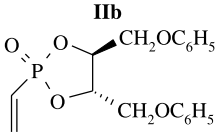
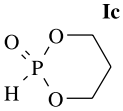
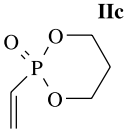
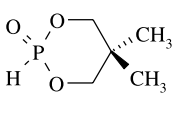
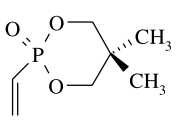
phosphites by coupling with vinyl bromide, in the presence of 1 equiv. of triethylamine and a catalytic amount of palladium tetrakis(triphenyl phosphine) in toluene, the reactions being performed at 70–100°C (Scheme 2).

No by-products were formed. It is worth mentioning that the crude phosphites are usually pure enough to be used without purification, since the only contaminant is a slight excess of diethyl phosphite. Following this method, the chiral vinyl phosphonates **IIb** and **IIc** can be easily obtained. Table 1 summarizes the yields obtained for each compound.

The limitations of the synthetic method presented here were found in the case of the simplest five-membered vinyl phosphonate, namely 2-oxo-2-vinyl-1,3,2-dioxaphospholane which cannot be obtained through this approach since the required phosphite is not stable and cannot be isolated.[13]

The fact that the coupling reaction occurs at different temperatures depending on the nature of the starting cyclic phosphite deserves some comments. Thus, six-membered ring phosphites react smoothly at 70–80°C, whereas five-membered ring phosphites require higher reaction temperatures. We observed also for these phosphites different $^{31}P$ chemical shifts. Thus five-membered ring phosphites 2-oxo-2-vinyl-1,3,2-dioxaphospholanes are always downfield ($\delta$=15–22 ppm) with respect to six-membered ring phosphites 2-oxo-2-vinyl-1,3,2-dioxaphosphorinanes ($\delta$=2–3 ppm). The same is true for the cyclic vinyl phosphonates prepared, i.e. $\delta$=26–33 ppm for five-membered compounds and $\delta$=10 ppm for six-membered analogues.[18] Similar trends were reported in comparative studies for several organophosphorus compounds.[19,20] Although the reasons for such features remain unclear, they lead to the conclusion that the ring size greatly influences the behaviour of those phosphonates. This is in agreement with previous studies[21] which have shown that five-membered cyclic phosphorus compounds behave differently than their six-membered analogues whose reactivity is closer to their acyclic counterparts.

**Table 1**. Yields for the cyclic phosphites **I** and vinyl phosphonates **II** prepared

| Cyclic phosphite | Yield (%) | Vinyl phosphonate | Yield (%) |
|---|---|---|---|
|  **Ia** | 72 |  **IIa** | 78 |
|  **Ib** | 94 |  **IIb** | 63 |
|  **Ic** | 96 |  **IIc** | 77 |
|  **Id** | 92 |  **IId** | 64 |
|  **Ie** | 86 |  **IIe** | 65 |

These compounds are well known to undergo a phosphite–phosphonate tautomerism with the phosphite tautomer and anion phosphite as the nucleophilic form and the phosphonates tautomer as the favored but non-nucleophilic form (Fig. 1).

These different reactivity and spectral data between phosphite compounds are partly due to stereoelectronic effects in five-membered and six-membered rings compounds. To estimate this we carried out the theoretical DFT calculations at the B3LYP/6-31G(d)//B3LYP/6-31G(d) on three phosphonate model structures: **C**, **D**, and **E**, and the corresponding nucleophilic phosphite anions **C′**, **D′**, and **E′**.[22,23]

These revealed that in structures **C** and **D**, axial exocyclic P–O and P–H bonds are longer than the equatorial ones (P–Oax 1.480 Å, P–Oeq 1.471 Å and P–Hax 1.414 Å, P–Heq 1.398 Å), as expected if $n_O-\sigma^*_{P-O}$ overlaps effectively take place for axial bonds. As a consequence, **C** which exhibits an axial P–O bond is more stable than its anomeric form **D** by 2.25 kcal mol$^{-1}$ (computed $\Delta G$ in gas phase), in agreement with previous calculations.[24,25] In contrast, in the single conformer of dioxaphospholane species **E**, P–O and P–H bond lengths range between the previous values (P–O 1.475 Å, P–H 1.403 Å). This strongly suggests that, in this case, $n_O-\sigma^*_{P-O}$ overlaps are less important than in six-membered ring specie **C**. Similar trends were observed for the anionic species **C′**, **D′**, and **E′**.[26] NBO analysis let appear an even more striking difference between these structures.[27] Whereas **D** and **E** were described with a double P–O bond, one $\sigma$ and one $\pi$, the extracyclic oxygen atom bearing two lone pairs, **C** exhibits a single $\sigma$ bond while the extracyclic oxygen bears three lone pairs. Thus, in this compound the extracyclic P–O bond should be seen as dative and this should promote the C′ anion phosphite from C by a migration of the proton. One could expect that species **C′** would have an enhanced nucleophilic character compared to **D′**, **E′**. Taking together, these results support the role of stereoelectronic effect ($n_O-\sigma^*_{P-Oax}$ overlaps) in the nucleophilic character of the phosphite compounds.[28,29]

In summary, the method described here constitutes a facile

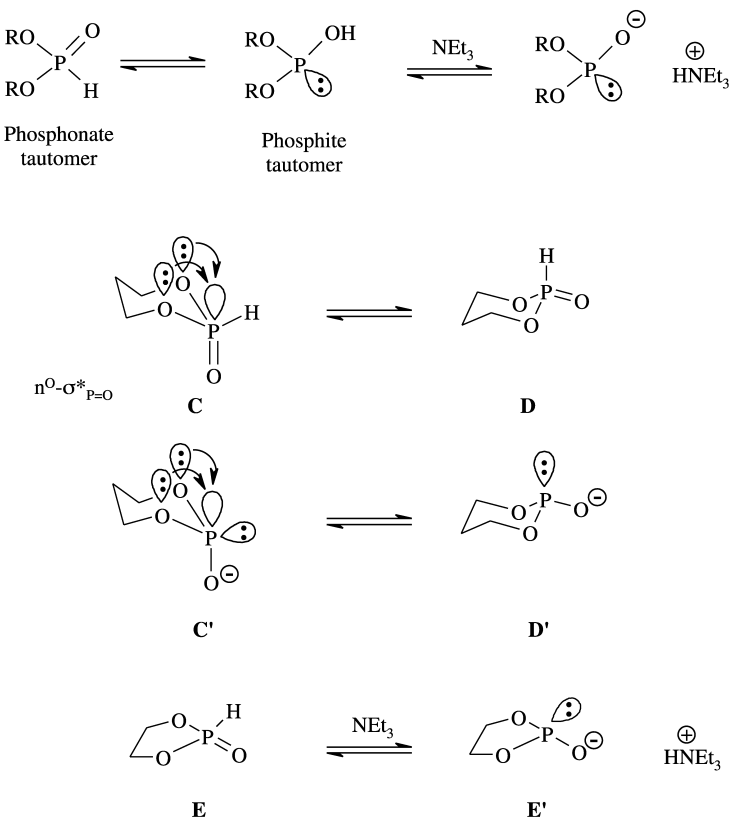



**Figure 1.** Phosphite–phosphinate tautomerism of **I**. Anomeric effect at cyclic phosphonate and phosphite anion.

synthesis of five- and six-membered cyclic vinyl phosphonates with different degrees of substitution on the ring, from cheap starting materials. We are currently studying the use of the chiral phosphites and vinyl phosphonates in asymmetric synthesis.

## 1. Experimental

Toluene was distilled from sodium and dichloromethane was distilled from calcium hydride. All solvents and reagents (except vinyl bromide) were degassed with dry nitrogen prior to use.

$^{1}H$, $^{13}C$, and $^{31}P$ NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AC 200 spectrometer. Chemical shifts were measured from residual chloroform ($\delta$=7.26 ppm for $^{1}H$ and $\delta$=77 ppm for $^{13}C$). 85% $H_3PO_4$ as external standard was used for $^{31}P$ chemical shifts. IR spectra were recorded on a Perkin–Elmer 298 Spectrometer as KBr films for liquids or KBr disks (1% in KBr) for solids. Elemental analyses were performed by the Service de Microanalyse de la Faculté de St Jérôme. Specific rotations were measured on a Perkin–Elmer 341C polarimeter. Melting points were measured on a Büchi apparatus and are uncorrected.

### 1.1. General procedure for the preparation of cyclic phosphates

A mixture of the diol (0.1 mol) and diethyl phosphite (14, 5 g; 0.105 mol; 5% excess) was placed in a 200 mL round bottomed flask equipped with a Claisen head, a condenser, and a receiving flask. The mixture was heated to 130–140°C under reduced pressure (150 Torr) and ethanol started to distill slowly. After ca. 4 h, ethanol evolution ceased and the reaction mixture was allowed to cool to room temperature. The dialkyl phosphites were used as such in the next step, and analytical samples were obtained by recrystallization or Kugelrhor distillation.

**1.1.1. 4,4,5,5-Tetramethyl-2-oxo-1,3,2-dioxaphospholane (Ia).** White solid, mp 105–106°C (THF/hexane, 1:1). Anal. calcd ($C_6H_{13}O_3P$): C 43.90; H 7.93. Found: C 43.71; H 7.67. $^{1}H$ NMR: 1.41 ($CH_3$, s); 1.51 ($CH_3$, s); 7.25 (1H, d, $^{1}J_{PH}$= 707.5 Hz). $^{13}C$ NMR: 23.94 ($CH_3$, $^{3}J_{PC}$=5.5 Hz); 24.65 ($CH_3$, d, $^{3}J_{PC}$=3.8 Hz); 88.98 (C–O, s). $^{31}P$ NMR: 15.6. IR ($cm^{-1}$): 2870, 2450, 1280, 1120.

**1.1.2. (4*S*,5*S*)-Bis(methoxymethyl)-2-oxo-1,3,2-dioxaphospholane (Ib).** Bp 115°C (0.3 Torr). Anal. calcd ($C_6H_{13}O_5P$): C 36.73; H 6.63. Found: C 36.76; H 6.86. $^{1}H$ NMR: 3.43 ($CH_3$, s); 3.44 ($CH_3$, s); 3.50–3.71 (4H, $OCH_2$, m); 4.53–4.67 (2H, CH–O, m); 7.73 (1H, d, $^{1}J_{PH}$=642 Hz). $^{13}C$ NMR: 58.98 ($CH_3$, s); 59.17 ($CH_3$, s); 72.43 ($OCH_2$, d, $^{3}J_{PC}$=3.6 Hz); 78.39 (CH–O, d, $^{2}J_{PC}$=32.7 Hz). $^{31}P$ NMR: 22.6. IR ($cm^{-1}$): 2990, 2870, 2450, 1280, 1120. $\alpha_D$ (25°C)= −38.3 ($c$=3.2, $CH_2Cl_2$).

**1.1.3. (4*S*,5*S*)-Bis(benzyloxymethyl)-2-oxo-1,3,2-dioxaphospholane (Ic).** Bp 200°C (0.05 Torr). Anal. calcd ($C_{18}H_{21}O_5P$): C 62.07; H 6.03. Found: C 62.07; H 6.09. $^{1}H$ NMR: 3.31–3.80 ($CH_2O$, m); 4.46–4.89 (6H, CH–O and PhC$H_2$O, m); 7.31 (10H, s); 7.40 (1H, d, $^{1}J_{PH}$=730 Hz). $^{13}C$ NMR: 69.62 ($OCH_2$, d, $^{3}J_{PC}$=3.6 Hz); 69.91 ($OCH_2$, d, $^{3}J_{PC}$=3.6 Hz); 73.57 ($C_6H_5OCH_2$, s); 73.73 ($C_6H_5OCH_2$, s); 78.42 (CH–O, d, $^{2}J_{PC}$=38.2 Hz); 127.59, 128.05, 128.57

137.12 and 137.22 (Carom.). $^{31}$P NMR: 22.9. IR (cm$^{-1}$): 2870, 2450, 1280, 1120. $\alpha_D$ (25°C)=−66.4 ($c$=2.8, $CH_2Cl_2$).

**1.1.4. 2-Oxo-1,3,2-dioxaphosphorinane (Id).** Bp 120°C (0.6 Torr). Anal. calcd ($C_3H_7O_3P$): C 29.51; H 5.74. Found: C 30.13; H 6.20. $^1$H NMR: 1.73–2.32 ($CH_2$, m); 3.37–4.59 ($OCH_2$, m); 6.93 (1H d, $^1J_{PH}$=675 Hz). $^{13}$C NMR: 27.95 ($CH_2$, d, $^3J_{PC}$=8.1 Hz); 67.51 ($OCH_2$, d, $^2J_{PC}$=6.3 Hz). $^{31}$P NMR: 2.4. IR (cm$^{-1}$): 2970, 2900, 2430, 1470, 1260.

**1.1.5. 5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphorinane (Ie).** Bp 120°C (0.02 Torr). Anal. calcd ($C_5H_{11}O_3P$): C 40.00; H 7.33. Found: C 40.07; H 7.40. $^1$HNMR: 0.90 ($CH_3$, s); 1.22 ($CH_3$, s); 4.00 (4H, m); 6.87 (1H, d, $^1J_{PH}$=675 Hz). $^{13}$CNMR: 20.66 ($CH_3$, s); 21.72 ($CH_3$, s); 32.15 ($Me_2C$, d, $^3J_{PC}$=6.3 Hz); 76 ($CH_2$, d, $^2J_{PC}$=6.3 Hz). $^{31}$P NMR: 3.3. IR (cm$^{-1}$): 2970, 2880, 2410, 1730, 1260.

### 1.2. General procedure for the preparation of cyclic vinyl phosphonates

A mixture of palladium tetrakis(triphenyl phosphine) (1.5 g; 1.3 mmol), cyclic phosphite (100 mmol), triethylamine (10 g; 99 mmol), vinyl bromide (14 g; 131 mmol) and toluene (30 mL) was heated to 70°C (for six-membered compounds) or 90–100°C (for five-membered analogues) with stirring under a nitrogen atmosphere in a thick wall Schlenck tube. A white precipitate appeared, and the reaction mixture then turned to a viscous mass, which characterizes the end of the reaction. The tube was cooled to room temperature, ethyl acetate (50 mL) was added, and the suspension was filtered. The solid was washed with ethyl acetate (4×30 mL) and the combined filtrates were evaporated in vacuo. The residue was passed over a short silica column eluting with EtOAc/ether (1:1), and the solvent was removed in vacuo. The vinyl phosphonates were purified by distillation (Kugelrohr), crystallization or flash chromatography.

**1.2.1. 4,4,5,5-Tetramethyl-2-oxo-2-vinyl-1,3,2-dioxaphospholane (IIa).** Bp 100°C (0.5 Torr). Anal. calcd ($C_8H_{15}O_3P$): C 50.53; H 7.89. Found: C 50.29; H 7.80. $^1$H NMR: 1.05 ($CH_3$, s); 1.18 ($CH_3$, s); 5.53–6.32 (3H, m). $^{13}$C NMR: 24.06 ($CH_3$, d, $^3J_{PC}$=5.3 Hz) and 24.72 ($CH_3$, d, $^3J_{PC}$=3.8 Hz); 88.33 (C–O, s); 126.71 (=C–P, d, $^1J_{PC}$=178.8 Hz); 136.95 (=$CH_2$, d, $^2J_{PC}$=1.2 Hz). $^{31}$P NMR: 26.2. IR (cm$^{-1}$): 2995, 1620, 1250, 995.

**1.2.2. (4*S*,5*S*)-Bis(methoxymethyl)-2-oxo-2-vinyl-1,3,2-dioxaphospholane (IIb).** Bp 130°C (0.02 Torr). Anal. calcd ($C_8H_{15}O_5P$): C 43.24; H 6.76. Found: C 43.65; H 7.00. $^1$H NMR: 3.41 ($CH_3$, s); 3.43 ($CH_3$, s); 3.54–3.73 ($OCH_2$, m); 4.58 (CH–O, t, $^3J_{PH}$=2.0 Hz); 5.93–6.56 (3H, m). $^{13}$C NMR: 59.38 ($CH_3$, s); 59.56 ($CH_3$, s); 71.84 ($OCH_2$, d, $^3J_{PC}$=5.5 Hz); 72.40 ($OCH_2$, d, $^3J_{PC}$=4.8 Hz); 78.29 (CH–O, d, $^2J_{PC}$=19.6 Hz); 124.77 (=CH–P, d, $^1J_{PC}$=179 Hz); 137.77 (=$CH_2$, s). $^{31}$P NMR: 30.5. IR (cm$^{-1}$): 2940, 2900, 1615, 1270, 1050. $\alpha_D$ (25°C)=−19.83 ($c$=1.8, $CH_2Cl_2$).

**1.2.3. (4*S*,5*S*)-Bis(benzyloxymethyl)-2-oxo-2-vinyl-1,3,2-dioxaphospholane (IIc).** Yellowish oil ($R_f$: 0.45 ether/ethyl acetate 1.5:1). Anal. calcd ($C_{20}H_{23}O_5P$): C 64.17; H 6.15. Found: C 64.01; H 6.31. $^1$H NMR: 3.58–3.73 ($OCH_2$, m); 4.45–4.62 (CH–O and PhC$H_2$O, m); 5.79–6.69 (3H, m); 7.16–7.30 (10H, m). $^{13}$C NMR: 69.28 ($OCH_2$, d, $^3J_{PC}$=5.5 Hz); 69.92 ($OCH_2$, d, $^3J_{PC}$=5 Hz); 73.51 (PhC$H_2$O, s); 73.66 (PhC$H_2$O, s); 78.45 (CH–O, d, $^2J_{PC}$=24.8 Hz); 124.32 (=CH–P, d, $^1J_{PC}$=158.8 Hz); 127.68, 127.92, 128.36, 133.30 and 133.65 (Carom.); 137.91 (=$CH_2$, s). $^{31}$P NMR: 33.2. IR (cm$^{-1}$): 3060, 2940, 2900, 1615, 1270, 1050. $\alpha_D$ (25°C)=−38.3 ($c$=3.2, $CH_2Cl_2$).

**1.2.4. 2-Oxo-2-vinyl-1,3,2-dioxaphosphorinane (IId).** Bp 105°C (0.3 Torr). Anal. calcd ($C_5H_9O_3P$): C 40.54; H 6.08. Found: C 40.86; H 5.87. $^1$H NMR: 1.75–2.42 ($CH_2$, m); 3.95–4.32 ($OCH_2$, m); 5.89–6.75 (3H, m). $^{13}$C NMR: 26.32 ($CH_2$, d, $^3J_{PC}$=8.1 Hz); 67.62 ($OCH_2$, d, $^2J_{PC}$=6.5 Hz); 124.91 (=CH–P, d, $^1J_{PC}$=177.5 Hz); 135.68 (=$CH_2$, s). $^{31}$P NMR: 10.1. IR (cm$^{-1}$): 2980, 2900, 1630, 1240, 1160.

**1.2.5. 5,5-Dimethyl-2-oxo-2-vinyl-1,3,2-dioxaphosphorinane (IIe).** White solid, mp 87°C (ethyl acetate/hexane, 1:1). Anal. calcd ($C_7H_{13}O_3P$): C 47.73; H 7.39. Found: C 47.84; H 7.32. $^1$H NMR: 1.04 ($CH_3$, s); 1.07 ($CH_3$, s); 3.84 ($OCH_2$, t, $^3J_{PH}$=11.2 Hz); 4.13 ($OCH_2$, t, $^3J_{PH}$=11.1 Hz); 5.90–6.62 (3H, m). $^{13}$C NMR: 20.99 ($CH_3$, s); 21.25 ($CH_3$, s); 32.20 ($Me_2C$, d, $^3J_{PC}$=6 Hz); 75.61 ($OCH_2$, d, $^2J_{PC}$=6 Hz); 123.78 (=CH–P, d, $^1J_{PC}$=182 Hz); 136.39 (=$CH_2$, d, $^2J_{PC}$=1.5 Hz). $^{31}$P NMR: 10.8. IR (cm$^{-1}$): 2970, 2910, 1615, 1260.

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