Synthesis of New α-Hydroxy-, α-Halogeno- and Vinylphosphonates Derived from 5,5-Dimethyl-1,3,2-dioxaphosphinan-2-one

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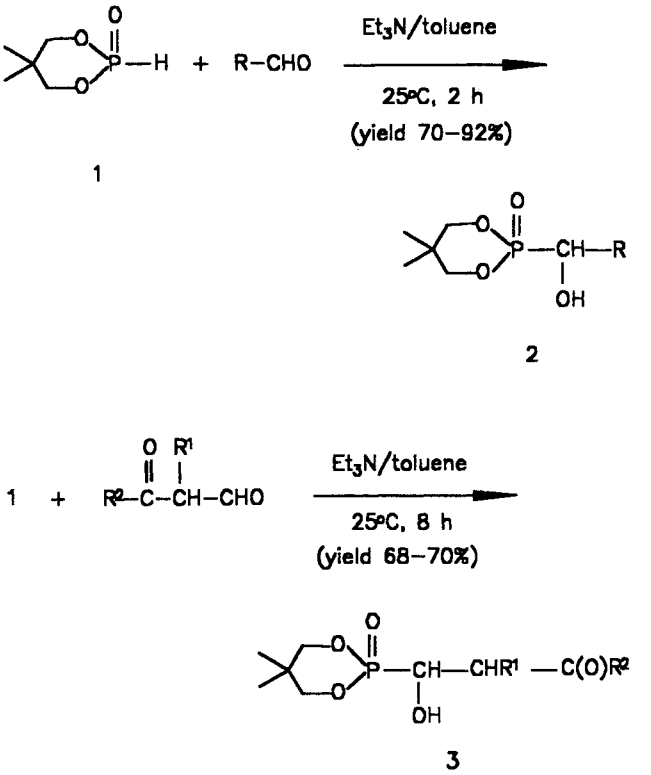
Several α-hydroxyphosphonates have been prepared by the Pudovik reaction of the cyclic phosphite 5,5-dimethyl-1,3,2-dioxaphosphinan-2-one with aldehydes and β-oxo aldehydes. These can be readily converted to α-chloro- or α-bromophosphonates in excellent yield by simply treating them with thionyl chloride or bromide. Reaction with phosphorus triiodide gave α-iodophosphonates and α-hydridophosphonates. The Pudovik products obtained from β-oxo aldehydes can be readily dehydrated to give vinylphosphonates.

α-Hydroxyphosphonates, which are products of the Pudovik reaction of a phosphite with an aldehyde,[1] and their halogeno derivatives can serve as useful precursors in organic synthesis. For instance, the hydroxy substituent can be replaced by other groups[2] to get a variety of phosphonate synthons. Some of their obvious applications are in the Wadsworth–Emmons and related reactions.[3] We report herein the synthesis of α-hydroxyphosphonates derived from 5,5-dimethyl-1,3,2-dioxaphosphinan-2-one, $HP(O)(OCH_2CMe_2CH_2O)$ **(1)** and their conversion to the halogeno and vinyl phosphonates. The phosphite **1** was chosen mainly to facilitate the formation of solid products that can be easily purified.

Treatment of the 1,3,2-dioxaphosphinane **1** with aldehydes or β-oxo aldehydes (existing in their enolic form in solution) in the presence of triethylamine readily leads to the Pudovik products **2a–j** and **3a–c** (Scheme 1). All the aromatic aldehydes and β-oxo aldehydes tried by us afforded the corresponding α-hydroxyphosphonates **2a–g** and **3a–c** in fair to excellent yield (68–92%) whereas the yields were much lower (25–40%) when aliphatic aldehydes were used **(2h** and **2j)**.

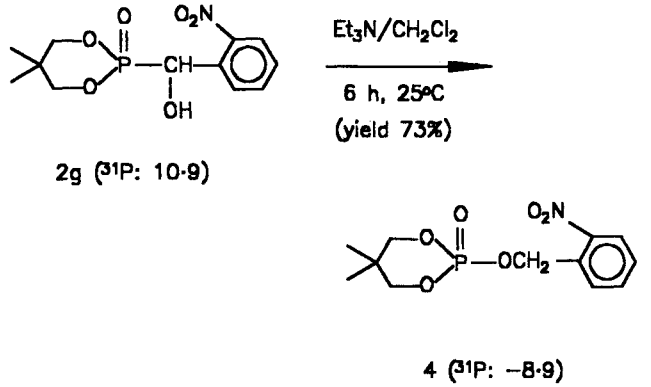
These products exhibit a characteristic peak at $\delta = 10-14$ [except for **2h** and **2j** which showed peaks at $\delta = 18.1$ and $\delta = 19.1$ respectively] in the ^{31}P NMR spectrum and a doublet in the ^{13}C NMR spectrum at $\delta = 68-73$ ($^1J_{P-C} \approx 155$ Hz).[1d] In the case of **3a** and **3c** both the reaction mixture and the recrystallized product showed a single stereoisomer [^1H, ^{31}P NMR]. However for **3b** the ^{31}P NMR spectrum showed two clearcut signals at $\delta = 13.0$ and 14.2 in 1:1 ratio (before as well as after recrystallization) suggesting the presence of isomers.

Compounds **2a–g** and **3a–c** are stable in air at room temperature for extended periods (up to one year) in the solid state and in solution (CH_2Cl_2, $CHCl_3$). Compound **2g** undergoes rearrangement to the phosphate ester when traces of triethylamine are present. Such rearrangements have been reported previously by the use of a strong base[1b,4] and in the case of the hydroxyphosphonate derived from fluorenone.[5] In contrast to the report by Wynberg et al.[4] where no such rearrangement was observed even after 12 hours in the reaction of 2-nitrobenzaldehyde with dimethyl phosphite, we obtained the phosphate ester **4** in over 70% yield when the reaction of



2	R	2	R	3	R^1	R^2
a	Ph	f	$4\text{-}NO_2C_6H_4$	a	Ph	Ph
b	$4\text{-}ClC_6H_4$	g	$2\text{-}NO_2C_6H_4$	b	$4\text{-}MeC_6H_4$	$4\text{-}Me\text{-}C_6H_4$
c	$2,4\text{-}Cl_2C_6H_3$	h	i-Pr	c	Ph	CH_2Ph
d	$4\text{-}MeC_6H_4$	i	Pr			
e	$3\text{-}MeC_6H_4$					

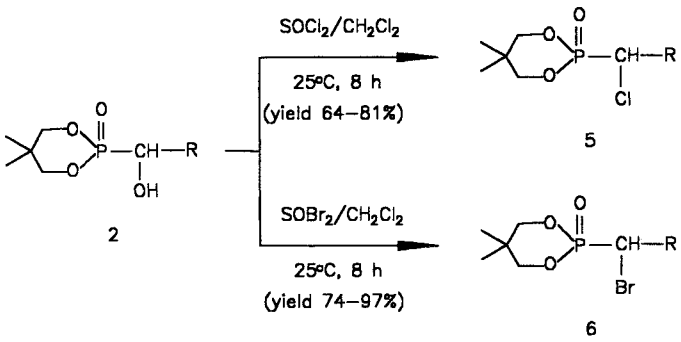
Scheme 1



Scheme 2

2-nitrobenzaldehyde and the phosphite **1** was allowed to proceed for 12 hours in toluene or 6 hours in CH_2Cl_2 (Scheme 2).

α-Hydroxyphosphonates have been converted to α-chlorophosphonates generally in modest yield using $SOCl_2$/pyridine,[6] SO_2Cl_2,[7] $POCl_3$[3e] or PPh_3/CCl_4.[8] Most of these methods suffer from drawbacks such as low yields, formation of side products, difficulty in separating the product from the reaction mixture or limitations in the type of substrate. Among the reagents $SOCl_2$, $N_4P_4Cl_8$ and PCl_5 checked by us for their effectiveness in converting **2b** to the chloride, thionyl chloride ($SOCl_2$) gave the best yields (75%) without any side products. Hence thionyl chloride was used to prepare **5a–e**, in 64–81% yield (Scheme 3). Reaction of **2h** with $SOCl_2$ under these conditions gave a mixture of uncharacterizable products along with unreacted starting material.



2 5 6

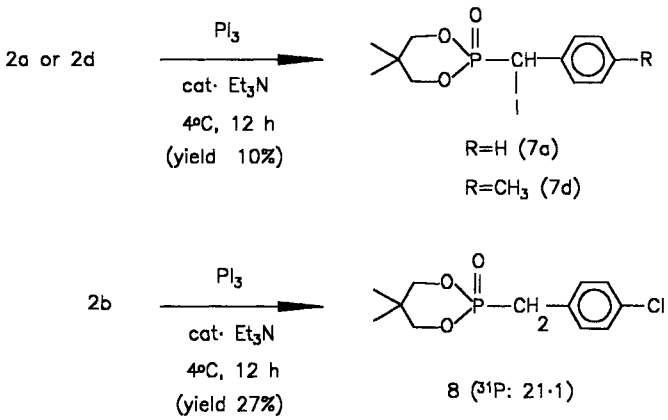
5, 6	R	5, 6	R
a	Ph	d	4-MeC_6H_4
b	4-ClC_6H_4	e	3-MeC_6H_4
c	2,4-$Cl_2C_6H_3$		

Scheme 3

The α-bromophosphonates **6a–e** are readily prepared in high yield (74–97%) by reacting **2a–e** with thionyl bromide (Scheme 3). We also tried PBr_3 in the case of **2a** but the yields were much lower.

The α-chloro **5a–e** and α-bromophosphonates **6a–e** can be easily distinguished from the hydroxyphosphonates by their ^{13}C NMR spectra; the P-*C*HX carbon appears as a doublet [$^1J_{P-C}$ = 155–160 Hz] at $\delta = \sim 72$ (X = OH), ~ 53 (X = Cl) and ~ 40 (X = Br). Isomeric products are obtained in some cases possibly due to the different disposition (axial or equatorial) of the substituents with respect to the dioxaphosphinane ring, for example **6d** [^{31}P: δ = 9.0 (70%), 8.5 (30%)] and **6e** [^{31}P: δ = 8.4 (60%), 8.8 (40%)]; separation could not be effected by fractional crystallization.

Attempts to obtain the α-iodophosphonates by treating **2a, 2b** and **2d** with phosphorus triiodide[9] met with limited success. The resulting iodo products are unstable in solution and liberate iodine. They also decompose during column chromatography. Only a small quantity (≈ 10% yield) of the iodophosphonates **7a** and **7d** could be isolated by performing a quick column chromatography separation (Scheme 4). In contrast, when **2b** was treated with PI_3 under similar conditions, we isolated 2-(4-chlorobenzyl)-5,5-dimethyl-1,3,2-dioxaphosphinan-2-one (**8**; Scheme 4); this compound can be easily characterized by its ^1H and ^{13}C NMR spectra. We do not know of any precedence for such a reduction with PI_3, although examples are known for reactions with P_2I_4.[10]



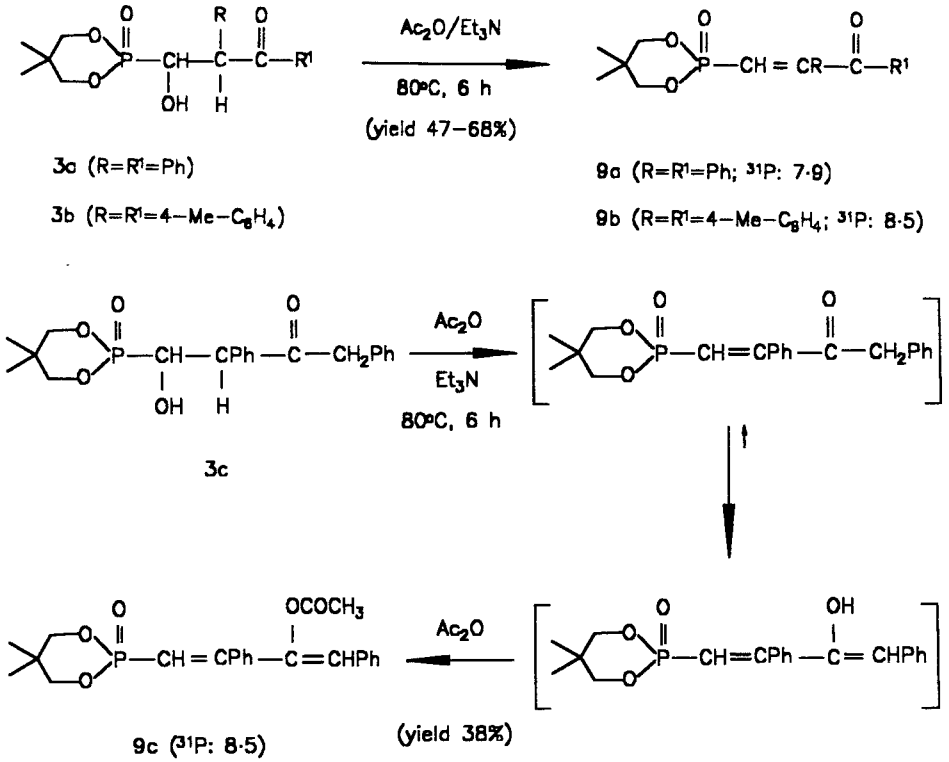
Scheme 4

An inspection of the structures of α-hydroxyphosphonates **3a–c** reveals that it should be possible for them to eliminate a water molecule to give vinylphosphonates. A similar dehydration has been observed by us for the allylated products of β-oxo aldehydes.[11] Indeed this reaction proceeds smoothly when **3a** and **3b** are treated with acetic anhydride/triethylamine, leading to the corresponding vinylphosphonates (Scheme 5). The initial dehydrated product obtained from **3c** (R = Ph, $R^1 = CH_2Ph$) has an enolizable C=O group and hence the final product is the acetylated phosphonate **9c** (Scheme 5). Although several routes are known for synthesizing vinylphosphonates,[2a,2b] to our knowledge, only one report is available on the synthesis of vinylphosphonates containing an oxo group.[12] In this report the authors utilize the reaction of the cyclic pentacoordinated 1,2-oxaphospholane $[CH_2CH{=}C(Me)O]P(OEt)_3$ with NBS (or Br_2).

Finally, as far as the utility of these compounds is concerned, we are currently investigating the Wadsworth–Emmons reaction on these compounds. For instance, one can readily obtain chlorostilbenes by treating **3** with BuLi/aldehyde, thus 1-chloro-1-phenyl-2-(4-tolyl) ethene (Ph(Cl)C=CH(4-Me=C_6H_4)) can be obtained in high yield (85%) by starting with **2a**. This and related reactions will be reported in a subsequent paper.

Chemicals were procured from Aldrich or local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[13] ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker 200 MHz spectrometer with chemical shifts [$CDCl_3$] measured against TMS (^1H, ^{13}C) or 85% H_3PO_4. IR spectra were recorded on a Perkin–Elmer 1310 spectrophotometer. Elemental analyses were carried out on a 240 CHN analyzer.

The β-oxo aldehydes used in the present study were prepared by procedures described earlier.[11] Compound **1** was synthesized using a literature procedure.[14]



Scheme 5

2-[Hydroxy(phenyl)methyl]-5,5-dimethyl-1,3,2-dioxaphosphinan-2-one (2a); Typical Procedure for 2a–j and 3a–c:

To a mixture of **1** (4.4 g, 29 mmol), benzaldehyde (3.1 g, 29 mmol) and toluene (20 mL) was added Et_3N (1.46 g, 14.5 mmol), cooling the flask if necessary. The mixture was stirred for 2 h at 25 °C and the white solid was filtered, washed with toluene (5 mL) and recrystallized (CH_2Cl_2/toluene, 1:1) to give **2a** (6.9 g, 92%).

All the other compounds **2b–j** and **3a–c** were prepared analogously using similar molar quantities. These compounds exhibited IR bands at $\nu_{OH} = 3150\ cm^{-1}$, ($\nu_{P=O} = 1240–1260\ cm^{-1}$, and $\nu_{P=O} = 1040–1080\ cm^{-1}$). Other data are given below.

2a: Yield: 92%; mp 151–153 °C.

^1H NMR: $\delta = 0.79, 1.11$ (2 s, 6 H, 2 CH_3), 3.20 (br, O*H*), 3.88–4.14 (m, 4 H, 2 OCH_2), 5.16 (d, $^2J = 14.0$ Hz, 1 H, C*H*OH), 7.23–7.57 (m, 5 H, *H*(Ar)).

^{13}C NMR: $\delta = 20.8, 21.8$ (2 CH_3), 32.4 (d, $^3J_{P-C} = 7.5$ Hz, CMe_2), 71.9 (d, $^1J = 157.0$ Hz, *C*HOH), 77.4 (d, $^2J \approx 7.0$ Hz, OCH_2), 127.0, 127.2, 128.3, 128.4, 136.5 (*C*(Ar)).

^{31}P NMR: $\delta = 13.3$.

Anal. calcd. for $C_{12}H_{17}O_4P$: C, 56.25; H, 6.69. Found: C, 56.50; H, 6.52.

2b: Yield: 90%; mp 174–175 °C.

^1H NMR: $\delta = 0.85, 1.11$ (2 s, 6 H, 2 CH_3), 3.94–4.20 (m, 4 H, 2 OCH_2), 5.15, (d, $^2J = 12.0$ Hz, 1 H, C*H*OH), 7.27–7.50 (m, 4 H, *H*(Ar)).

^{13}C NMR: $\delta = 21.0, 21.8$ (2 CH_3), 32.4 (d, $^3J = 7.5$ Hz, CMe_2), 71.3 (d, $^1J = 157.5$ Hz, *C*HOH), 77.4 (OCH_2), 114.7, 128.4, 128.5, 128.7, 135.0 (*C*(Ar)).

^{31}P NMR: $\delta = 12.9$.

Anal. calcd. for $C_{12}H_{16}ClO_4P$: C, 49.58; H, 5.55. Found: C, 49.51; H, 5.40.

2c: Yield: 82%; mp 208–210 °C.

^1H NMR: $\delta = 0.89, 1.11$ (2 s, 6 H, 2 CH_3), 3.85 (br, 1 H, O*H*), 3.88–4.18 (m, 4 H, OCH_2), 5.62 (d, $^2J = 12.0$ Hz, 1 H, C*H*OH), 7.28–7.75 (m, 3 H, *H*(Ar)).

Solubility was too low for recording ^{13}C NMR.

^{31}P NMR: $\delta = 12.9$.

Anal. calcd. for $C_{12}H_{15}Cl_2O_4P$: C, 44.33; H, 4.65. Found: C, 44.52; H, 4.36.

2d: Yield: 78%; mp 164 °C.

^1H NMR: $\delta = 0.82, 1.11$ (2 s, 6 H, 2 CH_3), 2.33 (s, 3 H, Ph–CH_3), 3.88–4.18 (m, 4 H, 2 OCH_2), 5.11 (d, $J \approx 12$ Hz, 1 H, C*H*OH), 7.10–7.42 (AB q 4 H, *H*(Ar)).

^{13}C NMR: $\delta = 20.8, 21.2, 21.8$ (3 CH_3), 32.4 (d, $^3J = 7.5$ Hz, CMe_2), 71.7 (d, $^1J = 157.6$ Hz, *C*HOH), 77.4 (d, $^2J \approx 6.0$ Hz, OCH_2), 127.0, 127.1, 129.1, 133.6, 138.0 (*C*(Ar)).

^{31}P NMR: $\delta = 13.6$.

Anal. calcd. for $C_{13}H_{19}O_4P$: C, 57.77; H, 7.09. Found: C, 57.20; H, 7.14.

2e: Yield: 80%; mp 142 °C.

^1H NMR: $\delta = 0.79, 1.10$ (2 s, 6 H, 2 CH_3), 2.33 (s, 3 H, CH_3), 3.83–4.19 (m, 4 H, 2 OCH_2), 4.80 (br, 1 H, O*H*), 5.08 (d, $J = 11.8$ Hz, C*H*OH), 7.03–7.31 (m, 4 H, *H*(Ar)).

^{13}C NMR: $\delta = 20.8, 21.4, 21.9$ (3 CH_3), 3.24 (d, $^3J = 7.5$ Hz, CMe_2), 71.9 (d, $J = 157.0$ Hz, *C*HOH), 77.4 (OCH_2), 124.1, 124.3, 127.7, 127.8, 128.3, 129.0, 136.6, 138.0 (*C*(Ar)).

^{31}P NMR: $\delta = 13.4$.

Anal. calcd. for $C_{13}H_{19}O_4P$: C, 57.77; H, 7.09. Found: C, 57.45; H, 7.00.

2f: [Note: When the reaction was allowed to continue longer than 15 min, the yield was reduced because of rearrangement]: Yield: 91%; mp 195–196 °C (dec.).

^1H NMR (CD_3OD): $\delta = 0.85, 1.15$ (2 s, 6 H, 2 CH_3), 3.85–4.11 (m, 2 H, OCH_2), 5.25 (d, $J = 12.0$ Hz, 1 H, C*H*OH), 7.57–8.24 (m, 4 H, *H*(Ar)).

Solubility was too low for recording ^{13}C NMR.

^{31}P NMR: $\delta = 10.9$.

Anal. calcd. for $C_{12}H_{16}NO_6P$: C, 47.84; H, 5.35; N, 4.65. Found: C, 47.55; H, 5.20; N, 4.55.

2g: [See note for **2f** above]: Yield: 70%; mp 176–178°C (dec.).

^{1}H NMR: $\delta = 0.60$, 0.95 (2s, 6H, 2 CH_3), 3.40–4.00 (m, 4H, OCH_2), 5.20 (d, $J \approx 12$ Hz, $CHOH$), 7.00–7.80 (m, 4H, H(Ar)).

Solubility was too low for recording ^{13}C NMR.

^{31}P NMR: $\delta = 10.3$.

Anal. calcd. for $C_{12}H_{16}NO_6P$: C, 47.84; H, 5.35; N, 4.65. Found: C, 47.65; H, 5.36; N, 4.60.

2h: Yield: 40%; mp 157°C.

^{1}H NMR: $\delta = 0.93$, 1.15 (2s, 6H, 2 CH_3), 1.04 (d, $J = 6.8$ Hz, 6H, 2 $CHCH_3$), 2.02–2.26 (m, 1H, $CHCH_3$), 3.83–4.08 (m, 4H, 2 OCH_2), 4.23–4.38 (m, 2H, $CHOH + OH$).

^{13}C NMR: $\delta = 17.5$ (d, $^3J = 6.2$ Hz, $CHCH_3$), 19.8 (d, $^3J = 11.0$ Hz, $CHCH_3$), 21.0, 22.0 (2 CH_3), 30.3 (d, $^2J = 3.2$ Hz, $CHMe_2$), 32.5 (d, $^3J = 7.3$ Hz, CMe_2 (ring)), 74.0 (d, $^1J = 154$ Hz, $CHOH$), 77.5 (d, $^2J = 7.2$ Hz, OCH_2).

^{31}P NMR: $\delta = 18.1$.

Anal. calcd. for $C_9H_{19}O_4P$: C, 48.64; H, 8.62. Found: C, 48.45; H, 8.56.

2j: Yield: 25%; mp 103°C.

^{1}H NMR: $\delta = 0.92$ (t, $J = 7.0$ Hz, 3H, CH_3), 1.06, 1.10 (2s, 6H, CH_3 (ring)), 1.35–1.92 (m, 4H, 2 CH_2), ≈3.0 (br, 1H, OH), 4.00–4.21 (m, 5H, 2 $OCH_2 + CHOH$).

^{13}C NMR: $\delta = 13.6$ (s, CH_3), 18.7 (d, $^3J = 13.5$ Hz, CH_2Me), 21.1, 21.8 (2 CH_3 (ring)), 32.5 (d, $^3J =$ = 7.0 Hz, CMe_2 (ring)), 33.5 (s, CH_2CHOH), 68.4 (d, $^1J = 157$ Hz, $CHOH$), 76.8 (s, OCH_2).

^{31}P NMR: $\delta = 19.1$.

3a: Yield: 70%; mp 184–186°C.

^{1}H NMR: $\delta = 0.94$, 1.20 (2s, 6H, 2 CH_3), 3.86–4.10 (m, 2H, OCH_2), 4.20–4.34 (m, 2H, OCH_2), 4.58–4.68 (dd, $J \approx 12.0$, 8.0 Hz, 1H, $CHOH$), 5.24–5.31 (dd, $J \approx 8.0$, 8.0 Hz, $CHPh$), 7.21–8.02 (m, 10H, H(Ar)).

^{13}C NMR: $\delta = 20.9$, 22.1 (2 CH_3), 52.0 ($CHPh$), 73.6 (d, $^1J = 163.0$ Hz, $CHOH$), 77.8 (buried in $CDCl_3$, OCH_2), 128.1, 129.2, 134.0 (C(Ar)).

^{31}P NMR: $\delta = 14.2$.

Anal. calcd. for $C_{20}H_{23}O_5P$: C, 64.16; H, 6.19. Found: C, 64.55; H, 6.26.

3b: Yield: 68%; mp 158–159°C.

^{1}H NMR: $\delta = 0.79$, 1.21 (2s, 6H, 2 CH_3), 2.29, 2.33 (2s, 6H, 2 CH_3), 3.42–4.62 (m, 5H, 2 $OCH_2 + CHOH$), 4.99–5.22 (m, 1H, $CHAr$), 7.08–7.92 (m, 8H, H(Ar)). The OCH_2, $CHOH$ and $CHAr$ regions were much more complicated than for **3a** and **3c**; J values could not be determined for $CHOH$ and $CHAr$ protons.

^{13}C NMR: $\delta = 20.5$, 21.1, 21.6, 22.2 (CH_3), 36.0 (CMe_2), 53.1 ($CHPh$), 71.5 ($J = 160.0$ Hz, $CHOH$), 78.9 (d, $J \approx 7$ Hz, OCH_2), 129.3, 129.8, 130.0, 137.5 (C(Ar)).

^{31}P NMR: $\delta = 13.0$, 14.2 (1:1 mixture of isomers).

3c: Yield: 69%; mp 182–184°C.

^{1}H NMR: $\delta = 0.90$, 1.21 (2s, 6H, 2 CH_3), 3.81 (d, $J \approx 2$ Hz, 1H, CH_2(A)Ph), 3.86–4.13 (m, 5H, 2 $OCH_2 + CH_2$(B)Ph), 4.41–4.52 (m, 2H, $CHOH$), 6.99–7.40 (m, 10H, H(Ar)).

^{13}C NMR: $\delta = 20.9$, 22.1 (2 CH_3), 32.6 (CMe_2), 49.8 (CH_2Ph), 56.6 ($CHPh$), 72.7 (d, $^1J = 155$ Hz, $CHOH$), 127.2, 128.2, 128.6, 129.2, 133.0 (C(Ar)).

^{31}P NMR: $\delta = 14.2$.

Anal. calcd. for $C_{21}H_{25}O_5P$: C, 64.94; H, 6.49. Found: C, 64.90; H, 6.81.

5,5-Dimethyl-2-(2-nitrobenzyloxy)-1,3,2-dioxaphosphinan-2-one (4); Typical Procedure for Rearrangement of 2f and 2g:

Et_3N (0.105 g, 1 mmol) was added to a suspension of **2g** (0.30 g, 1 mmol) in CH_2Cl_2 and the mixture was stirred at 25°C for 6h whereby a clear reddish solution was obtained. After removing the volatiles, the resulting yellow residue was crystallized from CH_2Cl_2/toluene (1:2) using activated charcoal to give **4** (0.22 g, 73%) as white crystals; mp 72°C.

^{1}H NMR: $\delta = 0.89$, 1.23 (2s, 6H, 2 CH_3), 3.81–4.19 (m, 4H, 2 CH_2), 5.49 (d, $^3J = 6.8$ Hz, 2H, OCH_2Ar), 7.52–8.15 (m, 4H, H(Ar)).

^{13}C NMR: $\delta = 20.0$, 20.4 (2 CH_3), 32.1 (d, $J \approx 5.5$ Hz, CMe_2), 65.5 (OCH_2Ar), 78.1 (d, $J \approx 6.5$ Hz, P–OCH_2), 129.1, 129.2 (C(Ar)).

^{31}P NMR: $\delta = -8.9$.

Anal. calcd. for $C_{12}H_{16}NO_6P$: C, 47,84; H, 5.35; N, 4.65. Found: C, 47.65; H, 5.30; N, 4.52.

Compound **2f** under similar conditions afforded only a semisolid which was a mixture of several products [^{31}P NMR: $\delta = -9.0$, -8.5, -4.9, 6.2, 6.5, 8.3, 20.4, 22.3].

2-[Chloro- or 2-[Bromo(phenyl)methyl]-5,5-dimethyl-1,3,2-dioxaphosphinan-2-one (5a and 6a); Typical Procedure for Chlorination to 5a–e and Bromination to 6a–e:

To a solution of **2a** (0.4 g, 1.56 mmol) in CH_2Cl_2 (5 mL) was added $SOCl_2$ (0.5 g, 0.3 mL, 4.2 mmol) (for **5a**) or $SOBr_2$ (0.8 g, 0.3 mL, 3.87 mmol) (for **6a**) and the mixture stirred at 25°C for 8h. Then water was cautiously added to destroy excess $SOCl_2/SOBr_2$ and the product was taken up in CH_2Cl_2 (10 mL). The solvent was removed and the residue crystallized from CH_2Cl_2/heptane to give **5a** or **6a**.

The IR spectra of **5** and **6** showed no ν_{OH} bands as expected; $\nu_{P=O}$ was observed at ca 1260 and 1060 cm^{-1}. Other details are given below.

5a: Yield: 0.35 g (81%); mp 150–152°C.

^{1}H NMR: $\delta = 0.95$, 1.18 (2s, 6H, 2 CH_3), 4.05–4.26 (m, 4H, OCH_2), 5.12 (d, $J = 13.8$ Hz, 1H, $CHCl$), 7.30–7.61 (m, 5H, H(Ar)).

^{13}C NMR: $\delta = 21.0$, 21.8 (2 CH_3), 32.6 (CMe_2), 54.0 (d, $^1J = 155.0$ Hz, $CHCl$), 78.1 ($^2J \approx 7$ Hz, OCH_2), 127.9, 128.9, 129.1 (C(Ar)).

^{31}P NMR: $\delta = 8.1$.

Anal. calcd. for $C_{12}H_{16}ClO_3P$: C, 52.47; H, 5.87. Found: C, 52.32; H, 5.92.

5b: Yield [using 0.4 g (1.38 mmol) of **2b**]: 0.32 g (75%); mp 151–152°C.

^{1}H NMR: $\delta = 0.96$, 1.17 (2s, 6H, 2 CH_3), 4.03–4.29 (m, 4H, 2 OCH_2), 5.08 (d, $J = 13.0$ Hz, 1H, $CHCl$), 7.28–7.52 (m, 4H, H(Ar)).

^{13}C NMR: $\delta = 21.0$, 21.8 (2 CH_3), 32.7 (d, $J = 8.0$ Hz, CMe_2), 53.2 (d, $^1J = 155$ Hz, $CHCl$), 78.3 (d, $J = 7.5$ Hz, OCH_2), 128.9, 130.1, 130.2, 132.3, 135.2 (C(Ar)).

^{31}P NMR: $\delta = 7.5$.

Anal. calcd. for $C_{12}H_{15}Cl_2O_3P$: C, 46.62; H, 4.89. Found: C, 46.40; H, 4.88.

5c: Yield: [using 0.4 g (1.23 mmol) of **2c**]: 0.27 g (64%); mp 105–106°C.

^{1}H NMR: $\delta = 1.02$, 1.20 (2s, 6H, 2 CH_3), 4.10–4.30 (m, 4H, 2 OCH_2), 5.65 (d, $^2J = 14$ Hz, 1H, $CHCl$), 7.27–7.89 (m, 3H, H(Ar)).

^{13}C NMR: $\delta = 21.1$, 21.7 (2 CH_3), 32.6 (CMe_2), 47.9 (d, $J = 156$ Hz, $CHCl$), 78.1 (d, $J \approx 7$ Hz, OCH_2), 128.0, 129.4, 130.8, 132.1, 135.9 (C(Ar)).

^{31}P NMR: $\delta = 7.5$.

Anal. calcd. for $C_{12}H_{14}Cl_3O_3P$: C, 41.95; H, 4.11. Found: C, 42.10; H, 4.21.

5d: Yield [using 0.4 g (11.48 mmol) of **2d**]: 0.32 g (75%); mp 184°C.

^{1}H NMR: $\delta = 0.97$, 1.18 (2s, 6H, 2 CH_3), 2.36 (s, 3H, Ph–CH_3), 4.03–4.25 (m, 4H, 2 OCH_2), 5.09 (d, $J = 13.6$ Hz, 1H, $CHCl$), 7.11–7.49 (AB q, 4H, H(Ar)).

^{13}C NMR: $\delta = 21.1$, 21.8 (2 CH_3), 32.6 (CMe_2), 53.9 (d, $^1J = 156$ Hz, $CHCl$), 78.0 (OCH_2), 128.7, 128.8, 129.4, 139.2 (C(Ar)).

^{31}P NMR: $\delta = 8.4$.

Anal. calcd. for $C_{13}H_{18}ClO_3P$: C, 54.08; H, 4.67. Found: C, 54.10; H, 4.55.

5e: Yield [using 0.4 g (1.48 mmol) of **2e**]: 0.348 g (81 %); mp 166 °C.

^{1}H NMR: δ = 0.92, 1.16 (2s, 6H, 2CH_3), 2.35 (s, 3H, Ph–CH_3), 4.01–4.22 (m, 4H, 2OCH_2), 5.08 (d, ^2J = 13.7 Hz, 1H, C*H*Cl), 7.09–7.41 (m, 4H, *H*(Ar)).

^{13}C NMR: δ = 20.0, 21.4, 21.8 (3 *C*H$_3$), 32.7 (d, ^3J = 8 Hz, *C*Me$_2$), 53.8 (d, ^1J = 155 Hz, *C*HCl), 78.2 (d, ^2J = 6 Hz, O*C*H$_2$), 125.9, 126.0, 128.6, 129.4, 129.5, 130.0, 133.6, 138.5 (*C*(Ar)).

^{31}P NMR: δ = 8.1.

Anal. calcd. for $C_{13}H_{18}ClO_3P$: C, 54.08; H, 4.67. Found: C. 53.95; H, 4.60.

6a: Yield: 0.394 g (79 %); mp 164–166 °C.

^{1}H NMR: δ = 0.89, 1.11 (2s, 6H, 2CH_3), 3.94–4.19 (m, 4H, 2CH_2), 5.10 (d, $J \approx$ 12 Hz, 1H, C*H*Br), 7.25–7.63 (m, 5H, *H*(Ar)).

^{13}C NMR: δ = 21.0, 21.7 (2 *C*H$_3$), 32.6 (d, J = 6.5 Hz, *C*Me$_2$), 40.5 (d, J = 153 Hz, *C*HBr), 77.7 (d, J = 6.5 Hz, O*C*H$_2$), 128.9, 129.2, 129.5, 129.6, 134.1 (*C*(Ar)).

^{31}P NMR: δ = 8.6.

Anal. calcd. for $C_{12}H_{16}BrO_3P$: C, 45.16; H, 5.05. Found: C, 45.61; H, 5.08.

6b: Yield [using 0.4 g (1.38 mmol) of **2b**]: 0.37 g (76 %); mp 155–156 °C.

^{1}H NMR: δ = 1.00, 1.14 (2s, 6H, 2CH_3), 4.02–4.31 (m, 4H, 2OCH_2), 5.01 (d, J = 12.7 Hz, 1H, C*H*Br), 7.29–7.61 (m, 4H, *H*(Ar)).

^{13}C NMR: δ = 21.3, 21.7 (2 *C*H$_3$), 32.8 (d, ^3J = 8 Hz, *C*Me$_2$), 39.8 (d, ^1J = 155 Hz, *C*HBr), 77.8 (d, ^2J = 8 Hz, O*C*H$_2$), 129.0, 130.8, 130.9, 132.7 (*C*(Ar)).

^{31}P NMR: δ = 8.4, 8.5 (two peaks).

Anal. calcd. for $C_{12}H_{15}BrClO_3P$: C, 40.76; H, 4.28. Found: C, 40.35; H, 4.18.

6c: Yield [using 0.4 g (1.23 mmol) of **2c**]: 0.43 g (91 %) mp 152–153 °C.

^{1}H NMR: δ = 1.02, 1.17 (2s, 6H, 2CH_3), 4.01–4.31 (m, 4H, 2CH$_2$), 5.58 (d, J = 12.7 Hz, 1H, C*H*Br), 7.23–8.00 (m, 3H, *H*(Ar)).

^{13}C NMR: δ = 21.2, 21.7 (2 C*H*$_3$), 32.8 (d, J = 7 Hz, *C*Me$_2$), 34.1 (d, J = 156 Hz, *C*HBr), 78.0 (d, $J \approx$ 7 Hz, O*C*H$_2$), 128.2, 129.4, 131.0, 133.1, 134.1, 135.8 (*C*(Ar)).

^{31}P NMR: δ = 8.1.

Anal. calcd. for $C_{12}H_{14}BrCl_2O_3P$: C, 37.14; H, 3.64. Found: C, 36.92; H, 3.70.

6d: Yield [using 0.4 g (1.48 mmol) of **2d**]: 0.366 g (74 %); mp 184–188 °C (mixture of isomers).

^{1}H NMR (major isomer, $\approx$ 70 %): δ = 0.97, 1.13 (2s, 6H, 2CH_3), 2.34 (s, 3H, Ph–CH_3), 3.96–4.30 (m, 4H, 2OCH_2), 5.03 (d, $J \approx$ 12 Hz, 1H, C*H*Br), 7.12–7.58 (AB q, 4H, *H*(Ar)).

^{1}H NMR (minor isomer, $\approx$ 30 %): δ = 1.00, 1.15 (2s, 6H, 2CH_3), 2.38 (s, 3H, Ph–CH_3), 3.96–4.30 (m, 4H, 2 OCH_2 (buried in the signals due to major isomer)), 4.97 (d, J = 11.6 Hz, 1H, C*H*Br), 7.22–7.77 (m, 4H, *H*(Ar)).

^{13}C NMR (major isomer): δ = 21.2, 21.7, 22.7 (3 *C*H$_3$), 32.8 (*C*Me$_2$), 40.6 (d, J = 155 Hz, *C*HBr), 77.7 (O*C*H$_2$), 128.5, 129.4, 129.6, 131.1, 133.2, 139.4 (*C*(Ar)).

^{13}C NMR (minor isomer): δ = 22.7 (*C*H$_3$), 39.3 (d, ^1J = 155 Hz, *C*HBr). Other signals buried in those of the major isomer.

^{31}P NMR: δ = 9.0 (br, major), 8.5 (minor).

Anal. calcd. for $C_{13}H_{18}BrO_3P$: C, 46.86; H, 5.44. found: C, 46.00; H, 5.27.

6e: Yield [using 0.4 g (1.48 mmol) of **2e**]: 0.48 g (97 %); mp 164–168 °C (mixture of isomers).

^{1}H NMR (major isomer, $\approx$ 60 %): δ = 1.01, 1.15 (2s, 6H, 2CH_3), 2.39 (s, 3H, Ph–CH_3), 3.96–4.30 (m, 4H, 2OCH_2), 4.98 (d, J = 12.7 Hz, 1H, C*H*Br), 7.09–7.59 (m, 3H, *H*(Ar)).

^{1}H NMR (minor isomer), 40 %): δ = 0.96, 1.14 (2s, 6H, 2CH_3), 2.35 (s, 3H, Ph–CH_3), 3.96–4.30 (m, buried in the signals of the major isomer), 5.01 (d, J = 12.7 Hz, 1H, C*H*Br).

^{13}C NMR (major isomer): δ = 21.2, 21.7, 23.0 (3s, *C*H$_3$), 32.7 (*C*Me$_2$), 39.7 (d, J = 154.5 Hz, *C*HBr), 77.7 (O*C*H$_2$), 122–140 (many signals, *C*(Ar)).

^{13}C NMR (minor isomer): δ = 21.5, 21.7, 22.7 (3 *C*H$_3$), 40.7 (*d*, J = 154 Hz, *C*HBr). Other signals buried in the signals due to the major isomer.

^{31}P NMR: δ = 8.4 (minor), 8.8 (major).

Anal. calcd. for $C_{13}H_{18}BrO_3P$: C, 46.86, H, 5.44. Found: C, 46.50; H, 5.32.

2-[Iodo(phenyl)methyl]-5,5-dimethyl-1,3,2-dioxaphosphinan-2-one (7a); Typical Procedure for the Reaction of 2a, 2b and 2d with Phosphorus Triiodide:[15]

To a mixture of PI_3 (2.48 g, 6 mmol) and CH_2Cl_2 (10 mL) was added a solution of **2a** (1.54 g, 6 mmol) and Et_3N (0.06 g, 0.6 mmol) in CH_2Cl_2 (10 mL) while cooling the flask in ice-water. The mixture was stirred at 25 °C for 1 h and kept at 4 °C for 12 h. Then ice-water was added and the mixture was extracted with CH_2Cl_2. The organic extracts were concentrated and the residue rapidly chromatographed (< 1 h) over a short column of silica gel using CH_2Cl_2/EtOAc to afford crude **7a** (0.2 g, 9 %). Pure material was obtained by quick recrystallization from CH_2Cl_2/hexane but the yield becomes significantly low and the solution turns violet indicating decomposition; mp 150–156 °C.

^{1}H NMR: δ = 0.95, 1.06 (2s, 6H, 2CH_3), 3.77–4.28 (m, 4H, OCH_2), 5.12 (d, ^2J = 12.8 Hz, 1H, C*H*I), 7.25–7.66 (m, 5H, *H*(Ar)).

^{31}P NMR: δ = 12.5.

Anal. calcd. for $C_{12}H_{16}IO_3P$: C, 39.36; H, 4.41. Found: C, 39.45; H, 4.43.

2-[Iodo(4-tolyl)methyl]-5,5-dimethyl-1,3,2-dioxaphosphinan-2-one **(7d)**:

In the reaction of **2d** with PI_3 the iodide **7d** (10 %, mp 194–195 °C was isolated. This compound decomposed very fast in solution [^{1}H NMR evidence].

^{1}H NMR: δ = 0.98, 1.10 (2s, 6H, 2CH_3), 3.80–4.30 (m, 4H, OCH_2), 5.15 (d, $^2J \approx$ 13.0 Hz, 1H, C*H*I), 7.00–7.50 (AB q, *H*(Ar)).

^{31}P NMR: δ = 12.4.

Anal. calcd. for $C_{13}H_{18}IO_3P$: C, 41.07; H, 4.77. Found: C, 40.59; H, 4.73.

2-(4-Chlorobenzyl)-5,5-dimethyl-1,3,2-dioxaphosphinan-2-one **(8)**:

In the reaction of **2b** with PI_3, the phosphonate **8** was isolated. Yield [using 0.35 g (1.2 mmol) of **2b**]: 0.09 g (27 %); mp 128 °C.

^{1}H NMR: δ = 0.85, 0.91 (2s, 6H, 2CH_3), 3.23 (d, ^2J = 22.1 Hz, 2H, CH_2P), 3.68 (dd, $^2J \approx$ 11 Hz, ^3J = 16 Hz, 2H, OCH_2(A)), 4.20 (dd, $^2J \approx$ 6.4 Hz, $^3J \approx$ 11 Hz, 2H, OCH_2(B)), 7.20–7.40 (m, 4H, *H*(Ar)).

^{13}C NMR: δ = 21.5, 21.6 (2 *C*H$_3$), 3.22 (d, ^1J = 135 Hz, *C*H$_2$P), 32.7 (d, ^3J = 6 Hz, *C*Me$_2$), 75.2 (d, ^2J = 5 Hz, O*C*H$_2$), 128.9, 129.0, 129.6, 129.8, 131.3, 131.4, 133.3 (*C*(Ar)).

^{31}P NMR: δ = 21.4.

Anal. calcd. for $C_{12}H_{16}ClO_3P$: C, 52.47; H, 5.87. Found: C, 52.00; H, 5.76.

A product analogous to **8** was observed in very small quantities (ca 2 %) in addition to **7a** in several fractions from the reaction of PI_3 with **2a** [^{1}H NMR: δ = 0.79, 0.82 (CH_3), 3.25 (d, $J \approx$ 18 Hz, CH_2), other signals buried in those due to **7a**; ^{31}P NMR: δ = 21.4] but could not be isolated in a pure state.

5,5-Dimethyl-2-(3-oxo-2,4-diphenylbut-2-enyl)-1,3,2-dioxaphosphinan-2-one (9a); Typical Procedure for the Dehydration of 3a–c:

To a mixture of **3a** (0.2 g, 0.53 mmol) and Et_3N (0.2 g, 2 mmol) was slowly added Ac_2O (0.2 g, 1.96 mmol) and the resulting clear solution stirred at 80 °C for 6 h. Then ice-water was added and the mixture stirred for 4 h to destroy excess Ac_2O. It was then extracted

with CH_2Cl_2, dried (Na_2SO_4) and concentrated to give a solid which was crystallized from CH_2Cl_2/heptane (2:1) to afford **9a** (0.13 g, 68%); mp 162°C.

^{1}H NMR: $\delta = 0.88$, 0.98 (2s, 6H, 2CH_3), 3.71–3.97 (m, 4H, OCH_2), 6.25 (d, $J = 14$ Hz, 1H, C=C*H*), 7.22–7.91 (m, 10H, *H*(Ar)).

^{13}C NMR: $\delta = 21.4$, 21.9 (2CH_3), 76.4 (OCH_2), 113.0 (d, $^1J \approx 190$ Hz, *C*=CH), 126.8, 128.9, 129.2, 129.8, 130.5, 134.2 (*C*(Ar) + *C*H=C).

^{31}P NMR: $\delta = 7.9$.

Anal. calcd. for $C_{20}H_{21}O_4P$: C, 67.41; H, 5.94. Found: C, 67.30; H, 5.84.

Relevant data for other reactions are given below:

9b: Yield [using 0.2 g (0.5 mmol) of **3b**]: 0.09 g (47%); mp 204–205°C.

^{1}H NMR: $\delta = 0.98$, 1.11 (2s, 6H, 2CH_3), 2.34, 2.37 (2s, 6H, 2Ph–CH_3), 3.85–4.08 (m, 4H, OCH_2), 6.30 (d, $^2J = 14.4$ Hz, C=C*H*), 7.22–7.95 (m, 8H, *H*(Ar)).

^{13}C NMR: $\delta = 21.3$, 21.8 (2CH_3), 76.3 (OCH_2), 11.5 (d, $^1J \approx 180$ Hz, *C*=CH), 126.6, 129.5, 129.8, 132.0, 140.4, 144.5 (*C*(Ar) + C=*C*H).

^{31}P NMR: $\delta = 8.5$.

Anal. calcd. for $C_{22}H_{25}O_4P$: C, 68.74; H, 6.56. Found: C, 69.23; H, 6.64.

9c: Yield: [using 0.2 g (0.52 mmol) of **3c**]: 0.08 g (38%); mp 156–158°C.

^{1}H NMR: $\delta = 0.79$, 1.12 (2s, 6H, 2CH_3), 2.38 (s. 3H, OC(O)CH_3), 3.52–3.75 (m, 4H, OCH_2), 5.87 (d, $^2J = 16$ Hz, 1H, C=C*H*–P), 6.13 (s, 1H, C*H*=C–OC(O)CH_3), 7.26–7.76 (m, 10H, *H*(Ar)).

^{13}C NMR: $\delta = 20.8$, 21.2, 21.9 (3, CH_3), 32.2 (*C*Me_2), 76.2 (d, $^2J = 6.5$ Hz, OCH_2), 111.9 (d, $^1J = 185$ Hz, Ph–*C*=CH–P), 126.3, 128.2, 128.9, 129.3, 129.6, 129.9, 154.0, 168.4, 191.0 (*C*(Ar) + PhCH=C + Ph–*C*=CH–P).

^{31}P NMR: $\delta = 10.5$.

Anal. calcd. for $C_{23}H_{25}O_5P$: C, 66.98; H, 6.11. Found: C, 67.10; H, 6.25.

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