# 2-Alkyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-ones α-Lithiated Carbanions. Synthesis, Stability, and Conformation

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The preparation and a conformational study of lithiated 2-alkyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-ones (2) in THF–hexane are described. These anions are present as two rapidly interconverting species with the P=O bond either axial (2a) or equatorial (2e). They are thermally unstable, but can be stabilised by the presence of one equivalent of LiBr or of lithium di-isopropylamide. A ^{31}P NMR study of the self condensation of the carbanions (2) showed that the phosphorus atom in the axial conformation (2a) is more electrophilic than in the equatorial one (2e). An X-ray structural study of 2,5,5-trimethyl-1,3,2-dioxaphosphorinan-2-one is described.

Owing to the enhanced sensitivity of the phosphorus atom to nucleophilic attack, cyclic phosphonates are useful intermediates in organic syntheses.[1] 2-Alkyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-ones (1) have potential as synthetic intermediates, because they are stable, solid, well crystallised compounds (single isomer) readily obtained through easy and efficient reactions. This prompted us to study the formation and the stability of the parent α-lithiated carbanions (2). This paper deals with the formation of such carbanionic species either by action of alkyl-lithium reagents upon six-membered cyclic phosphates (3) (Route a) or by direct metallation of six-membered cyclic phosphonates (1) (Route b). A study of the stability of these carbanions under a variety of conditions has been made.

(1) (2)
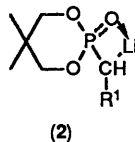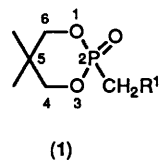
R^1 = H, Me, Et, Pr. The arrow between the oxygen atom of the phosphoryl group and the lithium atom represents a favourable orbital overlap which gives a preferred orientation for the substituents of the carbon atom bonded to the phosphorus atom.

Results

Route a: Alkylation of a Six-membered Cyclic Phosphate (3).—Nucleophilic attack of the phosphorus atom of phosphates $(RO)_3P(O)$ by an alkyl-lithium R^1CH_2Li easily affords α-lithiated α-phosphonylated carbanions[2] (Scheme 1).

Scheme 1.
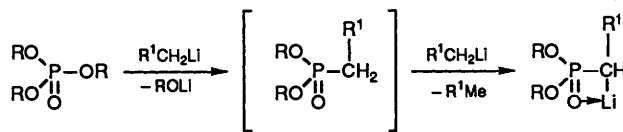
This reaction has been extended to 1,3,2-dioxaphosphorinanes (3). We chose three Z groups with increasing leaving capability (OEt, SEt, Cl). Addition of a cyclic phosphate (3) to cooled (− 70 °C) BuLi in THF–hexane (1:1) followed by gentle warming to 0 °C fails to give a clean, single reaction. Although

the results do depend on the nature of the Z group, we always observed the formation of two of the three compounds (2), (4), and (5) (Scheme 2).

Scheme 2.
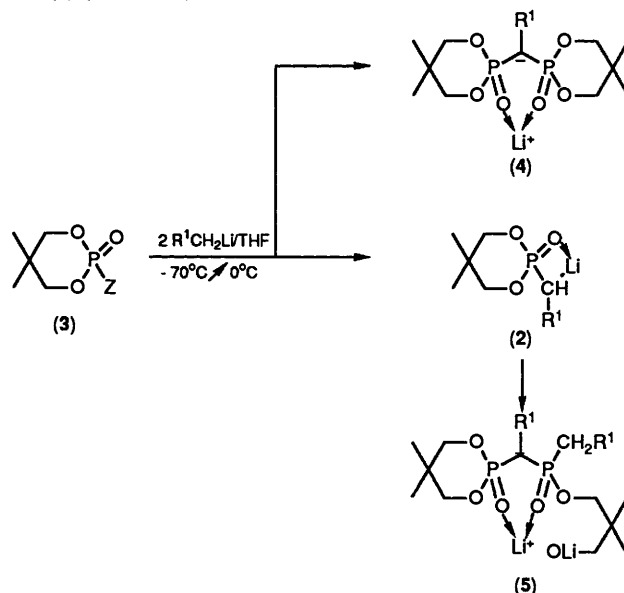
When Z = Cl, ^{31}P NMR spectroscopy shows a mixture of the expected carbanion (2) (δ + 43.0 ppm) and of the lithiated alkylidene diphosphonate (4) (δ + 35.0 ppm) in a 85:15 ratio. When Z = SEt, the (2):(4) ratio becomes 60:40. When Z = OEt, we get a mixture of (2) and its self-condensation product (5) (two multiplets, + 52.2 and + 31.1 ppm). Compounds (2), (4), and (5) were identified by independent reactions. Thus, (2) and (5) were obtained by metallation of (1; R^1 = Pr) (*cf.* route b). Addition of (3; Z = Cl) to (2) prepared according to route b in presence of LDA (1 equiv.) afforded (4) quantitatively.[3] The observed side-product (4) evidences the sensitivity of the phosphorus atom in cyclic phosphates to nucleophilic attacks, unlike trialkyl phosphates which under the same conditions never undergo this reaction. Since we could not overcome these side-reactions, we had to return to a classical metallation pathway.

Route b: Metallation of Six-membered Cyclic Phosphonates (1).—First, we had to look for an efficient synthesis of the

2-alkyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-ones (1).[4,5,13] These are now prepared through fast, easy, and reproducible reactions. All isolated intermediates were pure enough to be used without any further purification. Overall yields are in the range 77–83% (Scheme 3).
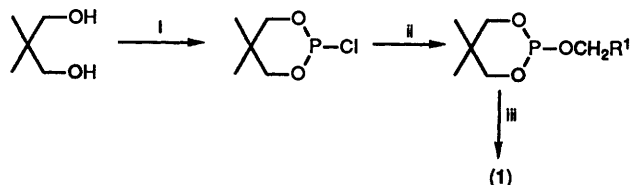
Scheme 3. R^1 = H, Me, Et, Pr. *Reagents and conditions:* i, PCl_3, CH_2Cl_2; ii, R^1CH_2OH, NEt_3/THF; iii, R^1CH_2I, heat.

Metallation of (1) by BuLi was carried out in THF–hexane (1:1) at low temperature (– 70 °C). The thermal stability of the carbanions (2) is lower than that of the acyclic phosphonylated carbanions.[6] On warming to 0 °C, the primary carbanion (2; R^1 = H) undergoes self-condensation around –35 °C whereas the secondary carbanions (2; R^1 = alkyl) undergo self-condensation around 0 °C (Scheme 4). This occurs because of the high electrophilicity of the phosphorus atom *and* the polarisation of the P–C bond in the metallated species. Although increasing the size of R^1 does not prevent this reaction, it does slow it down. The self-condensation products (5) are characterised in their ^{31}P NMR spectra by an AB system (two multiplets, +30, and +60 ppm, J_{PP} 20–50 Hz).
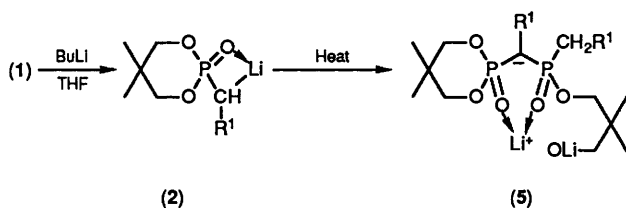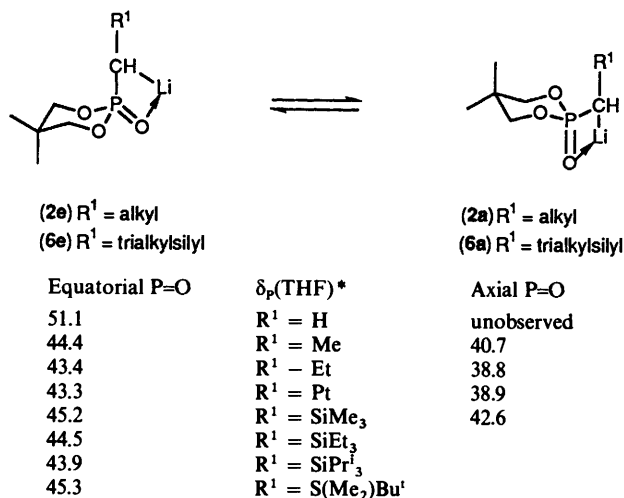
Scheme 4.

Variable low-temperature ^{31}P NMR spectroscopy showed that the carbanions (2) exist as a mixture of two interconverting conformations, either free in solution (2a) (highfield sharp singlet) with the phosphoryl group being in the axial position, or aggregated (2e) (lowfield multiplet or broad peak, depending on the temperature), in which the phosphoryl group adopts the equatorial position[5,7] (Scheme 5). The equilibrium between these conformations depends on the size of R^1. The interconversion rate decreases when the size of the alkyl substituent R^1 increases. However, when R^1 = H, we observed a multiplet only, between –80 and 0 °C, which is due either to a fast conformational equilibrium or, more probably, to the aggregated, equatorial conformation.

When we silylated the unstable cyclic carbanion (2; R^1 = H), we found that it was stable at 20 °C. Thus, α-silylated α-phosphonylated carbanions (6) are stable at room temperature, with all the trialkylchlorosilanes used. Depending on the bulkiness of the silyl group, the conformational equilibrium between (6a) and (6e) may occur, or not. With Me_3SiCl, both (6a) and (6e) are observed at room temperature (ratio 65:35), whereas Et_3SiCl, Pr^iSiCl, and $Bu^t(Me_2)_2SiCl$ only afford (6e) as we deduced from the ^{31}P NMR data (Scheme 5).

The presence of either lithium di-isopropylamide (LDA) or LiBr both break the aggregates and stabilise cyclic α-lithiated α-phosphonylated carbanions. We have already reported that addition of 1 equiv. of LDA to an α-lithiated α-phosphonylated carbanion stabilises the metallated species (Figure 1) with no significant variation of ^{31}P chemical shift.[8] The stability of the

| (2e) R^1 = alkyl | | (2a) R^1 = alkyl |
| (6e) R^1 = trialkylsilyl | | (6a) R^1 = trialkylsilyl |

Equatorial P=O	δ_P(THF)*	Axial P=O
51.1	R^1 = H	unobserved
44.4	R^1 = Me	40.7
43.4	R^1 = Et	38.8
43.3	R^1 = Pt	38.9
45.2	R^1 = $SiMe_3$	42.6
44.5	R^1 = $SiEt_3$	
43.9	R^1 = $SiPr^i_3$	
45.3	R^1 = $S(Me_2)Bu^t$	

* Spectra were recorded at –30 °C for R^1 = alkyl, and at room temperature for R^1 = trialkylsilyl.

Scheme 5.

carbanions (2) associated to LDA is greater in the order R^1 = H < Me < Et < Pr. It does not prevent the conformational flipping of the six-membered ring: the ^{31}P NMR spectrum exhibits a singlet at 25 °C, whose chemical shift is the half-sum of the two chemical shifts attributed to (2a) and (2e) (Scheme 6). Yet the interaction between the LDA negative centre and the phosphorus atom positive centre is weaker for steric reasons than that observed with acyclic phosphonylated carbanions. In fact, the 5,5-dimethyl group hampers the access of the bulky LDA to the phosphorus when the phosphoryl group is in the axial position. When the phosphoryl group is in an equatorial position, the phosphorus atom becomes less electrophilic because it is masked by the three oxygen atom lone pairs.

R^1	δ_P(THF)
H	50.3
Me	42.5
Et	41.6
	41.4

(2; LDA)
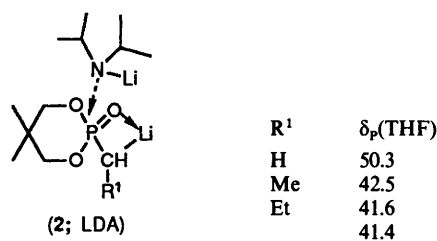
Figure 1.

Lithium bromide has a greater stabilising effect, albeit more subtle. When lithium salts (1 equiv.) are added to a solution of (2), ^{31}P NMR spectroscopy shows that the aggregates have completely disappeared, and the spectrum exhibits a sharp singlet (2; LiBr), whatever the temperature. It has the same chemical shift as (2e) in salt-free solution (Figure 2). Addition of LiBr breaks the aggregates, every metallated species being individually associated to a lithium cation provided by the salt. Since in the aggregates the cohesion is due to chelated lithium cations provided by other carbanions of the medium, the phosphorus environment remains unchanged. The interconversion between (2e) and (2a) has been completely shifted towards the equatorial position (2e). All α-lithiated α-phosphonylated cyclic carbanions (2; LiBr) are observed at 0 °C, by ^{31}P NMR spectroscopy, without degradation, the lithium cation being chelated by the three oxygen atoms and preventing both the ring conformational flipping and attack at the phosphorus atom (Figure 2).
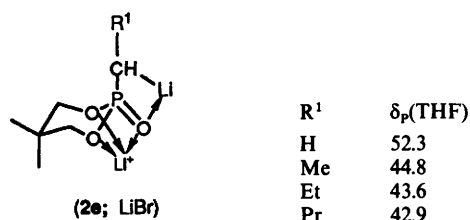
R¹	δ_P(THF)
H	52.3
Me	44.8
Et	43.6
Pr	42.9

(2e; LiBr)

Figure 2.

Discussion

An X-ray structure of (1; R^1 = H) (Figure 3) was realised in order to get some geometrical information about the environment of the phosphorus atom.
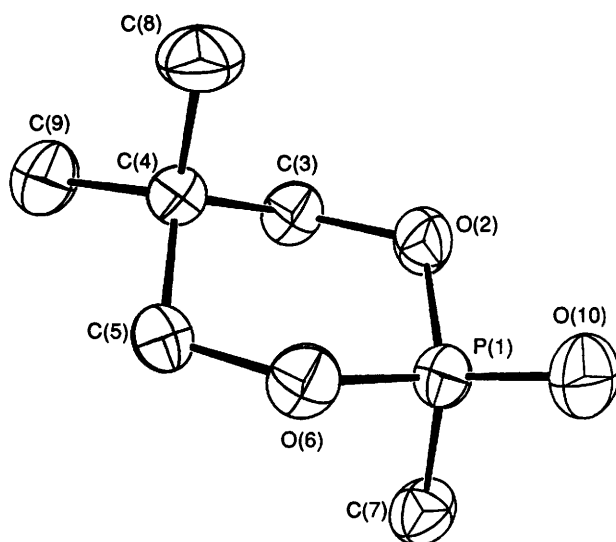

Figure 3.

As expected, the phosphoryl group is in its preferred equatorial position. The intracyclic O–P–O angle is 104.8° (2) (average from the two molecules of the asymmetrical unit), smaller than the perfect tetrahedral one (109.48°) (Table 1). Thus the phosphorus atom is slightly unhindered in comparison with an acyclic phosphonate, where no favoured access to the phosphorus electrophilic centre is available. This contribution enhances its reactivity.

We can assume that at low temperature the favoured conformation of the metallated species is the equatorial one (2e), with both the negative charge and the phosphoryl group in their preferred positions. Moreover, the aggregations, which we evidenced in the variable-temperature NMR spectra, are a self-protection of the phosphorus centre. Therefore, the equatorial conformer (2e) is stable, or at least the more stable, in solution. In contrast, since the axial conformer (2a) cannot aggregate, it is more reactive, and self-condenses to afford (5) once a suitable temperature for this reaction has been reached. The equilibrium between (2a) and (2e) is slowly displaced by the disappearance of (2a) until all the carbanion has undergone self-condensation.

Conclusions

Direct formation of six-membered cyclic phosphonates by action of an alkyl-lithium reagent upon the parent phosphate cannot be performed owing to a higher electrophilicity of the

phosphorus centre. In counterpart, this enhanced reactivity could be exploited in 2-alkyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-ones which have potential in organic synthesis.

The carbanions (2) exist as an equilibrium of two conformers, (2a) and (2e), which are more reactive than their acyclic analogues. Two new types of stabilisation have been evidenced, specific to cyclic α-phosphonylated α-lithiated carbanions: self-stabilisation by aggregation of one conformer (2e), and individual stabilisation by addition of 1 equiv. of lithium bromide. In the latter case, conformation (2e) is the most stable one in the conformational equilibrium.

Experimental

All reactions, excluding hydrolysis, were carried out under an inert atmosphere and scrupulously anhydrous conditions. Improved syntheses of known compounds are described for compounds (3) and (1).

X-Ray Structure Determination for (1; R^1 = H).—Crystals of (1; R^1 = H), $C_6H_{13}O_3P$ were grown at 20 °C from a dichloromethane–hexane solution of the compound. Data were collected at 19° ± 1° on an Enraf Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf Nonius supplied SDP package. The compound crystallises in space group $P2_12_12_1$, a = 6.411(1), b = 13.252(1), c = 19.520(2) Å; V = 1 658.29(55) Å³; Z = 8; d_c = 1.315 g/cm³; Mo-K_α radiation (l = 0.710 73 Å) graphite monochromator; μ = 2.7 cm⁻¹; $F(000)$ = 704. A total of 2 780 unique reflections were recorded in the range 2° ≤ 2q ≤ 60.0° of which 616 were considered as unobserved [F^2 < 3.0 σ (F^2)], leaving 2 164 for solution and refinement. The structure was solved by direct methods, yielding a solution for the whole molecule. The hydrogen atoms were refined with fixed B's in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final R factors were R = 0.036, R_ω = 0.048, GOF = 1.03. The following crystallographic results are available, on request, from the Cambridge Crystallographic Data Centre:* table of positional parameters and estimated standard deviations (hydrogen and non-hydrogen atoms), table of refined displacement parameter expressions—β's table of bond distances (hydrogen atoms), table of bond angles (hydrogen and non-hydrogen atoms), table of root-mean-square amplitudes of anisotropic displacement, and table of general displacement parameter expressions—U's.

2-*Chloro*-5,5-*dimethyl*-1,3,2-*dioxaphosphorinan*-2-*one* (3; Z = Cl).—Phosphorus oxychloride (32.2 g, 0.21 mol) in dichloromethane (200 ml) was added to 2,2-dimethylpropan-1,3-diol (20.8 g, 0.2 mol) in a 1 l flask. The solvent was removed on a rotatory evaporator at ambient temperature to eliminate the HCl produced. The resulting oil when heated on a water-bath at 50 °C for 1 h afforded quantitatively, a white solid, m.p. 106–108 °C (lit.,¹⁰ 104.5–106 °C); δ_P($CDCl_3$) 5.4; δ_C($CDCl_3$) 18.2 (s, 5-Me), 20.2 (s, 5-Me), 31.0 (s, 5-C), and 77.9 (2 C, d, *J* 7 Hz, OCH_2).

2-*Ethoxy*-5,5-*dimethyl* 1,3,2-*dioxaphosphorinan*-2-*one*.—To a solution of sodium ethoxide (7.5 g, 0.11 mol) in tetrahydro-

* See 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans 1*, 1990, Issue 1.

Table 1. Table of positional parameters and their estimated standard deviations.

Atom	x	y	z
P(1)	0.969 75(9)	0.111 59(4)	0.071 27(3)
O(2)	0.767 9(3)	0.108 1(1)	0.024 87(8)
C(3)	0.741 5(4)	0.022 5(2)	−0.021 4(1)
C(4)	0.748 5(4)	−0.076 8(2)	0.017 9(1)
C(5)	0.958 8(4)	−0.084 4(2)	0.053 6(1)
O(6)	0.995 7(3)	0.000 4(1)	0.099 40(8)
C(7)	1.185 0(4)	0.135 9(2)	0.016 4(1)
C(8)	0.571 1(4)	−0.083 8(2)	0.070 2(1)
C(9)	0.737 3(5)	−0.163 6(2)	−0.033 2(2)
O(10)	0.946 6(3)	0.183 2(1)	0.127 85(9)
P(2)	0.248 6(1)	0.096 62(5)	0.328 49(3)
O(11)	0.214 9(3)	0.214 9(1)	0.328 78(8)
C(12)	0.242 5(4)	0.272 4(2)	0.265 8(1)
C(13)	0.448 4(4)	0.251 2(2)	0.231 6(1)
C(14)	0.462 1(4)	0.137 7(2)	0.217 6(1)
O(15)	0.444 5(3)	0.079 6(1)	0.281 07(9)
C(16)	0.029 5(5)	0.042 3(2)	0.285 9(2)
C(17)	0.451 0(6)	0.306 2(2)	0.162 2(1)
C(18)	0.633 0(4)	0.285 0(2)	0.275 0(1)
O(20)	0.282 3(4)	0.057 4(2)	0.397 52(9)

Table 2. Table of bond distances in Å.

Atoms 1–2	Distance	Atoms 1–2	Distance
P(1)–O(2)	1.580(2)	P(2)–O(11)	1.583(2)
P(1)–O(6)	1.581(2)	P(2)–O(15)	1.576(2)
P(1)–C(7)	1.776(4)	P(2)–C(16)	1.783(3)
P(1)–O(10)	1.463(2)	P(2)–O(20)	1.460(2)
O(2)–C(3)	1.459(3)	O(11)–C(12)	1.457(3)
C(3)–C(4)	1.523(3)	C(12)–C(13)	1.506(4)
C(4)–C(5)	1.521(3)	C(13)–C(14)	1.532(4)
C(4)–C(8)	1.531(4)	C(13)–C(17)	1.537(4)
C(4)–C(9)	1.524(4)	C(13)–C(18)	1.523(4)
C(5)–O(6)	1.455(3)	C(14)–O(15)	1.464(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

furan (150 ml) was added dropwise, with stirring, 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (18.4 g, 0.1 mol) dissolved in tetrahydrofuran (60 ml). The temperature was kept at 20 °C with a water-bath. After being stirred for 1 h the solution was quenched by addition of water (40 ml) and the aqueous phase was extracted with dichloromethane–ether (1:1; 3 × 50 ml). The organic layers were dried (MgSO$_4$), filtered, and concentrated under reduced pressure to give a clear oil (16.7 g, 86%), b.p. (0.3 mmHg), 94–95 °C; δ_P(CDCl$_3$) −10.2; δ_C(CDCl$_3$) 15.1 (d, J 6 Hz, OCH$_2$CH$_3$), 19.2 (s, 5-Me), 20.5 (s, 5-Me), 31.2 (d, J 6 Hz, 5-C), 62.4 (d, J 6 Hz, OCH$_2$CH$_3$), and 76.7 (2 C, d, J 6 Hz, $\overline{C}$CH$_2$OPO$\overline{C}$H$_2$).

2-Ethylthio-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (**3**; Z = EtS).—To a solution of sodium thiolate (9.2 g, 0.11 mol) in tetrahydrofuran (150 ml) was added dropwise with stirring the dioxaphosphorinanone (**3**; Z = Cl) (18.4 g, 0.1 mol) dissolved in tetrahydrofuran (60 ml). The temperature was kept at 20 °C with a water-bath. After being stirred for 1 h, the solution was quenched by the addition of water (40 ml) and the aqueous phase was extracted with dichloromethane–ether (1:1); 3 × 50 ml). The combined extracts were dried (MgSO$_4$), filtered, and concentrated under reduced pressure to give a light pink oil (18 g, 85%), b.p. (0.3 mmHg) 110–115 °C; δ_P(CDCl$_3$) +17.6; δ_C(CDCl$_3$) 15.4 (d, J 5 Hz, SCH$_2$CH$_3$), 19.2 (s, 5-Me), 20.7 (s, 5-

Me), 23.3 (d, J 3 Hz, SCH$_2$), 31.3 (d, J 6 Hz, 5-C), and 76.7 (2 C, d, J 7 Hz, OCH$_2$).

2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane[13] (*Scheme 3*).—Phosphorus trichloride (30.1 g, 0.22 mol) in dichloromethane (300 ml) was added to 2,2-dimethylpropane-1,3-diol (20.8 g, 0.2 mol) in a 1-l flask. The flask was immediately adapted to a rotatory evaporator and the solvent slowly removed under reduced pressure at ambient temperature to yield, quantitatively, a clear liquid; b.p. (1.5 mmHg) 47 °C; δ_P(CDCl$_3$) +143.9 (146.7[11]); δ_C(CDCl$_3$) 22.2 (s, CH$_3$), 32.6 (d, J 4 Hz, 5-C), and 70.7 (s, OCH$_2$).

2-Alkoxy-5,5-dimethyl-1,3,2-dioxaphosphorinanes.[12]—The appropriate anhydrous alcohol (0.2 mol) in tetrahydrofuran (50 ml) was added dropwise at room temperature with vigorous stirring to crude 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane and triethylamine (21.2 g, 0.21 mol) in tetrahydrofuran (300 ml). The solution was stirred for 1 h and then filtered and the filtrate concentrated under reduced pressure to give a colourless liquid. Methanol (R = Me):[13] δ_P(CDCl$_3$) +120.1; ethanol (R = Et):[13] δ_P(CDCl$_3$) +119.0; propanol (R = Pr): δ_P(CDCl$_3$) +119.1; butanol (R = Bu): δ_P(CDCl$_3$) +119.3.

2-Alkyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-ones[13] (**1**) (*Scheme 3*).—A mixture of crude 2-alkoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane (*ca.* 0.2 mol) and alkyl iodide (0.1 mol) was heated for 3 h at 95 °C and then stored overnight. The crude product was then treated with hexane (100 ml), filtered, and washed several times with hexane to afford a white solid: R = Me (26.9 g, 82%), m.p. 122 °C (lit.,[13] 117–120 °C), δ_P(CDCl$_3$) +24.7, δ_C(CDCl$_3$) 8.97 (1 Me, d, J 136.0 Hz, PCH$_3$), 21.1 (2 Me, s, 5-Me), 32.3 (s, 5-C), and 75.0 (2 CH$_2$, d, J 6 Hz, OCH$_2$); R = Et (29.4 g, 83%), m.p. 110 °C (Found: C, 47.9; H, 8.5. C$_7$H$_{15}$O$_3$P requires C, 47.2; H, 8.5%); δ_P(CDCl$_3$) +28.2; δ_C(CDCl$_3$) 5.13 (s, PCH$_2$CH$_3$), 15.5 (d, J 137.2 Hz, PCH$_2$), 20.2 (2 Me, s, 5-Me), 31.3 (s, 5-C), and 73.6 (2 CH$_2$, d, J 6 Hz, OCH$_2$); R = Pr (29.8 g, 78%), m.p. 82 °C (Found: C, 49.8; H, 8.8. C$_8$H$_{17}$O$_3$P requires C, 50.0; H, 8.9%), δ_P(CDCl$_3$) +26.9, δ_C(CDCl$_3$) 14.2 (d, J 16 Hz, PCH$_2$CH$_2$), 14.8 [s, P(CH$_2$)$_2$CH$_3$], 20.4 (2 Me, s, 5-Me), 24.7 (d, J 135.8 Hz, PCH$_2$), 31.5 (s, 5-C), 73.6 (2 CH$_2$, d, J 6 Hz, OCH$_2$); R = Bu (30.8 g, 77%), m.p. 72 °C (Found: C, 52.6; H, 9.4. C$_9$H$_{19}$O$_3$P requires C, 52.4; H, 9.3%), δ_P(CDCl$_3$) +27.4, δ_C(CDCl$_3$) 12.7 [s, P(CH$_2$)$_3$CH$_3$], 20.6 (2 Me, s, 5-Me), 22.6 (d, J 135.9 Hz, PCH$_2$), 22.7 (d, J 16 Hz, PCH$_2$CH$_2$), 23.3 [s, P(CH$_2$)$_2$CH$_2$], 31.7 (s, 5-C), and 73.9 (2 CH$_2$, d, J 6 Hz, OCH$_2$).

Metallation: General Procedure.—Six-membered cyclic phosphonates (**1**) (0.01 mol) in tetrahydrofuran (15 ml) were added with stirring at −70 °C to butyl-lithium (*ca.* 1.4M in hexane) in a mixture of hexane–tetrahydrofuran (1:1). After 10 min at low temperature, the metallation was complete. To stabilise the carbanion, previously dried lithium bromide (0.01 mol) can be introduced into the solution before the addition of (**1**). When the stabilisation is performed with lithium di-isopropylamide, this reagent is used in two-fold excess as the metallating agent.

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