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Direct Transformation of Trialkyl Phosphates into Organolithium Compounds by a DTBB-Catalysed Lithiation†

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Abstract: The reaction of different alkylic or phenylic phosphates **1** with an excess of lithium powder and a catalytic amount of DTBB (5 mol %) in the presence of an electrophile -Barbier-type reaction conditions- in THF at -30°C leads to the formation of the expected products **2**, resulting from the reaction of the *in situ* generated organolithium compound with the corresponding electrophile.

INTRODUCTION

Organolithium compounds are very useful intermediates in preparative organic chemistry, above all in carbon-carbon bond formation processes[1]. The preparation of these type of carbanionic reagents starts usually from alkyl halides, the most general method being a halogen-lithium exchange with lithium metal. Other methodologies for this purpose, which involve direct lithiation (deprotonation), transmetallation (from mercury- or tin-containing starting materials), reductive cleavage of ethers or thioethers and lithium addition to unsaturated systems, are far less used[1]. Recently[2], we reported that the use of a catalytic amount of an arene [mainly naphthalene or 4,4'-di-*tert*-butylbiphenyl (DTBB)] in lithiation processes with lithium powder is a very effective and powerful lithiation combination, which permits the preparation of very reactive organolithium compounds under mild reaction conditions. By means of this methodology we have prepared functionalised organolithium compounds[3] (from functionalised chlorinated materials[2,4], carbonylic derivatives[5] and saturated heterocycles[6]) and dilithiated intermediates[7]. This procedure has been also used as a new way for the preparation of organolithium compounds starting from sulfides[2], sulfonates[8a], sulfates[8b,c], sulfones[8d] and nitriles[8e]. In this paper we report the direct transformation of trialkyl phosphates into organolithium compounds by means of a DTBB-catalysed lithiation with lithium powder[9,10] and the *in situ* reaction of these intermediates with electrophiles (Barbier-type conditions). By this methodology is possible (1) the indirect conversion of alcohols into alkyllithium derivatives through the corresponding phosphates, and (2) the *in situ* manipulation of halide-free solutions of organolithium compounds.

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† This paper is dedicated to Prof. A. R. Katritzky on occasion of his 65th birthday.

RESULTS AND DISCUSSION

The reaction of trialkyl and triphenyl phosphates **1a-e** with an excess of lithium powder (1:14 molar ratio) and a catalytic amount of DTBB (1:0.1 molar ratio) in the presence of the corresponding electrophile (Me_3SiCl, $PhMe_2SiCl$, PhCHO, Et_2CO, PhCOEt; 1:3 molar ratio) -Barbier-type reaction conditions- in THF at -30°C led, after hydrolysis with water, to the corresponding compounds **2aa-ec** (Scheme 1 and Table 1). In all cases only one of the alkyl or phenyl groups of the starting phosphate could be transformed into the corresponding organolithium intermediate, so yields in Table 1 are referred to the stoichiometry shown in Scheme 1 (Table 1, footnote b). The exception was the allylic derivative **1b**: in this case the three allyl groups were converted into allyllithium (Table 1, entries 3-5), this method being useful for the indirect transformation of allyl alcohol into allyllithium[11,12]. On the other hand, in many reactions with carbonyl compounds as electrophiles a small amount (<10%) of the corresponding pinacol-type products was detected by GLC.

$$(RO)_3PO \xrightarrow{i,ii} RE$$

2

1a : R=Et
1b : R=$CH_2CH{=}CH_2$
1c : R=Pr^i
1d : R=Bu^n
1e : R=Ph

Scheme 1. *Reagents and conditions*: i, Li powder, DTBB cat. (5 mol %), E^+=Me_3SiCl, $PhMe_2SiCl$, PhCHO, Et_2CO, PhCOEt, THF, -30°C; ii, H_2O.

Starting materials **1a-e** were easily prepared from the corresponding alcohols and phosphorus oxychloride in benzene under basic reaction conditions[12].

We then applied the reaction shown in Scheme 2 to mixed phosphates, namely diethyl and diphenyl derivatives , **1f-j** and **1k-n**, respectively (Scheme 2 and Table 2). As expected from the results obtained above, diethyl allyl and benzyl derivatives , **1f** and **1j** respectively, gave only allylic and benzylic products **2ba-bc** (Table 2, entries 1-3) and **2ja-jd** (Table 2, entries 8-11), respectively.The other mixed diethyl phosphates **1g-i** afforded a mixture of both possible reaction products (RE and R'E; Scheme 2 and Table 2, entries 5-7). In the case of diphenyl derivatives **1k-n** we found a different behaviour: we obtained a mixture of reaction products RE+R'E in all cases -even when an allyl or benzyl group is present in the starting phosphate (**1l** or **1n**; Table 2, entries 13 and 15)- except for **1m**, in which the phenylic derivative **2eb** was the only reaction product isolated (Table 2, entry 14). As in the case of the reaction shown in Scheme 1, a small amount (<10%) of the corresponding pinacol-type product was usually detected as by-product when carbonyl compounds were used as electrophilic reagents.

Table 1. DTBB-Catalysed Lithiation of Trialkyl Phosphates **1a-e** and Reaction with Electrophiles E^+. Isolation of Compounds **2**

Entry	Starting phosphate	Electrophile E^+	Product[a]			
			No.	R	E	Yield (%)[b]
1	**1a**	PhCHO	**2aa**	Et	PhCHOH	90
2	**1a**	PhCOEt	**2ab**	Et	PhC(OH)Et	82
3	**1b**	PhMe$_2$SiCl	**2ba**	CH$_2$CH=CH$_2$	PhMe$_2$Si	44[c]
4	**1b**	PhCHO	**2bb**	CH$_2$CH=CH$_2$	PhCHOH	64[c]
5	**1b**	PhCOEt	**2bc**	CH$_2$CH=CH$_2$	PhC(OH)Et	74[c]
6	**1c**	PhCHO	**2ca**	Pr^i	PhCHOH	37
7	**1c**	PhCOEt	**2cb**	Pr^i	PhC(OH)Et	37
8	**1d**	Et$_2$CO	**2da**	Bu^n	Et$_2$COH	90
9	**1d**	PhCHO	**2db**	Bu^n	PhCHOH	86
10	**1e**	Me$_3$SiCl	**2ea**	Ph	Me$_3$Si	87
11	**1e**	PhCHO	**2eb**	Ph	PhCHOH	54
12	**1e**	PhCOEt	**2ec**	Ph	PhC(OH)Et	31

[a] All products **2** were >95% pure (GLC and 300 MHz ^{1}H NMR). [b] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting material **1** for the stoichiometry shown in Scheme 1. [c] This yield corresponds to the stoichiometry **1**→3 **2**.

Mixed phosphates **1f-n** were easily prepared from commercially available diethyl or diphenyl chlorophosphate and the corresponding alcohol in THF under basic reaction conditions.

From the yields and products ratio shown in Tables 1 and 2 we conclude than the facility of transforming an alkyl phosphate into an organolithium compound, depending on the group R, can be adequately indicated in the following series:

allyl ≈ benzyl > phenyl > primary alkyl >> secondary alkyl

which is in good agreement with the relative stability of the corresponding carbanionic intermediates.

$$(R'O)_2P(O)OR \xrightarrow{i,ii} RE \text{ and/or } R'E$$

2

1f : $R'=Et, R=CH_2CH=CH_2$
1g : $R'=Et, R=Pr^i$
1h : $R'=Et, R=Bu^n$
1i : $R'=Et, R=Ph$
1j : $R'=Et, R=PhCH_2$
1k : $R'=Ph, R=Et$
1l : $R'=Ph, R=CH_2CH=CH_2$
1m : $R'=Ph, R=Pr^i$
1n : $R'=Ph, R=PhCH_2$

Scheme 2. *Reagents and conditions*: i, Li powder, DTBB cat. (5 mol %), $E^+=Me_3SiCl$, $PhMe_2SiCl$, Pr^iCHO, PhCHO, Et_2CO, $\overline{(CH_2)_5C}O$, PhCOEt, THF, -30°C; ii, H_2O.

Table 2. DTBB-Catalysed Lithiation of Mixed Phosphates **1f-n** and Reaction with Electrophiles E^+. Isolation of Compounds **2**

Entry	Starting phosphate	Electrophile E^+	Product[a]		
			No. [ratio]	E	Yield (%)[b]
1	**1f**	$PhMe_2SiCl$	**2ba**[c]	$PhMe_2Si$	74
2	**1f**	PhCHO	**2bb**[c]	PhCHOH	90
3	**1f**	PhCOEt	**2bc**[c]	PhC(OH)Et	94
4	**1f**	$\overline{(CH_2)_5C}O$	**2bd** ($R=CH_2CH=CH_2$)	$\overline{(CH_2)_5C}OH$	43
5	**1g**	PhCHO	**2aa**[c]+**2ca**[c] [4.3/1][d]	PhCHOH	48[e]
6	**1h**	PhCHO	**2aa**[c]+**22db**[c] [1.2/1][d]	PhCHOH	87[e]
7	**1i**	PhCHO	**2aa**[c]+**2eb**[c] [1/1][d]	PhCHOH	32
8	**1j**	Me_3SiCl	**2ja** ($R=PhCH_2$)	Me_3Si	63
9	**1j**	Pr^iCHO	**2jb** ($R=PhCH_2$)	Pr^iCHOH	71
10	**1j**	PhCHO	**2jc** ($R=PhCH_2$)	PhCHOH	86
11	**1j**	$\overline{(CH_2)_5C}O$	**2jd** ($R=PhCH_2$)	$\overline{(CH_2)_5C}OH$	42
12	**1k**	PhCHO	**2eb**[c]+**2aa**[c] [6.8/1][d]	PhCHOH	47[e]
13	**1l**	PhCHO	**2bb**[c]+**2eb**[c] [1.8/1][d]	PhCHOH	25[e]
14	**1m**	PhCHO	**2eb**[c]	PhCHOH	66
15	**1n**	PhCHO	**2jc** ($R=PhCH_2$)+**2eb**[c] [1.4/1][d]	PhCHOH	49[e]

[a,b] See footnotes a and b in Table 1. [c] See Scheme 1 and Table 1. [d] By GLC . [e] Global yield.

EXPERIMENTAL PART

General.- For general information see reference 8c. Phosphorus oxychloride, diethyl and diphenyl chlorophosphate and triethyl phosphate, as well as the other reagents were commercially available (Aldrich, Fluka).

Preparation of Trialkyl Phosphates **1a-e**. *General Procedure*[13].- To a cooled (-10°C) solution of the corresponding alcohol (60 mmol) and pyridine (66 mmol) in dry benzene (6 ml) was added dropwise phosphorous oxychloride (20 mmol) during *ca.* 15 min. The resulting solution was then refluxed for 2 h. After cooling at room temperature the resulting mixture was hydrolysed with water (10 ml) and extracted with diethyl ether (2x20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr) to yield crude phosphates **1a-e** in pure form (>90% from 300 MHz ^{1}H NMR and GLC), which was used for the lithiation step without further purification. Yields, physical and spectroscopical data, as well as literature references, follow.

Triallyl Phosphate (**1b**)[14]: R_f 0.34 (hexane/ethyl acetate: 1/1); t_r 9.81 min; ν_{max} (film) 3080, 3010, 1645 (HC=C), 1270 (P=O) and 1020 cm^{-1} (P-O); δ_H 4.56 (6 H, ddt, *J*=8.2, 5.6, 1.4, 3xCH$_2$O), 5.26 (3 H, dt, *J*=10.4, 1.2, 3xC*H*$_2$=C), 5.37 (3 H, dq, *J*=17.2, 1.4, 3xC*H*$_2$=C) and 5.88-6.01 (3 H, m, 3xCH); δ_C 68.1 (3 C, d, *J*=5.5, 3xCH$_2$O), 118.2 (3 C, 3x*C*H$_2$=C) and 132.4 (3 C, d, *J*=6.8, 3xCH); *m/z* 177 (M$^+$-41, 5%), 137 (12), 79 (13), 57 (12) and 41 (100).

Triisopropyl Phosphate (**1c**)[15]: R_f 0.25 (hexane/ethyl acetate: 1/1); t_r 8.26 min; ν_{max} (film) 1265 (P=O) and 995 cm^{-1} (P-O); δ_H 1.33 (18 H, d, *J*=6.2, 6xMe), 4.54-4.69 (3 H, m, 3xCH); δ_C 23.6 (6 C, d, *J*=4.7, 6xMe) and 71.9 (3 C, d, *J*=6.1, 3xCH); *m/z* 209 (M$^+$-15, 1%), 141 (15), 125 (56), 99 (100), 45 (16), 43 (50) and 41 (27).

*Tri-*n*-butyl Phosphate* (**1d**)[15]: R_f 0.41 (hexane/ethyl acetate: 1/1); t_r 12.65 min; ν_{max} (film) 1275 (P=O) and 1025 cm^{-1} (P-O); δ_H 0.87 (9 H, t, *J*=7.4, 3xMe), 1.28-1.41 (6 H, m, 3xC*H*$_2$Me), 1.55-1.64 (6 H, m, 3xC*H*$_2$CH$_2$O) and 3.96 (6 H, q, *J*=6.7, 3xCH$_2$O); δ_C 13.45 (3 C, 3xMe), 18.55 (3 C, 3x*C*H$_2$Me), 32.2 (3 C, d, *J*=6.9, 3x*C*H$_2$CH$_2$O) and 67.2 (3 C, d, *J*=6.1, 3xCH$_2$O); *m/z* 267 (M$^+$+1, <1%), 211 (22), 155 (25), 99 (100) and 41 (11).

Triphenyl Phosphate (**1e**)[15]: R_f 0.58 (hexane/ethyl acetate: 1/1); t_r 17.83 min; m.p. 48-49°C (hexane/ethyl acetate); ν_{max} (KBr) 3050, 1585, 1480 (HC=C), 1290 (P=O) and 1175 cm^{-1} (P-O); δ_H 7.17-7.26 and 7.31-7.38 (9 H and 6 H, respectively, 2 m, ArH); δ_C 120.05 (6 C, d, *J*=4.9, 6xArCH), 125.55 (3 C, 3xArCH), 129.8 (6 C, 6xArCH) and 150.4 (3 C, d, *J*=7.4, 3xArC); *m/z* 328 (M$^+$+2, 2%), 327 (M$^+$+1, 22), 326 (M$^+$, 88), 325 (79), 233 (22), 232 (17), 228 (15), 215 (32), 170 (37), 169 (35), 168 (19), 152 (12), 141 (17), 140 (12), 139 (14), 94 (26), 93 (16), 77 (100), 66 (11), 65 (76), 64 (10), 63 (16), 51 (59) and 50 (16).

Preparation of Mixed Phosphates **1f-n**. *General Procedure.*- To a cooled (0°C) solution of the corresponding alcohol (20 mmol) and triethylamine (25 mmol) in dry THF (10 ml) was added dropwise the corresponding diethyl or diphenyl chlorophosphate (20 mmol) during *ca.* 15 min. and the mixture was stirred 8 h allowing the temperature to rise to 20°C. Then, the mixture was hydrolysed with water (10 ml) and extracted with diethyl ether (2x20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) yielding pure title compounds. Yields, physical and spectroscopic data, as well as literature references, follow.

Allyl Diethyl Phosphate (**1f**)[16]: R_f 0,22 (hexane/ethyl acetate: 1/1); t_r 8.23 min; ν_{max} (film) 3070, 1640 (HC=C), 1265 (P=O) and 1025 cm^{-1} (P-O); δ_H 1.34 (6 H, t, *J*=7.1, 2xMe), 4.08-4.18 (4 H, m, 2xC*H*$_2$Me), 4.51-4.56 (2 H, m, C*H*$_2$CH), 5.25, 5.37 (1 H each, 2 d, *J*=10.4 and 17.1, respectively, 2xC*H*$_2$=C) and 5.89-6.00 (1 H, m, C*H*=CH$_2$); δ_C 15.95 (2 C, d, *J*=6.7, 2xMe), 63.65 (2 C, d, *J*=5.8, 2x*C*H$_2$Me), 67.75 (d, *J*=5.5, *C*H$_2$CH), 117.9 (*C*H$_2$=C) and 132.5 (d, *J*=7.1, *C*H=CH$_2$); *m/z* 195 (M$^+$+1, 2%), 194 (M$^+$, 4), 167 (28), 166 (12), 139 (15), 138 (46), 137 (14), 127 (22), 125 (27), 121 (11), 109 (13), 99 (100), 82 (17), 81 (37), 57 (19) and 41 (28).

Diethyl Isopropyl Phosphate (**1g**)[17]: R_f 0.29 (hexane/ethyl acetate: 1/1); t_r 7.68 min; ν_{max} (film) 1260 (P=O) and 1020 cm^{-1} (P-O); δ_H 1.31-1.36 (12 H, m, 4xMe), 4.10 (4 H, dq, J=7.8, 7.1, 2xCH$_2$) and 4.59-4.70 (1 H, m, CH); δ_C 16.05 (2 C, d, J=6.9, 2x*Me*CH$_2$), 23.55 (d, J=5.1, *Me*CH), 63.4 (2 C, d, J=5.9, 2xCH$_2$) and 72.3 (d, J=5.8, CH); m/z 181 (M$^+$-15, 16%), 155 (34), 154 (14), 153 (13), 127 (58), 125 (27), 109 (19), 99 (100), 82 (17), 81 (33), 45 (19), 43 (36) and 41 (19).

n-*Butyl Diethyl Phosphate* (**1h**)[18]: R_f 0.28 (hexane/ethyl acetate: 1/1); t_r 9.39 min; ν_{max} (film) 1265 (P=O) and 1025 cm^{-1} (P-O); δ_H 0.94 [3 H, t, J=7.3, *Me*(CH$_2$)$_3$], 1.34 (6 H, t, J=7.1, 2x*Me*CH$_2$O), 1,38-1,48, 1,62-1,72 [2 H each, 2 m, Me(C*H*$_2$)$_2$], 4.04 (2 H, q, J=6.7, CH$_2$C*H*$_2$O) and 4.11 (4 H, quintet, J=7.1, 2xMeC*H*$_2$O); δ_C 13.5 [*Me*(CH$_2$)$_3$], 16.05 (2 C, d, J=6.7, 2x*Me*CH$_2$O), 18.6 (Me*C*H$_2$CH$_2$), 32.2 (d, J=6.8, *C*H$_2$CH$_2$O), 63.5 (2 C, d, J=5.9, 2xMe*C*H$_2$O) and 67.25 (d, J=6.0, CH$_2$*C*H$_2$O); m/z 211 (M$^+$+1, <1%), 210 (M$^+$, <1), 155 (82), 127 (56), 125 (13), 109 (13), 99 (100) and 81 (21).

Diethyl Phenyl Phosphate (**1i**)[19]: R_f 0.32 (hexane/ethyl acetate: 1/1); t_r 11.50 min; ν_{max} (film) 3050, 3030, 1590, 1485 (HC=C), 1270 (P=O) and 1025 cm^{-1} (P-O); δ_H 1.35 (6 H, td, J=7.1, 1.0, 2xMe), 4.17-4.27 (4 H, m, 2xCH$_2$) and 7.14-7.36 (5 H, m, ArH); δ_C 16.0 (2 C, d, J=6.7, 2xMe), 64.5 (2 C, d, J=6.3, 2xCH$_2$), 119.9 (2 C, d, J=4.6, 2xArCH), 124.9, 129.6 (1 C and 2 C, respectively, 3xArCH) and 150.7 (d, J=6.6, ArC); m/z 231 (M$^+$+1, 2%), 230 (M$^+$, 35), 201 (11), 187 (12), 109 (12), 105 (11), 104 (54), 99 (13), 94 (100), 81 (27), 77 (33), 66 (15), 65 (45), 63 (12) and 51 (19).

Benzyl Diethyl Phosphate (**1j**)[20]: R_f 0.22 (hexane/ethyl acetate: 1/1); t_r 12.55 min; ν_{max} (film) 3060, 3020, 1495 (HC=C), 1270 (P=O) and 1020 cm^{-1} (P-O); δ_H 1.30 (6 H, t, J=7.1, 2xMe), 4.09 (4 H, quintet, J=7.1, 2xC*H*$_2$Me), 5.07 (2 H, d, J=8.1, C*H*$_2$Ph) and 7.31-7.41 (5 H, m, ArH); δ_C 16.0 (2 C, d, J=6.8, 2xMe), 63.7 (2 C, d, J=5.9, 2x*C*H$_2$Me), 68.9 (d, J=5.5, *C*H$_2$Ph), 127.75, 128.35, 128.45 (ArCH) and 136.0 (d, J=6.8, ArC); m/z 246 (M$^+$+2, 1%), 245 (M$^+$+1, 8), 244 (M$^+$, 50), 215 (23), 188 (20), 187 (31), 153 (14), 138 (16), 125 (23), 118 (25), 111 (15), 107 (65), 105 (13), 99 (11), 92 (10), 91 (100), 90 (23), 89 (14), 82 (11), 81 (16), 79 (15), 77 (20) and 65 (26).

Ethyl Diphenyl Phosphate (**1k**)[21]: R_f 0.48 (hexane/ethyl acetate: 1/1); t_r 14.90 min; ν_{max} (film) 3060, 3030, 1590, 1485 (HC=C), 1285 (P=O) and 1035 cm^{-1} (P-O); δ_H 1.35 (3 H, t, J=7.1, Me), 4.27-4.37 (2 H, m, CH$_2$) and 7.15-7.35 (10 H, m, ArH); δ_C 15.95 (d, J=6.6, Me), 65.35 (d, J=6.3, CH$_2$), 119.95 (4 C, d, J=4.9, 4xArCH), 125.15, 129.65 (2 C and 4 C, respectively, 6xArCH) and 150.5 (2 C, d, J=7.1, 2xArC); m/z 280 (M$^+$+2, 2%), 279 (M$^+$+1, 21), 278 (M$^+$, 96), 277 (33), 263 (10), 250 (40), 249 (71), 232 (12), 175 (11), 174 (10), 170 (70), 169 (40), 168 (11), 165 (16), 157 (18), 141 (14), 140 (11), 139 (11), 105 (25), 104 (66), 95 (12), 94 (93), 93 (17), 81 (17), 78 (14), 77 (100), 76 (13), 66 (36), 65 (91), 64 (15), 63 (24), 51 (59), 50 (18) and 47 (11).

Allyl Diphenyl Phosphate (**1l**)[22]: R_f 0.54 (hexane/ethyl acetate: 1/1); t_r 15.41 min; ν_{max} (film) 3050, 3030, 1645, 1585, 1485 (HC=C), 1290 (P=O) and 1015 cm^{-1} (P-O); δ_H 4.73 (2 H, ddt, J=8.7, 5.6, 1.4, CH$_2$O), 5.26 (1 H, dq, J=10.4, 1.2, 1xC*H*$_2$=C), 5.37 (1 H, dq, J=17.1, 1.5, 1xC*H*$_2$=C), 5.87-6.00 (1 H, m, C*H*=CH$_2$), 7.15-7.26 and 7.30-7.37 (6 H and 4 H, respectively, 2 m, ArH); δ_C 69.4 (d, J=5.9, CH$_2$O), 118.9 (*C*H$_2$=C), 120.0 (4 C, d, J=5.0, 4xArCH), 125.3 (2 C, 2xArCH), 129.7 (4 C, 4xArCH), 131.75 (d, J=6.9, *C*H=CH$_2$) and 150.45 (2 C, d, J=7.1, 2xArC); m/z 291 (M$^+$+1, 3%), 290 (M$^+$, 19), 117 (27), 116 (22), 115 (37), 94 (36), 77 (26), 65 (46), 63 (10), 51 (22) and 41 (100).

Isopropyl Diphenyl Phosphate (**1m**)[23]: R_f 0.51 (hexane/ethyl acetate: 1/1); t_r 15.05 min; ν_{max} (film) 3060, 3030, 1590, 1485 (HC=C), 1280 (P=O) and 1015 cm^{-1} (P-O); δ_H 1.35 (6 H, dd, J=6.2, 0.8, 2xMe), 4.80-4.95 (1 H, m, C*H*Me) and 7.13-7.35 (10 H, m, ArH); δ_C 23.4 (2 C, d, J=5.1, 2xMe), 74.75 (d, J=6.4, *C*HMe), 119.95 (4 C, d, J=5.0, 4xArCH), 125.05, 129.55 (2 C and 4 C, respectively, 6xArCH) and 150.55 (2 C, d, J=7.1, 2xArC); m/z 294 (M$^+$+2, 3%), 293 (M$^+$+1, 22), 292 (M$^+$, 85), 277 (34), 251 (46), 250 (98), 249 (96), 232 (30), 171 (16), 170 (83), 169 (46), 168 (19), 156 (23), 152 (11), 141 (20), 140 (19), 139 (16), 118 (15), 115 (10), 109 (11), 100 (14), 95 (19), 94 (100), 93 (26), 81 (13), 78 (11), 77 (90), 76 (12), 66 (40), 65 (91), 64 (15), 63 (28), 51 (53), 50 (17), 43 (76), 42 (17) and 41 (65).

Benzyl Diphenyl Phosphate (**1n**)[24]: R_f 0.55 (hexane/ethyl acetate: 1/1); t_r 18.84 min; m.p. 47°C (hexane/ethyl acetate); ν_{max} (KBr) 3080, 3040, 1585, 1485 (HC=C), 1285 (P=O) and 1010 cm^{-1} (P-O); δ_H 5.25 (2 H, d, J=8.6, CH_2), 7.13-7.20 and 7.24-7.33 (6 H and 9 H, respectively, 2 m, ArH); δ_C 70.55 (d, J=6.1, CH_2), 120.0 (4 C, d, J=4.9, 4xArCH), 125.25 (2 C), 128.0 (2 C), 128.55 (2 C), 128.7, 129.7 (4 C)(11xArCH), 135.1 (d, J=7.3, 1xArC) and 150.45 (2 C, d, J=7.4, 2xArC); m/z 342 (M^++2, 1%), 341 (M^++1, 7), 340 (M^+, 33), 167 (35), 166 (16), 165 (13), 91 (100) and 65 (23).

DTBB-Catalysed Lithiation of Phosphates **1** *and Reaction with Electrophiles. Isolation of Compounds* **2**. *General Procedure*.- To a blue suspension of lithium powder (100 mg, 14 mmol) and DTBB (26 mg, 0.10 mmol) in dry THF (5 ml) was slowly added (30-60 min) a solution of the corresponding phosphate **1** (1 mmol) and the electrophile (3 mmol) in THF (4 ml) at -30°C. After 10 min stirring at the same temperature, the reaction mixture was hydrolysed with water (5 ml), neutralysed with 2 N hydrochloric acid and extracted with diethyl ether (2x20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr) to give a residue, which was purified by flash chromatography (silica gel, hexane/ethyl acetate) yielding pure products **2**. Yields are included in Tables 1 and 2. Compounds **2aa**[8c], **2ab**[8c], **2bb**[8a], **2bd**[8a], **2ca**[8c], **2da**[8c], **2db**[8c], **2ea**[8c], **2eb**[8c], **2ec**[5a], **2jb**[8a], **2jc**[8a] and **2jd**[8a] have been characterised by comparison of their physical and spectroscopic data with those previously described by us[5,8]. Physical and spectroscopic data for the rest of compounds **2**, as well as the literature references, follow.

Allyldimethylphenylsilane (**2ba**)[25]: R_f 0.47 (hexane); t_r 8.47 min; ν_{max} (film) 3050, 3030, 1620, 1580, 1480 (HC=C) and 1240 cm^{-1} (SiMe); δ_H 0.28 (6 H, s, 2xMe), 1.75 (2 H, d, J=8.0, CH_2Si), 4.82-4.89 (2 H, m, CH_2=CH), 5.70-5.84 (1 H, m, CH=CH_2), 7.32-7.37 and 7.49-7.52 (3 H and 2 H, respectively, 2 m, ArH); δ_C -3.5 (2 C, 2xMe), 23.65 (CH_2Si), 113.35 (CH_2=C), 127.7, 128.95, 133.6, 138.65 (ArC) and 134.6 (CH=CH_2); m/z 135 (M^+-41, 100%), 107 (16), 105 (38) and 43 (19).

3-Phenyl-5-hexen-3-ol (**2bc**)[26]: R_f 0.37 (hexane/ethyl acetate: 6/1); t_r 9.68 min; ν_{max} (film) 3460 (OH), 3060, 3020, 1635, 1600 and 1490 cm^{-1} (HC=C); δ_H 0.76 (3 H, t, J=7.4, Me), 1.78-1.90 (2 H, m, CH_2Me), 2.02 (1 H, s, OH), 2.49 (1 H, dd, J=13.7, 8.6, 1xCH_2CH=CH_2), 2.72 (1 H, ddt, J=13.7, 6.1, 1.3, 1xCH_2CH=CH_2), 5.07-5.16 (2 H, m, CH_2=CH), 5.58 (1 H, dddd, J=17.1, 10.1, 8.6, 6.1, CH=CH_2), 7.20-7.25 and 7.31-7.41 (1 H and 4 H, respectively, 2 m, ArH); δ_C 7.75 (Me), 35.2 (CH_2Me), 46.9 (CH_2CH=CH_2), 75.95 (CO), 119.45 (CH_2=CH), 125.35, 126.35, 128.0, 145.7 (ArC) and 133.55 (CH=CH_2); m/z 135 (M^+-41, 100%), 105 (48), 91 (11), 77 (50), 57 (96), 51 (21), 43 (18) and 41 (64).

2-Methyl-3-phenyl-3-pentanol (**2cb**)[27]: R_f 0.42 (hexane/ethyl acetate: 6/1); t_r 9.79 min; ν_{max} (film) 3480 (OH), 3050, 3020, 1600 and 1490 cm^{-1} (HC=C); δ_H 0.70 (3 H, t, J=7.4, MeCH$_2$), 0.73, 0.95 (3 H each, 2 d, J=6.8 each, 2xMeCH), 1.58 (1 H, s, OH), 1.89 (2 H, q, J=7.4, CH_2), 2.05 (1 H, septet, J=6.8, CHMe), 7.18-7.20 and 7.21-7.38 (1 H and 4 H, respectively, 2 m, ArH); δ_C 7.9, 16.6, 17.5 (3xMe), 32.0 (CH_2), 37.5 (CHMe), 79.3 (CO), 125.9, 126.1, 127.7 and 145.05 (ArC); m/z 149 (M^+-29, 15%), 136 (10), 135 (97), 105 (16), 91 (12), 78 (10), 77 (27), 57 (100), 51 (16), 43 (80) and 41 (45).

Benzyltrimethylsilane (**2ja**)[28]: R_f 0.43 (hexane); t_r 7.23 min; ν_{max} (film) 3050, 3010, 1595, 1485 (HC=C) and 1245 cm^{-1} (Si-Me); δ_H -0.04 (9 H, s, 3xMe), 2.05 (2 H, s, CH_2), 6.89-7.06 and 7.12-7.21 (3 H and 2 H, respectively, 2 m, ArH); δ_C -1.95 (3 C, 3xMe), 27.05 (CH_2), 123.8, 128.0, 128.1 and 140.45 (ArC); m/z 166 (M_++2, 1%), 165 (M^++1, 2), 164 (M^+, 11), 121 (12), 91 (26), 73 (100), 65 (18), 45 (12) and 43 (14).

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