Journal of Organometallic Chemistry, 466 (1994) 89–94

Side-chain metallation of diethyl phosphonotoluenes

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(Received April 16, 1993)

Abstract

Ortho and *para*-diethylphosphonotoluenes are regioselectively lithiated using lithium diisopropylamide in tetrahydrofuran at −70°C at the benzylic positions. The lithiated species react with *para*-anisaldehyde or chlorotrimethylsilane to give the corresponding carbinols or trimethylsilylated derivatives in excellent yields. In contrast, the extent of metallation of *meta*-diethylphosphonotoluene does not exceed 60% under the same conditions.

Key words: Phosphorus; Metallation; Toluene

1. Introduction

As with the aromatic ring itself [1], metallation on the side chain of toluenes **1** is greatly facilitated by heteroatom *ortho* substitution [2] (Scheme 1). Numerous functional substituents Z *ortho* to a methyl group on an aromatic ring promote regioselective metallation at the benzylic position. Subsequent treatment of the lithiated intermediate **2** with an electrophilic reagent leads to various polyfunctional aromatic compounds **3** useful for natural product syntheses [3]. On the contrary, the same metallation–electrophilic substitution sequence applied to the *meta* or *para* isomers is often more difficult and less regioselective than for the *ortho* isomer [4–8].

To our knowledge, no example of metallation of phosphonotoluenes has been described so far. For the phosphate series, Watanabe *et al.* [9] recently reported a synthesis of benzofurans via the lithiation (Li^sBu in tetrahydrofuran (THF) at −105°C) of *ortho*-tolyl tetramethylphosphorodiamidates (**1**) (Z = O–P(O)$(NMe_2)_2$).

Having previously described an efficient synthesis of the three isomers (*ortho, meta* and *para*) of diethyltolylphosphonates **4** by photophosphonylation of the corresponding bromotoluenes [10], we wished to know whether these molecules could be metallated on the side chain.

2. Results

We studied first the metallation of the potentially more reactive *ortho* isomer **4**-*o*. We chose *para*-methoxybenzaldehyde to trap the presumed intermediate benzylic carbanion, **5**-*o*. In so far as the resulting oxanion **6**-*o* was protected from further deprotonation, we used only one equivalent of lithiated base (B–Li) (Scheme 2).

We tested four metallating systems: n-butyllithium (Li^nBu), *n*-butyllithium complexed with one equivalent of tetramethylethylene diamine (Li^nBu + TMEDA), tert-butyllithium (Li^tBu) and lithium diisopropylamide (LDA). In order to minimize possible nucleophilic attack by the basis system at the phosphonate moiety, all metallations were carried out at −70°C in THF for 30 min before the addition of the electrophile. After acidification, the crude mixtures were analysed by ^{31}P NMR spectroscopy. The results are reported in Table 1.

Table 1 clearly shows the superiority of LDA over the other metallation reagents, in the conditions of the reaction. The recovery of phosphonotoluene **4**-*o* in runs 1–3 indicates that the metallation of **4**-*o* was slower with other reagents than with LDA; moreover, with the very nucleophilic system Li^nBu + TMEDA

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0022-328X/94/$7.00
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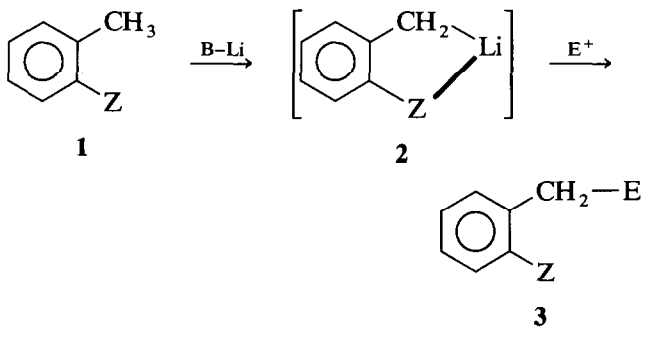


Scheme 1.

(run 2), competitive attack at the phosphonate group probably occurred (see later in the *meta* series). Finally, pure carbinol **7**-*o* was isolated with an 85% yield from run 4.

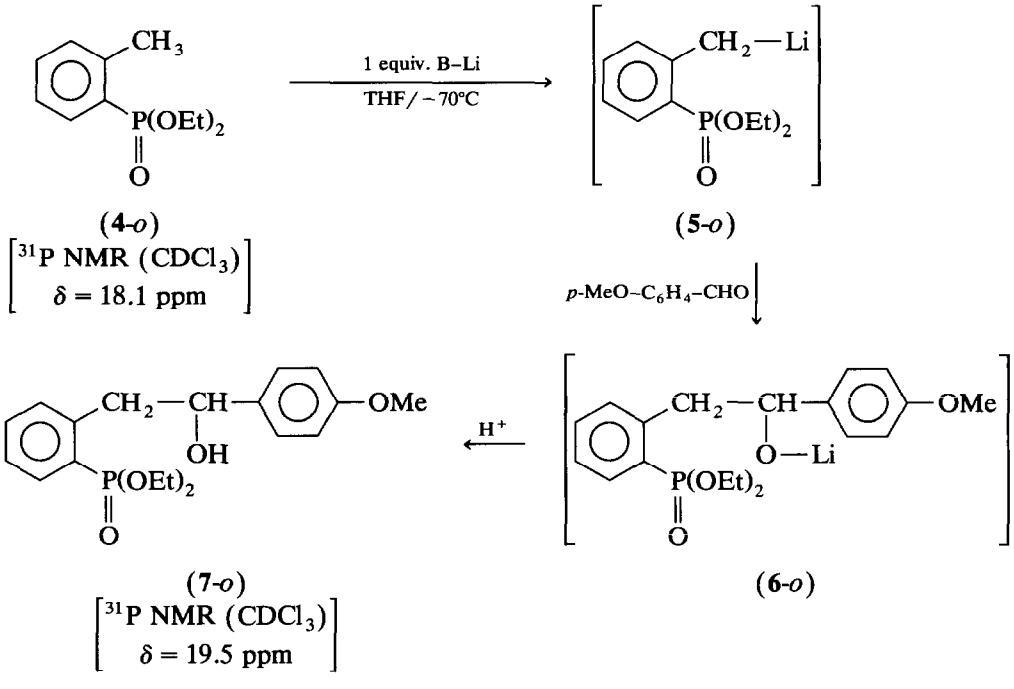
Metallations of the **4**-*m* and **4**-*p* isomers were attempted under the experimental conditions used in run 4 (Scheme 3).

The outcomes of these reactions showed marked differences from the *ortho* isomer. As established from ^{31}P NMR measurements carried out on the crude reaction mixtures, only 3% of **4**-*p* was recovered (run 6), reflecting its relatively easy metallation (Table 2).

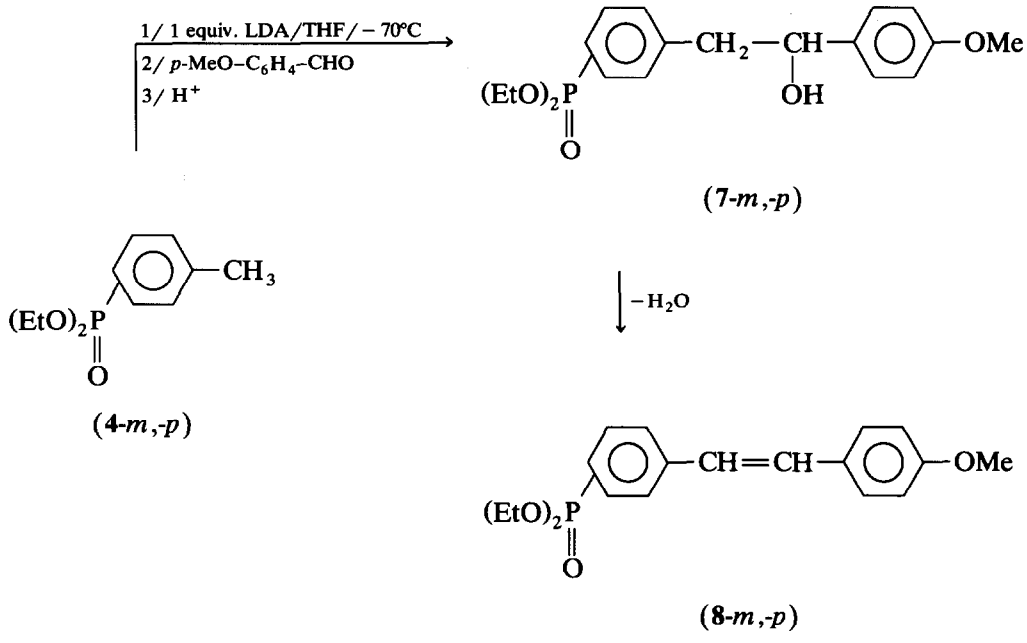
In the case of **4**-*m* the characteristic red colour of the metallated product was formed at a much later stage, indicating a slower side-chain deprotonation; after quenching with *para*-anisaldehyde, the quantity of recovered substrate was at least 40% (run 5) and this could not be significantly reduced by raising the temperature and lengthening the time of metallation. Moreover we detected (^{31}P and ^{1}H NMR spectroscopy) small amounts of stilbene derivatives **8** resulting from the dehydration of the carbinols **7** during acidic hydrolysis. Carbinols **7**-*m* and **7**-*p* were isolated, characterized and then converted under acidic conditions into the stilbene derivatives **8**-*m* and **8**-*p* respectively (see Section 4). The absence of such a stilbene derivative in the *ortho* series may be explained by an intramolecular hydrogen bond between hydroxy and phosphonic groups in the carbinol **7**-*o*.

In a second set of experiments, we studied the reaction of the lithiated carbanions **5** with chlorotrimethylsilane (Scheme 4).

The high reactivity of triorganosilicon chlorides towards carbanions even at low temperature is well known and is widely used to characterize organolithium compounds [11]. However, in contrast with the lithium alkoxide (as **5**-*o* in Scheme 2) resulting from the condensation of a carbonylated electrophile, the silylated phosphonate **10** arising from quenching by Me_3SiCl may be deprotonated in the presence of the unreacted basic carbanion **5**. Under these conditions, complete silylation of the substrate was never obtained. Thus, in an experiment analogous to run 9 (Table 3), when one molar equivalent of LDA was used, ^{31}P NMR analysis of the crude product composition revealed 61% formation of silylated phosphonate **10**-*p* and 39% recovery of



Scheme 2.

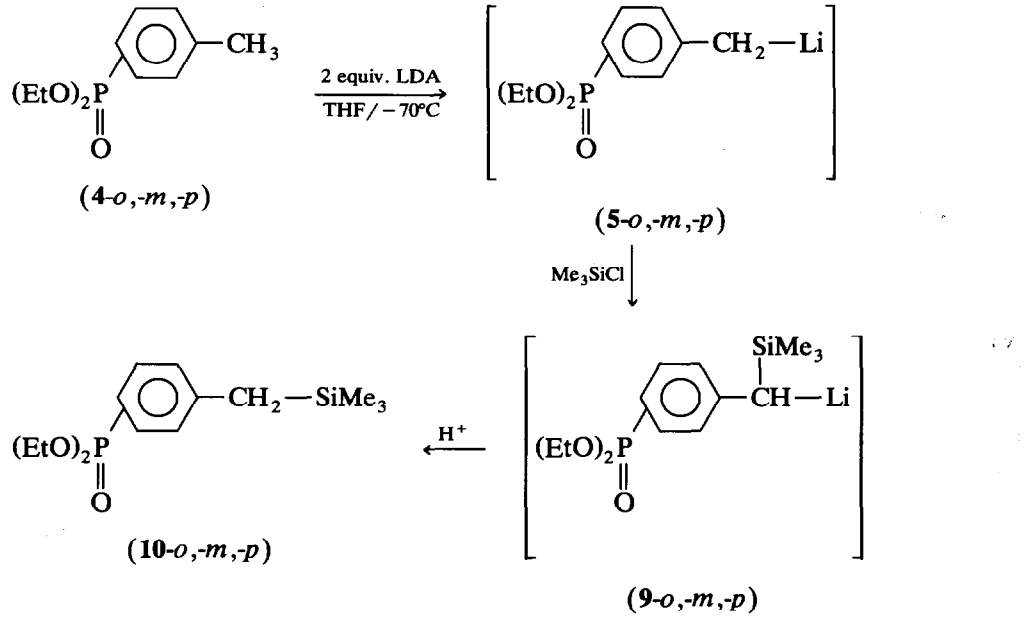


Scheme 3.

starting material **4**-*p*. To overcome this, we used two equivalents of LDA: one for the initial deprotonation of the substrate and one for the deprotonation of the product as it formed. In the last step of the process, the carbanion **9** was hydrolysed to give **10**. The results are reported in Table 3.

In runs 7 and 9, the crude product exhibited the single ^{31}P NMR signal of phosphonate **10**. In run 8, the crude product was a mixture of **10**-*m* and **4**-*m* (52% and 48% respectively, as determined by ^{31}P NMR measurements).

In our last experiment, phosphonotoluene **4**-*m* was metallated by the system Li^{n}Bu + TMEDA at −70°C for 30 min and then treated with Me_3SiCl. ^{31}P NMR analysis of the crude reaction mixture revealed the presence of the phosphinate **11**-*m* (49%), the phos-



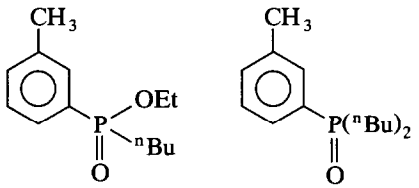
Scheme 4.

TABLE 1. Percentage composition [a] of the reaction mixtures of metallated phosphonotoluene **4-*o*** when trapped with *para*-anisaldehyde

Run	Metallating reagent (B–Li)	**4-*o*** (%)	**7-*o*** (%)	Other (%)
1	Li^{n}Bu	62	38	–
2	Li^{n}Bu + TMEDA	52	38	10 [b]
3	Li^{t}Bu	54	46	–
4	LDA	–	100	–

[a] ^{31}P NMR ($CDCl_3$) analysis via the ratio of peak areas. [b] Two additional unidentified peaks were detected at $\delta = 43.1$ ppm and $\delta = 44.8$ ppm.

phine oxide **12-*m*** (41%) and the starting phosphonate **4-*m*** (10%). No trace of silylated phosphonate **10-*m*** was detected.



(**11-*m***) (**12-*m***)

3. Discussion and conclusion

The present study establishes the usefulness of LDA as a non-nucleophilic base for proton abstraction, under very mild conditions, at the benzylic position of diethyl phosphonotoluenes **4**. For all three isomers, the presence on the aromatic ring of the electron-withdrawing phosphonate group undoubtedly facilitates the benzylic deprotonation, in comparison with toluene itself, which requires a more powerful metallating reagent [12].

However, our metallation-trapping experiments indicate that, whereas side-chain deprotonation is almost quantitative for *ortho* and *para* isomers, it does not exceed 60% for the *meta* isomer. Although we propose no hypothesis concerning the relative importance of kinetic or thermodynamic control in such metallation processes [13], we can, in part, rationalize the noticeable difference in the susceptibilities of the three isomers to metallation. For both *ortho* and *para* isomers a mesomeric resonance stabilization of the corresponding benzylic anions probably occurs, in addition to the inductive effect that favours formation of such isomers. Moreover, for the *ortho* isomer, intramolecular coordination of the lithium cation with the phosphonic group certainly reinforces the stabilization of the anion. In contrast, for the *meta* isomer, only the moderate inductive effect of the phosphonyl group can be involved. This effect is apparently insufficient to promote complete metallation at the side chain in the presence of lithiated dialkylamides (we checked that lithium 2,2,6,6-tetramethylpiperidide gave no better results than LDA). Moreover, as shown by the last experiment, with the very powerful reagent Li^{n}Bu + TMEDA, nucleophilic substitution at the phosphonate group completely suppresses deprotonation at the benzylic position.

In conclusion, apart from the limitation of the *meta* isomer, metallation–electrophilic substitution methodology is useful for regioselective functionalization at the benzylic position of diethylphosphonotoluenes [14]. Some of these functionalized aromatic phosphonates have already aroused much interest because of their potential therapeutic properties [15].

TABLE 2. Constitution and ^{31}P NMR analysis [a] of the crude mixtures of metallated phosphonotoluenes **4-*m*** (run 5) and **4-*p*** (run 6) when trapped with *para*-anisaldehyde

Run	Phosphonotoluene **4**; $\delta(^{31}P)$ (ppm); amount (%)	Carbinol **7**; $\delta(^{31}P)$ (ppm); amount (%)	Phosphonostilbene **8**; $\delta(^{31}P)$ (ppm); amount (%)
5	**4-*m***; 18.0; 40	**7-*m***; 17.9; 55	**8-*m***; 17.6; 5
6	**4-*p***; 18.1; 3	**8-*p***; 18.0; 90	**8-*p***; 17.8; 7

[a] In $CDCl_3$ solution, the percentage of each constituent was determined by ^{31}P NMR integration measurements.

TABLE 3. ^{31}P NMR, yields and boiling points of the silylated phosphonates **10**

Run	Phosphonate	δ (^{31}P NMR ($CDCl_3$)) (ppm)	Yield [a] (%)	B.p. at 0.3 Torr (°C)
7	**10-*o***	19.1	84	128
8	**10-*m***	18.9	31	120
9	**10-*p***	18.8	86	124

[a] Yields of distilled products pure by GPC, and ^{31}P and ^{1}H NMR spectroscopy.

4. Experimental section

Diethyl tolylphosphonates **4** were prepared by photophosphonylation of the corresponding bromotoluenes as previously described [10]. All the metallation reactions were carried out under an inert atmosphere. THF was distilled from sodium-benzophenone ketyl before use. Commercially available solutions of Li^{n}Bu in hexane were titrated with a standardized solution of benzylic alcohol in toluene, in the presence of 2,2′-biquinoline as indicator. IR spectra were recorded on a Beckman 4250 spectrophotometer. ^{1}H NMR spectra were recorded on Varian T-60 and Bruker AC 200

spectrometers using tetramethylsilane as internal reference. ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer using 85% H_3PO_4 as external reference. Gas-phase chromatography (GPC) was performed on a Girdel 300 chromatograph equipped with a 2 m OV 17 column. Elemental microanalyses were carried out on a Carlo Erba 1106 analyser. Melting points were taken on a Kofler apparatus and are uncorrected. Mass spectra were obtained with a JEOL AX 500 spectrometer (EI, 70 eV).

4.1. General procedure for the generation of benzylic carbanions 5

To a stirred 1.6 M solution of Li^{n}Bu in hexane (5.5 ml, 8.8 mmol) at −20°C was added dropwise diisopropylamine (0.9 g, 8.8 mmol) in THF (10 ml). After 15 min, the mixture was cooled to −70°C and diethyltolylphosphonate **4** (2 g, 8.8 mmol) in THF (5 ml) was slowly added. Stirring was continued at −70°C for 30 min while the mixture turned red.

4.2. Reaction of 4-methoxybenzaldehyde with benzylic carbanions 5: preparation of phosphonocarbinols 7

para-Anisaldehyde (1.2 g, 8.8 mmol) in THF (5 ml) was dropped at −70°C into a solution of the benzylic carbanion **5** (prepared as described above) and stirred at −70°C while the mixture turned dark green. The reaction was monitored by GPC analysis of hydrolysed samples. No more changes in the mixture were detected after about 30 min. The mixture was allowed to warm to room temperature and then treated with 3 M aqueous HCl (10 ml), when it turned light yellow. The aqueous phase was extracted with dichloromethane (3 × 15 ml) and the combined organic layers dried ($MgSO_4$). The solvent was evaporated under reduced pressure to give the crude product, which was analysed by ^{31}P and ^1H NMR spectroscopy and then purified by chromatography over SiO_2 (eluent, diethylether), giving the pure carbinol **7** as a viscous oil.

7-*o*: 2.73 g, 7.5 mmol; yield, 85%. IR (film): ν(OH) 3280 cm^{-1}. ^{31}P NMR ($CDCl_3$): 19.5 ppm. ^1H NMR ($CDCl_3$). 1.25 (t, $J = 7$ Hz, 6H, 2 × CH_3CH_2O); 3.25 (d, $J = 6$ Hz, 2H, CH_2CH); 3.7 (s, 3H, CH_3O); 4.1 (qui, $J = 7$ Hz, 4H, 2 × OCH_2CH_3); 4.75 (t, $J = 6$ Hz, 1H, $CHCH_2$); 5.2 (s, 1H, OH); 6.8–8.0 (m, 8H, 2 × C_6H_4) ppm. Anal. Found: C, 62.5; H, 7.0. $C_{19}H_{25}O_5P$ calc.: C, 62.63; H, 6.87%.

7-*m*: 0.98 g, 2.7 mmol; yield, 31%. IR (film): ν(OH) 3270 cm^{-1}. ^{31}P NMR ($CDCl_3$): 17.9 ppm. ^1H NMR ($CDCl_3$): 1.25 (t, $J = 7$ Hz, 6H, 2 × CH_3CH_2O); 3.3 (d, $J = 6$ Hz, 2H, CH_2CH); 3.65 (s, 3H, CH_3O); 4.1 (qui, $J = 7$ Hz, 4H, 2 × OCH_2CH_3); 4.5 (s, 1H, OH); 4.7 (t, $J = 6$ Hz, 1H, $CHCH_2$), 6.8–7.7 (m, 8H, 2 × C_6H_4) ppm. Anal. Found: C, 62.8; H, 6.7%.

7-*p*: 2.29 g, 6.3 mmol; yield, 71%. IR (film): ν(OH) 3285 cm^{-1}. ^{31}P NMR ($CDCl_3$): 18.0 ppm. ^1H NMR ($CDCl_3$): 1.25 (t, $J = 7$ Hz, 6H, 2 × CH_3CH_2O); 3.1 (d, $J = 6$ Hz, 2H, CH_2CH); 3.3 (s, 1H, OH); 3.65 (s, 3H, CH_3O); 4.7 (t, $J = 6$ Hz, 1H, $CHCH_2$); 6.6–7.7 (m, 8H, 2 × C_6H_4) ppm. Anal. Found: C, 62.7; H, 7.2%.

4.3. Dehydration of phosphonocarbinols 7-m and 7-p: preparation of phosphonostilbenes 8-m and 8-p

To phosphonocarbinol **7**(*-m,-p*) (0.4 g, 1.1 mmol) in toluene (10 ml) were added some molecular sieves (4 Å) and *para*-tolylsulfonic acid (about 5 mg). The mixture was stirred for 4 h at 90–100°C and then cooled to room temperature. Diethylether (3 ml) and an aqueous saturated solution of $NaHCO_3$ (5 ml) were added. The separated organic layer was washed with the $NaHCO_3$ solution (5 ml) and then water (5 ml), and it was then dried over $MgSO_4$. The solvent was removed under reduced pressure to afford the crude product which exhibited a single ^{31}P NMR signal.

8-*m*: the crude oil was purified by chromatography over SiO_2 (eluent, diethylether) to give a light-yellow oil (0.22 g, 0.63 mmol; yield, 57%). ^{31}P NMR ($CDCl_3$): 17.6 ppm. ^1H NMR ($CDCl_3$): 1.3 (t, $J = 7$ Hz, 6H, 2 × CH_3CH_2O); 3.8 (s, 3H, CH_3O); 4.1 (qui, $J = 7$ Hz, 4H, 2 × OCH_2CH_3); 7.0 (AB system, $J = 16$ Hz, 2H, CH=CH); 6.8–8.0 (m, 8H, 2 × C_6H_4) ppm. Anal. Found: C, 65.5; H, 6.8. $C_{19}H_{23}O_4P$ calc.: C, 65.89; H, 6.64%.

8-*p*: the crude pasty solid was purified by crystallization from diethylether giving white spangles (0.29 g, 0.85 mmol; yield, 77%, melting point 122°C). ^{31}P NMR ($CDCl_3$): 17.8 ppm. ^1H NMR ($CDCl_3$): 1.3 (t, $J = 7$ Hz, 6H, 2 × CH_3CH_2O); 3.8 (s, 3H, CH_3O); 4.15 (qui, $J = 7$ Hz, 4H, 2 × OCH_2CH_3); 7.1 (AB system, $J = 16$ Hz, 2H, CH=CH); 6.9–7.9 (m, 8H, 2 × C_6H_4) ppm. Anal. Found: C, 65.7; H, 6.4%.

4.4. Reaction of chlorotrimethylsilane with benzylic carbanions 5: preparation of phosphonotolyltrimethylsilanes 10

A solution of benzylic carbanion **5** (8.8 mmol) was prepared at −70°C in THF from diethyltolylphosphonate **4** (8.8 mmol) and LDA (17.6 mmol (two equivalents)). Chlorotrimethylsilane (0.96 g, 8.8 mmol) in THF (10 ml) was added dropwise at −70°C to the stirred solution of carbanion **5**. The mixture progressively turned orange. The progress of the reaction was monitored by CPG analysis, and no more starting phosphonate was detected after about 30 min. The mixture was warmed to room temperature and treated with water (20 ml). The aqueous layer was extracted with diethylether (2 × 15 ml) and then with dichloromethane (15 ml), and the combined organic layers were dried

($MgSO_4$). The solvent was removed under reduced pressure to give the crude product which was analysed by ^{31}P NMR spectroscopy. The crude oil was purified by distillation, affording the pure oily phosphonotolyltrimethylsilane **10**.

10-*o*: 2.21 g, 7.4 mmol; yield, 84%; boiling point (b.p.), 128°C at 0.3 Torr. ^{31}P NMR ($CDCl_3$): 19.1 ppm. ^1H NMR ($CDCl_3$): 0.1 (s, 9H, $(CH_3)_3Si$ 1.2 (t, $J = 7$ Hz, 6H, $2 \times CH_3CH_2O$); 2.6 (s, 2H, CH_2Si); 4.1 (qui, $J = 7$ Hz, 4H, $2 \times OCH_2CH_3$); 6.9–8.0 (m, 4H, C_6H_4) ppm.

10-*m*: 0.82 g, 2.7 mmol; yield, 31%; b.p., 120°C at 0.3 Torr. ^{31}P NMR ($CDCl_3$): 18.9 ppm. ^1H NMR ($CDCl_3$): 0.15 (s, 9H, $(CH_3)_3Si$); 1.2 (t, $J = 7$ Hz, 6H, $2 \times CH_3CH_2O$); 2.3 (s, 2H, CH_2Si); 3.9 (qui, $J = 7$ Hz, 4H, $2 \times OCH_2CH_3$), 7.0–7.7 (m, 4H, C_6H_4) ppm.

10-*p*: 2.27 g, 7.6 mmol; yield, 86%; b.p., 124°C at 0.3 Torr. ^{31}P NMR ($CDCl_3$) 18.8 ppm. ^1H NMR ($CDCl_3$): 0.1 (s, 9H, $(CH_3)_3Si$); 1.25 (t, $J = 7$ Hz, 6H, $2 \times CH_3CH_2O$); 2.1 (s, 2H, CH_2Si); 4.0 (t, $J = 7$ Hz, 4H, $2 \times OCH_2CH_3$); 6.9–7.7 (m, 4H, C_6H_4) ppm.

4.5. Isolation and characterization of the phosphinate 11-m and the phosphine oxide 12-m

To a stirred 1.6 M solution of Li^{n}Bu in hexane (11 ml, 17.6 mmol) and TMEDA (2.05 g, 17.6 mmol) at −70°C was added dropwise diethyl *meta*-tolylphosphonate **4**-*m* (2 g, 8.8 mmol) in THF (10 ml). Stirring was continued for 1 h at −70°C while the mixture turned pale orange. Chlorotrimethylsilane (1.0 g, 9.2 mmol) in THF (5 ml) was then added at −70°C, and no significant change in the mixture colour was observed. After hydrolysis and the usual work-up, analysis of the crude product (2.2 g) by ^{31}P NMR spectroscopy ($CDCl_3$) revealed the presence of three main constituents at $\delta = 18.0$ ppm, 39.5 ppm and 43.5 ppm in percentages of 10%, 41% and 49%, respectively. Distillation under reduced pressure of the crude oil gave first the starting phosphonate **4**-*m* (0.06 g; b.p., 110°C at 0.6 Torr). ^{31}P NMR ($CDCl_3$): 18.0 ppm [10]. Then two main fractions were obtained.

11-*m*: 0.7 g; b.p., 128°C at 0.6 Torr. ^{31}P NMR ($CDCl_3$) 43.5 ppm. ^1H NMR ($CDCl_3$): 1.1 ($\approx$ t, $J \approx 6$ Hz, 3H, $CH_3(CH_2)_3$), 1.5 (t, $J = 7$ Hz, 6H, $2 \times CH_3CH_2O$); 1.3–2.0 (m, 6H, $(CH_2)_3CH_3$); 2.65 (s, 3H, $CH_3\Phi$), 4.25 (qui, $J = 7$ Hz, 4H, $2 \times OCH_2CH_3$); 7.3–7.9 (m, 4H, C_6H_4) ppm. MS *m/e*: 240 ($M^{\cdot+}$), 198 ($M^{\cdot+} - CH_2{=}CHCH_3$), 170, 155, 91.

12-*m*: 0.6 g; b.p., 150°C at 0.6 Torr. ^{31}P NMR ($CDCl_3$): 39.5 ppm. ^1H NMR ($CDCl_3$): 1.1 ($\approx$ t, $J \approx 6$ Hz, 6H, $2 \times CH_3(CH_2)_3$); 1.3–2.3 (m, 12H, $2 \times (CH_2)_3CH_3$); 2.65 (s, 3H, $CH_3\Phi$); 7.3–7.9 (m, 4H, C_6H_4) ppm. MS *m/e*: 252 ($M^{\cdot+}$), 223 ($M^{\cdot+} - C_2H_5$), 196 ($M^{\cdot+} - CH_2{=}CHCH_2CH_3$), 168, 154, 139, 91.

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