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Studies on the Efficient Generation of Phosphorus–Carbon Bonds via a Rearrangement of P^{III} Esters Catalysed by Trimethylhalosilanes

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Dedicated to Prof. Dr. Marian Mikolajczyk on the occasion of his 70th birthday

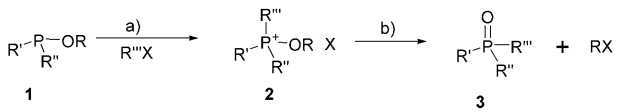
Abstract: Halotrimethylsilanes Me_3SiX (X = Br, I) catalyse rearrangements of tricoordinate phosphorus esters R′R″P–OR into the corresponding phosphoryl systems R′R″P(O)R. This provides a simple and efficient route to a variety of structures containing phosphorus–carbon bonds, under mild conditions and with good yields. The reaction mechanism was investigated in detail by ^{31}P NMR spectroscopy and independent synthesis of the reaction intermediates. It has been demonstrated that the primary products of this catalytic reaction are halogeno P^{III} structures R′R″PX and silyl ethers $ROSiMe_3$ and that they subsequently react to give the corresponding phosphorus silyl esters—$Me_3SiOPR'R''$—and alkyl halides RX. At higher temperatures these intermediates then react to form R′R″P(O)R compounds. This paper also features the surprising observation that when esters Ph_2POR and halotrimethylsilanes Me_3SiX (X = Br, I) are used in 2:1 ratio, phosphonium salts $Ph_2R_2P^+X^-$ and trimethylsilyl diphenylphosphinate—$Ph_2P(O)OSiMe_3$—are formed as the major products. Experimental evidence indicates that the mechanisms of both reactions are fundamentally different from that of the Michaelis–Arbuzov reaction. Me_3SiCl is not reactive and this paper explains why.

Keywords: asymmetric catalysis · C–P bond formation · Michaelis–Arbuzov reaction · organophosphorus chemistry · reaction mechanisms

Introduction

Interest in C–P bond-formation procedures has recently been growing, due to the use of this class of compounds in organic synthesis, catalysis and the preparation of medicinal agents.[1] In our laboratories we have been using the interactions of P^{III} esters and amides with halotrimethylsilanes as a tool in organophosphorus chemistry and in the synthesis of biophosphates.[2] These studies led us to the area of Michaelis–Arbuzov-like rearrangements. The reaction, originally discovered by Michaelis in 1898, was explored in great detail by Arbuzov.[3] The Michaelis–Arbuzov rearrangement provides a versatile approach to compounds containing C–P bonds and is widely employed in the synthesis of phosphonic esters, phosphinic esters and phosphine oxides. The classic Michaelis–Arbuzov reaction requires rather drastic thermal conditions, but its efficiency can be improved in ionic liquid solvents[4a] and by use of microwave-assisted heating.[4b] It has been shown that photochemically induced rearrangement is also possible.[5]

It is generally accepted that the Michaelis–Arbuzov reaction proceeds in two steps. Formation of the phosphonium salt (Scheme 1, step a) is followed by rapid dealkylation by



Scheme 1.

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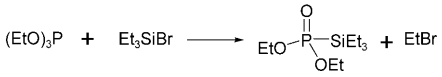
the counterion X^- (Scheme 1, step b), yielding the compound **3** and an alkyl halide. When the alkyl groups of a P^{III} species and the alkyl halide are identical, the process amounts to isomerisation.

Step a (Scheme 1) is essentially an S_N2 reaction. Step b (Scheme 1) involves S_N2 displacement at carbon. Reviews on the mechanistic aspects of Michaelis–Arbuzov reaction and its synthetic utility are available.[6]

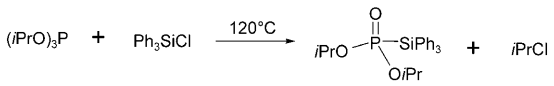
Normally the Michaelis–Arbuzov reaction proceeds without a catalyst, but in some cases catalysts are needed. In view of the fact that the Michaelis–Arbuzov rearrangement has been known for nearly 110 years, however, the number of catalytic processes described is relatively small. Catalytic rearrangements with use of a small quantity of methyl iodide are limited to a few relatively simple phosphites. Consumption of the catalyst and formation of undesired side products have been observed.[7] Certain metal halides also serve as catalysts. A single clear-cut example of catalysis by nickel(II) chloride has been described by a German group;[8] most recently, oxophilic Lewis acids have been successfully employed.[9] Some organic compounds have also been used as catalysts.[6c]

The Michaelis–Arbuzov rearrangement serves as a model for a large number of reactions between P^{III} esters and electrophilic reagents, so it was natural that some of the earliest studies on silicon-organophosphorus chemistry attempted to extend the Michaelis–Arbuzov reaction to the formation of phosphorus–silicon bonds. The first paper in this field, published as early as 1948 by Arbuzov and Pudovik, postulated the formation of compounds containing P–Si bonds (Scheme 2).[10]



Scheme 2.

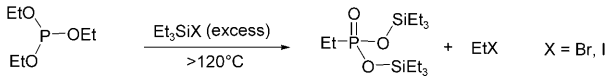
Later on, Ferguson and Glidewell prepared the fully identified compound $Ph_3Si–P(O)(OiPr)_2$ through an Michaelis–Arbuzov-type reaction between $P(OiPr)_3$ and Ph_3SiCl at 120 °C for a period of 6 h (Scheme 3).[11]



Scheme 3.

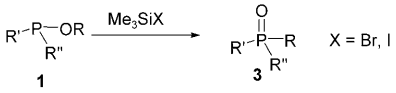
Surprisingly, in 1950 Malatesta found that treatment of triethylphosphite with an excess of triethylhalosilane Et_3SiX (X = Br, I) yielded a bis(triethylsilyl) ethylphosphonate, containing a P–C bond (Scheme 4).[12]

Scheme 4 does not follow the classic Arbuzov reaction route. Burgarenko et al. confirmed Malatesta's observations and demonstrated that the ester $(EtO)_2P–OSiEt_3$ is formed



Scheme 4.

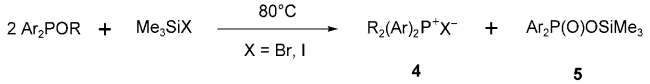
in this reaction.[13] Our preliminary investigations into the interactions of P^{III} systems with iodosilanes R_3SiI indicated that the reaction was catalytic in nature. This led us to devise a novel route to the formation of carbon–phosphorus bonds under relatively mild thermal conditions (Scheme 5).[2c]



Scheme 5.

Recently Renard et al. published a similar observation, giving just a few synthetically useful examples.[14] They suggested—without any experimental evidence—the intermediate formation of a $P^{III}OSiMe_3$ structure, subsequently undergoing Michaelis–Arbuzov rearrangement. For us, the mechanistic challenge was to explain how P^{III} silyl esters are formed by the reaction of P^{III} alkyl esters and halotrimethylsilanes; these studies were undertaken in order to clarify this problem unambiguously. We also wanted to emphasise the importance of this reaction (Scheme 5), which provides access to a wide range of organophosphorus compounds of interest both in organic synthesis and as ligands in organometallic chemistry under thermal conditions much milder than those commonly used in the celebrated Michaelis–Arbuzov reaction.

During these studies we found to our surprise that when alkyl diarylphosphinites (Ar_2POR) and halotrimethylsilanes are allowed to react in a 2:1 ratio the reaction follows an entirely different course (Scheme 6). This opens a new route to phosphonium salts of type **4**.



Scheme 6.

Results and Discussion

Catalytic rearrangement of P^{III} esters: Catalytic rearrangement of P^{III} esters as shown in Scheme 5 is reminiscent of the classic Arbuzov rearrangement. However, the conditions this reaction requires are appreciably milder. The activator of choice is bromotrimethylsilane (Me_3SiBr), which allows the reaction to occur at or below 80 °C, in 2 to 12 h. Iodotrimethylsilane (Me_3SiI) is somewhat more active, but to give

reproducible results it must be pure. No reaction is observed with Me_3SiCl even under solvolytic conditions. The rearrangement operates successfully for a broad range of substrates. The starting materials are P^{III} esters, easily obtained from the corresponding alcohols. Average yields of the products isolated are 60% and can be as high as 90%. The recommended protocol is simply heating in a carefully dried glass vessel, either without any solvent or in toluene solution, with 10–20 mol% catalyst. The reaction can also be successfully carried out in a sealed glass tube.[2,14] Crude products were purified by silica gel chromatography. Table 1 gives selected examples.

Table 1. Catalytic rearrangements of P^{III} esters into P^{V} compounds containing P–C bonds.[a]

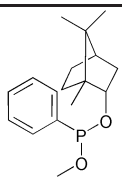
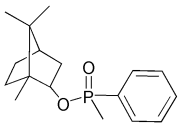
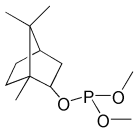
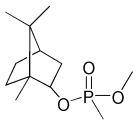
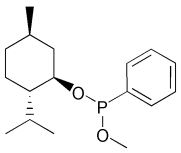
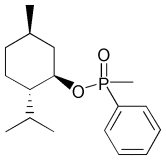
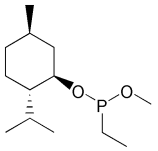
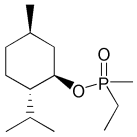
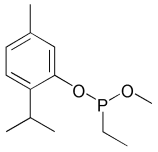
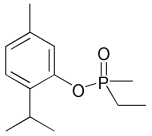
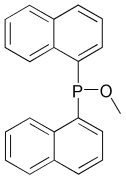
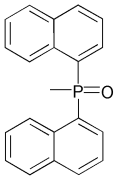
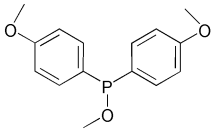
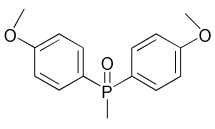
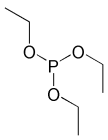
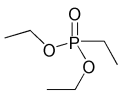
Entry	Substrate	Product	Catalyst, Yield [%][b]
1			Me_3SiBr, 66
2			Me_3SiBr, 65
3			Me_3SiBr, 60
4			Me_3SiBr, 50
5			Me_3SiBr, 60
6			Me_3SiBr, 65
7			Me_3SiBr, 75
8			Me_3SiI, 25

Table 1. (Continued)

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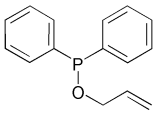
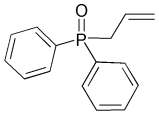
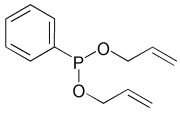
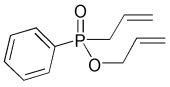
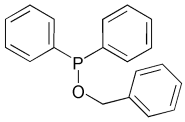
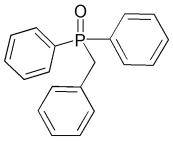
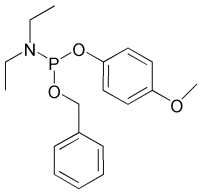
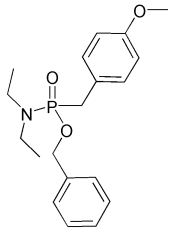
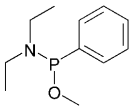
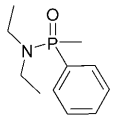
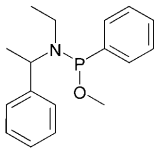
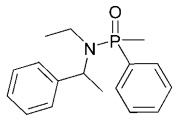
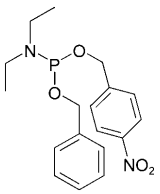
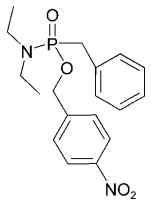
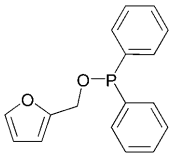
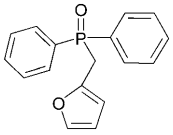
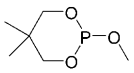
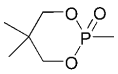
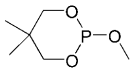
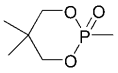
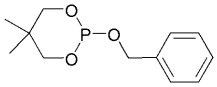
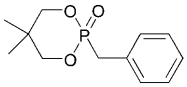
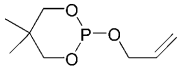
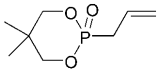
9			Me_3SiBr, 85
10			Me_3SiBr, 73
11			Me_3SiBr, 90
12			Me_3SiBr, 70
13			Me_3SiBr, 65
14			Me_3SiBr, 95
15			Me_3SiBr, 62
16			Me_3SiBr, 80
17			Me_3SiI, 80
18			Me_3SiBr, 99
19			Me_3SiBr, 90
20			Me_3SiBr, 90

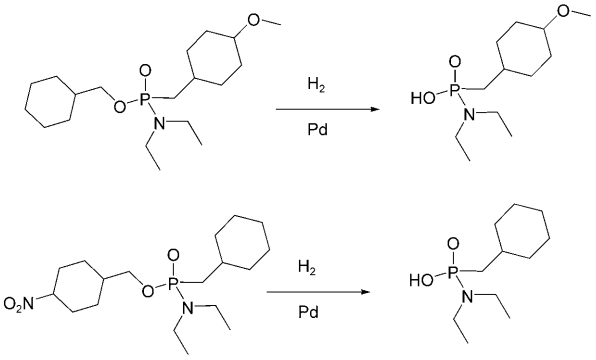
[a] Reaction conditions: **1** (1.5 mmol), Me_3SiX (20% mol), 80 °C, 5–12 h. [b] Yield of isolated product.

The reactions listed in Table 1 provide convenient access routes to esters of phosphonic and phosphinic acids and phosphine oxides. It is known that P^{III} esters containing allyloxy groups—P^{III}–OCH_2–CH=CH_2—rearrange into the corresponding phosphoryl compounds containing the P–C bond—P(O)CH_2–CH=CH_2—without any catalyst.[15] We were able to demonstrate that catalytic reactions activated by Me_3SiX (X = Br, I) (entries 9, 10 and 20) proceed at least ten times more rapidly than those performed without an activator, which corroborates the observed formation of P^{III}–Br intermediates, in a manner similar to that shown in Scheme 8 (below), in all the above cases.

The compounds of entries 1, 2, 4 and 5 (Table 1), containing chiral centres at their P(O) groups, are all 1:1 mixtures of diastereomers. During their purification by silica gel chromatography, negligible separation of diastereomers was observed. In contrast, the P(O) compound of entry 3 was readily separated. The more rapidly eluting diastereomer has the R_P configuration, as was established by NOESY experiments, taking advantage of the Overhauser effect.[16] Auxiliary stereocenters at carbon (entries 1–4) are not affected; this was firmly established by ^{31}P NMR and ^{1}H NMR spectroscopy.

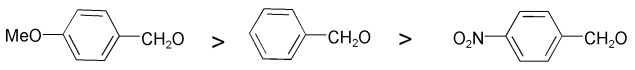
After $P^V \rightarrow P^{III}$ reduction, the compounds listed in Table 1 have the potential to be employed as useful ligands. It is well known that the P–OR group may act as a leaving group in reactions with organometallic compounds, leading to the formation of new P–C bonds.[17] Another possibility is the removal of an auxiliary carbon chiral moiety by hydrogenolysis (entry 14).[18]

In cases involving P^{III} mixed benzyl esters containing either an electron-donating group (entry 12) or an electron-withdrawing group (entry 15), the structures of the P^V compounds formed were established by Pd/C-catalysed hydrogenolysis (Scheme 7).



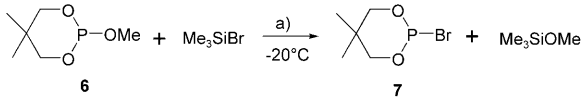
Scheme 7.

The relative propensity for rearrangement of benzyl groups is in the order:



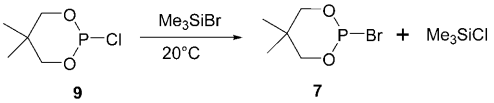
Systems containing amido groups (entries 12–15 Table 1) at P^{III} phosphorus centres and similar structures are also attractive as phosphitylating reagents. When coupled with alcohols, they can be subsequently transformed into new P^{III} esters, which can be rearranged into phosphonates of potential biological or medicinal interest

The mechanism of catalytic rearrangement: Precise model studies using P^{III} esters derived from neopentyl glycol clearly support the mechanism of catalytic rearrangement postulated by us in a preliminary paper.[2b] A typical Me_3SiBr-catalysed rearrangement of methyl ester **6** proceeds in three distinct steps. The first, leading to phosphorobromide **7** and involving interaction of a P^{III} **6** ester with bromotrimethylsilane, takes place even at 20 °C, reaching completion within 2 h, in almost quantitative yield (Scheme 8).



Scheme 8.

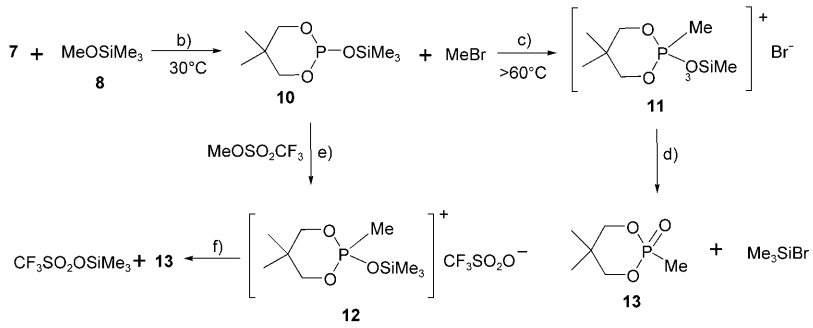
The identity of bromide **7** ($\delta_P = 162.1$ ppm) and its reaction with diisopropylamine to afford the corresponding phosphoroamidite ($\delta_P = 114.4$ ppm) were confirmed by ^{31}P NMR spectroscopy. Similar reactions were carried out with iodotrimethylsilane. The identity of $MeOSiMe_3$ was established by its spectral properties [$\delta_H = 3.22$ ppm (s, 3H; CH_3O), 0.03 ppm (s, 9H; $Si(CH_3)_3$)] and by comparison with an authentic specimen. The bromide **7** ($\delta_P = 162.9$ ppm) was independently prepared in very high yield from the chloridite **9** by treatment with Me_3SiBr at 20 °C as shown in Scheme 9.[19]



Scheme 9.

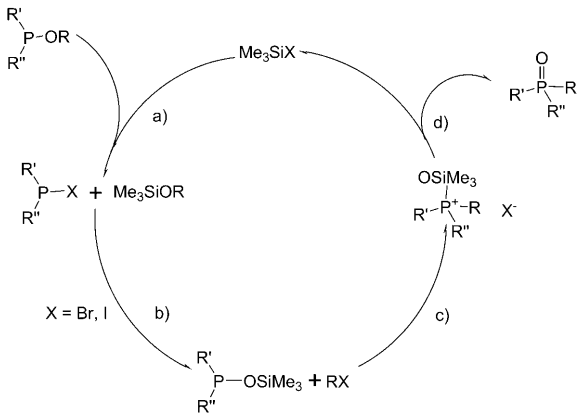
In the second step the bromide **7** reacts with ether **8** at a somewhat higher temperature of 30 °C (Scheme 10, reaction a). The silylphosphate **10** ($\delta_P = 110.1$ ppm), formed in almost quantitative yield, is identical with the specimen ($\delta_P = 109.8$ ppm) prepared by silylation of the corresponding H-phosphonate. The third step involves a Michaelis–Arbuzov-like reaction with methyl bromide produced in situ. This reaction proceeds at temperatures above 60 °C and leads to the final methylphosphonate **13** ($\delta_P = 26.8$ ppm) in almost quantitative yield (Scheme 10, reactions c and d). Formation of the intermediate phosphonium salt **11**, decomposing into the phosphonate **13**, seems to be obvious. In classic Michaelis–Arbuzov reactions this type of phosphonium salt, showing moderate stability, is only observed when a counterion

of low nucleophilicity is present. In this study an analogous phosphorus salt **12** ($\delta_P = 34.2$ ppm) was prepared from the ester **10** and methyl trifluoromethanesulfonate (reaction e), subsequently decomposing into the phosphonate **13** and trimethylsilyl trifluoromethanesulfonate (reaction f).



Scheme 10.

As anticipated, the removal of methyl bromide prior to reaction b led to the formation of silylphosphate **10** as the only reaction product. Methyl bromide was removed from the system by blowing argon through the reacting substrates, in the absence of any solvent. The experimental observations regarding the rearrangement of a variety of P^{III} esters and activators Me_3SiX (X = Br, I) are in agreement with the catalytic cycle presented in Scheme 11.



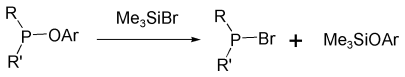
Scheme 11. Reactions a, b, c and d correspond to those given in Schemes 8 and 10.

The cycle proposed in Scheme 11 is consistent with the observation that compounds R′R″P–X (X = Br, I) containing chiral centres at their phosphorus atoms are formed as diastereomers in 1:1 R_P/S_P ratios. This results in ready halide–halide exchange via symmetric trigonal bipyramids, in which the pairs of halide atoms are situated in the apical positions. The catalytic rearrangement discussed in this paper (Table 1, entries 1, 2, 3, 4 and 14) proceeds without breakage of C–O or C–N bonds at auxiliary chiral centres. Therefore, their configurations in P^{III} substrates and in P^{V} products must be the same.

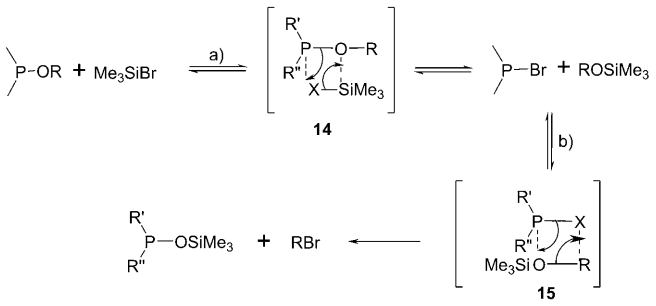
Aryloxy esters RR′P–OAr react with halotrimethylsilanes Me_3SiX (X = Br, I) as shown in Scheme 12.

In agreement with the proposal catalytic cycle (Scheme 11), the above reaction stops with halogen–phosphorus bond formation (step a). This is because the subsequent step b leading to $P^{III}OSiMe_3$ esters would involve aromatic nucleophilic displacement, which requires an excessive amount of energy. The reaction shown in Scheme 12 is of interest in synthetic phosphorus chemistry.

The formation of products containing halogen–phosphorus bonds and $P^{III}OSiMe_3$ esters by the consecutive reactions a and b (Scheme 13) can be postulated as involving nucleophilic substitution at the three-coordinate phosphorus atom.



Scheme 12.



Scheme 13.

On the basis of our earlier studies,[2b,d] a mechanism via the highly polar four-centre 2+2 transition states **14** and **15** (Scheme 13) seems to be more likely for reactions a and b than others involving nucleophilic attack of phosphorus on silicon to give intermediates with higher coordination numbers at the phosphorus centre. The geometries of the reactive complexes confirm a four-centre mechanism of interaction between the reactants in steps a and b. The geometries of the transition states, however, suggest that significant charge separation must take place, resulting in oxonium cation–halide anion ion-pairs (TS (a) and TS (b) in Figure 1).

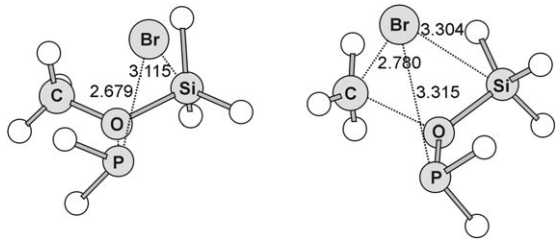
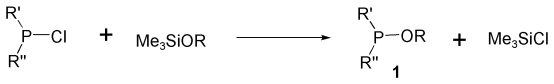


Figure 1. Transition state geometries for $H_2POMe+H_3SiBr$ and H_2PBr+H_3SiOMe reactions, respectively.

Substitution reactions at tetrahedral silicon are more associative than those at carbon, due to the large size and availability of low-lying 3d orbitals. Intermediates such as R_3Si^+ are highly improbable in the presence of nucleophiles.[22]

It is intriguing why chlorotrimethylsilane (Me_3SiCl) is not effective in promoting a mechanism similar to that shown in Scheme 8, even at elevated temperatures and under solvolytic conditions. This contrasting behaviour is likely to be due to the strength of the silicon-chlorine bond and the fact that the reaction between Me_3SiCl and ester **1** (Scheme 9) takes a different course from those described in Schemes 5 and 9. Even if the $P^{III}Cl$ system is formed, it is reasonable to assume that it may readily react with Me_3SiOR, regenerating the substrates (Scheme 14).



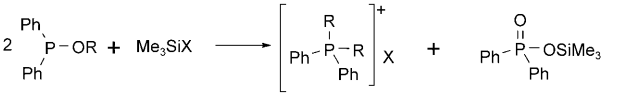
Scheme 14.

The reaction shown above is a very efficient method of preparing P^{III}–OR esters of high purity from readily available $P^{III}Cl$ chlorides.[23] As demonstrated earlier, our studies show that $P^{III}X$ (X = Br, I) reacts with Me_3SiOR in quite a different manner (Scheme 11, reaction a).

The presence of an excess of bromotrimethylsilane has practically no effect on the rearrangement shown in Scheme 5. However, at temperatures above 100 °C and after prolonged reaction times, bromotrimethylsilane can react further with the >P(O)-OR esters to give silyl esters > $P(O)OSiMe_3$.[24] The unusual behaviour of P^{III} esters containing two phenyl groups (Ph_2POR) is discussed below.

Synthesis of $[Ar_2PR_2]^+X^-$ phosphonium salts through the interaction of diarylphosphinites (Ar_2POR) with Me_3SiX (X = Br, I): When using P^{III} esters containing two phenyl groups attached to their phosphorus centres with halotrimethylsilanes in 2:1 ratio, we found that the reaction takes a surprisingly different course. Instead of the regular rearrangement products, phosphonium salts $Ph_2R_2P^+X^-$ **17** (Table 2) are formed in excellent yields. The oxygen atoms present in esters Ph_2P–OR **16** are transferred to form the trimethylsilyl ester of diphenylphosphonic acid (**18**). In formal terms, the reaction shown in Table 2 generates two new C–P bonds in excellent yields. Phosphonium salts **17** are readily separable from ester **18**. The silyl ester **18** very readily hydrolyses to give the corresponding phosphinic acid ($Ph_2P(O)OH$). The solubility of this compound in water, dichloromethane and other common solvents is low, so it can readily be separated from phosphonium salts **17**. This stable acid was therefore used to estimate the yields of ester **18**, which were close to those observed for **17**. The reaction seems be more convenient than the alkylation of diphenylalkylphosphanes—Ph_2P–R+R′X→$Ph_2RR'P^+X^-$—in those cases in which esters **16** are more readily accessible then the corresponding phosphines.[1a]

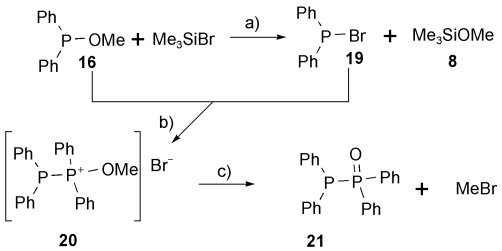
Table 2. Reactions between Ph_2P–OR and Me_3SiX in 2:1 ratio.[a]



Entry	R	X	Yield[b] [%] of **17**
1	CH_3	Br	95
2	C_2H_5	Br	90
3	$CH_2CH{=}CH_2$	Br	95
4	CH_2Ph	Br	85
5	CH_3	I	60
6	C_2H_5	I	72

[a] Phosphonous ester **16** (6.0 mmol), TMS–X (Br, I) (3.0 mmol), room temperature, either without solvent for 12 h or in toluene, 80 °C for 6 h. [b] Yield of isolated product.

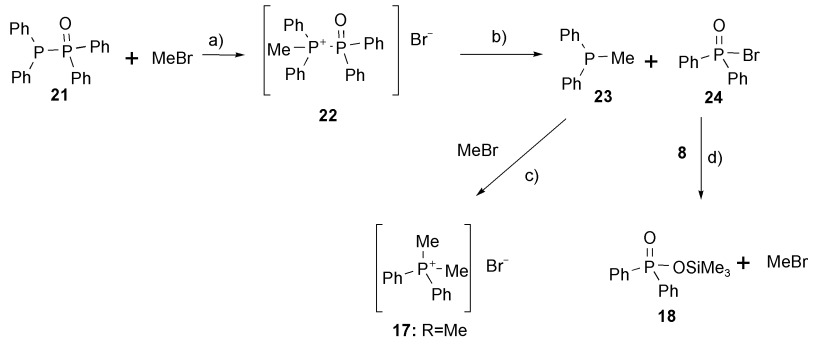
Rationale for the formation of phosphonium salt 17: To interpret the reactions leading to phosphonium salts **17** and the ester **18** we employed the model system Ph_2POMe (**16**, R = Me) and Me_3SiBr in 2:1 ratio. These substrates were allowed to react at 20 °C in toluene solution. After 5 min the following compounds were observed (Scheme 15): unchanged ester **16** ($\delta_P = 117.0$ ppm), the bromide **19** (Ph_2PBr), the silyl ester **8** and the compound Ph_2P–P(O)Ph_2 [**21**, δ_P = 34.28 ppm (d, $J_{P,P} = 220.9$ Hz), −23.49 ppm (d, $J_{P,P}$ = 220.9 Hz)].[25] This last compound is formed as shown in Scheme 15, by reactions a, b and c. After having been kept for 30 min this mixture was fully converted into compound **21**, containing the phosphorus-phosphorus bond, and silyl ester $Ph_2P(O)OSiMe_3$ (**18**) as the main products. Compound **21** is most probably formed via the intermediate phosphoni-



Scheme 15.

um salt **20**. The bromide **19** was identified by transformation into the corresponding diisopropyl-phosphinoamidite—$Ph_2P{-}Br + HNiPr_2 \rightarrow Ph_2P{-}NiPr_2$ ($\delta_P = 47.3$ ppm)—and was identical to that prepared from chlorodiphenylphosphine ($Ph_2P{-}Cl + Me_3SiBr \rightarrow$ **19** $+ Me_3SiCl$; $\delta_P = 72.0$ ppm).

When the temperature of the system was raised to 90 °C, the further changes shown in Scheme 16 were observed. Signals corresponding to methyldiphenylphosphine (**23**, $\delta_P = -28.2$ ppm) and diphenylphosphonic bromide (**24**, $\delta_P = 39.6$ ppm) appeared along with those for the phosphonium salt **17** ($\delta_P = 21.1$ ppm) and trimethylsilyl diphenylphosphinate (**18**, $\delta_P = 22.0$ ppm). After 12 h, compounds **17** and **18** were exclusively present.



Scheme 16.

Reaction a, involving electrophilic attack of methyl bromide on the P^{III} centre of compound **21**, is likely to proceed via the phosphonium salt **22**, which decomposes into **23** (reaction b) and **24** ($\delta_P = 39.6$ ppm). Reaction c, between the phosphine **23** and methyl bromide, affords the phosphonium salt **17** (R = Me). The parallel reaction between **24** and silyl ether **8** leads to the ester **18** ($\delta_P = 22.0$ ppm) and methyl bromide. Transformations a, c and d were validated by independent synthesis from authentic specimens. Reaction of types a and d have, to the best of our knowledge, not been described. The methyl bromide involved in reactions a and b (Scheme 16) is formed in reactions a (Scheme 15) and d (Scheme 16). We have here a unique combination of several chemical reactions leading to final products **17** and **18**. The answer to the question of why this process is limited to $Ph_2P{-}OR$ compounds is not clear. Tentatively, this could be accounted for in terms of a pronounced tendency to form the structure $Ph_2P{-}P(O)Ph_2$ (**21**).

Conclusions

A new general strategy for the formation of carbon–phosphorus bonds has been developed. $P^{III}{-}OR$ esters rearrange in the presence of catalytic amounts of halogenosilanes Me_3SiX (X = Br, I) into the corresponding $>P(O)R$ structures under mild thermal conditions and in good yields. It has been finally established that the rearrangement proceeds through four well defined steps and is initiated by halogen transfer from the halogenosilanes to P^{III} esters to give P^{III} halides. This method is therefore fundamentally different from the Michaelis–Arbuzov reaction. The observation that phosphonium salts $Ph_2P^+R_2X^-$ are formed as the major products when $Ph_2P{-}OR$ is allowed to react with Me_3SiX (X = Br, I) in 2:1 ratio is unexpected and noteworthy. A mechanistic scheme for this reaction based on extended synthetic model studies and ^{31}P spectroscopy is proposed. Our study illustrates a fascinating peculiarity of silicon and phosphorus chemistry and opens up synthetic opportunities more convenient than the classic Michaelis–Arbuzov reaction. This paper illustrates the wide applicability of the catalytic method for the synthesis of new C–P systems, including phosphono- and phosphinoamidates.

Experimental Section

General methods: The solvents were reagent grade and were distilled and dried by conventional methods before use. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254, Merck). The products were purified by flash chromatography on silica gel 60 (Merck 0.063 mm, 230–400 mesh ASTM). NMR spectra were obtained on a Bruker AC 200 instrument. δ values are reported in ppm relative to Me_4Si as standard for ^1H NMR and ^{13}C NMR, relative to H_3PO_4 as external standard for ^{31}P NMR, and relative to CCl_3F as external standard for ^{19}F NMR. The signals are expressed as s (singlet), d (doublet), t (triplet) or m (multiplet). Coupling constants (J) are in Hz. MS spectra were performed on a Finnigan MAT 95 spectrometer. All reactions were performed in flame-dried glassware under dry argon. All reagents were obtained from Aldrich Chemical Co.

General procedure for phosphine oxides (phosphinates or phosphonates): A P^{III} ester (1.5 mmol) was introduced by syringe into a three-necked flask containing a magnetic stirrer and fitted with a reflux condenser and septum. Catalyst Me_3SiBr or Me_3SiI (20 %) was then added at room temperature by injection, and the mixture was heated at 80 °C for 5–12 h. The crude reaction mixture was allowed to cool to room temperature, and was either recrystallised or subjected to silica gel column chromatography or distillation under reduced pressure, yielding pure phosphine oxide (phosphinate or phosphonate).

***O*-(1*S*)-Bornyl-(*R*)$_P$- and (*S*)$_P$-methyl(phenyl)phosphinate**[26] (Table 1, entry 1): ^1H NMR (200.13 MHz, $CDCl_3$): $\delta = 7.79$–7.69 (m, 4H), 7.51–7.37 (m, 6H), 4.53–4.30 (m, 2H), 2.34–2.02 (m, 2H), 1.99–1.85 (m, 4H), 1.62 (d, $J = 14.4$ Hz, 3H), 1.61 (d, $J = 14.4$ Hz, 3H), 1.48–1.15 (m, 6H), 1.10–0.95 (m, 2H), 0.89 (s, 3H), 0.80 (s, 3H), 0.78 (s, 3H), 0.73 (s, 3H), 0.71 (s, 3H), 0.62 ppm (s, 3H); ^{13}C ($CDCl_3$): $\delta = 12.9$, 15.6 (d, $J = 103$ Hz), 18.3, 19.5, 26.1, 27.7, 36.6, 44.5, 47.0, 49.2, 80.6 (d, $J = 6$ Hz), 128.0 (d, $J = 12$ Hz), 130.7 (d, $J = 8$ Hz), 131.6, 132.2 ppm (d, $J = 94$ Hz); ^{31}P NMR ($CDCl_3$): $\delta = 41.1$, 41.3 ppm (1:1); MS (CI): m/z: 293 $[M+H]^+$.

***O*-(1*S*)-Bornyl-(*S*)$_P$-methyl(phenyl)phosphinate** (more slowly eluting diastereoisomer): $[\alpha]_D^{25} = -43.7$ ($c = 1.03$, CH_2Cl_2); ^1H NMR (200.13 MHz, $CDCl_3$): $\delta = 7.81$–7.70 (m, 2H), 7.61–7.34 (m, 3H), 4.41–4.30 (m, 1H), 2.37–2.21 (m, 1H), 2.03–1.90 (m, 1H), 1.64 (d, $J = 14.5$ Hz, 3H), 1.79–1.51 (m, 2H), 1.35–1.14 (m, 3H), 0.79 (s, 3H; CH), 0.73 (s, 3H), 0.63 ppm (s, 3H); ^{13}C NMR (50.28 MHz, $CDCl_3$): $\delta = 13.15$, 16.28 (d, $J_{P,C} = 101.9$ Hz),

18.63, 19.80, 26.42, 27.97, 37.83, 44.88, 47.36, 49.49 (d, $J=6.0$ Hz), 81.00 (d, $J=6.7$ Hz), 128.32 (d, $J=12.7$ Hz), 131.05 (d, $J=10.0$ Hz), 131.96, 132.68 ppm (d, $J=128.2$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=41.56$ ppm; MS (CI): m/z: 293 $[M+H]^+$.

***O*-(1*S*)-Bornyl-(*R*)$_P$-methyl(phenyl)phosphinate** (more rapidly eluting diastereoisomer): $[\alpha]_D^{25}=+17.0$ ($c=1.01$, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): $\delta=$ 7.73–7.54 (m, 2H), 7.45–7.26 (m, 3H), 4.46–4.36 (m, 1H), 1.97–1.77 (m, 2H), 1.68–1.36 (m, 2H), 1.54 (d, $J=14.4$ Hz), 1.25–1.04 (m, 2H), 0.98–0.83 (m, 1H), 0.83 (s, 3H), 0.73 (s, 3H), 0.66 ppm (s, 3H); ^{13}C NMR (50.28 MHz, $CDCl_3$): $\delta=12.99$, 15.79 (d, $J=102.9$ Hz), 18.47, 19.68, 26.30, 27.81, 36.76, 44.61, 47.17, 49.38 (d, $J=4.6$ Hz), 81.52 (d, $J=6.7$ Hz), 128.17 (d, $J=12.7$ Hz), 130.81 (d, $J=10.1$ Hz), 131.69, 132.72 ppm (d, $J=$ 128.2 Hz); ^{31}P NMR ($CDCl_3$): $\delta=41.10$ ppm; MS (CI): m/z: 293 $[M+H]^+$.

***O*-Bornyl-*O*-methyl methylphosphonate** (Table 1, entry 2): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=4.56$–4.47 (m, 1H), 3.64 (dd, $J=11.01$, 3.7 Hz, 3H), 2.29–2.09 (m, 1H), 1.94–1.22 (m, 3H), 1.16 (d, $J=9.32$ Hz, 3H), 1.12–0.81 (m, 3H), 0.79 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): $\delta=10.2$ (d, $J=$ 146 Hz), 12.6, 18.1, 19.3, 25.8, 27.4, 36.7, 44.3, 46.9, 48.8 (d, $J=6$ Hz), 51.0 (d, $J=7$ Hz), 81.1 ppm (d, $J=8$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=31.2$, 31.6 ppm (1:1); MS (CI): m/z: 247 $[M+H]^+$.

***O*-Menthyl methyl(phenyl)phosphinate**[27] (Table 1, entry 3): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.86$–7.73 (m, 4H), 7.56–7.26 (m, 6H), 4.34–4.17 (m, 2H), 2.37–2.07 (m, 6H), 1.97–1.76 (m, 4H), 1.67 (d, $J=14.45$ Hz, 3H), 1.62 (d, $J=14.30$ Hz, 3H), 1.06–0.68 ppm (m, 18H); ^{13}C NMR ($CDCl_3$): $\delta=15.6$, 20.0, 20.8, 21.7, 22.7, 25.6, 31.3, 33.9, 43.3, 48.5, 76.0, 128.2 (d, $J=13$ Hz), 130.6 (d, $J=10$ Hz), 131.7 (d, $J=3$ Hz), 133.8 ppm (d, $J=129$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=40.0$, 40.6 ppm; MS (CI): m/z: 295 $[M+H]^+$.

***O*-Menthyl ethyl(methyl)phosphinate**[28] (Table 1, entry 4): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=4.20$–4.03 (m, 1H), 2.17–1.93 (m, 2H), 1.77–1.58 (m, 4H), 1.47–1.17 (m, 5H), 1.16–0.94 (m, 6H), 0.89–0.65 ppm (m, 9H); ^{13}C NMR ($CDCl_3$): $\delta=5.5$ (d, $J=5$ Hz), 12.8 (d, $J=91$ Hz), 15.0, 20.3, 21.2, 22.1, 23.3 (d, $J=95$ Hz), 24.8 (d, $J=4$ Hz), 30.7, 33.4, 42.9 (d, $J=7$ Hz), 47.8 (d, $J=6$ Hz), 74.8 ppm (d, $J=8$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=54.9$, 55.5 ppm (1:2); MS (CI): m/z: 247 $[M+H]^+$.

***O*-(2-Isopropyl-5-methylphenyl) ethyl(methyl) phosphinate** (Table 1, entry 5): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.22$ (s, 1H), 7.12 (d, $J=$ 7.84 Hz, 1H), 6.89 (d, $J=7.87$ Hz, 1H), 3.23–3.10 (m, 1H), 2.27 (s, 3H), 2.00–1.82 (m, 2H), 1.55 (d, $J=13.30$ Hz, 3H), 1.31–1.14 ppm (m, 9H); ^{13}C NMR ($CDCl_3$): $\delta=5.5$ (d, $J=5$ Hz), 12.3 (d, $J=90$ Hz), 20.1, 22.4 (d, $J=96$ Hz), 22.3, 26.0, 119.8, 124.7, 125.8, 135.1, 136.0, 147.7 ppm (d, $J=$ 9 Hz); ^{31}P NMR ($CDCl_3$): $\delta=55.6$ ppm; MS (CI): m/z: 241 $[M+H]^+$.

Methyl[di(1-naphthyl)]phosphine oxide (Table 1, entry 6): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=8.63$–8.58 (m, 2H), 8.04–7.85 (m, 6H), 7.54–7.40 (m, 6H), 2.32 ppm (d, $J=12.98$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta=18.0$ (d, $J=75$ Hz), 124.4, 126.3, 126.4, 127.2, 128.8, 129.4, 131.4, 132.9, 132.2, 133.7 ppm; ^{31}P NMR ($CDCl_3$): $\delta=34.0$ ppm; MS (CI): m/z: 317 $[M+H]^+$.

Bis(4-methoxyphenyl)(methyl)phosphine oxide (Table 1, entry 7): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.56$–7.47 (m, 4H), 6.79 (d, $J=$ 6.86 Hz, 4H), 3.77 (s, 6H), 1.97 ppm (d, $J=13.25$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta=16.4$ (d, $J=75$ Hz), 55.2, 123.0 (d, $J=112$ Hz), 114.0 (d, $J=$ 13 Hz), 132.5 (d, $J=12$ Hz), 162.3 ppm; ^{31}P NMR ($CDCl_3$): $\delta=35.4$ ppm; MS (CI): m/z: 277 $[M+H]^+$.

Diethyl ethylphosphonate (Table 1, entry 8): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=3.90$ (m, 4H), 1.61 (m, 2H), 1.13 (t, $J=7.0$ Hz, 6H), 0.93 ppm (dt, $J=18.4$, 7.7 Hz, 3H); ^{31}P NMR ($CDCl_3$); $\delta=33.54$ ppm; ^{1}H NMR and ^{31}P NMR date were consistent with those previously reported.[29]

Allyl diphenyl phosphinoxide[30] (Table 1, entry 9): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.76$–7.63 (m, 4H), 7.47–7.03 (m, 6H), 5.83–6.63 (m, 1H), 5.15–5.04 (m, 2H), 3.15–3.04 ppm (dd, $J=14.5$, 7.33 Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta=35.9$ (d, $J=69$ Hz), 120.8 (d, $J=11$ Hz), 126.8 (d, $J=9$ Hz), 128.4 (d, $J=12$ Hz), 130.8 (d, $J=9$ Hz), 131.7 (d, $J=$ 3 Hz), 132.2 ppm (d, $J=99$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=29.9$ ppm.

Allylphenylphosphinic acid allyl ester (Table 1, entry 10): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.77$–7.59 (m, 2H), 7.51–7.33 (m, 3H), 5.95–5.55 (m, 2H), 5.48–4.84 (m, 4H), 4.54–4.40 (m, 1H), 4.30–4.13 (m, 1H), 2.76 (dd, $J=18.28$, 69 Hz, 1H), 2.67 ppm (dd, $J=18.03$, 7.46 Hz); ^{13}C NMR ($CDCl_3$) $\delta=133.9$ (d, $J=7$ Hz), 133.3 (d, $J=3$ Hz), 132.7 (d, $J=10$ Hz), 130.9 (d, $J=125$ Hz), 129.4 (d, $J=13$ Hz), 127.9 (d, $J=9$ Hz), 121.4 (d, $J=13$ Hz), 118.6, 65.9 (d, $J=6$ Hz), 36.9 ppm (d, $J=97$ Hz, ^{1}H); ^{31}P NMR ($CDCl_3$): $\delta=41.5$ ppm; ^{31}P NMR and ^{13}C NMR data were consistent with those previously reported.[15d]

Benzyl diphenylphosphine oxide[31] (Table 1, entry 11): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.75$–7.58 (m, 4H), 7.57–7.24 (m, 6H), 7.21–7.07 (m, 5H), 3.65 ppm (d, 2H, $J=13.75$ Hz); ^{13}C NMR ($CDCl_3$): $\delta=37.9$ (d, $J=66$ Hz), 126.5 (d, $J=3$ Hz), 128.3 (d, $J=12$ Hz), 129.9 (d, $J=5$ Hz), 130.9 (d, $J=9$ Hz), 131.5 (d, $J=3$ Hz), 133.0 ppm; ^{31}P NMR ($CDCl_3$): $\delta=$ 29.6 ppm; MS (FAB): m/z: 293.3 $[M+1]^+$.

Benzyl *N*,*N*-diethyl *P*(4-methoxybenzyl)phosphoamidite (Table 1, entry 12): H NMR (200.13 MHz, CD_3OD): $\delta=7.35$–7.24 (m, 5H), 7.21 (dd, $J=2$, 8.5 Hz, 2H), 6.81 (d, $J=8$ Hz, 2H), 5.01 (dd, $J=12.4$, 12.0 Hz, 1H), 4.81 (dd, $J=12.4$, 12.0 Hz, 1H), 3.73 (s, 1H, 3.73), 3.13 (dd, $J=$ 20.6 Hz, 1H), 3.03 (dd, $J=20.6$ Hz, 1H), 3.02 (m, 2H), 2.93 (m, 2H), 0.92 ppm (t, $J=7$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta=13.9$, 33.3 (d, $J=$ 125.9 Hz), 38.5, 54.9, 64.6 (d, $J=5.9$ Hz), 113.6 (d, $J=2.5$ Hz), 123.8 (d, $J=8.2$ Hz), 127.2, 128.1, 127.7, 130.6 (d, $J=6.7$ Hz), 136.6 (d, $J=7.5$ Hz), 158.1 ppm; ^{31}P NMR (CD_3OD): $\delta=32.0$ ppm; MS (CI): m/z: 348.2 $[M+H]^+$.

***N*,*N*-Diethyl-*P*-methyl-*P*-phenyl phosphinamide** (Table 1, entry 13): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.73$–7.58 (m, 2H), 7.44–7.26 (m, 3H), 3.11–2.83 (m, 4H), 1.61 (d, $J=13.59$ Hz, 3H), 1.02 ppm (t, $J=$ 7.06 Hz, 6H); ^{13}C NMR ($CDCl_3$): $\delta=14.8$ (d, $J=91$ Hz), 13.9 (d, $J=$ 7 Hz), 39.0 (d, $J=4$ Hz), 127.9 (d, $J=12$ Hz), 130.7 (d, $J=10$ Hz), 130.9 (d, $J=3$ Hz), 133.4 ppm (d, $J=126$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=35.7$ ppm; MS (CI): m/z: 212 $[M+H]^+$.

***N*-Ethyl-(1*S*)-*N*-(1-phenylethyl) (R_P,S_P) *P*-methyl *P*-phenyl phosphinamide** (Table 1, entry 14): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.89$–7.77 (m, 4H), 7.51–7.45 (m, 8H), 7.36–7.20 (m, 8H), 4.84–4.60 (m, 2H), 3.09–2.84 (m, 4H), 1.79 (d, $J=13.53$ Hz, 3H), 1.74 (d, $J=13.48$ Hz, 3H), 1.63 (d, $J=7.02$ Hz, 3H), 1.49 (d, $J=7.03$ Hz, 3H), 1.25–0.79 ppm (m, 6H); ^{13}C NMR ($CDCl_3$): $\delta=14.9$ (d, $J=92$ Hz), 15.1 (d, $J=92$ Hz), 16.2, 16.9, 18.0, 18.5, 36.5, 52.5 (d, $J=4$ Hz), 53.0 (d, $J=3$ Hz), 126.4, 126.5, 127.1 (d, $J=9$ Hz), 127.5, 127.8 (d, $J=13$ Hz), 130.6 (d, $J=10$ Hz), 130.9, 133.4 (d, $J=125$ Hz), 133.5 (d, $J=125$ Hz), 141.2 (d, $J=7$ Hz), 141.3 ppm (d, $J=$ 4 Hz); ^{31}P NMR ($CDCl_3$): $\delta=35.2$, 35.8 ppm (1:1); MS (CI): m/z: 288 $[M+H]^+$.

***N*-Ethyl-(1*S*)-*N*-(1-phenylethyl) *P*-methyl *P*-phenyl phosphinamide** (rapidly eluting): $[\alpha]_D=-54.4$ ($c=1.04$ in CH_2Cl_2); ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.90$–7.79 (m, 2H), 7.51–7.44 (m, 5H), 7.49–7.08 (m, 3H), 4.84–4.68 (m, 1H), 3.12–2.71 (m, 2H), 1.79 (d, $J=13.56$ Hz, 3H), 1.49 (d, $J=7.02$ Hz, 3H), 0.85 ppm (t, $J=7.13$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta=$ 15.2 (d, $J=93$ Hz), 17.1, 18.2, 36.7 (d, $J=4$ Hz), 52.7 (d, $J=4$ Hz), 126.6, 127.3, 127.7, 128.0 (d, $J=12$ Hz), 130.8 (d, $J=10$ Hz), 131.1(d, $J=3$ Hz), 133.6 (d, $J=125$ Hz), 141.5 (d, $J=4$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=$ 35.3 ppm; MS (CI): m/z: 288 $[M+H]^+$.

***N*-Ethyl-(1*S*)-*N*-(1-phenylethyl) *P*-methyl *P*-phenyl phosphinamide** (more slowly eluting): $[\alpha]_D=-45.8$ ($c=1.03$ in CH_2Cl_2); ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta=7.87$–7.76 (m, 2H), 7.50–7.42 (m, 3H), 7.35–7.19 (m, 5H), 4.75–4.15 (m, 1H), 3.06–2.88 (m, 2H), 1.74 (d, $J=13.55$ Hz, 3H), 1.62 (d, $J=7.04$ Hz, 3H), 0.81 ppm (t, $J=7.10$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta=15.6$ (d, $J=92$ Hz), 17.0, 19.0, 37.0 (d, $J=4$ Hz), 53.4 (d, $J=$ 4 Hz), 126.9, 127.4, 127.9, 128.2 (d, $J=13$ Hz), 131.0 (d, $J=10$ Hz), 131.3(d, $J=3$ Hz), 133.9 (d, $J=125$ Hz), 141.7 ppm (d, $J=5$ Hz); ^{31}P NMR ($CDCl_3$): $\delta=35.8$ ppm; MS (CI): m/z: 288 $[M+H]^+$.

4-Nitrobenzyl *P*-benzyl *N*,*N*-diethylphosphonamidate (Table 1, entry 15): H NMR (200.13 MHz, CD_3OD): $\delta=8.12$ (d, $J=8.7$ Hz, 2H), 7.39 (d, $J=$ 8.6 Hz, 2H), 7.31–7.24 (m, 5H), 5.10 (dd, $J=13.4$, 13.4 Hz, 1H), 4.85 (dd, $J=13.4$, 13.4 Hz, 1H), 3.22 (dd, $J=20.6$ Hz, 1H), 3.14 (dd, $J=20.6$ Hz, 1H), 3.06 (m, $J_{P,H}=6.9$ Hz, 2H), 2.97 (m, $J_{P,H}=6.9$ Hz, 2H), 0.94 ppm (t, $J=7.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta=13.9$, 34.3 (d, $J=125.9$ Hz), 38.4 (d, $J=4.8$ Hz), 63.1 (d, $J=6.06$ Hz), 123.3, 126 (d, $J=3.6$ Hz), 127.3, 128.2 (d, $J=2.4$ Hz), 129 (d, $J=6.0$ Hz), 131 (d, $J=8.4$ Hz), 144.1 (d, $J=$

7.2 Hz), 147.1 ppm; ^{31}P NMR (CD_3OD): $\delta = 32.4$ ppm; MS (CI): m/z: 363.2 $[M+H]^+$.

2-Furylmethyl diphenylphosphine oxide (Table 1, entry 16): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 7.75$–7.65 (m, 5H), 7.57–7.33 (m, 5H), 7.23–7.22 (m, 1H), 6.23–6.20 (m, 1H), 6.10–6.06 (m, 1H), 3.75 ppm (d, $J = 14.00$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 31.1$ (d, $J = 69$ Hz), 108.8 (d, $J = 6$ Hz), 110.6 (d, $J = 3$ Hz), 128.3 (d, $J = 11$ Hz), 130.9 (d, $J = 9$ Hz), 131.8 (d, $J = 2$ Hz), 132.8, 141.8 (d, $J = 3$ Hz), 145.1 ppm (d, $J = 8$ Hz); ^{31}P ($CDCl_3$): $\delta = 28.4$ ppm; MS (FAB): m/z: 283.2 $[M+1]^+$. ^{1}H NMR data were consistent with those previously reported.[32]

2,5,5-Trimethyl-1,3,2-dioxaphosphorinan-2-one (Table 1, entries 17 and 18): ^{13}C NMR ($CDCl_3$): $\delta = 9.5$ (d, $J = 142$ Hz), 21.1, 32.4 (d, $J = 6$ Hz), 74.7 ppm (d, $J = 6$ Hz); ^{31}P NMR ($CDCl_3$): $\delta = 25.4$ ppm. ^{31}P NMR and ^{13}C NMR data were consistent with those previously reported.[33]

2-Benzyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one[34] (Table 1, entry 19): ^{13}C NMR ($CDCl_3$): $\delta = 21.0$, 21.2, 32.3 (d, $J = 6$ Hz), 32.6 (d, $J = 136$ Hz), 75.0 (d, $J = 7$ Hz), 126.9 (d, $J = 4$ Hz), 128.4 (d, $J = 3$ Hz), 129.7 (d, $J = 6$ Hz), 130.8 ppm (d, $J = 10$ Hz); ^{31}P NMR ($CDCl_3$): $\delta = 22.3$ ppm.

2-Allyl-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (Table 1, entry 20): ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 5.91$–5.67 (m, 1H), 5.10–4.92 (m, 2H), 3.97–3.89 (m, 2H), 3.36–3.22 (m, 2H), 2.50 (dd, $J = 21.86$, 7.31 Hz, 1H), 2.46 (dd, $J = 21.85$, 7.31 Hz, 1H), 0.69 (s, 3H), 0.38 ppm (s, 3H); ^{13}C NMR (C_6D_6): $\delta = 20.9$, 21.1, 29.7 (d, $J = 133$ Hz), 32.2 (d, $J = 9$ Hz), 74.7 (d, $J = 6$ Hz), 120.0 (d, $J = 16$ Hz), 126.3 ppm (d, $J = 13$ Hz); ^{31}P NMR (C_6D_6): $\delta = 22.3$ ppm; MS (CI): m/z: 191 $[M+H]^+$.

***N,N*-Diethyl-*P*-(4-methoxybenzyl)phosphonamidic acid**: ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 11.6$ (br s, 1H), 7,15 (dd, $J = 2.3$, 8.4 Hz, 2H), 6.78 (d, $J = 8.4$ Hz, 2H), 3.74 (s, 1H), 2.96 (m, 2H), 2.90 (m, 2H), 0.94 ppm (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (C_6D_6): $\delta = 14.4$, 34.5 (d, $J = 125$ Hz), 39.1 (d, $J = 4$ Hz), 54.8, 113.3, 125 (d, $J = 9.0$ Hz), 130.5 (d, $J = 6.0$ Hz), 157.8 ppm (d, $J = 4$ Hz); ^{31}P NMR (C_6D_6): $\delta = 30.6$ ppm; MS (FAB): m/z: 258.1 $[M+H]^+$.

2-Bromo-5,5-dimethyl-1,3,2-dioxaphosphinane:[35] Me_3SiBr (1.2 mmol) was added dropwise under argon at room temperature to a solution of 2-chloro-5,5-dimethylphosphinane (1 mmol) in methylene chloride (50 mL). After the system had been stirred for 2 h at room temperature, the solvent was removed under reduced pressure and the crude product was purified by vacuum distillation (70 °C, 15 mmHg; 72 °C, 18 mmHg). ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 4.02$–3.94 (m, 2H; CH_2–O), 3.16–3.06 (m, 2H; CH_2–O), 0.83 (s, 3H; CH_3), 0.15 ppm (s, 3H; CH_3); ^{13}C (C_6D_6): $\delta = 73.43$ (d, $J_{P,C} = 3.0$ Hz; 2 × CH_2–O), 33.14 (d, $J_{P,C} = 4.5$ Hz; $C(CH_3)_3$), 22.86 (CH_3), 22.42 ppm (CH_3); ^{31}P NMR (C_6D_6): $\delta = 162.1$ ppm.

General procedure for the preparation of phosphonium salts: A P^{III} ester (6.0 mmol) was introduced by syringe into a three-necked flask containing a magnetic stirrer and fitted with a reflux condenser and a septum. TMSBr (3.0 mmol) or TMSI (3.0 mmol) was then added at room temperature by injection, and the mixture was heated at 80 °C for 5–12 h. The crude reaction mixture was allowed to cool to room temperature and was either recrystallised or subjected to silica gel column chromatography, to yield the pure salt.

Dimethyl diphenyl phosphonium bromide (Table 2, entry 1): ^{1}H NMR (200.13 MHz, CD_3OD): $\delta = 7.96$–7.48 (m, 10H), 2.62 ppm (d, $J = 14.42$, 6H); ^{13}C NMR (CD_3OD): $\delta = 9.2$ (d, $J = 57$ Hz), 122.7 (d, $J = 88$ Hz), 131.2 (d, $J = 13$ Hz), 133.1 (d, $J = 11$ Hz), 135.7 ppm (d, $J = 3$ Hz); ^{31}P NMR (CD_3OD): $\delta = 21.1$ ppm; MS (FAB, +ve): m/z: 215.

Diethyl diphenyl phosphonium bromide (Table 2, entry 2): ^{1}H NMR (200.13 MHz, CD_3OD): $\delta = 7.99$–7.48 (m, 10H), 3.33–2.29 (m, 4H), 1.28 (t, $J = 7.52$ Hz, 3H), 1.18 ppm (t, $J = 7.50$ Hz, 3H); ^{13}C NMR (CD_3OD): $\delta = 6.1$ (d, $J = 5$ Hz), 14.5 (d, $J = 51$ Hz), 119.3 (d, $J = 83$ Hz), 131.4 (d, $J = 12$ Hz), 134.1 (d, $J = 10$ Hz), 135.9 ppm (d, 3 Hz); ^{31}P NMR (CD_3OD): $\delta = 31.0$ ppm; MS (FAB, +ve): m/z: 243.1.

Diallyl diphenyl phosphonium bromide[36] (Table 2, entry 3): ^{1}H NMR (200.13 MHz, CD_3OD): $\delta = 7.89$–7.37 (m, 10H), 5.81–5.57 (m, 2H), 5.44–5.31 (m, 4H), 3.90 ppm (dd, $J = 15.48$, 7.11 Hz, 4H); ^{13}C NMR (CD_3OD): $\delta = 26.6$ (d, $J = 50$ Hz), 118.4 (d, $J = 83$ Hz), 124.0 (d, $J = 9$ Hz), 126.2 (d, $J = 13$ Hz), 131.3 (d, $J = 12$ Hz), 134.2 (d, $J = 9$ Hz), 136.3 ppm; ^{31}P NMR (CD_3OD): $\delta = 22.3$ ppm; MS (FAB, +ve): m/z: 267.0.

Dibenzyl diphenyl phosphonium bromide[36] (Table 2, entry 4): H NMR (200.13 MHz, CD_3OD): $\delta = 7.88$–7.78 (m, 2H), 7.71–7.53 (m, 8H), 7.31–7.14 (m, 6H), 7.08–6.95 (m, 4H), 4.52 ppm (d, $J = 14.61$ Hz, 4H); ^{13}C NMR (CD_3OD): $\delta = 29.8$ (d, $J = 46$ Hz), 118.0, 128.9, 129.4, 130.0, 130.9, 131.8, 135.3, 136.1 ppm; ^{31}P NMR (CD_3OD): $\delta = 26.0$ ppm; MS (FAB, +ve): m/z: 367.0.

Dimethyl diphenyl phosphonium iodide[36] (Table 2, entry 5): ^{1}H NMR (200.13 MHz, CD_3OD): $\delta = 7.97$–7.66 (m, 10H), 2.64 ppm (d, $J = 14.40$ Hz, 6H); ^{13}C NMR (CD_3OD): $\delta = 9.2$ (d, $J = 57.1$ Hz), 122.6 (d, $J = 82$ Hz), 131.2 (d, $J = 13$ Hz), 133.0 (d, $J = 11$ Hz), 135.0 ppm (d, $J = 3$ Hz); ^{31}P NMR (CD_3OD): $\delta = 21.1$ ppm; MS (FAB, +ve): m/z: 216.0.

Diethyl diphenyl phosphonium iodide[36] (Table 2, entry 6): ^{1}H NMR (200.13 MHz, CD_3OD): $\delta = 8.00$–7.34 (m, 10H), 3.98–2.98 (m, 4H), 1.37–1.13 ppm (m, 6H); ^{13}C NMR (CD_3OD): $\delta = 6.1$ (d, $J = 5$ Hz), 14.6 (d, $J = 51$ Hz), 119.3 (d, $J = 83$ Hz), 131.4 (d, $J = 12$ Hz), 134.2 (d, $J = 9$ Hz), 136.0 ppm (d, $J = 3$ Hz); ^{31}P NMR (CD_3OD): $\delta = 31.0$ ppm; MS (FAB, +ve): m/z: 243.0.

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