The synthesis of stable 1,3,4-triphenylphospholes

Tuula-A Niemi,[a] Paul L. Coe *[a] and Stephen J. Till [b]

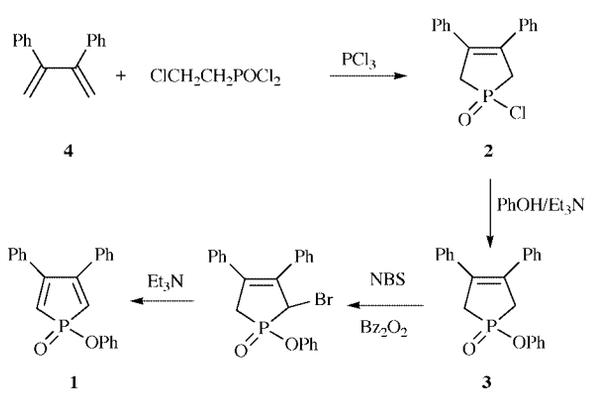
[a] *School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, UK B15 2TT*
[b] *DERA Malvern, Worcestershire, UK WR14 3PS*

Received (in Cambridge, UK) 25th January 2000, Accepted 22nd March 2000

The first syntheses of 1,3,4-triphenylphosphole, 2-bromo-1,3,4-phenylphosphole and 2,5-dibromo-1,3,4-triphenylphosphole are described. These phospholes, unlike most of the known derivatives, are difficult to oxidise and they and their corresponding oxides show little tendency to dimerise. The NBS mediated bromination of 1,3,4-triphenyl-2,5-dihydrophosphole oxide led to the desired precursors of the corresponding phospholes and in one case unexpectedly yielded a phosphole oxide directly. Some reactions including the formation of organolithium reagents and their derivatisation are reported. McMurry reactions of derived formylphospholes to give coupled products are described and some copper mediated reactions are also discussed.

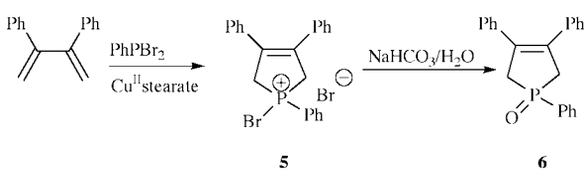
Introduction

Although there is a considerable literature[1] concerned with five membered aromatic phosphorus heterocycles, the phospholes, it has been found that the oxidative stability of most of the known phospholes, except for certain penta-substituted compounds, is very low. This has the consequence that because of the formation of the phosphole oxides which readily dimerise, there is little information on the isolation and chemistry of stable derivatives. The first phosphole was in fact synthesised as late as 1959.[2] Most of the recent work on the chemistry of phospholes has been carried out by the Mathey group with 3,4-dimethyl-1-phenylphosphole and its 2-bromo derivative and their work has been well reviewed.[3] These workers were able, in spite of the inherent problems of preparation and stability of the starting material, to prepare a number of functionalised compounds and to study their chemistry. We were interested in the formation of *stable* phospholes which were substituted at the 2 or 5 positions with functionality *e.g.* halogen which was capable of being easily transformed in order to study their chemistry. Westheimer[4] reported the synthesis of 1-phenoxy-3,4-diphenylphosphole 1-oxide **1** and showed that it did not dimerise. Scheme 1 shows the reactions of 2,3-



Scheme 1

diphenylbutadiene with 2-chloroethyl dichlorophosphinite and phosphorus trichloride and then that of the intermediate 1-chloro-3,4-diphenyl-2,5-dihydrophosphole 1-oxide **2**, without isolation, with phenol to give the phenoxy derivative **3**. By a sequence involving bromination and then dehydrobromination with excess triethylamine the phosphole oxide **1** was obtained. This method was subsequently adapted by Quin[5] and by Nakayama[6] to prepare 1,3,4-triphenyl-3-phospholene-1-oxide **6** as shown in Scheme 2. Quin reacted 2,3-diphenylbutadiene



Scheme 2

with dibromophenylphosphine in the presence of copper(II) stearate followed by reaction of the intermediate phospholium bromide **5** with aqueous sodium bicarbonate to give the desired phosphole oxide **6**. No further reactions of **6** have been reported. Nakayama prepared **6** in a more vigorous reaction using dichlorophenylphosphine and 2,3-diphenylbutadiene in the presence of magnesium at 215 °C, and not surprisingly the yield in this reaction was rather low and so we did not consider it suitable for our purposes. We thus felt that a combination of the Westheimer and Quin procedures might allow the possibility of preparing our desired 1,3,4-triphenylphosphole oxide. Having obtained **6**, which we believed would not dimerise rapidly, we planned to convert it by the methods used by Mathey to obtain the desired phospholes.

Results and discussion

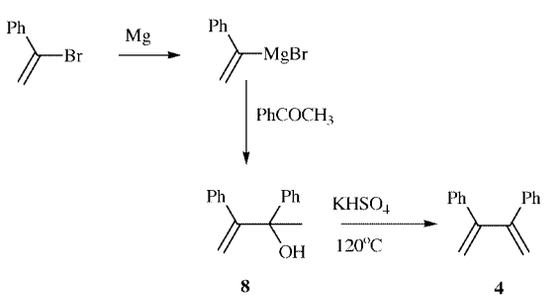
The first problem we encountered in our synthetic plan was to obtain 2,3-diphenylbutadiene **4**. There are some reported routes to **4** which when this work was commenced was not commercially available and is still very expensive and impure. There are a variety of routes available as shown below and we considered most of them before choosing the one we eventually used. An obvious method to prepare **4** was to follow the precedent used for the preparation of the dimethyl analogue: that of dehydration of a suitably substituted butane-2,3-diol. This method involves heating the diol with trace amounts of fused potassium hydrogen sulfate. A worrying feature of these descriptions (see below) seemed to be the variable yield obtained (between 15 and 100%), depending on the author, using essentially the same chemistry. Hayden and Alder[7]

DOI: 10.1039/b000692k

claimed almost quantitative yields of the diene and so we investigated their reaction conditions. In our hands, although we were able to obtain very high carbon recoveries, we always obtained the pinacolone rearrangement product 3,3-diphenylbutanone as by far the major product. Even under our best conditions the yield of the diene never exceeded 25% of the product and was usually not more than 10% in accord with the results described by Dodson *et al.*[8] In contrast Brettle[9] reported a 68% yield for the same reaction. Clearly there is an inherent difficulty, which we could not master, in this reaction. An alternative route appeared to be the Wittig reaction of methylenetriphenylphosphorane with benzil, as described by De Groot *et al.*,[10] but the yield here was only 15% and involved somewhat tedious column chromatography to remove the triphenylphosphine oxide formed in the reaction. Since we require multi-gram quantities of the products this was not a viable alternative.

A second possibility was the coupling of α-bromostyrene using either a nickel or palladium catalyst. Such reactions have been reported, the former by Caubere *et al.*[11] and the latter by Luo.[12] The former report suggested to us that although the desired diene could be obtained on a small scale the reaction was very sensitive to the method of catalyst preparation, to profound solvent effects, which led to an alternative product, and to problems of scale. The Luo method again appears to be attractive but we were concerned with the scale up and the high cost of the catalyst. Thus, we needed to find an alternative route which overcame these objections.

We eventually discovered a report in the Japanese patent literature by Kondo[13] who had shown that the pinacol–pinacolone rearrangement could be avoided by using 2,3-diphenyl but-3-en-2-ol **8** as starting material. We were able to prepare **8** by reaction of 2-phenylethenylmagnesium bromide (α-styrylmagnesium bromide) with acetophenone in 77% isolated yield. Although 2-bromo-2-phenylethene is commercially available we found that most commercial samples are highly contaminated with the polymeric material and are very difficult to purify. We thus used freshly prepared material[14] in all of our reactions. The dehydration of **8** was readily achieved by heating the alcohol with freshly fused potassium hydrogen sulfate at 120 °C followed by vacuum distillation of the diene **4** from the reaction mixture, as shown in Scheme 3. Having solved



Scheme 3

this problem we were able to repeat the reaction of **4** with dibromophenylphosphine under Quins conditions to obtain the desired phospholene oxide **6**. Unfortunately, as was found by Quin, the yields in the reaction were rather low. The phospholium bromide **5** crystallises from the petroleum ether solvent on cooling and we found that by cropping this product each day for up to ten days we could obtain an overall yield of **6**, after hydrolysis of **5**, of 71%. We also found that the reaction could be substantially scaled up and this allowed us to obtain abundant supplies of the phosphole oxide **6** (25% overall from styrene).

The next stage in our synthesis was the conversion of **6** to 1,3,4-triphenylphosphole oxide using the Westheimer procedure with NBS and base. Since our major objective was to prepare

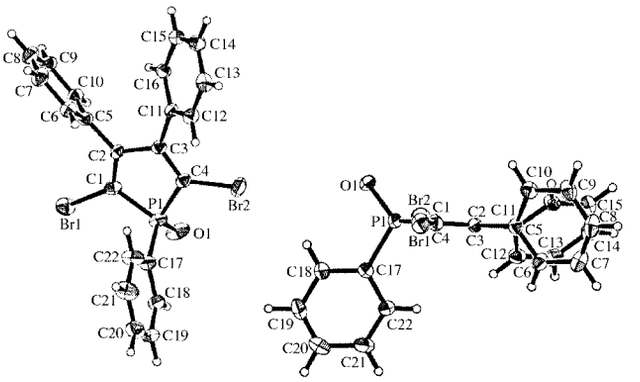
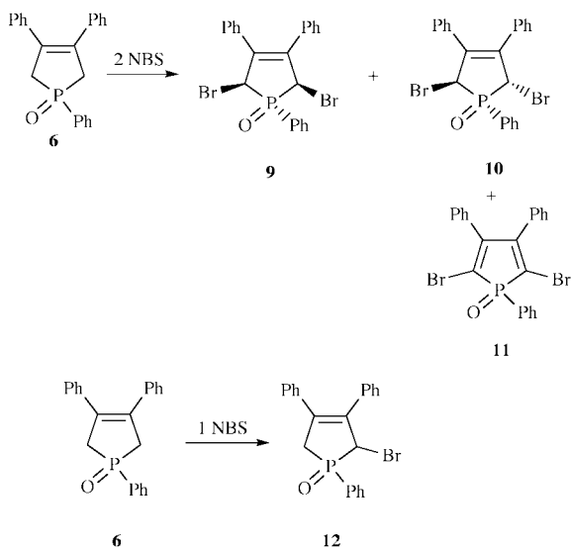


Fig. 1 X-Ray structure of 2,5-dibromo-1,3,4-triphenylphosphole 1-oxide.

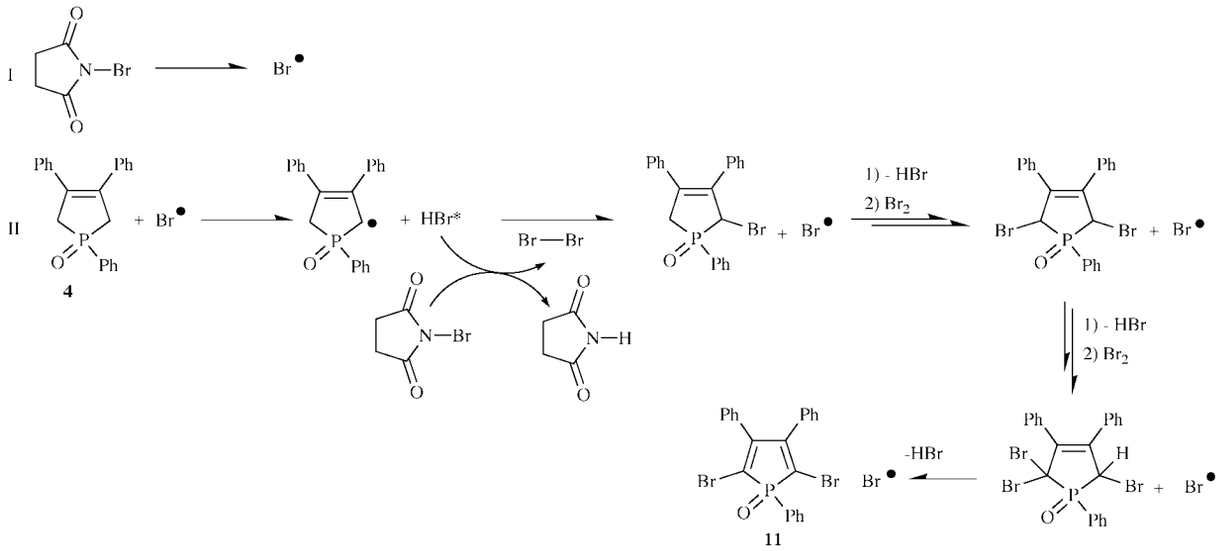
functionalised phospholes we decided to attempt to prepare the required bromodihydrophosphole oxides directly rather than in a stepwise manner. Thus, we adapted Westheimers method using 2 equivalents of NBS in the hope of preparing the 2,5-dibromo derivative in one step. The reaction of **6** with NBS in DCM using purified benzoyl peroxide as catalyst at 40 °C afforded a mixture of three products in the ratio 1.4 : 1 : 1 (see Scheme 4). The mixture was readily separated by column



Scheme 4

chromatography. The products were identified, using a combination of ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and elemental analysis, as *trans*,*trans*-2,5-dibromo-1,3,4-triphenyl-2,5-dihydrophosphole oxide **9**, *cis*,*trans* 2,5-dibromo-1,3,4-triphenyl-2,5-dihydrophosphole oxide **10**, and 2,5-dibromo-1,3,4-triphenylphosphole oxide **11**. It was possible to distinguish the pairs of diastereoisomers **9** and **10** by means of the ^{1}H and ^{13}C spectra since the *trans*,*trans* isomer has a plane of symmetry giving only therefore one NMR signal for the 2 and 5 protons and also for the 2 and 5 carbon atoms. Further, there is only a small $^{2}J_{PH\alpha}$ coupling characteristic of *trans*,*trans* isomers.[15] The *cis*,*trans* isomer does not have the symmetry plane and shows two signals for the 2 and 5 protons and carbon atoms. The dibromophosphole oxide **11** was a totally unexpected product and to confirm the structure we carried out an X-ray analysis. The structure is shown in Fig. 1. As can be seen the three phenyl rings and the oxide oxygen are almost orthogonal to the planar phosphole and this fits well with energy minimised MOPAC calculations.

This result raises some interesting mechanistic questions and we decided to try to find an answer to the possible pathway leading to the phosphole oxide **11**. We carried out a series of



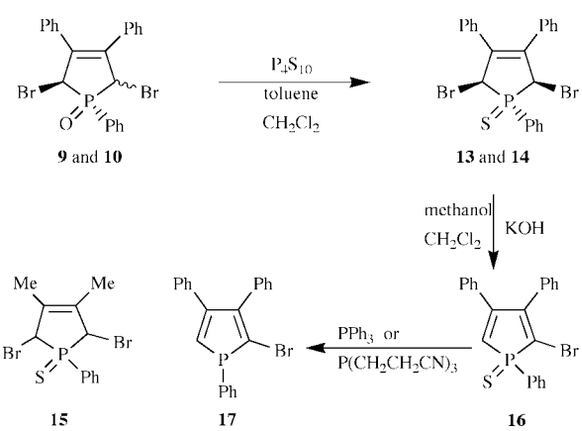
Scheme 5

Table 1 The reaction of 1,3,4-triphenylphospholene 1-oxide **6** with *N*-bromosuccinimide

Entry	NBS	$(PhCO)_2O_2$	Reaction time/h	Yield (%)		
				9	**10**	**11**
1	2.0 equiv.	cat.	18	55.5	14	30.5
2	2.0 equiv.	excess	18	59	20	21
3	2.0 equiv.	none	18	57	14	29
4	3.0 equiv.	cat.	18	50	12	38
5	3.0 equiv.	none	240			100

reactions varying the amount of catalyst to NBS ratio, and the NBS to substrate ratio. The results are shown in Table 1 from which it is clear that the amount of NBS used is important in determining the products formed and that the catalyst, as expected, merely speeds up the reaction. Interestingly the results also show that either the rate of formation of **9** is faster than that of **10** or that the rate of decomposition of **10** to **11** is faster than **9** to **11**. We believed from our original experiment, where after 6 h the ratio of **9**:**10** was 1.4:1, that **10** reacted to give **11** faster than **9**. In a separate experiment using a 1:1 mixture of **9** and **10** and 2 equivalents of NBS the ratio of **9**:**10** was 1.6:1 after 12 h, the only other product being **11**. The proposed mechanism is shown in Scheme 5. We were unable to obtain any evidence for the formation of the proposed tribromo intermediate from NMR spectra of the reaction mixture and we assume that the rate of dehydrobromination to **11** is very fast. We have so far been unable to carry out the reaction within the NMR probe. From a synthetic point of view however these results were extremely useful. By using three equivalents of NBS we were able to prepare multi-gram quantities of **11**. Similarly the use of two equivalents of NBS afforded a mixture of **9** and **10** and the use of one equivalent of NBS, after a simple column separation, gave 2-bromo-1,3,4-triphenyl-2,5-dihydrophosphole oxide **12**. The latter was characterised by standard physical methods.

We now had three potential precursors to the desired phospholes. These results are shown in Scheme 5. Two problems now remained to be solved, firstly to convert the dihydrophosphole oxides to phosphole oxides and then to convert these by a deoxygenation process to the phospholes. When we began this work the favoured method of carrying out the latter process was to convert the dihydrophosphole oxides by reaction with phosphorus pentasulfide to the corresponding sulfides. After dehydrobromination the resulting phosphole sulfides were then treated with either triphenylphosphine or better with tris-(β-cyanoethyl)phosphine to afford the corresponding phospholes.[15] During the course of this study Mathey showed that it was possible to deoxygenate the phosphole oxides directly, in good yield, by reaction with trichlorosilane in the presence of pyridine,[16] a reaction known to reduce phosphine oxides to phosphines. We have now compared both methods using our phosphole derivatives with some surprising results. The first reactions we tried were the conversions of the dibromodihydrophosphole oxides **9** and **10** to the sulfides **13** and **14** respectively (Scheme 6). We found that each diastereoisomer reacted



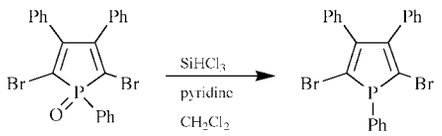
Scheme 6

smoothly in virtually quantitative yield to give the corresponding sulfide with retention of configuration at phosphorus as was reported by Mathey[15] for the formation of the dimethyl compound **15**. The assignment of structure was based on the small αH to P couplings characteristic of the *trans* arrangement and on the appearance of only one signal in the ^1H and ^{13}C NMR spectra of the symmetrical *trans*,*trans* compound as outlined above for the starting oxide.

We next investigated the dehydrobromination of **13** and **14**. Westheimer[4] had used triethylamine as the base to obtain **1** whereas Mathey[15] had used methanolic potassium hydroxide to dehydrobrominate 2,5-dibromo-3,4-dimethyl-1-phenyl-2,5-dihydrophosphole 1-sulfide **15**. We tried both of these reagents quite successfully with the methanolic potassium hydroxide giving the higher yield. The reaction of the *trans*,*trans* isomer **13** was much faster than the *cis*,*trans* derivative **14** (30 min as against 4 h for completion of the reaction). Both **13** and **14** gave exactly the same product, as would be expected, namely

2-bromo-1,3,4-triphenylphosphole 1-sulfide **16**. We were now concerned with removal of the sulfide, and first tried the desufurisation with triphenylphosphine which was quite successful, all of the starting material being consumed as shown by ^{31}P NMR spectroscopy, but unfortunately it was impossible to separate the phosphole from unreacted triphenylphosphine. We were, however, able to carry out a very straightforward desulfurisation using tris(β-cyanoethyl) phosphine which afforded 2-bromo-1,3,4-triphenylphosphole **17** in 88% yield. These results are shown in Scheme 6. The phosphole was characterised by physical means. The new phosphole showed no tendency to dimerise and was found to oxidise only very slowly. A sample kept in air afforded only a few percent of oxide after six months and a sample in dry nitrogen appears to be totally unchanged after two years. The small amount of oxide present in the sample, unlike almost all other phosphole oxides reported, does not appear to have dimerised.

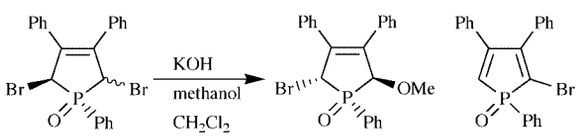
At this time in our work an improved deoxygenation route described above became available and we decided to use this method instead of the somewhat unpleasant sulfide route. Thus, we reacted the phosphole oxide **11** with trichlorosilane using the Mathey conditions (Scheme 7) and obtained an 81%



11 **18**

Scheme 7

yield of a pale yellow solid which was shown by physical methods to be the desired 2,5-dibromo-1,3,4-triphenylphosphole **18**. This phosphole was also quite stable; it did not readily oxidise in air, but as with **17**, a sample left in air for some months did show some oxidation, but in a nitrogen atmosphere it seems to be unchanged after at least one year. In principle we should have been able to prepare **17** directly *via* its oxide, which in turn should be available from dehydrobromination of **9** and **10** as for the sulfide. Thus, we reacted **9** and **10** as separate diastereoisomers. In each case we obtained largely one product which showed a band at 31.5 ppm in its ^{31}P NMR spectrum. This was unlike any other product we had found previously in this series. The ^{1}H spectrum showed a doublet signal in the methoxy region with a proton–phosphorus coupling of 11 Hz. This suggested we had replaced a bromine atom with a methoxy group in a simple nucleophilic displacement process. This was confirmed by mass spectrometry, which showed the characteristic isotopic distribution for a monobromo- compound. This confirmed the product as 2-bromo-5-methoxy-1,3,4-triphenyl-2,5-dihydrophospholene oxide **19**. Thus, we were unable to prepare **17** from the oxide (Scheme 8). This change in reactivity



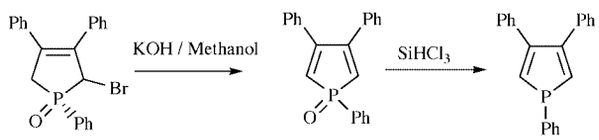
9,10 **19** **20**

Scheme 8

on going from the phosphole sulfide to the oxide was quite unexpected from previous literature results. We presume that this is due to the greater electronegativity of the oxygen atom on phosphorus making the α-carbon atom more positive and hence more reactive towards nucleophiles and therefore allowing this reaction to compete with dehydrobromination.

In a separate experiment using a mixture of **9** and **10** under slightly milder conditions we were able to obtain a mixture of the desired bromophosphole oxide **20** and **19** suggesting there is indeed a competition between the two reactions. We were also able to show that bromination of **20** with elemental bromine followed by dehydrobromination in a "one pot" reaction yielded the dibromophosphole oxide **11** identical to that obtained from the NBS reaction of **6** above (Scheme 5).

To complete our objectives we wished to make 1,3,4-triphenylphosphole. This should be available from the deoxygenation of the corresponding phosphole oxide, which in turn could be prepared by dehydrobromination of the dihydrophosphole oxide derivative **12**. Reaction of the latter with methanolic potassium hydroxide readily afforded the required phosphole oxide in good yield (Scheme 9). We found no evi-



12 **4** **21**

Scheme 9

dence for the nucleophilic substitution reaction which we had observed with the dibromo analogue above. The phosphole oxide, which was again characterised by the usual physical means, showed no evidence of rapid dimerisation and even after one year only trace amounts of the dimer were evident from the ^{31}P NMR spectrum. Deoxygenation of the phosphole oxide with trichlorosilane–pyridine gave 1,3,4-triphenylphosphole **21** in 79% yield. The phosphole was characterised in the usual way. We had thus achieved the first objective of the study with the preparation of the three stable phospholes. It is important to note the crucial role of ^{31}P NMR spectroscopy in structural determination in this area. The dihydrophosphole and phosphole sulfides were generally observed to show phosphorus resonances at 55–60 ppm and *ca.* 50 ppm respectively, whereas the corresponding oxides had resonances at *ca.* 40 and 35 ppm. The phospholes all showed resonances at rather lower fields depending on their substitution but in the range of 5–22 ppm. This enabled us to monitor reactions very easily and also to check on the ease of oxidation or dimerisation of the products so that appropriate precautions could be taken to counter these processes. A similar set of reactions of the dihydrophosphole oxide **6** but with NIS failed to yield the corresponding iodo compounds, only the starting material being recovered.

We were now in a position to study further functionalisation of the phospholes to enable us to proceed towards our objective of synthesising macrocyclic derivatives. In the light of the work of Mathey[1] we first studied the formation and reactions of organolithium derivatives as a means of functionalising our phospholes. Since the dibromophosphole **18** was more readily available and could possibly lead more directly to our objective, we concentrated our initial studies on this derivative. We tried a number of different conditions for the halogen–metal interchange and these results are summarised in Table 2. Aliquots were taken at the reaction temperature indicated and the resulting solutions were examined by ^{31}P NMR spectroscopy to determine the approximate product ratios. We were somewhat surprised to find that the reaction apparently did not take place at some temperature between −75 and −30 °C and even at −75 °C did not go to completion, whereas at −100 °C complete conversion to the lithio compound was seen. As yet we have no real explanation for this observation: it would imply the usual halogen–metal interchange is reversed with increasing temperature. In a simple experiment we found that hydrolysis of a sample taken from a solution taken at −100 °C showed complete conversion to the lithium derivative. After warming the mixture to −75 ° C and allowing it to stand at this temperature

Table 2 The reaction of 2,5-dibromo-1,3,4-triphenylphosphole with organolithium reagents

Organolithium	*T*/°C	Yield (%)		
		18	**17**	**21**
n-BuLi	−100	15	85	none
n-BuLi	−75	50	50	none
n-BuLi	−30	100	none	none
n-BuLi	20	100	none	none
MeLi–LiBr	−100	94	6	none
MeLi–LiBr	−75	98.5	1.5	none
MeLi–LiBr	−30	100	none	none
MeLi–LiBr	20	100	none	none
tert-BuLi	−100	64	16	20
tert-BuLi	−75	68	16	16
tert-BuLi	−30	90	5	5
tert-BuLi	20	100	none	none

for a short time before sampling, starting material was present to approximately 50% and on repeating this process at −20 °C only starting material could be detected. A repeat of this experiment confirmed this result. We also carried out the same type of reaction using methyllithium–lithium bromide, *tert*-butyllithium and methylmagnesium bromide. We found that in general these reagents were less reactive than *n*-butyllithium but when reaction did occur the same unusual temperature effects were observed. Further study on this reaction may clear up this anomaly.

As we could carry out the interchange to yield the lithium reagent **22** quite successfully at −100 °C we proceeded with reactions at this temperature. Since we planned to try to join phospholes together with unsaturated carbon chains, we felt an obvious route was to use the McMurry reaction which has been applied very successfully in the preparation of macrocyclic furan derivatives.[17] Thus, we required the appropriate carbaldehydes for this coupling. We found the best conditions for the reaction were to treat the lithium reagent **22** with a slight excess of *N*-methylformanilide at −100 °C in THF as solvent. In this way the bromophosphole **17** and the dibromophosphole **18** afforded the corresponding aldehydes **23** and **24** in fair yield. As was discovered by Mathey[16] for the corresponding 3,4-dimethyl compound, the dibromophosphole did not form the dilithio derivative. We found that under similar conditions **22** reacted with propanal to yield the expected alcohol **25,** but attempts to isolate this material completely pure all yielded only the dehydrated product **26**. These compounds were characterised by physical means. Reaction of **22** with iodine afforded an inseparable mixture of the starting material 10% and the bromoiodo compound **27** 90%. These could be readily identified by GC/MS. Reaction of **22** with phenyldichlorophosphine afforded a mixture of two products. The major component was the phosphine **28**, identified by physical means, but we were unable to identify the minor component. The composition of the phosphine **28** at first sight was unexpected but this can be readily rationalised in terms of the known halogen exchange reactions between phosphines. There are two possibilities which could account for the formation of **28**: either the phenyldichlorophosphine exchanges chlorine for bromine with the bromide ions present in the butyllithium, and the bromophosphine then reacts with **22,** or more likely the chlorophosphine formed by straightforward reaction of the dichlorophenylphosphine with **22** exchanges with lithium bromide. A suggested method of distinguishing between these possibilities has been made† as follows: if the exchange proceeds to produce **28** *via* addition to give a phosphoranide intermediate the first pathway would be expected to be faster since the phosphorus atom would bear three halogen atoms compared to two for the other route. It may be possible to distinguish between the two pathways therefore by converting **28** to the corresponding chloride by exchange with PCl_3 and then to study the rate of its reaction with bromide ion using ^{31}P NMR spectrocopy. Equally the exchange reaction of $PhPCl_2$ with bromide could be studied in the same way. Somewhat to our surprise we have so far been unable to react **22** successfully with carbon dioxide or with acyl halides.

Having obtained the aldehydes **23** and **24** we were now in a position to attempt the McMurry reaction and we chose to do this on the more readily available aldehyde **24**. We tested out the reaction conditions using furfural and were able to obtain the desired coupled product in 93% yield as a single isomer shown to be the *E* isomer in agreement with the literature.[18] A similar reaction with the aldehyde **24** afforded a pale orange solid in 71% yield which was characterised by physical means and was shown to be the expected ethene **29**. Both the ^1H and ^{31}P NMR spectra revealed the presence of two diastereoisomeric mixtures in the ratio of appoximately 90 : 10 due to the *E* and *Z* arrangements of the phenyl groups attached to phosphorus. The double bond was in the *E*-configuration, in common with the furfural derived product. The mass spectrum showed an interesting feature which was very useful in confirming the structure. The mass of the molecule was so high (it contained more than 40 carbon atoms) that it was possible to distinguish not only the bromine isotope ratios but also the natural abundance ratios of the carbon atoms. The observed pattern was a complete match to the computer generated unique pattern for the molecule. As a further check on the method we prepared the corresponding 3,4-dimethyl derivative **30** from 2-bromo-3,4-dimethylphosphole-5-carbaldehyde[16] which was again a diastereomeric mixture with similar NMR characteristics to those found for **29**.

We next investigated some copper coupling reactions of the lithium reagent **22** and the dibromophosphole **18.** In the light of the work of Mathey[15] we reacted **22** with copper(II) chloride and obtained a mixture of products in moderate yield which could be separated by column chromatography to yield the expected dimer **31** (33%) the reduced dimer **32** (19%) unreacted starting phosphole **18** (12%) and the phosphole (**17**) formed from the hydrolysis of **22**. The new products were characterised by physical means. Reaction of **18** with copper(I) cyanide under a variety of conditions always afforded mixtures of products which we could not completely separate, but from which we could obtain a mixture of the dimers **31** (50%) and **32** (16%) as shown by GC/MS and a small (19%) yield of the desired nitrile **33**, which was partially characterised by physical means. The formation of coupled products in these copper assisted reactions are quite commonly found[19] and it would appear in our case this reaction is the favoured one. These reactions are summarised in Scheme 10. We have thus shown that the new phospholes lead to a number of derivatives which have scope for further developments in this interesting area of chemistry.

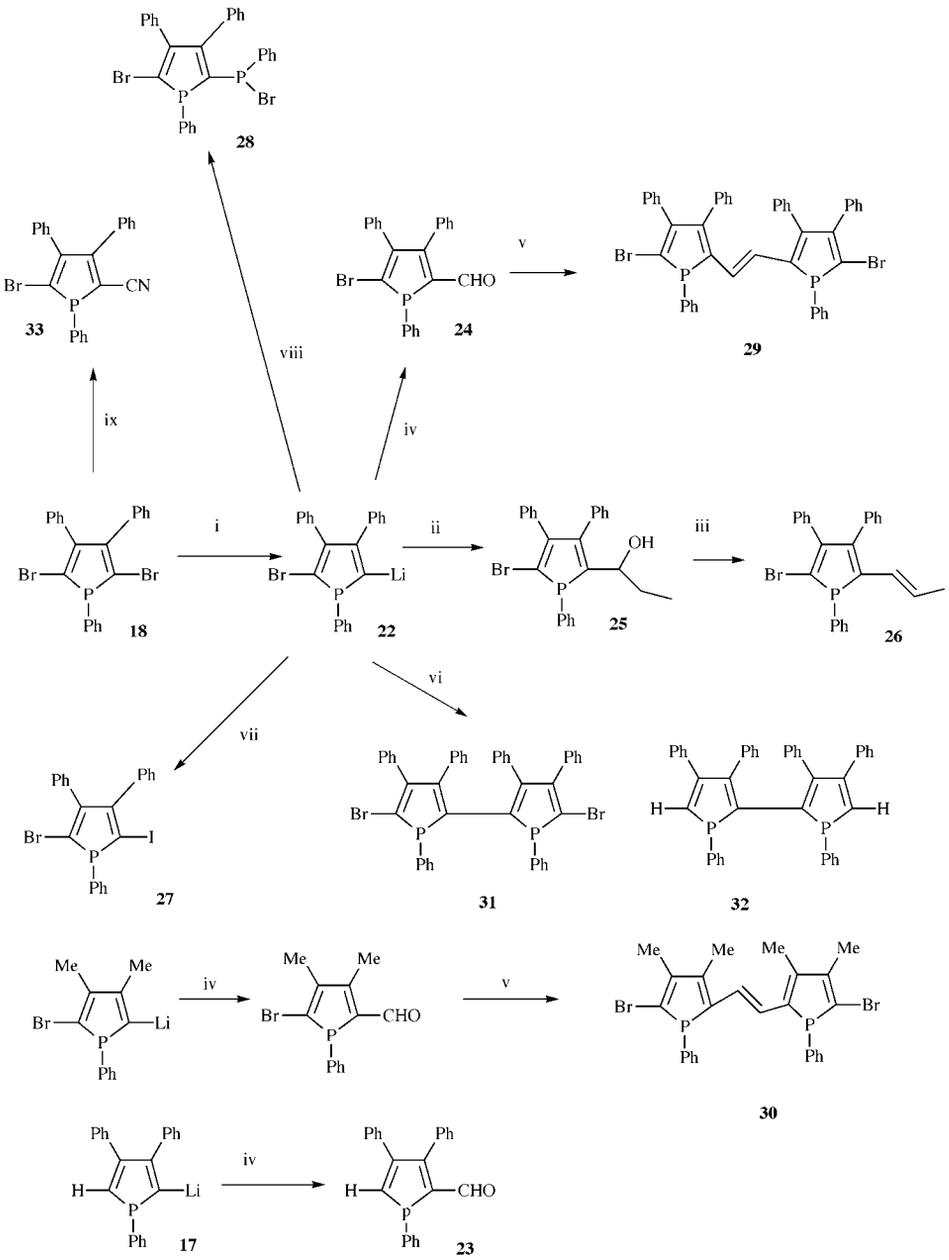
Experimental

NMR spectra were recorded using a Bruker AC-300 spectrometer. TMS was used as the internal standard for ^1H (300.13 MHz) and ^{13}C (75.47 MHz) spectra. H_3PO_4 (85%) was used as external reference for ^{31}P (121.50 MHz) spectra. Mass spectra were recorded on a VG Prospec triple focussing spectrometer. X-Ray spectra were recorded using a Rigaku Raxis 2C spectrometer. Matrix Silica 60 (35–70 micron) was used for column chromatography (Fisher Scientific Co.). SilicaGel 60 covered aluminium sheets were used for TLC.

Preparation of 2,3-diphenylbut-3-en-2-ol 8

1-Bromo-1-phenylethene (82.4 g, 0.45 mol) in dry ether (150 cm^3) was added dropwise at such a rate to maintain gentle reaction (over 2.5 h) to a suspension of magnesium turnings (13.1 g,

† We thank a referee for this suggestion.



Scheme 10 *Reagents*: i, BuLi; ii, PrCHO; iii, silica; iv, PhNHCHO; v, $TiCl_4$–Zn; vi, CuCl; vii, CuI; viii, $PhPCl_2$; ix, CuCN.

0.54 mol) in ether (30 cm^3). When the addition was complete the mixture was stirred for 40 min and then acetophenone (52.5 cm^3, 0.45 mol) was added over 2 h. The reaction mixture was stirred for a further 4 h when saturated ammmonium chloride solution (70 cm^3) was added and the mixture was neutralised with HCl (3 M, 130 cm^3). The ether layer was separated and combined with the ether extracts of the aqueous layer (5 × 200 cm^3). The dried ($MgSO_4$) ether layers were evaporated and the residue distilled *in vacuo* to yield 2,3-diphenylbut-3-en-2-ol **8** (77.5 g, 76%), bp 127–130 °C/0.5 mmHg (lit.,[8] 127–148 °C/0–1 mmHg); δ_H ($CDCl_3$), 7.4 (m, 10H, 2Ph), 5.7 (m, 2H, =CH), 2.4 (s, 1H, OH), 1.8 (s, 3H, CH_3); MS *m*/*z* 224 [M^+].

Preparation of 2,3-diphenylbuta-1,3-diene 7

Compound **8** (64.9 g, 0.3 mol), freshly fused potassium hydrogen sulfate (1.5 g) and phenyl-β-naphthylamine (0.04 g) were heated together for 40 min at 120 °C at 7–8 mmHg and the mixture was distilled at 0.01 mmHg to yield 2,3-diphenylbuta-1,3-diene **7** (27.3 g, 46%), mp 41–43 °C (lit.,[8] 46–47 °C) (from methanol); δ_H ($CDCl_3$) 7.2–7.5 (m, 10H, 2Ph), 5.6 (d, $^2J_{HH}$ 1.5, 2H, =CH), 5.4 (d, $^2J_{HH}$ 1.5, 2H, =CH); MS *m*/*z* 206 [M^+].

Preparation of 1,3,4-triphenyl-2,5-dihydrophosphole 1-oxide 6

The butadiene **4** (25.5 g, 0.12 mol), copper(II) stearate (0.25 g) and dibromophenylphosphole (40 g, 0.15 mol) in petroleum ether (bp 60–80 °C, 170 cm^3) were stirred at 60 °C for 16 days but after each day the precipitated product was filtered off. The combined precipitates were treated with ice cold saturated sodium bicarbonate solution (150 cm^3) The aqueous layer was extracted with DCM (6 × 50 cm^3), the combined extracts were dried ($MgSO_4$) and the solvent evaporated to yield 1,3,4-triphenyl-2,5-dihydrophosphole 1-oxide **6** (29.3 g, 71%), mp 160–162 °C (from CCl_4) (lit.,[6] 162–165 °C); δ_H ($CDCl_3$) 7.9–7.8 (m, 2H, PhP), 7.6–7.5 (m, 3H, PhP), 7.3–7.1 (m, 10H, PhC), 3.5–3.2 (m, 4H, CH_2); δ_P ($CDCl_3$) 48.1; MS *m*/*z* 330 [M^+].

Reaction of 1,3,4-triphenyl-2,5-dihydrophosphole 1-oxide with *N*-bromosuccinimide

The phospholene oxide **4** (1.3 g, 3.9 mmol), *N*-bromosuccinimide (1.4 g, 7.9 mmol) and benzoyl peroxide (0.15 g) in chloroform (35 cm^3) were heated together under reflux for 6 h. The mixture was cooled to room temperature and the solvent evaporated. The residue was shaken with a small amount of

DCM and the resulting suspension filtered. The filtrate was passed through a column of silica (eluant ethyl acetate–hexane 1:1) to yield three products identified as (i) *trans*,*trans*-2,5-dibromo-1,3,4-triphenyl-2,5-dihydrophosphole 1-oxide **9** (0.34 g) as a gum (Found: C, 53.8; H, 3.4%. $C_{22}H_{17}Br_2OP$ requires C, 54.1; H, 3.5%); δ_H ($CDCl_3$) 7.9 (m, 2H, PhP), 7.6 (m, 1H, PhP), 7.5 (m, 2H, PhP), 7.3 (m, 10H, PhC), 5.0 (d, 2H, $^2J_{HP}$ 3.3, CHBr); δ_C ($CDCl_3$), 141.2 (d, $^1J_{CP}$ 12.4, C_{ipso}-PhP), 135.1 (d, $^2J_{CP}$ 10.2, PhC=C), 133.6 (Ar), 131.1 (d, $^2J_{CP}$ 8.8, C_{ortho}-PhP), 129.2 (Ar), 127(Ar), 45 (d, $^1J_{CP}$ 70.1, CHBr); δ_P ($CDCl_3$) 28.9; MS *m*/*z* 490/488/486 (1:2:1) [M^+], 409/407 (1:1) [$M - Br^+$], 328 [$M - Br_2^+$]; (ii) *cis,trans*-2,5-dibromo-1,3,4-triphenyl-2,5-dihydrophosphole 1-oxide **10** (0.25 g) as a gum (Found: C, 54.1; H, 3.2%. $C_{22}H_{17}Br_2OP$ requires C, 54.1; H, 3.5%); δ_H ($CDCl_3$) 7.9 (m, 2H, PhP), 7.6 (m, 1H, PhP), 7.5 (m, 2H, PhP), 7.2 (m, 6H, PhC), 7.1 (m, 4H, PhC), 5.5 (d, $^2J_{HP}$ 10.7, CHBr), 5.2 (s, 1H, CHBr); δ_C ($CDCl_3$) 139.8 (d, $^1J_{CP}$ 11.9, C_{ipso}-PhP), 134.9 (d, $^2J_{CP}$ 9, PhC=C), 134.4 (d, $^2J_{CP}$ 9, PhC=C), 133.7 (C_{ortho}-PhC), 132.1 (d, $^2J_{CP}$ 8.8, C_{ortho}-PhP), 128.9 (Ar), 127.8 (C_{ipso}-PhC), 46.3 (d, $^1J_{CP}$ 65.6, CHBr), 45.3 (d, $^1J_{CP}$ 67.3, CHBr); δ_P ($CDCl_3$) 28.9 (m); MS *m*/*z* 490/488/486 (1:2:1) [M^+], 409/407 (1:1) [$M - Br^+$], 328 [$M - Br_2$]; and (iii) 2,5-dibromo-1,3,4-triphenylphosphole 1-oxide **11** (0.26 g), mp 210 °C (decomp.) (Found: C, 54.1; H, 3.3%. $C_{22}H_{15}Br_2OP$ requires C, 54.4; H, 3.1%); δ_H ($CDCl_3$) 8.0–7.9 (m, 2H, PhP), 7.7–7.6 (m, 1H, PhP), 7.6–7.5 (m, 2H, PhP), 7.3–7.2 (m, 6H, PhC), 7.1–7.0 (m, 4H, PhC); δ_C ($CDCl_3$) 153.2 (d, $^2J_{CP}$ 26, PhC=C), 133.5 (PhP), 133 (d, $^1J_{CP}$ 11.9, C_{ipso}-PhP), 131.4 (d, $^2J_{CP}$ 10.5, C_{ortho}-Ph-P), 129.1 (Ar), 128.9 (C_{meta}-PhC), 124.4 (d, $^1J_{CP}$ 110.2, C_{ipso}-PhP), 115.3 (d, $^1J_{CP}$ 102.3, CBr); δ_P ($CDCl_3$), 32.4 (m); MS *m*/*z* 488/486/484 (1:2:1) [M^+], 407/405 (1:1) [$M - Br^+$].

X-Ray data for compound 11.‡ Empirical formula: $C_{22}H_{15}Br_2OP$. $M = 486.13$. Crystal system orthorhombic, unit cell dimensions $a = 12.6240$ Å, $b = 24.696$ Å, $c = 6.000$ Å, $V = 1870$ Å^3, $Z = 4$, $D_c = 1.726$ mg m^{-3}, $\mu = 4.428$ mm^{-1}. Crystal size $0.50 \times 0.14 \times 0.10$ mm. $F(000)$ 960. θ range for data collection 1.65 to 26.34°. Index ranges $-15 \le h \le 15$, $-29 \le k \le 27$, $-7 \le l \le 7$. Reflections collected 11014. Independent reflections 3417 [R(int) = 0.422]. Refinement method full matrix least squares on F^2. Data/restraints/parameters 3417/0/235. Goodness of fit on F^2 1.069. Final R indices [$I > 2E(I)$]. $R_1 = 0.0366$, $wR_2 = 0.0821$. R indices all data $R_1 = 0.0422$, $wR_2 = 0.0821$. $w = [E^2(F_o^2) + (0.037P)^2 + 0.74P]$. $P = (F_0^2 = 2F_c^2)/3$. Flack parameter 0.008. Largest diff. peak and hole 0.331 and −0.461 e Å^{-3}.

Synthesis of 2-bromo-1,3,4-triphenyl-2,5-dihydrophosphole 1-oxide 12

Reaction of **6** (95.0 g, 15 mmol) with *N*-bromosuccinimide (2.7 g, 15 mmol) and benzoyl peroxide (0.15 g) as above afforded a mixture of four products and some unreacted starting material. The mixture was separated by column chromatography into two fractions using toluene–ethyl acetate (2:5) as eluant. The first fraction (2.5 g) was shown to be a mixture of **9**, **10** and **11** above, the second fraction was shown to be a mixture of starting material and a new component. This fraction was re-separated using toluene–ethyl acetate (1:3) as eluant to give unreacted starting material (0.6 g) and 2-bromo-1,3,4-triphenyl-2,5-dihydrophosphole 1-oxide **12** (2.0 g, 33%) as gum; (Found: C, 46.4; H, 4.2%. $C_{22}H_{18}BrOP$ requires C, 46.6; H, 4.4%); δ_H ($CDCl_3$) 7.9–7.8 (m, 2H, PhP), 7.6–7.5 (m, 3H, Ph-P), 7.3–7.1 (m, 10H, PhC), 5.0 (d, $^2J_{HP}$ 3.7, 1H, CHBr), 3.8–3.1(m, 2H, CH_2); δ_C ($CDCl_3$) 138.9 (C_{ipso}-PhP), 137.6 (d, $^2J_{CP}$ 14.1, PhP), 136.4 (d, $^2J_{CP}$ 11.3, Ph-P), 129.1, 135.8 (d, $^3J_{CP}$ 9, C_{ipso}-PhC), 133 (Ar), 130.7 (d, $^2J_{CP}$ 8.5, PhP), 129.4 (Ar), 128.7 (Ar), 128.5 (Ar), 50.9 (d, $^1J_{CP}$ 69, CHBr), 35.3 (d, $^1J_{CP}$ 68.4, CH_2); δ_P ($CDCl_3$), 41.5; MS *m*/*z* 410/408 (1:1) [M^+], 328 [$M - Br^+$].

Synthesis of *trans*,*trans*-2,5-dibromo-1,3,4-triphenyl-2,5-dihydrophosphole 1-sulfide 13

The phospholene oxide **9** (0.7 g, 1.43 mmol) and phosphorus pentasulfide (0.32 g, 0.73 mmol) were refluxed together in toluene–dichloromethane (50 cm^3, 1:1) for 5 h. The mixture was filtered through Celite and the solvents evaporated to yield, as a single component by TLC analysis, *trans*,*trans*-2,5-dibromo-1,3,4-triphenyl-2,5-dibromophosphole-1-sulfide **13** (0.72 g, 99%) as a gum (Found mass 501.913224. Required mass ($C_{22}H_{17}{}^{79}Br_2PS$) 501.915533); δ_H ($CDCl_3$) 8.0 (m, 2H, PhP), 7.6 (m, 1H, PhP), 7.5 (m, 2H, Ph-P), 7.3 (m, 10H, PhC), 5.2 (d, 2H, $^2J_{HP}$ 2.2, CHBr); δ_C ($CDCl_3$) 142.3 (d, $^2J_{CP}$ 9, PhC=C), 135.2 (d, $^1J_{CP}$ 8.5, C_{ipso}-PhP), 133.1 (C_{ortho}-Ph-C), 131.5 (d, $^2J_{CP}$ 9.6, C_{ortho}-PhP), 129.8 (C_{ipso}-PhC), 129.2 (Ar), 51.3 (d, $^1J_{CP}$ 50.9, CHBr); δ_P ($CDCl_3$) 56.5; MS *m*/*z* 506/504/502 (1:2:1) [M^+], 425/423 (1:1) [$M - Br^+$], 344 [$M - Br_2^+$].

Synthesis of *cis*,*trans*-2,5-dibromo-1,3,4-triphenyl-2,5-dihydrophosphole 1-sulfide 14

In the same way as above, except that reflux was only necessary for 90 min, the phospholene oxide **10** (0.8 g) afforded *cis*,*trans*-2,5-dibromo-1,3,4-triphenyl-2,5-dihydrophosphole 1-sulfide **14** (0.75 g) as a gum (Found mass 501.91438. Required mass ($C_{22}H_{17}{}^{79}Br_2PS$) 501.915533); δ_H ($CDCl_3$), 8.2 (m, 2H, PhP), 7.6 (m, 3H, PhP), 7.3 (m, 10H, PhC), 5.5 (d, 2H, $^2J_{HP}$ 6.9, CHBr), 5.4 (s, 1H, CHBr); δ_C ($CDCl_3$), 140.8 (d, $^1J_{CP}$ 9, C_{ipso}-PhP), 135.2 (d, $^2J_{CP}$ 8.5, PhC=C), 134.6 (d, $^2J_{CP}$ 8.5, PhC=C), 133.3 (C_{ortho}-Ph-C), 132.4 (d, $^2J_{CP}$ 9.6, C_{ortho}-PhP), 129.2 (C_{ipso}-PhC), 128.9 (Ar), 52.4 (d, $^1J_{CP}$ 58, CHBr), 51.8 (d, $^1J_{CP}$ 50.9, CHBr); δ_P ($CDCl_3$) 62; MS *m*/*z* 506/504/502 (1:2:1) [M^+], 425/423 (1:1) [$M - Br^+$], 344 [$M - Br_2^+$].

Synthesis of 2-bromo-1,3,4-triphenylphosphole 1-sulfide 16

To the phospholene sulfide **13** (0.8 g, 1.58 mmol) in DCM (15 cm^3) KOH (0.18 g, 3.17 mmol) in methanol (4 cm^3) was added dropwise over 20 min. The mixture was stirred for a further 30 min (in a similar experiment for 4 h with **14**) and then water (10 cm^3) was added. The organic layer and the DCM extracts of the aqueous layer (6×10 cm^3) were combined, dried ($MgSO_4$) and the solvent removed to leave a pale yellow solid which on recrystallisation from methanol–ether afforded 2-bromo-1,3,4-triphenylphosphole 1-sulfide **16** (0.57 g, 85%) mp 155 °C (decomp.) (Found: C, 62.2; H, 3.9%. $C_{22}H_{16}BrPS$ requires C, 62.4; H, 3.8%); δ_H ($CDCl_3$) 8.0–7.9 (m, 2H, PhP), 7.6–7.5 (m, 3H, PhP), 7.3–7.0 (m, 10H, PhC), 6.6 (d, 1H, $^2J_{HP}$ 28.7, CH=C); δ_C ($CDCl_3$) 157.2 (d, $^1J_{CP}$ 12.4, PhP), 150.3 (d, $^2J_{CP}$ 12.4, Ph-P), 135.2 (d, $^3J_{CP}$ 11.9, PhP), 133.6 (d, $^3J_{CP}$ 12.4, Ph-C), 130.9 (d, $^2J_{CP}$ 11.9, Ph-C), 129.3 (Ar), 128.4 (Ar), 128.1 (Ar), 125.3 (d, $^1J_{CP}$ 65.5, C5), 124.3 (d, $^1J_{CP}$ 83.6, CBr); δ_P ($CDCl_3$) 51.3; MS *m*/*z* 424/422 (1:1) [M^+], 390 [$M - S^+$] (Found mass 501.91438. Required mass ($C_{22}H_{17}{}^{79}Br_2PS$) 501.915533).

Synthesis of 1,3,4-triphenylphosphole 1-oxide

2-Bromo-1,3,4-triphenyl-2,5-dihydrophosphole 1-oxide **12** (0.5 g, 1.22 mmol) in DCM (10 cm^3) was refluxed with KOH (0.14 g, 2.44 mmol) in methanol (4 cm^3) for 5 h. The mixture was treated with 0.5 M HCl (5 cm^3) and the organic layer and the combined DCM extracts of the aqueous layer (6×10 cm^3) were dried ($MgSO_4$). The solvent was removed to yield a pale yellow solid which was purified by column chromatography using toluene–ethyl acetate (1:3) as eluant to give 1,3,4-triphenylphosphole 1-oxide (0.32 g, 79%), mp 165 °C (decomp.) (Found: C, 80.3; H, 5.4%. $C_{22}H_{17}PO$ requires C, 80.5; H, 5.2%); δ_H ($CDCl_3$) 7.5–7.4 (m, 2H, PhP), 7.3 (m, 3 H, PhP), 7.2–7.1 (m,

‡ CCDC reference number 207/422. See http://www.rsc.org/suppdata/p1/b0/b000692k/ for crystallographic files in .cif format and tables of crystal data, structure refinement, atomic coordinates, bond lengths and angles.

10H, PhC), 7 (d, 2H, $^2J_{HP}$ 36.4, CH=C); δ_C ($CDCl_3$) 152 (d, $^2J_{CP}$ 8.5, PhC=C), 138.4 (d, $^3J_{CP}$ 4, Ph-C), 134.4 (Ar), 133.9 (d, $^2J_{CP}$ 19.2, PhP), 130.5 (d, $^3J_{CP}$ 10.2, Ph-P), 129.5 (Ar), 128.8 (Ar), 128.4 (Ar), 128 (Ar), 127.3 (Ar), 125.3 (d, $^1J_{CP}$ 97.2, CH=C); δ_P ($CDCl_3$) 5.0 (Found mass 312.10663. Required mass ($C_{22}H_{17}P$) 312.10679).

Synthesis of 2-bromo-1,3,4-triphenylphosphole 17

2-Bromo-1,3,4-triphenylphosphole 1-sulfide **16** (1.0 g, 2.36 mmol) and tris(2-cyanoethyl)phosphine (2 g) in dry toluene (45 cm^3) were refluxed for 6 h and then the cooled mixture was allowed to stand overnight at room temperature. The mixture was filtered through Celite and the solvent evaporated to yield a pale yellow solid which was purified by column chromatography on silica using hexane–ethyl acetate (4:1) as eluant to afford 2-bromo-1,3,4-triphenylphosphole **17** (0.8 g, 86%), mp 165–170 °C (decomp.) (Found: C, 67.2; H, 4.2%. $C_{22}H_{16}BrP$ requires C, 67.5; H, 4.1%); δ_H ($CDCl_3$) 8.0–7.9 (m, 2H, PhP), 7.6–7.5 (m, 3H, PhP), 7.4–7.1 (m, 10H, PhC), 6.9 (d, 1H, $^2J_{HP}$ 36.8, CH=C); δ_P ($CDCl_3$) 15.9.

Synthesis of 2,5-dibromo-1,3,4-triphenylphosphole 18

Pyridine (5.0 cm^3, 61.7 mmol) in DCM (30 cm^3) was slowly added to a solution of trichlorosilane (2.9 cm^3, 28.3 mmol) in DCM (20 cm^3) under nitrogen at 0 °C. The white suspension was stirred for a further 30 min and then 2,5-dibromo-1,3,4-triphenylphosphole oxide **11** in DCM (30 cm^3) was added dropwise over 30 min at 0 °C. After the addition was complete the mixture was refluxed for 3 h, cooled and poured into saturated sodium bicarbonate containing ice. The suspension formed was filtered through Celite, the filtrate extracted with DCM (4 × 30 cm^3) and the combined extracts and DCM washings (100 cm^3) of the Celite were dried ($MgSO_4$). The solvent was evaporated to give a yellow solid which was purified by column chromatography under nitrogen using hexane–ethyl acetate (4:1) as eluant to yield 2,5-dibromo-1,3,4-triphenylphosphole **18** (1.9 g), mp 170 °C (decomp.) (Found: C, 56.5; H, 3.3%. $C_{22}H_{15}Br_2P$ requires C, 56.2; H, 3.2%); δ_H ($CDCl_3$) 7.6 (m, 2H, PhP), 7.5 (m, 3H, PhP), 7.3–7.1 (m, 10H, PhC); δ_C ($CDCl_3$) 150.8 (d, $^2J_{CP}$ 7.9, C=CPh), 135.6 (Ar), 134.3 (d, $^1J_{CP}$ 20.91, Ph-P), 131.1 (Ar), 129.7 (Ar), 129.4 (d, $^2J_{CP}$ 8.5, Ph-P), 128.3 (d, $^2J_{CP}$ 13.6, Ph-P), 128 (Ar), 127.9 (Ar), 124.2 (d, $^1J_{CP}$ 20.9, CBr); δ_P ($CDCl_3$) 22.4 (Found mass 467.929923. Required mass ($C_{22}H_{15}{}^{79}Br_2P$). 467.927811).

Synthesis of 1,3,4-triphenylphosphole 21

1,3,4-Triphenylphosphole 1-oxide (0.88 g, 2.68 mmol) was reacted with trichlorosilane (0.69 cm^3, 8.58 mmol) as described above to yield 1,3,4-triphenylphosphole **21** (0.42 g, 50%) mp 155–160 °C (decomp.) (Found: C, 84.4; H, 5.8%. $C_{22}H_{17}P$ requires C, 84.6; H, 5.5%); δ_H ($CDCl_3$) 7.5–7.4 (m, 2H, PhP), 7.3 (m, 3H, PhP), 7.2–7.1 (m, 10H, PhC), 7 (d, 2H, $^2J_{HP}$ 28.7, CH=C); δ_C ($CDCl_3$) 152 (d, $^2J_{CP}$ 8.5, PhP), 138.4 (d, $^3J_{CP}$ 4, PhC), 134.4 (Ar), 133.9 (d, $^2J_{CP}$ 19.2, Ar), 130.5 (d, $^1J_{CP}$ 10.2, Ar), 129.5 (Ar), 128.8 (Ar), 128 (Ar), 127.3 (Ar) 125.3 (d, $^1J_{CP}$ 97.2), 124.3; δ_P ($CDCl_3$) 5.0; MS *m/z* 312 [M^+].

Reaction of 2,5-dibromo-1,3,4-triphenyl-2,5-dihydrophosphole 1-oxides 9 and 10 with potassium hydroxide in methanol

To a mixture of the dihydrophosphole oxides **9** and **10** (0.8 g) in DCM (15 cm^3) was added KOH (0.18 g) in methanol dropwise over 20 min. The mixture was stirred at 18 °C for a further 30 min, water (10 cm^3) was added and the aqueous layer extracted with DCM (6 × 10 cm^3). The combined organic layer and the DCM extracts were dried ($MgSO_4$) and the solvent evaporated to yield a gummy white solid purified by column chromatography on silica using hexane–ethyl acetate (4:1) as eluant to yield (i) 2-bromo-5-methoxy-1,3,4-triphenyl-2,5-dihydrophosphole 1-oxide **19** (0.6 g) as a gum (Found: C, 62.6; H, 4.4%. $C_{23}H_{20}BrO_2P$ requires C, 62.9; H, 4.6%) δ_H ($CDCl_3$) 7.9–7.8 (m, 2H, PhP), 7.5–7.3 (m, 3H, PhP), 7.2–7.00 (m, 10H, PhC), 6.8 (s, 1H, CHBr), 6.5 (d, 1H, $^2J_{HP}$ 13.6, CHOMe), 3.7 (d, $^4J_{HP}$ 10.9, 3H, OMe); δ_P ($CDCl_3$) 31.5; MS *m/z* 359 [M^+], and (ii) 2-bromo-1,3,4,-triphenylphosphole 3-oxide (0.1 g) **20** see below.

Preparation of 2-bromo-1,3,4-triphenylphosphole-3-oxide 20

To a mixture of the dibromophopholene oxides **9** and **10** (3 g) in DCM (50 cm^3) at 0 °C was added KOH (0.68 g) in methanol (10 cm^3) over 30 min at such a rate to maintain the temperature at 0 °C. The mixture was stirred at 0 °C for a further 4 h and was then worked up as above to yield a mixture of largely one product with traces of **19** and unreacted starting material as indicated by ^{31}P NMR spectroscopy. The mixture was purified by column chromatography to remove the minor impurities to afford 2-bromo-1,3,4-triphenylphosphole 1-oxide (1.9 g) as a gummy solid (Found: C, 64.7; H, 3.7%. $C_{22}H_{16}BrOP$ requires C, 64.9; H, 4.0%); δ_H ($CDCl_3$) 7.9–7.8 (m, 2H, Ar), 7.6–7.5 (m, 3H, Ar), 7.2–7.0 (m, 10H, Ar), 6.5 (d, 1H, $^2J_{HP}$ 27.6, CH=); δ_C ($CDCl_3$) 155.2 (d, $^1J_{CP}$ 12.4, PhP), 149.3 (d, $^2J_{CP}$ 12.4, Ph-P), 135.4 (d, $^3J_{CP}$ 11.9, PhP), 135.7 (d, $^3J_{CP}$ 12.4, Ph-C), 130.4 (d, $^2J_{CP}$ 11.9, Ph-C), 129.3 (Ar), 128.6 (Ar), 127.8 (Ar), 125.6 (d, $^1J_{CP}$ 65,5, C5), 124.1 (d, $^1J_{CP}$ 83.6, CBr); δ_P ($CDCl_3$) 36.9; MS *m/z* 407/405 [M^+].

A general method for the preparation of 5-bromo-2-lithio-1,3,4-triphenylphosphole 22

The dibromophosphole **18** (1.0 g, 2.13 mmol) was dissolved in THF–ether (2:1, 45 cm^3) in a nitrogen atmosphere. The mixture was cooled to −100 °C using a liquid nitrogen–ethanol slush bath. *N*-Butyllithium (1.09 cm^3, 1.89 M in hexanes) pre-cooled to −78 °C was added dropwise with stirring and the mixture stirred for 45 min at −100 °C. This solution was then used for further reactions.

Temperature effects on the solutions of 5-bromo-2-lithio-1,3,4-triphenylphosphole. A solution of the lithium reagent prepared above was taken. After the stirring for 45 min stage, a sample (2 cm^3) was hydrolysed with 3 M HCl (0.5 cm^3) and diluted with DCM (3 cm^3). The organic layer was washed with water (2 × 2 cm^3), dried ($MgSO_4$) and the solvent evaporated. The residue was examined by ^{31}P NMR spectroscopy. This procedure was repeated with the solution at −75, −40 and +20 °C. The results we obtained are shown in Table 2 together with those using different organometallic reagents.

Preparation of 1,3,4-triphenylphosphole-2-carbaldehyde 23

The lithium reagent from the bromophosphole **17** (0.25 g) at −100 °C was treated with *N*-methylformanilide (0.09 cm^3) in THF (3 cm^3), the mixture was stirred for 30 min and then worked up by hydrolysis with 3 M HCl and extraction with DCM (4 × 5 cm^3) the combined organic layers were dried (MgSO4) and the solvent evaporated to yield a mixture (0.3 g) which was separated by column chromatography to yield triphenylphosphole **21** (0.1 g) identical with an authentic specimen and 1,3,4-triphenylphosphole-2-carbaldehyde **23** (0.15 g), mp decomposed above 165 °C; δ_H ($CDCl_3$) 9.6 (d, 1H, $^3J_{HP}$ 13.3, CHO), 7.9–7.2 (m, 15H, Ar), 7.0–6.9 (d, 1H, $^2J_{HP}$ 39.1, CH=); δ_P ($CDCl_3$) 6.8 (Found mass 340.10168, required mass ($C_{23}H_{17}OP$) 349.10170).

Preparation of 5-bromo-1,3,4-triphenylphosphole-2-carbaldehyde 24

The lithium reagent **22** from the dibromophosphole **18** (0.97 g, 2.06 mmol) was treated with *N*-methylformanilide (0.25 cm^3, 2.06 mmol) at −100 °C and the mixture stirred for 7 h at this temperature. Work up as above afforded a pale yellow solid (0.35 g) which was purified by column chromatography under

nitrogen using ethyl acetate–hexane (1:6) as eluant to yield 5-bromo-1,3,4-triphenylphosphole-2-carbaldehyde **24** (0.28 g), mp decomposed above 170 °C (Found C, 65.6; H, 3.7%. $C_{23}H_{16}BrOP$ requires C, 65.9; H, 3.9%); δ_H ($CDCl_3$) 9.5 (d, 1H, $^3J_{HP}$ 12.5, CHO), 7.6–7.5 (m, 2H, Ar), 7.5–7.4 (m, 3H, Ar), 7.3–7.1, (m, 10H, Ar); δ_C ($CDCl_3$) 188.2 (d, 1H, $^2J_{HP}$ 13.0, CHO), 162.5 (d, $^2J_{HP}$ 10.2, Ar), 151.1 (d, $^2J_{HP}$ 6.8, Ar), 146.1 (d, $^3J_{HP}$ 6.7, Ar), 140.8 (d, $^1J_{CP}$ 15.8, C-CHO), 137 (d, $^1J_{CP}$ 17, CBr), 130 (Ar), 128 (Ar), 127.5 (Ar); δ_P ($CDCl_3$) 16.4 (Found mass 418.01252, required mass ($C_{23}H_{16}BrOP$) 418.01222).

Reaction of 22 with propanal

The lithium reagent **22** from the dibromophosphole **18** (0.5 g, 1.05 mmol) was reacted as above with propanal (0.08 cm^3, 1.05 mmol) in ether (5 cm^3) and the mixture stirred for 5 h at −100 °C. After work up as above a mixture of an oil (0.3 g) of the two diastereoisomeric pairs of 1-(5-bromo-1,3,4-triphenylphosphol-2-yl)propan-1-ol **25** in the ratio 62:38 was obtained. Attempts to purify this mixture failed due to the ready dehydration to the alkene **26**. Spectral details of **25**: δ_H ($CDCl_3$) 7.7–7.6 (m, 2H, Ar), 7.5–7.4 (m, 3H, Ar), 7.0 (m, 10H, Ar), 4.5 (m, 1H, CHOH) 2.0 (m, 2H, CH_2 minor isomer), 1.8 (2H, CH_2 major isomer), 0.9 (t, 3H, $^3J_{HH}$ 7.4, CH_3 major isomer), 0.6 (t, 3H, $^3J_{HH}$ 7.4, CH_3 minor isomer); δ_P ($CDCl_3$) 12.4 (62%), 12.7 (38%); MS *m/z* 449 $[M]^+$, 431 $[M - H_2O]^+$.

The alcohol **25** (0.2 g) was passed down a silica column using ethyl acetate–hexane (1:6) as eluant to afford 1-(5-bromo-1,3,4-triphenylphosphol-2-yl)propene **26** (0.1 g) as an oil which polymerised on heating, δ_H ($CDCl_3$) 7.6–7.5 (m, 2H, Ar), 7.4–7.3 (m, 3H, Ar), 7.2–7.0 (m, 10H, Ar), 6.3 (m, 1H, $^3J_{HP}$ 15.1, $^2J_{HH}$ 1.8, $^3J_{HH}$ 0.7, CH), 5.9 (m, $^2J_{HH}$ 1.8, $^2J_{HH}$ 6.6, CH), 1.6 (dq, $^2J_{HH}$ 0.7, $^3J_{HH}$ 6.6, CH_3); δ_P ($CDCl_3$) 14.4 (Found mass 430.04854. Required mass ($C_{25}H_{20}BrP$) 430.04860).

Reaction of 22 with iodine

A solution of **22** from the dibromophosphole **18** (1.0 g, 2.13 mmol) was treated at −100 °C with iodine (0.28 g, 2.2 mmol) in ether (5 cm^3) for 30 min. The mixture was worked up as above to afford a pale yellow solid (0.95 g) which was shown to be an inseparable mixture by GC and GC/MS of 2-bromo-5-iodo-1,3,4-triphenylphosphole **27** (905) and 2-bromo-1,3,4-triphenylphosphole (10%). Found for **27**: MS *m/z* 518/516 $[M]^+$, 390/392 (1:1) $[M - I]^+$; δ_P ($CDCl_3$) 32.8. This mixture could be used for copper assisted reactions (see below).

Reaction of 22 with dichlorophenylphosphine

The lithiocompound **22** from the dibromophosphole **18** (1.0 g, 2.13 mmol) was reacted with dichlorophenylphosphine (0.14 cm^3, 1.07 mmol) in ether and the mixture stirred at −100 °C for 6 h. Work up as above yielded a yellow solid (0.45 g) shown by TLC to be a mixture of a major and minor components. Separation of the mixture by column chromatography ethyl acetate–hexane (1:1) as eluant afforded (i) bromo(5-bromo-1,3,5-triphenylphosphol-2-yl)phenylphosphine **28** (0.38 g), mp decomposed at 175 °C; δ_H ($CDCl_3$) 7.6–7.0 (m, 20H, Ar); δ_P ($CDCl_3$) 27.5 (d, J_{PP} 61), 25.1 (d, J_{PP} 61); MS *m/z* 580/578/576 1:2:1 $[M]^+$ (Found mass 575.94068. Required mass ($C_{28}H_{20}Br_2P$) 575.94070) and (ii) an unidentified product (0.08 g).

Preparation of 1,2-bis(5-bromo-1,3,4-triphenylphosphol-2-yl)-ethene 29

Titanium tetrachloride (0.24 cm^3, 2.15 mmol) was added dropwise over 20 min to a suspension of zinc powder (0.28 g, 4.29 mmol) in THF (7 cm^3) at 0 °C. When the addition was complete the mixture was heated at reflux for 2 h, cooled to rt and the aldehyde **24** (0.60 g, 1.43 mmol) in THF (25 cm^3) was added dropwise. The mixture was then refluxed for a further 3 h then cooled and poured into 10% aqueous potassium carbonate solution. The resulting suspension was continuously extracted with ether for 40 h. The ether extract was dried ($MgSO_4$) and the solvent removed to leave an orange solid. The solid was washed several time with ice cold ether to yield a mixture of diastereoisomers of (*E*)-1,2-bis(5-bromo-1,3,4-triphenylphosphol-2-yl)ethene **29** (0.41 g) mp >300 °C (Found: C, 68.3; H, 4.2%. $C_{46}H_{32}Br_2P_2$ requires C, 68.6; H, 4.00%); δ_H ($CDCl_3$) 7.6–7.2 (m, 30H + 30H major and minor isomers, Ar), 6.8 (d, 2H, minor $^3J_{HP}$ 6.6, CH=CH), 6.6 (d, 2H, $^3J_{HP}$ 7, CH=CH); δ_P ($CDCl_3$) 14.3 (major isomer), 14.2 (minor isomer); MS *m/z* 804/806/808 (1:2:1) $[M]^+$ (Found mass 804.03328. Required mass ($C_{46}H_{32}Br_2P_2$) 804.034600.

Preparation of 1,2-bis(5-bromo-3,4-dimethyl-1-phenylphosphol-2-yl)ethene 30

In the same way as above 2,3-dibromo-3,4-dimethyl-1-phenylphosphole-2-carbaldehyde (1.20 g, 6.10 mmol)[16] was reacted with the McMurry reagent to yield 1,2-bis(5-bromo-3,4-dimethyl-1-phenylphosphol-2-yl)ethene **30** (0.8 g) as a mixture of diastereoisomers, mp decomposed 200 °C (Found: C, 55.6; H, 4.1%. $C_{26}H_{24}Br_2P_2$ requires C, 55.9; H, 4.3%); δ_H ($CDCl_3$) 7.8–7.2 (m, 10H, Ar) 6.8 (d, 2H $^3J_{HP}$ 12.1, CH=CH minor isomer), 6.7 (d, 2H, $^3J_{HP}$ 13.2, CH=CH major isomer); δ_P ($CDCl_3$) −2.4 (major), −2.6 (minor); MS *m/z* (1:2:1) 558/556/554 $[M]^+$.

Preparation of bi(5-bromo-1,3,4-triphenylphosphol-2-yl) 31

Copper(II) chloride was added to a stirred solution of **22** from the dibromophosphole **18** in THF at −100 °C. The mixture was stirred for 5 h and worked up as above to yield a mixture of three compounds (0.6 g), one of which was starting material. Separation by column chromatography using ethyl acetate–hexane 1:1 as eluant afforded (i) bi(5-bromo-1,3,4-triphenylphosphol-2-yl) **31** (0.25 g), mp >250 °C (Found: C, 67.5; H, 3.6%. $C_{44}H_{30}Br_2P_2$ requires C, 67.7; H, 3.9%); δ_H ($CDCl_3$) 7.9–7.2 (m, Ar); δ_P ($CDCl_3$) 26.9; MS *m/z* 782/780/778 (1:2:1) $[M]^+$, and (ii) bi(1,3,4-triphenylphosphol-2-yl) **32** (0.15 g), mp >250 °C; δ_H ($CDCl_3$) 7.9–7.0 (m, 36H, Ar), 6.9 (d, 2H, $^2J_{HP}$ 38.7, CH=); δ_P ($CDCl_3$) 20.9 (Found mass 622.19688. Required mass ($C_{44}H_{32}P_2$) 622.19792).

Reaction of phosphole 18 with copper(I) cyanide

A mixture of the dibromophosphole **18** (1.0 g, 2.13 mmol) and copper(I) cyanide (0.42 g, 4.69 mmol) in dry DMF (35 cm^3) was heated at reflux for 6 h. The mixture was poured into ferric chloride solution in 3 M HCl (10 cm^3) and the mixture warmed for 30 min. The aqueous layer was extracted with toluene (3 × 30 cm^3), the combined extracts were dried ($MgSO_4$) and the toluene evaporated to yield a pasty solid (0.4 g) shown by TLC to be three components. The mixture was separated by column chromatography to yield (i) **31** (0.15 g), (ii) **32** (0.07 g), and (iii) 5-bromo-1,3,4-triphenylphosphole-2-nitrile **33** (0.02 g); δ_H ($CDCl_3$) 7.8–7.1 (m, Ar); δ_P ($CDCl_3$) 26.7; MS *m/z* 417/415 (1:1) $[M]^+$.

References

1 F. Mathey, *Chem. Rev.*, 1988, **88**, 429.
2 F. C. Leavitt, T. A. Manuel and F. Johnson, *J. Am. Chem. Soc.*, 1959, **81**, 3163; E. H. Braye and W. Hubel, *Chem. Ind.* (*London*), 1959, 1250.
3 F. Mathey, *Phosphorus*, *Sulfur*, 1994, **87**, 139.
4 F. B. Clarke and F. H. Westheimer, *J. Am. Chem. Soc.*, 1971, **93**, 4591.
5 L. D. Quin, E. Middlemas, N. S. Rao, R. W. Miller and A. J. McPhail, *J. Am. Chem. Soc.*, 1982, **104**, 2912.
6 S. Nakayama, M. Yoshifugi, R. Okazaki and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 546.
7 K. Alder and J. Hayden, *Liebigs Ann. Chem.*, 1950, **570**, 201.
8 R. M. Dodson, V. Srinivasan, K. S. Sharma and R. F. Sauers, *J. Org. Chem.*, 1972, **37**, 2367.

9 R. Brettle and Sa'ad M. Shibil, *J. Chem. Soc.*, *Perkin Trans. 1*, 1981, 2917.
10 A. De Groot, B. Evenhuis and H. Wynberg, *J. Org. Chem.*, 1968, **33**, 2214.
11 R. Vanderesse, Y. Fort, S, Becker and P. Caubere, *Tetrahedron Lett.*, 1986, **27**, 3517.
12 F. T. Luo, S.-L. Fwa and W.-S. Wang, *Tetrahedron Lett.*, 1992, **33**, 3345.
13 Y. Kondo, M. Takaki and R. Asami, *Kobunshi Ronbunshi*, 1989, **46**, 769; *Chem. Abstr.*, 1990, **112**, 139866m. (We thank Professor Kondo for an English translation of this reference.)
14 L. Brandsma and H. Verkruijsse, *Preparative Polar Organometallic Chem.*, Springer-Verlag, Berlin, 1981, 1.
15 E. Deschamps and F. Mathey, *Bull. Soc. Chim. Fr.*, 1992, **129**, 486.
16 E. Deschamps, L. Ricard and F. Mathey, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1158.
17 G. Markel, J. Steigler, P. Kreitmeier, T. Burgermeister, F. Kastner and S. Dove, *Helv. Chim. Acta.*, 1997, **80**, 14.
18 R. M. Kellogg, M. B. Green and H. Wynberg, *J. Org. Chem.*, 1967, **32**, 3993.
19 (*a*) J. M. Klunder and G. H. Posner, in *Comprehensive Organic Synthesis*, eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 3, p. 207; (*b*) D. W. Knight, in *Comprehensive Organic Synthesis*, eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 3, p. 481.