Synthesis and chemistry of 10,11-dihydro-5-phenyl-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxide,† the 5-propyl analogue and related phosphonium salts

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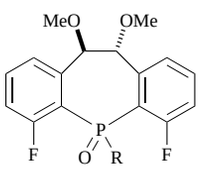
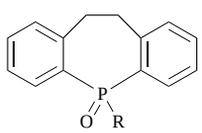
The preparation of the title compounds is greatly improved by combining seven steps (three lithiations, three substitutions and an oxidation) into a one-pot procedure. The hydrolysis of the related phosphonium salts, the lithiation of the *P*-propyl phosphepine oxides and their reaction with electrophiles are described.

Our programme of development[1,2] of dibenzophosphepines such as **1** as chiral auxiliaries based on our diphenylphosphinoyl chemistry[3] required a preliminary study of the synthesis and Horner–Wittig chemistry of simple achiral 10,11-dihydro-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxides such as **2** (R = Ph, Pr). We report full details of this study together with some unexpected results encountered along the way.

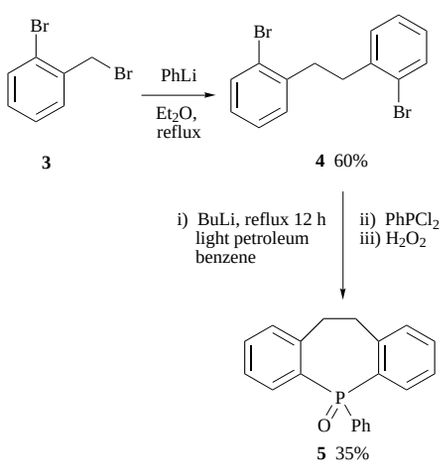


1



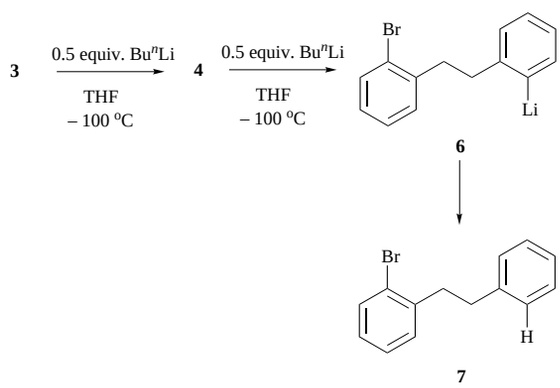
2

The simple phosphepine oxide **2** (R = Ph) has been made several times[4–6] in poor yield by the lithiation of dibromobibenzyl **4**, itself prepared by lithiation of 2-bromobenzyl bromide **3** (Scheme 1). The conversion of **3** into **4** used PhLi in refluxing diethyl ether[7] occurs in 60% yield while the best reported (35% yield by Segall *et al.*[4]) cyclisation to **5** required Bu^{n}Li in boiling benzene prior to the addition of the electrophile.



Scheme 1

Parham *et al.*[8] had meanwhile reported that lithiation of **3** with one equivalent of Bu^{n}Li in THF at −100 °C gave *mono*-bromobibenzyl **7** by further lithiation of **4** (Scheme 2). Half the Bu^{n}Li is needed to lithiate half of the molecules of **3** present by exchange with the benzylic bromide. This lithiated species then reacts with unreacted **3**. The remaining half of Bu^{n}Li lithiates one of the aryl bromides of the coupled product **4** to give **6** which is protonated during work-up.



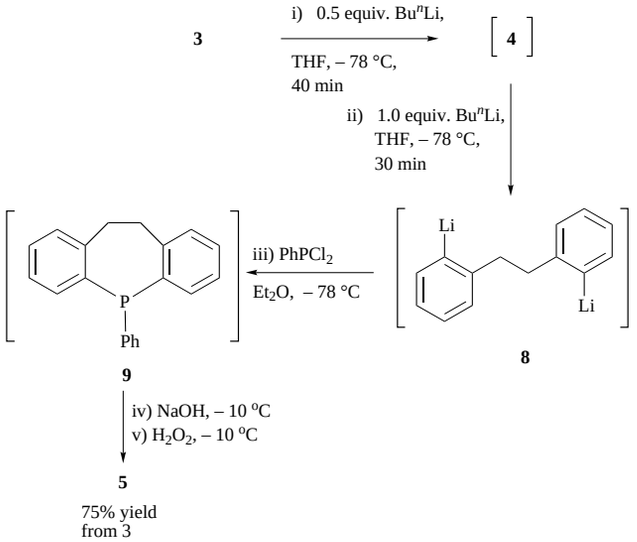
Scheme 2

We reasoned that both lithiation reactions could probably be performed in one pot in THF at −78 °C and that side products in the first lithiation, such as **6**, which would be quenched and removed when **4** is isolated, would be intermediates in the subsequent dilithiation of **4**. Hence telescoping the two lithiations into one pot could enhance the yield—none of **6** would be lost as unwanted **7**. This improvement was remarkably successful. Treatment of **3** with 0.5 equiv. of Bu^{n}Li in THF at −78 °C for 40 min gave **4**. Without isolation this solution was treated with a further 1.0 equiv. of Bu^{n}Li in THF at −78 °C for 30 min to give 2,2′-dilithiobibenzyl which was then quenched with $PhPCl_2$ to give the phosphepine and immediately oxidised to the phosphine oxide **5** (Scheme 3). The best yield in previous preparations had been obtained by Segall *et al.* (21% from **3**)[4] but we obtained a 75% yield in a one-pot process involving a formal seven steps—three bromine–lithium exchanges, one S_N2 reaction at a benzylic position, two nucleophilic substitutions at phosphorus and an oxidation.

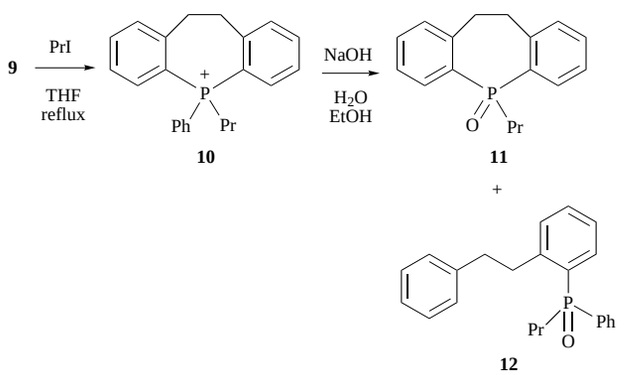
Our normal procedure for making alkyldiphenylphosphine oxides[3] involves the alkaline hydrolysis of alkyltriphenylphosphonium salts. The equivalent here would be the alkylation of the phosphine **9** and the hydrolysis of the resulting phosphonium salt **10** (Scheme 4). Allen *et al.*[9] had already established that such phosphonium salts prefer exocyclic cleavage to give 5-alkylphosphepines rather than endocyclic cleavage to give open chain compounds such as **12**.

We could prepare the phosphine **9** by reduction of the phosphine oxide **5** with trichlorosilane[10] in 77% yield and then the

† Phosphepine was formerly known as phosphepin.



Scheme 3 One-pot synthesis of 10,11-dihydro-5-phenyl-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxide from 2-bromobenzyl bromide



Scheme 4

phosphonium salt **10** in 86% yield. We preferred the procedure of Coumbe *et al.*[11] in which the phosphine oxide **5** is reduced with poly(methylhydrosiloxane) (PMHS) and alkylated without isolation of the intermediate phosphine to give **10** in 88% yield from **5**. In our experience the Coumbe procedure is preferable, providing that the phosphonium salt crystallises during work-up. If isolated phosphine is required, trichlorosilane reduction is to be preferred.

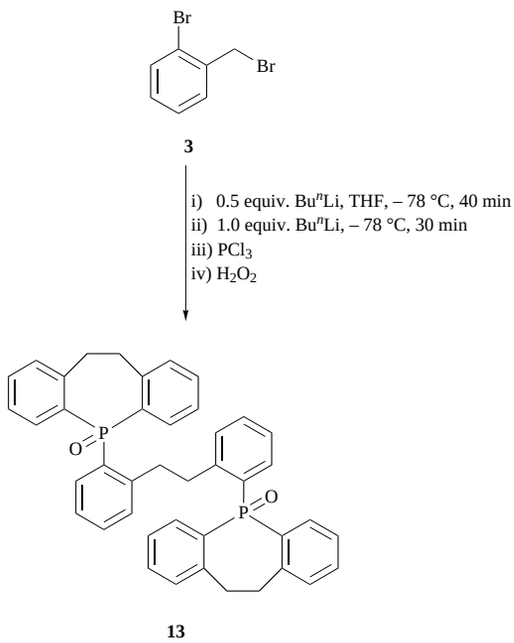
It is worth noting that we preferred to prepare **9** *in situ* from its oxide **5** rather than using **9** obtained initially from the ring closure. This is because phosphine oxide **5**, being air-stable and easy to recrystallise, was easier to purify than **9** as well as being a convenient compound to store.

Hydrolysis of **10** under the conditions of Allen *et al.*[9] gave an 87% yield of the desired phosphine oxide **11** and only a small amount (9%) of ring opened product **12**. These products were easily separated by flash chromatography. This preparation of **11** involves the one-pot formation of the *P*-phenyl compound **5** (a one-pot reduction, alkylation and then hydrolysis) all in good yield (75 × 88 × 87% = 57% overall). We could improve on this by using the direct synthesis shown in Scheme 3 using dichloro(propyl)phosphine (PrPCl$_2$) instead of PhPCl$_2$. This direct route gave 66% overall yield of **11**.

However this route to 5-alkyl dibenzo[*b*,*f*]phosphepine oxides does depend on the rather erratic commercial availability of alkyl dichlorophosphines. We made PrPCl$_2$ from PrMgCl *via* the organozinc reagent[12,13] and PCl$_3$, though this gave only 33% yield of PrPCl$_2$. This dichlorophosphine later became commercially available as are MePCl$_2$ and EtPCl$_2$. Either method (phosphonium salt hydrolysis or dilithiated aryl reaction with PrPCl$_2$) gave the propyl compound **11** on a gram scale. Both phosphepine oxides **5** and **11** have a characteristic AA′BB′ pattern for the diastereotopic pairs of protons in the –CH$_2$CH$_2$– backbone linking the two benzene rings, no doubt as a result of the twisted conformation observable by X-ray crystallography.[14]

Attempts to find an alternative and more general route

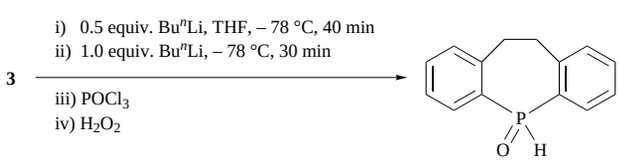
Since PhPCl$_2$ and PrPCl$_2$ reacted cleanly with the dilithiated intermediate **8**, it seemed an obvious extension to use PCl$_3$ and add whatever group was required on the phosphorus atom after ring closure. This reaction led instead to a remarkable new compound, the bis(phosphine oxide) **13** (Scheme 5). Identification came from a FAB mass spectrum and the presence in the proton NMR spectrum of both the characteristic AA′BB′ pattern of the backbone of the phosphepine and a benzylic singlet.



Scheme 5

This compound is formed from no less than six molecules of **3** as well as two of PCl$_3$ (or three molecules of **8** and two of PCl$_3$) and represents a remarkable piece of molecular recognition by small molecules. Approximately eight separate steps are needed to bring the eight molecules of starting material together. Though **13** is never formed in good yield (maximum 34%) it kept cropping up when we tried to use a number of different electrophiles with the dilithiated intermediate **8**.

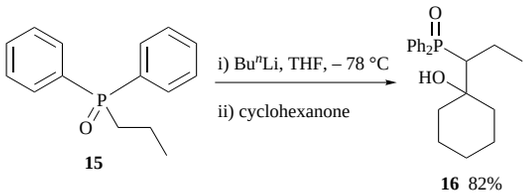
Attempts to use POCl$_3$ in the same way led instead to 2,2′-dichlorobibenzyl and a trace (7%) of the secondary phosphine oxide **14** with a characteristic $^1J_{PH}$ of 484 Hz in the NMR spectrum (Scheme 6). Attempts to use PhPOCl$_2$ or PrPOCl$_2$ gave no useful results.



Scheme 6

Chemistry of lithium derivatives of phosphepines

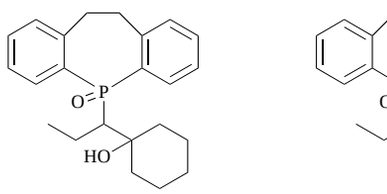
We have made extensive use of the addition of lithiated alkyldiphenylphosphine oxides to carbonyl compounds[3] and it was important to establish how well the seven-membered cyclic analogues performed. We have previously studied the five-membered cyclic analogues, the dibenzophospholes,[15,16] which show some important differences from the simple Ph$_2$PO compounds. We repeated a typical reaction, the addition of prop-

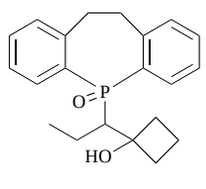


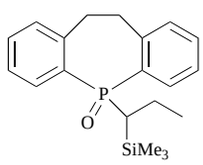
Scheme 7

yldiphenylphosphine oxide **15** to cyclohexanone (Scheme 7), to get a direct comparison without variation in operator's skill. The adduct **16** was formed in 82% yield.

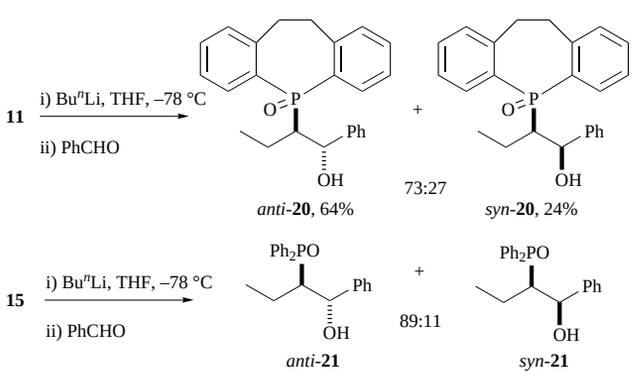
The phosphepine oxide **11** gave, if anything, a slightly higher yield of adduct **17**. With cyclobutanone under the same conditions, adduct **18** was isolated in 62% yield but this could be improved to 73% using our internal quench procedure.[17] An internal quench (*i.e.* Me_3SiCl was added to **11** *followed* by LDA) also gave an excellent yield of the silyl compound **19**.[18]







A direct comparison between the benzaldehyde adducts allowed an assessment of the stereochemical capabilities of the lithiated phosphepine oxides. Adducts **20** were formed in identical yield (88%) but with rather lower selectivity than adducts **21** (Scheme 8). We do not of course suggest that the phosphepine oxides have any advantages over the simple diphenylphosphine oxides—the significant observation is that these results enhance the potential of the chiral analogues[1,2] in asymmetric synthesis simply because phosphepine **11** shows essentially the same chemistry as the acyclic compounds. This work continues.



Scheme 8

Experimental

Flash chromatography[19] was performed using Merck 9385 Kieselgel 60. Thin layer chromatography (TLC) was performed using commercially available glass plates coated with Merck silica Kieselgel $60F_{254}$. High performance liquid chromatography (HPLC) was performed using a Dynamax prepacked silica column (25 cm × 21.4 mm internal diameter) using a Gilson model 303 pump and a Cecil Instruments CE212A UV detector at 254 nm. All solvents were distilled before use. Light petroleum refers to the fraction with bp 40–60 °C. Anhydrous solvents were distilled from $LiAlH_4$ in the case of Et_2O and THF, from CaH_2 in the case of CH_2Cl_2, MeOH, hexane and toluene, and from $CaCl_2$ in the case of CCl_4. Triphenylmethane was used as indicator for THF.

Melting points were determined on a Reichert hot stage microscope and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer.

All NMR instruments used were made by Bruker. Proton, carbon, phosphorus and fluorine NMR spectra were recorded using the AC 250, WM 250 or AM 400 Fourier transform spectrometers, using an internal deuterium lock. Carbon spectra were determined with broad band decoupling and an attached proton test (APT). Signals from carbon atoms with an odd number of attached protons are designated ($^+$) while those with an even number are designated ($^-$). *J* Values are given in Hz.

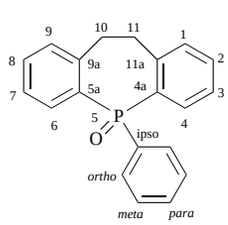
All mass spectra were determined by electron impact (EI) unless otherwise stated. Other methods used were chemical ionisation (Cl) and fast atom bombardment (FAB). All three methods were performed on a Kratos MS890 spectrometer by technical staff. Microanalyses were performed by technical staff using either Carlo Erba 1106 or Perkin-Elmer 240 automatic analysers.

When using *n*-butyllithium, and especially when using *sec*-butyl- or *tert*-butyl-lithium, best results were obtained using Hamilton 1700 series gas-tight Teflon tipped microsyringes (<1000 μl) which did not require lubrication, and Hamilton 1000 series gas-tight Teflon tipped syringes (>1 cm^3) lubricated with poly(dimethylsiloxane) 200® fluid with a viscosity of 100 centistokes.

Key to NMR assignments

The notation used for aromatic protons and carbon assignments is as follows. Aromatic protons are referred to by their ring position followed by '-ArH'. The 'C' in 'ArC' is the numbered carbon within that ring and not a carbon attached to the ring. Carbons outside the ring are italicised when 'Ar' is included in the assignment *e.g.* 129.0^+ ($^4J_{CF}$ 2.3, Ar*C*H). When a carbon nucleus is observed to couple to only one other nucleus then it is not referred to as a doublet. Any greater multiplicity, such as a double doublet, is noted.

Protons and carbons which form part of a phosphepine system are numbered according to the system indicated below. The



exocyclic portion is assigned using the labels ipso, *ortho*, *meta* and *para*. When two *ortho* positions are non-equivalent, *ortho'* is also used and their positions illustrated.

In an instance when a compound contains a heterocyclic portion and an exocyclic ring and it is clear which portion an atom belongs to, but not the exact position, then the labels 'het' and 'exo' are used respectively in the assignment.

When coupling constants refer to the coupling between two protons, or between two unassigned nuclei, then no subscripts follow '*J*'.

General procedure for the medium scale preparation of 2,2′-dilithiobibenzyl 8

2-Bromobenzyl bromide (13.1 g, 52.4 mmol) was dissolved in dry THF (400 cm^3) under argon and cooled to −78 °C. *n*-Butyllithium (13.2 cm^3 of a 2 mol dm^{-3} solution in cyclohexane mixed with 15 cm^3 of dry Et_2O, 26.4 mmol) was added dropwise to the stirred solution over 10 min. At this rate of addition the temperature of the reactants did not exceed −68 °C. After stirring for a further 40 min, the second portion of *n*-butyllithium (29.4 cm^3 of a 2 mol dm^{-3} solution in cyclohexane with 50 cm^3 of dry Et_2O, 58.8 mmol) was added dropwise over 20 min. After stirring for 15 min at −78 °C, the dilithiobibenzyl solution was ready for use.

General procedure for the small scale preparation of 2,2′-dilithiobibenzyl 8

2-Bromobenzyl bromide (2.02 g, 8.08 mmol) was dissolved in dry THF (50 cm^3) under argon and cooled to −78 °C. *n*-Butyllithium (3.00 cm^3 of a 1.5 mol dm^{-3} solution in hexane, 4.50 mmol) was added dropwise to the stirred solution. After stirring for a further 40 min, the second portion of *n*-butyllithium (5.65 cm^3 of a 1.5 mol dm^{-3} solution in hexane, 8.48 mmol) was added dropwise. After stirring for 30 min at −78 °C, the dilithiobibenzyl solution was ready for use.

10,11-Dihydro-5-phenyl-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxide 5

2-Bromobenzyl bromide (13.1 g, 52.4 mmol) was lithiated as above (medium scale method). Dichloro(phenyl)phosphine (4.4 cm^3, 32.4 mmol) dissolved in Et_2O (10 cm^3) was added dropwise over 20 min. At this rate of addition the temperature of the reactants was maintained below −70 °C. Analysis by gas chromatography after 18 min indicated that the reaction was complete. The reaction mixture was allowed to warm. When the temperature had reached −10 °C, NaOH (10 cm^3 of 6 mol dm^{-3} solution) was added to the vigorously stirred mixture followed by H_2O_2 (30 cm^3 of a 30% solution, 0.26 mol). After 35 min, Et_2O (25 cm^3) was added and the reaction mixture washed with brine (3 × 30 cm^3) and concentrated by evaporation under reduced pressure. Any remaining water was removed as an azeotrope with toluene. The residue was purified by flash chromatography, eluting with 3:1 EtOAc–hexane to yield the phosphine oxide (5.94 g, 75%) as prisms, mp 190.5–192.5 °C (from EtOAc) (lit.,[4] 185 °C, from benzene); δ_H(400 MHz; $CDCl_3$) 8.32 (2 H, ddd, $^3J_{PH}$ 12.5, *J* 7.6 and 1.2), 7.51–7.31 (10 H, m), 7.24–7.13 (2 H, m), 3.24–3.17 (2 H, m, $ArCH_AH_BCH_{A'}H_{B'}Ar$) and 3.03–2.96 (2 H, m, $ArCH_AH_B$-$CH_{A'}H_{B'}Ar$); δ_C(100.6 MHz; $CDCl_3$) 143.8$^-$ ($^2J_{PC}$ 11, 9a-ArC), 136.6$^-$ ($^1J_{PC}$ 103, ipso-PhC), 133.5$^+$ (J_{PC} 7), 132.4$^+$ ($^4J_{PC}$ 2, 2-ArC), 131.4$^+$ ($^4J_{PC}$ 3, *p*-PhC), 130.8$^+$ (J_{PC} 11), 130.1$^-$ ($^1J_{PC}$ 100, 4a-ArC), 130.0$^+$ (J_{PC} 12), 128.5$^+$ (J_{PC} 12), 126.3$^+$ (J_{PC} 11) and 34.1$^-$ ($^3J_{PC}$ 2, Ar*C*H). In another experiment, in which phenylphosphonic dichloride [$PhP(O)Cl_2$] was used as the electrophile, the yield was 36%.

10,11-Dihydro-5-propyl-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxide 11

2-Bromobenzyl bromide (2.71 g, 10.8 mmol) was lithiated as above (small scale method). Freshly distilled dichloro(propyl)-phosphine (0.77 cm^3 in 9.2 cm^3 of THF, 5.67 mmol) was added dropwise to the stirred solution at −78 °C. After 2 h at −78 °C, the reaction mixture was allowed to warm to room temperature and stirred overnight. Water (40 μl) was added followed by silica (approx. 1 g) and the solvent evaporated under reduced pressure. Flash chromatography gave the phosphine which was dissolved in CH_2Cl_2 (25 cm^3). Water (10 cm^3) was added and the mixture stirred vigorously as aqueous H_2O_2 (3 cm^3 of a 30% solution) was added dropwise. After 30 min, the layers were separated and the aqueous layer further extracted with CH_2Cl_2 (2 × 15 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Flash chromatography, eluting with EtOAc, gave the *phosphine oxide* (904 mg, 66%) as rectangular prisms, mp 121–122 °C (from EtOAc–hexane); R_f (EtOAc) 0.18; $\nu_{max}(CHCl_3)$/cm^{-1} 1592 (Ar), 1573 (Ar) and 1174 (P=O); δ_H(250 MHz; $CDCl_3$) 8.23 (2 H, ddd, $^3J_{PH}$ 12.1, *J* 7.1 and 1.6, 4 and 6-ArH), 7.47–7.34 (4 H, m), 7.23–7.18 (2 H, m), 3.43–3.34 (2 H, m, $ArCH_AH_BCH_{A'}H_{B'}Ar$), 3.11–3.01 (2 H, m, $ArCH_AH_B$-$CH_{A'}H_{B'}Ar$), 2.15–2.03 (2 H, m, PCH_2), 1.60–1.41 (2 H, m, PCH_2CH_2) and 0.90 (3 H, td, *J* 7.2 and $^4J_{PH}$ 0.8, CH_2Me); δ_C(62.9 MHz; $CDCl_3$) 142.9$^-$ ($^2J_{PC}$ 11.3, 9a-ArC), 133.2$^+$ (J_{PC} 6.1), 131.3$^-$ ($^1J_{PC}$ 91.9, 4a-ArC), 131.1$^+$ ($^4J_{PC}$ 2.6, 2-ArC), 129.7$^+$ (J_{PC} 11.8), 126.3$^+$ (J_{PC} 10.5), 37.1$^-$ ($^1J_{PC}$ 70.8, PCH_2), 34.9$^-$ (Ar*C*H_2), 15.7$^-$ ($^2J_{PC}$ 4.1) and 15.3$^+$ ($^3J_{PC}$ 15.6, CH_2Me); *m*/*z* 270 (27%, M^+), 228 (100, $M - C_3H_6$) and 227 (66, $M - C_3H_7$) (Found: M^+, 270.1175. $C_{17}H_{19}OP$ requires *M*, 270.1174).

10,11-Dihydro-5-phenyl-5*H*-dibenzo[*b*,*f*]phosphepine 9

Trichlorosilane (190 μl, 1.88 mmol) was added to a suspension of phosphine oxide **5** (226 mg, 0.743 mmol) in dry toluene (10 cm^3) and the mixture was refluxed overnight. After cooling, sodium hydroxide (5 cm^3 of a 10% aqueous solution) was added to the reaction mixture which was extracted with CH_2Cl_2 (2 × 25 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography, eluting with 9:1 hexane–Et_2O, to give the phosphine (195 mg, 77%) as plates, mp 97–98 °C (from EtOH) (lit.,[4] 94 °C, from EtOH); R_f (Et_2O–hexane, 1:9) 0.47; δ_H(400 MHz; $CDCl_3$) 7.36–7.23 (9 H, m, ArH), 7.17–7.11 (4 H, m, ArH) and 3.18 (4 H, s with 2 very small side bands, CH_2CH_2); δ_C(100.6 MHz; $CDCl_3$) 145.8–125.6 ($^+$ and $^-$, several lines) and 34.6$^-$ ($^3J_{PC}$ 3.0, $ArCH_2$) (Found: M^+, 288.1079. $C_{20}H_{17}P$ requires *M*, 288.1068).

10,11-Dihydro-5-phenyl-5-propyl-5*H*-dibenzo[*b*,*f*]phosphepin-5-ium iodide 10

The phosphine **9** (195 mg, 0.677 mmol) and propyl iodide (330 μl, 3.38 mmol) were refluxed in THF (2.5 cm^3) for 14 h. The THF was removed under reduced pressure and the remaining solids were washed with hexane to give the *phosphonium salt* (267 mg, 86%) as hexagonal prisms, mp 207–209 °C (from CH_2Cl_2–hexane); $\nu_{max}(CHCl_3)$/cm^{-1} 1591 (Ar), 1574 (Ar) and 1439 (P-Ph); δ_H(250 MHz; $CDCl_3$) 7.98 (2 H, ddd, $^3J_{PH}$ 14.0, *J* 7.7 and 1.1, 4-ArH), 7.73–7.44 (11 H, m), 3.49 (2 H, m, PCH_2), 3.30 (4 H, AB m virtually a singlet, $ArCH_2$), 1.59 (2 H, septet, *J* 7.9 and $^3J_{PH}$ 7.9, PCH_2CH_2) and 1.20 (3 H, td, *J* 7.2 and $^4J_{PH}$ 1.4, CH_2Me); δ_C(62.9 MHz; $CDCl_3$) 148.1$^-$ ($^2J_{PC}$ 8.4, 9a-ArC), 135.1$^+$ ($^4J_{PC}$ 2.8, 2-ArC), 134.8$^+$ (J_{PC} 11.0), 134.4$^+$ ($^4J_{PC}$ 2.8, *p*-PhC), 132.5$^+$ (J_{PC} 10.5), 132.0$^+$ (J_{PC} 11.7), 130.3$^+$ (J_{PC} 12.6), 128.2$^+$ (J_{PC} 12.6), 122.5$^-$ ($^1J_{PC}$ 85.2, 4a-ArC), 116.1$^-$ ($^1J_{PC}$ 80.4, ipso-PhC), 35.1$^-$ (J_{PC} Ar*C*H_2), 26.7$^-$ ($^1J_{PC}$ 51.6, PCH_2), 16.9$^-$ ($^2J_{PC}$ 4.1, PCH_2CH_2) and 15.2$^+$ ($^3J_{PC}$ 17.4, CH_2Me); *m*/*z* (100%, M^+) [Found (FAB): M^+, 331.16290. $C_{23}H_{24}P^+$ requires *M*, 331.16155].

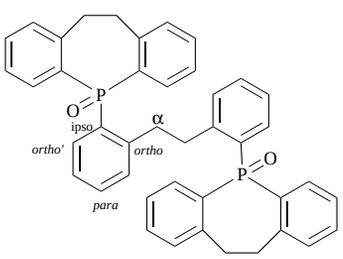
One-pot formation of 10,11-dihydro-5-phenyl-5-propyl-5*H*-dibenzo[*b*,*f*]phosphepin-5-ium iodide 10 by reduction and alkylation

Polymethylhydrosiloxane (890 μl, 41 mmol of hydride) was added to a suspension of phosphine oxide **5** (615 mg, 2.02 mmol) in dry THF (4 cm^3). Titanium isopropoxide (600 μl, 2.02 mmol) was added and the mixture refluxed for 3 h 20 min before propyl iodide (1.05 cm^3, 10.7 mmol) was added. After the mixture had been refluxed for 14 h, it was allowed to cool and hexane (2 cm^3) was added. The mixture was cooled in ice and the precipitate filtered from the supernatant and washed with hexane to give the phosphepinium salt (818 mg, 88%) as a yellow solid.

Preparation of 10,11-dihydro-5-propyl-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxide 11 by hydrolysis of phosphepin-5-ium salt 10

Sodium hydroxide (6 cm^3 of a 2 M solution) was added to phosphepinium iodide **10** (346 mg, 0.755 mmol) suspended in EtOH (10 cm^3) and the mixture was refluxed for 18 h. Ethanol was evaporated under reduced pressure, water (5 cm^3) added and the mixture was extracted with CH_2Cl_2 (3 × 15 cm^3). The combined extracts were dried ($MgSO_4$), evaporated under reduced pressure and the products separated by flash chromatography, eluting with EtOAc, to give the phosphine oxide **11** (178 mg, 87%) and, from endocyclic cleavage, phosphine oxide **12** (23 mg, 9%); R_f (EtOAc) 0.43; δ_H(400 MHz; $CDCl_3$) 7.69–7.62 (3 H, m), 7.50–7.40 (4 H, m), 7.33–7.19 (4 H, m), 7.13 (1 H, t, *J* 7.3), 7.06 (2 H, d, *J* 7.1), 3.17–3.03 (2 H, m, PhCH_AH_B), 2.79 (1 H, ddd, *J* 13.3, 11.2 and 5.7, ArCH_CCH_D), 2.55 (1 H, ddd, *J* 13.3, 10.6 and 6.2, ArCH_CCH_D), 2.42–2.29 (1 H, m, PCH_A), 2.28–2.17 (1 H, m, PCH_B), 1.85–1.67 (1 H, br m, PCH_2CH_A), 1.66–1.50 (1 H, br m, PCH_2CH_B) and 1.03 (3 H, td, *J* 7.2 and $^4J_{PH}$ 0.6).

In another experiment, hydrolysis of phosphepinium salt **10** in aqueous sodium hydroxide gave 42% of **11** and 12% of **12**. In another experiment, hydrolysis in aqueous methanol gave a 77% yield of **11** and a 4% yield of **12**.



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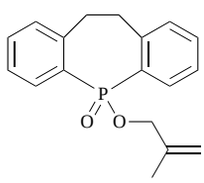

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5,5′-(Bibenzyl-2,2′-diyl)bis(10,11-dihydro-5*H*-dibenzo[*b*,*f*]-phosphepine 5-oxide) 13 by attempted formation of phosphinate ester 22

Sodium 2-methylprop-2-enolate was prepared by adding 2-methylprop-2-en-1-ol (680 μl in 5 cm^3 of THF, 8.08 mmol) to NaH (415 mg of 60 wt%, 10.4 mmol) and stirring at room temperature for 30 min. Bromobenzyl bromide (2.02 g, 8.08 mmol) was reacted by the small scale method above. Freshly distilled phosphorus trichloride (458 μl in 2.3 cm^3 of THF, 5.25 mmol) was added dropwise to the stirred solution at −78 °C. The reaction mixture was allowed to warm to room temperature overnight and then cooled to −78 °C. The sodium 2-methylprop-2-enolate solution was added dropwise. The reactants were allowed to warm to room temperature and stirred for 2 h before H_2O_2 (10 cm^3 of an approx. 33% solution, 88 mmol) was added dropwise. Saturated aqueous NH_4Cl (5 cm^3) was added to the mixture followed by saturated aqueous $NaHCO_3$ (5 cm^3) and H_2O_2 (10 cm^3). Volatile materials were removed under reduced pressure and the remaining solution was extracted with CH_2Cl_2 (4 × 50 cm^3), washed with brine (20 cm^3), dried and concentrated under reduced pressure. Separation of the products by flash chromatography, eluting with 5% methanol in EtOAc gave 10,11-dihydro-5-butyl-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxide (342 mg, 30%); R_f (EtOAc–MeOH, 19:1) 0.44; tentatively identified spectroscopically. It had ν_{max}($CHCl_3$)/cm^{-1} 1592 (Ar), 1573 (Ar) and 1162 (P=O); δ_H(250 MHz; $CDCl_3$) 8.22 (2 H, ddd, $^3J_{PH}$ 12.1, *J* 7.1 and 1.7, 4 and 6-ArH), 7.46–7.34 (4 H, m), 7.22–7.17 (2 H, m), 3.43–3.33 (2 H, m, ArCH_AH_B-C$H_{A'}H_{B'}$Ar), 3.10–3.00 (2 H, m, ArCH_AH_BC$H_{A'}H_{B'}$Ar), 2.16–2.03 (2 H, m, PCH_2), 1.49–1.21 (4 H, m, $PCH_2CH_2CH_2$) and 0.80 (3 H, t, *J* 7.2, CH_2*Me*); δ_C(100.6 MHz; $CDCl_3$) 143.0$^-$ ($^2J_{PC}$ 11.1, 9a-ArC), 133.3$^+$ (J_{PC} 6.0), 132.0$^+$ ($^4J_{PC}$ 2.4, 2-ArC), 129.8$^+$ (J_{PC} 11.8), 126.4$^+$ (J_{PC} 10.5), 35.0$^-$ (Ar*C*H_2), 34.8$^-$ ($^1J_{PC}$ 70.9, PCH_2), 24.0$^-$ ($^2J_{PC}$ 4.8, PCH_2CH_2), 23.9$^-$ ($^3J_{PC}$ 15.9, PCH_2-CH_2CH_2) and 13.6$^+$ (CH_2*Me*) and the *bis*(*phosphine oxide*) **13** (294 mg, 34%) as rectangular prisms, mp >230 °C (from EtOAc–EtOH); R_f (EtOAc–MeOH, 19:1) 0.33; ν_{max}($CHCl_3$)/cm^{-1} 1592 (Ar) and 1162 (P=O); δ_H(400 MHz; $CDCl_3$) 8.08 (4 H, ddd, $^3J_{PH}$ 12.8, *J* 7.7 and 1.1, 4 and 6-ArH), 7.43–7.29 (12 H, m), 7.19–7.13 (6 H, m), 6.95 (2 H, dd, *J* 7.1 and 4.7), 3.25–3.18 (4 H, m, ArCH_AH_BC$H_{A'}H_{B'}$Ar), 3.06–2.99 (4 H, m, ArCH_AH_B-C$H_{A'}H_{B'}$Ar) and 2.65 (4 H, s, α-CH_2); δ_C(100.6 MHz; $CDCl_3$) 145.2$^-$ ($^2J_{PC}$ 8.8, *o*-ArC), 143.4$^-$ ($^2J_{PC}$ 10.6, 9a-ArC), 133.5$^+$ (J_{PC} 12.7, exo-C), 133.0$^+$ (J_{PC} 7.4, het), 132.7$^-$ ($^1J_{PC}$ 107.1, ipso-ArC), 132.17$^+$ (2-ArC), 132.15$^-$ ($^1J_{PC}$ 98.1, 4a-ArC), 131.8$^+$ (*p*-ArC), 131.2$^+$ (J_{PC} 10.1, exo-C), 130.0$^+$ (J_{PC} 11.8, het), 126.4$^+$ (J_{PC} 11.3, het), 125.6$^+$ (J_{PC} 12.8, exo), 35.4$^-$ ($^3J_{PC}$ 5.0, α-CH_2) and 33.8$^-$ (10-CH_2); *m*/*z* 635 (<0.9%, M^+ + 1) and 51 (100, C_4H_3) [Found (+FAB): M^+ + H, 635.2288. $C_{42}H_{36}O_2P_2$ + H requires *M*, 635.2269].

Formation of dichlorobibenzyl by attempted formation of phosphinic acid under reverse addition conditions

2-Bromobenzyl bromide (2.17 g, 8.68 mmol) was reacted by the small scale method above and then rapidly added *via* cannula to a stirred solution of freshly distilled phosphorus oxychloride (0.75 cm^3, 5.25 mmol) in dry THF (10 cm^3) under argon at −78 °C. The reactant temperature rose to −38 °C during the addition. The reaction mixture was allowed to warm to room temperature and left overnight. It was cooled to 0 °C and saturated aqueous $NaHCO_3$ (3 cm^3) was added. THF was removed under reduced pressure before HCl (60 cm^3 of a concentrated solution) was added. The mixture was extracted with CH_2Cl_2 (4 × 30 cm^3) and EtOAc (30 cm^3). The combined extracts were concentrated by evaporation under reduced pressure and acidic products were extracted from the residue by dissolving it in EtOAc (50 cm^3) and extracting with saturated aqueous $NaHCO_3$ (3 × 10 cm^3). The aqueous extract was acidified with concentrated H_2SO_4 (6 cm^3) and extracted with CH_2Cl_2 (3 × 30 cm^3). This organic extract was dried ($MgSO_4$) and evaporated under reduced pressure. The residue (397 mg) contained little of the desired product and was discarded. The products remaining in the non-acidic portion of the reaction mixture were separated by flash chromatography, eluting with EtOAc, to give dichlorobibenzyl (609 mg, 56%), R_f (hexane) 0.34; δ_H(250 MHz; $CDCl_3$) 7.39–7.33 (2 H, m), 7.18–7.08 (6 H, m) and 3.30 (4 H, s); δ_C(100.6 MHz; $CDCl_3$) 139.1$^-$, 134.2$^-$, 130.7$^+$, 129.6$^+$, 127.7$^+$, 126.9$^+$ and 34.0$^-$; *m*/*z* (26%, M^+) and 125 (100, $ArCH_2$) and 10,11-dihydro-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxide **14** (67 mg, 7%).

General procedure for the reaction of phosphine oxides with carbonyl compounds

n-Butyllithium (130 μl of a 1.5 M solution in hexane, 0.195 mmol, 1.06 equiv.) was added dropwise to a stirred solution of the phosphine oxide (0.184 mmol) in dry THF (1.5 cm^3) under argon at −78 °C. After stirring at −78 °C for 45 min, the aldehyde or ketone (0.267 mmol in THF solution, 1.4 equiv.) was added dropwise. After stirring for 20 min at −78 °C, the reaction mixture was allowed to warm to 0 °C and stirred for 30 min before saturated aqueous NH_4Cl (1 cm^3) was added. The THF was removed under reduced pressure, water was added (5 cm^3) and the mixture was extracted with CH_2Cl_2 (3 × 5 cm^3). The combined extracts were dried ($MgSO_4$) and the product was purified by flash chromatography.

1-(1-Diphenylphosphinoylpropyl)cyclohexan-1-ol 16

Diphenyl(propyl)phosphine oxide (45 mg, 0.184 mmol) was reacted as above with cyclohexanone to give, after flash chromatography, eluting with 1:1 EtOAc–hexane, the *alcohol* (52 mg, 82%) as needles, mp 201–202.5 °C (from EtOAc); R_f (EtOAc–hexane, 1:1) 0.27; ν_{max}($CHCl_3$)/cm^{-1} 3386 (br, O-H), 1602 (Ar) and 1168 (P=O or C-O); δ_H(400 MHz; $CDCl_3$) 7.86–7.81 (2 H, m, *o* and *o*′-Ph_AH), 7.78–7.73 (2 H, m, *o* and *o*′-

Ph_BH), 7.49–7.40 (6 H, m), 4.60 (1 H, s, OH), 2.25 (1 H, dt, $^2J_{PH}$ 8.9 and *J* 4.3), 1.93–1.82 (2 H, m), 1.70–1.24 (9 H, m), 1.13–1.04 (1 H, m) and 0.80 (3 H, t, *J* 7.5, CH_2*Me*); δ_C(100.6 MHz; $CDCl_3$) 136.1–128.3 (Ph_2PO), 75.3$^-$ ($^2J_{PC}$ 4.2, COH), 48.6$^+$ ($^1J_{PC}$ 66.8, PCH), 39.5$^-$ ($^3J_{PC}$ 6.1, HOCC_AH_2), 36.0$^-$ ($^3J_{PC}$ 8.5, HOCC_BH_2), 25.6$^-$ (PCHCH_2), 21.9$^-$ (HOCCH$_2C_AH_2$), 21.8$^-$ (HOCCH$_2C_BH_2$), 18.6$^-$ (HOCCH$_2$CH$_2CH_2$) and 15.8$^+$ ($^3J_{PC}$ 6.3, Me); *m*/*z* 342 (39%, M^+), 324 (24, M − H_2O), 244 [66, M − $(CH_2)_5$CO], 299 [100, M − $(CH_2)_5$CO − Me], 202 (84, Ph_2POH) and 201 (72, Ph_2PO) (Found: M^+, 342.1742. $C_{21}H_{27}O_2P$ requires *M*, 342.1749).

syn-(1*RS*,2*RS*)- and *anti*-(1*RS*,2*SR*)-2-Diphenylphosphinoyl-1-phenylbutan-1-ol 21

Diphenyl(propyl)phosphine oxide (45 mg, 0.184 mmol) was reacted as above with benzaldehyde to give, after flash chromatography eluting with EtOAc, the alcohols **21** previously characterised by Buss and Warren[20] (57 mg, 88%) in an 89:11, *anti*:*syn* ratio by ^{1}H NMR spectroscopy; *anti*-**21**, R_f (EtOAc) 0.51; *syn*-**21**, R_f (EtOAc) 0.37; δ_H(400 MHz; $CDCl_3$) 8.00–7.95 (2 H^{anti}, m), 7.84 (2 H^{anti}, m), 7.77–7.73 (2 H^{syn}, m), 7.57–6.99 (11 H^{anti} and 13 H^{syn}, m), 5.60 (1 H^{syn}, d, *J* 4.7, OH), 5.26 (1 H^{anti}, d, $^3J_{PH}$ 9.4, PCHC*H*OH), 5.06 (1 H^{syn}, br dt, $^3J_{PH}$ 15.9 and 4.8, PCHC*H*OH), 4.83 (1 H^{anti}, s, OH), 2.63 (1 H^{syn}, br td, *J* 11.2 and $^2J_{PH}$ 4.6, PCH), 2.39 (1 H^{anti}, q, $^2J_{PH}$ 5.5 and *J* 5.5, PCH), 1.97–1.82 (1 H^{anti}, m, PCHCH_ACH$_B$), 1.69–1.54 (1 H^{anti} and 1 H^{syn}, m, PCHCH$_A$C$H_B{}^{anti}$ and PCHCH_ACH$_B{}^{syn}$), 1.51–1.42 (1 H^{syn}, m, PCHCH$_A$CH_B), 0.62 (3 H^{syn}, t, *J* 7.4, CH_2*Me*) and 0.36 (3 H^{anti}, t, *J* 7.5, CH_2*Me*).

syn-(1*RS*,2*RS*)- and *anti*-(1*RS*,2*SR*)-10,11-Dihydro-5-(1-phenyl-1-hydroxybutan-2-yl)-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxide 20

Propylphosphepine oxide **11** (50 mg, 0.185 mmol) was reacted as above with benzaldehyde to give, after flash chromatography eluting with EtOAc, the alcohols **20** (61 mg, 88%) in a 73:27, *anti*:*syn* ratio by ^{1}H NMR spectroscopy; *anti*-**20**, R_f (EtOAc–hexane, 1:1) 0.27; *syn*-**20**, R_f (EtOAc–hexane, 1:1) 0.13; δ_H(400 MHz; $CDCl_3$) 8.35 (1 H^{anti}, dd, $^3J_{PH}$ 11.6 and *J* 7.7, 4 or 6-ArH), 8.25 (1 H^{anti}, dd, $^3J_{PH}$ 11.8 and *J* 7.5, 4 or 6-ArH), 8.19 (1 H^{syn}, dd, $^3J_{PH}$ 12.0 and *J* 7.5, 4 or 6-ArH), 7.53–6.90 (11 H^{anti} and 12 H^{syn}, m, ArH), 5.66 (1 H^{syn}, d, $^3J_{PH}$ 9.2, OH), 5.49 (1 H^{anti}, s, OH), 5.27 (1 H^{anti}, d, $^3J_{PH}$ 9.1, PCHC*H*OH), 5.18 (1 H^{syn}, ddd, $^3J_{PH}$ 26.9, *J* 9.2 and 4.3, PCHC*H*OH), 3.52 (1 H^{anti}, dd, *J* 16.5 and 9.5, ArCH_AH$_B$), 3.46 (1 H^{anti}, dd, *J* 16.5 and 9.8, ArCH$_A$$H_B$), 3.41–3.30 (2 H^{syn}, m, ArCH_AH$_B$CH_CH$_D$Ar), 3.15 (1 H^{anti}, dd, *J* 16.5 and 10.7, CH_CH$_D$Ar), 3.08 (1 H^{anti}, dd, *J* 17.0 and 10.3, CH$_C$$H_D$Ar), 3.01–2.93 (2 H^{syn}, m, ArCH$_A$$H_BCH_C$$H_D$-Ar), 2.65 (1 H^{syn}, td, *J* 10.3 and $^2J_{PH}$ 4.3, PCH), 2.21 (1 H^{anti}, dt, $^2J_{PH}$ 6.1 and *J* 4.2, PCH), 1.96–1.85 (1 H^{syn}, m, PCH-CH_AH$_B$), 1.79–1.52 (2 H^{anti}, m, PCHCH_2), 1.50–1.37 (1 H^{syn}, m, PCHCH$_A$$H_B$), 0.93 (3 H^{syn}, t, *J* 7.4, CH_2*Me*) and 0.27 (3 H^{anti}, t, *J* 7.5, CH_2*Me*).

10,11-Dihydro-5-[1-(1-hydroxycyclohexyl)propyl]-5*H*-dibenzo-[*b*,*f*]phosphepine 5-oxide 17

Propylphosphepine oxide **11** (50 mg, 0.185 mmol) was reacted as above with cyclohexanone to give, after flash chromatography, eluting with 1:1 EtOAc–hexane, the *alcohol* (58 mg, 85%) as fine needles, mp 242–243.5 °C (from EtOAc–EtOH); R_f (EtOAc–hexane, 1:1) 0.29; ν_{max}($CHCl_3$)/cm^{-1} 3375 (br, O-H), 1592 (Ar) and 1159 (P=O); δ_H(400 MHz; $CDCl_3$) 8.24 (1 H, ddd, $^3J_{PH}$ 11.7, *J* 7.6 and 1.2, 4 or 6-ArH), 8.17 (1 H, ddd, $^3J_{PH}$ 11.9, *J* 7.6 and 0.7, 4 or 6-ArH), 7.53–7.32 (4 H, m), 7.23 (1 H, t, *J* 6.1, 2 or 8-ArH), 7.15 (1 H, t, *J* 6.0, 2 or 8-ArH), 4.89 (1 H, s, OH), 3.64–3.57 (1 H, m, ArCH_ACH$_B$), 3.47 (1 H, dd, *J* 17.2 and 6.1, CH_CH$_D$Ar), 3.11–3.01 (2 H, m, ArCH$_A$$H_BCH_C$$H_D$Ar), 2.27 (1 H, td, *J* 5.7 and $^2J_{PH}$ 3.2, PCH), 1.94–1.36 [10 H, m, $(CH_2)_5$], 1.26–1.13 (1 H, br m, PCHCH_AH$_B$), 1.02–0.91 (1 H, br m, PCHCH$_A$$H_B$) and 0.75 (3 H, t, *J* 7.5, Me); δ_C(100.6 MHz; $CDCl_3$) 142.0–125.9 (Ar_2PO), 76.0$^-$ ($^2J_{PC}$ 4.4, COH), 49.9$^+$ ($^1J_{PC}$ 66.0, PCH), 39.4$^-$ ($^3J_{PC}$ 3.7, HOCC_AH_2), 36.4$^-$ ($^3J_{PC}$ 3.7, HOCC_BH_2), 34.6$^-$ (ArC_AH_2), 32.8$^-$ (ArC_BH_2), 25.6$^-$ (PCHCH_2), 22.3$^-$ (HOCCH$_2C_AH_2$), 22.2$^-$ (HOCCH$_2C_BH_2$), 18.8$^-$ (HOCCH$_2$CH$_2CH_2$) and 14.9$^+$ ($^3J_{PC}$ 4.1, Me); *m*/*z* 368 (9.1%, M^+), 350 (4, M − H_2O), 270 [8, M − $(CH_2)_5$CO] and 228 (70, Ar_2POH) (Found: M^+, 368.1906. $C_{23}H_{29}O_2P$ requires *M*, 368.1905).

10,11-Dihydro-5-[1-(1-hydroxycyclobutyl)propyl]-5*H*-dibenzo-[*b*,*f*]phosphepine 5-oxide 18

Propylphosphepine oxide **11** (50 mg, 0.185 mmol) was reacted as above with cyclobutanone to give, after flash chromatography, eluting with 1:1 EtOAc–hexane, the *alcohol* (46 mg, 73%) as rectangular prisms, mp 229.5–231 °C (from EtOAc); R_f (EtOAc–hexane, 1:1) 0.32; ν_{max}($CHCl_3$)/cm^{-1} 3362 (O-H), 1592 (Ar), 1262 (P=O or C-O) and 1170 (P=O or C-O); δ_H(400 MHz; $CDCl_3$) 8.22–8.15 (2 H, m, 4 and 6-ArH), 7.51–7.33 (4 H, m), 7.27–7.23 (1 H, m), 7.20–7.17 (1 H, m), 5.68 (1 H, s, OH), 3.59–3.42 (2 H, m, ArCH_AH$_B$CH_CH$_D$Ar), 3.12–3.03 (2 H, m, ArCH$_A$$H_BCH_C$$H_D$Ar), 2.29 (1 H, dt, $^2J_{PH}$ 7.0 and *J* 4.6, PCH), 2.16–1.57 (6 H, m), 1.55–1.45 (2 H, m) and 0.64 (3 H, t, *J* 7.5, CH_2*Me*); δ_C(100 MHz; $CDCl_3$) 142.5$^-$ ($^2J_{PC}$ 12.3, 9a or 11a-ArC), 142.3$^-$ ($^2J_{PC}$ 11.1, 9a or 11a-ArC), 133.4$^+$ (J_{PC} 5.3), 133.2$^+$ (J_{PC} 6.3), 132.61$^-$ ($^1J_{PC}$ 92.4, 4a or 5a-ArC), 132.60$^+$ (J_{PC} 2.4), 132.1$^+$ (J_{PC} 2.4), 130.5$^+$ (J_{PC} 11.9), 129.7$^-$ ($^1J_{PC}$ 88.5, 4a or 5a-ArC), 129.6$^+$ (J_{PC} 11.8), 126.6$^+$ (J_{PC} 10.6), 126.4$^+$ (J_{PC} 10.3), 79.3$^-$ ($^2J_{PC}$ 5.7, COH), 52.0$^+$ ($^1J_{PC}$ 65.0, PCH), 37.4$^-$ ($^3J_{PC}$ 4.0, COHC_AH_2), 37.1$^-$ ($^3J_{PC}$ 13.8, COHC_BH_2), 34.6$^-$ (Ar$C_AH_2C_B$-H_2Ar), 33.6$^-$ ($^3J_{PC}$ 1.2, Ar$C_AH_2C_BH_2$Ar), 19.2$^-$, 15.1$^-$ and 14.6$^+$ (Me); *m*/*z* 340 (5.6%, M^+), 325 (18, M − Me), 312 (7, M − CH_2=CH_2) and 228 (100, Ar_2POH) (Found: M^+, 340.1592. $C_{21}H_{25}O_2P$ requires *M*, 340.1592).

10,11-Dihydro-5-(1-trimethylsilylpropyl)-5*H*-dibenzo[*b*,*f*]-phosphepine 5-oxide 19

Lithium diisopropylamide (215 μl of a 0.42 M solution in THF, 0.090 mmol) was added dropwise to a stirred solution of phosphine oxide **11** (20.3 mg, 0.752 mmol) and trimethylsilyl chloride (47 μl, 0.37 mmol) in THF (1 cm^3) at −78 °C under argon. After stirring at −78 °C for 1 h 10 min, TLC indicated that the reaction had gone to completion. During the course of the reaction no red colour developed but the reaction mixture turned a slight yellow colour. The mixture was allowed to warm to room temperature, quenched with aqueous saturated NH_4Cl (1 cm^3) and extracted with CH_2Cl_2 (3 × 5 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography to give the *phosphine oxide* (22 mg, 86%) as rectangular prisms, mp 98–100 °C (from hexane); R_f (EtOAc) 0.47; ν_{max}($CHCl_3$)/cm^{-1} 1592 (Ar) and 1252 (P=O); δ_H(400 MHz; $CDCl_3$) 8.25–8.20 (2 H, m, 4 and 6-ArH), 7.42–7.33 (4 H, m), 7.20–7.14 (2 H, m), 3.62–3.47 (2 H, m, ArCH_AH$_B$C$H_{A'}$-$H_{B'}$Ar), 3.07–2.99 (2 H, m, ArCH$_A$$H_BCH_{A'}$$H_{B'}$Ar), 1.96–1.80 (1 H, m, PCHCH_AH$_B$), 1.75–1.59 (1 H, m, PCHCH$_A$$H_B$), 1.43 (1 H, dt, *J* 9.7 and 4.9, PCHSi), 0.73 (3 H, t, $^4J_{PH}$ 7.4, CH_2*Me*) and −0.04 (9 H, d, $^4J_{PH}$ 0.6, $SiMe_3$); δ_C(100.6 MHz; $CDCl_3$) 142.5$^-$ ($^2J_{PC}$ 11.6, 9a or 11a-ArC), 141.6$^-$ ($^2J_{PC}$ 10.8, 9a or 11a-ArC), 134.2–129.5 ($^+$ and $^-$, several lines), 126.5–125.9 ($^+$, several lines), 34.7$^-$ (ArC_AC_BAr), 34.2$^+$ ($^1J_{PC}$ 60.3, PCHSi), 34.1$^-$ (ArC_AC_BAr), 18.8$^-$ ($^2J_{PC}$ 3.9, PCHCH_2), 16.0$^+$ ($^3J_{PC}$ 4.6, CHCH_2*Me*) and −0.5 ($^3J_{PC}$ 1.3, $SiMe_3$); *m*/*z* 342 (17%, M^+), 327 (93, M − Me), 300 (100, M − C_3H_6) and 228 (76, M − MeCH=CHSiMe_3) (Found: M^+, 342.1563. $C_{20}H_{27}$OPSi requires *M*, 342.1569).

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