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Preparation of chiral α-diazophosphonic acid derivatives

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Abstract—The chiral α-diazophosphonic acid derivatives **3**, **6** and **8** were prepared from (−)-ephedrine and (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diaminocyclohexane; preliminary experiments suggest that the chiral auxiliary exerts little influence in the dirhodium(II) acetate catalysed O–H and N–H insertion reactions. © 2001 Elsevier Science Ltd. All rights reserved.

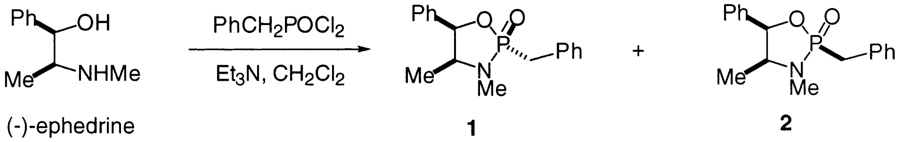
1. Introduction

Despite their ready availability,[1] α-diazophosphonates and related derivatives have found rather limited use in organic synthesis, their major role being the use of dimethyl (or diethyl) diazomethylphosphonate in the preparation of alkynes.[2,3] Although the rhodium carbenes formed in the dirhodium(II) acetate catalysed decomposition of diazophosphonates undergo typical reactions such as intramolecular cyclopropanation,[4] intramolecular C–H insertion,[5] and O–H and N–H insertion reactions,[6–8] such reactions are much less used than the corresponding reactions of their diazocarbonyl counterparts.[9] In an attempt to extend the utility of α-diazophosphonic acid derivatives in synthesis, we have prepared the first examples of chiral α-diazophosphonyl compounds, and briefly investigated the diastereoselectivity in their X–H (X = O, N) insertion reactions, having previously studied the corresponding reactions of chiral α-diazoesters.[10,11]

2. Results and discussion

The α-diazophosphonic acid derivatives chosen for study were based on the (−)-ephedrine-derived oxazophospholidine and *trans*-1,2-bis(*N*-methylamino)-cyclohexane-derived benzodiazaphosphole frameworks; both of these systems have been shown to be effective chiral auxiliaries in phosphorus chemistry.[12–14] Thus, benzylphosphonic acid diethyl ester was converted into the phosphonic acid dichloride, reaction of which with (−)-ephedrine gave the desired 2-benzyl-1,3,2-oxazaphospholidine as described in the literature (Scheme 1).[13] The two diastereomers (epimeric at phosphorus) were readily separated to give the (2*R*)-isomer **1** and the (2*S*)-isomer **2**.

Initial attempts to prepare the corresponding diazo compounds centred on direct diazo-transfer.[1] However, the use of 4-toluenesulfonyl azide as diazo-transfer reagent proved unsatisfactory, and it was only when **1** was treated with LDA followed by 4-nitrobenzenesulfonyl azide[15] that the diazo compound **3** was formed, along with the corresponding azide **4** (Scheme 2). The competition being azido- and diazo-transfer has been noted previously, for example, by Evans et al.[16] Unfortunately, the diazo compound **3** and azide **4** proved extremely difficult to separate, and eventually the diazo compound was only obtained in low yield, still contaminated with traces of the azide.



Scheme 1.

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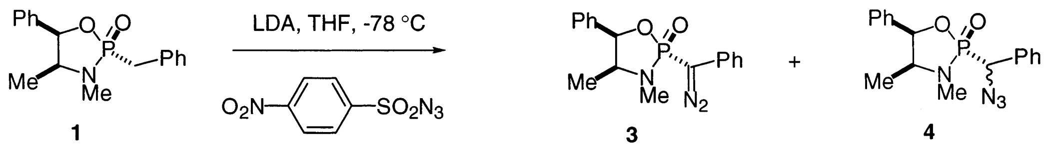


Scheme 2.

An alternative route was therefore developed in which the diazo group was already present in the precursor. Diethyl α-diazobenzyl phosphonate **5**[17] was converted into the corresponding phosphonic acid by treatment with trimethylsilyl bromide; reaction with oxalyl chloride followed by (−)-ephedrine gave a mixture of the diastereomeric diazo compounds (Scheme 3). The diastereomers were readily separated and gave the pure diazophosphonyl derivatives **3** and **6** albeit in extremely poor yield.

The synthesis of the diazo compound **8** proved simpler; the known diazophosphole-2-oxide **7**[14] was subjected to the above diazo-transfer conditions, and although the azide **9** was also formed, the desired diazo compound **8** could be readily obtained pure by recrystallisation (Scheme 4). The crystals of **8** proved suitable for analysis by X-ray crystallography, which confirmed the structure (Fig. 1).

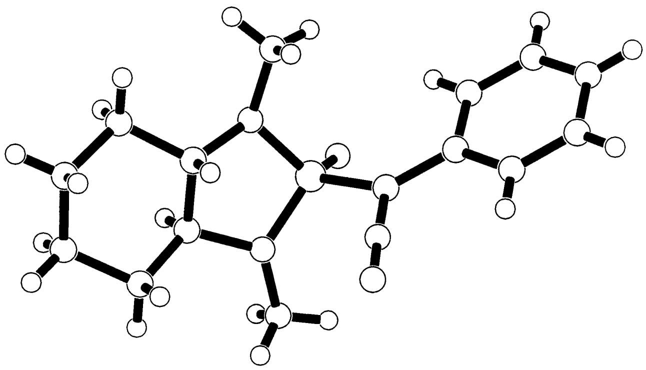


Figure 1. X-Ray crystal structure of (3a*S*,7a*S*)-2-diazobenzyl-1,3,3a,4,5,6,7,7a-octahydro-1,3-dimethyl-1*H*-1,3,2λ^5-benzodiazaphosphole-2-oxide **8**.

With three homochiral α-diazophosphonic acid derivatives available, a brief investigation of their reactivity was carried out to ascertain if the derived rhodium carbenes exhibited any diastereoselectivity in their subsequent insertion reactions. Therefore the diazophosphonyl derivative **8** was treated with a catalytic amount of dirhodium(II) acetate in the presence of 2-propanol or benzyl carbamate. Unfortunately no products resulting from carbene insertion into the respective O–H or N–H bonds could be isolated. The corresponding reactions of the P-stereogenic diazo compounds **3** and **6** did however lead to the formation of insertion products in good yield (Scheme 5), although the diastereoselectivity of the reactions (as determined by ^{31}P NMR analysis of the initial product mixture) was poor (15–32%).

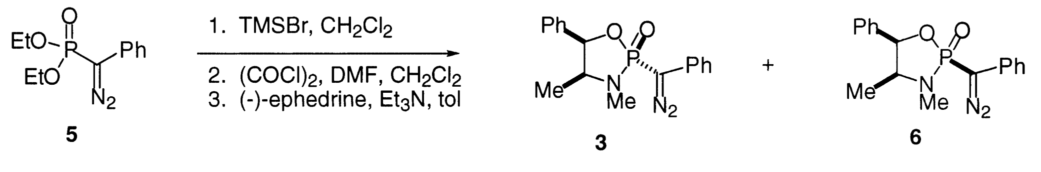
3. Conclusion

We have prepared the first examples of chiral α-diazophosphonic acid derivatives. Initial experiments (and the X-ray structure of compound **8**) suggest that the two chiral auxiliaries investigated exert little influence over the subsequent reactions of the derived rhodium carbenes, in direct contrast to similar reactions of diazoesters, $R^*O_2CC(=N_2)Ph$, where the chiral group can impart significant asymmetric induction (up to ~75% d.e.) in O–H insertion reactions.

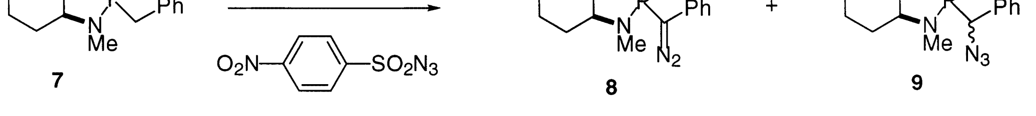
4. Experimental

4.1. General experimental

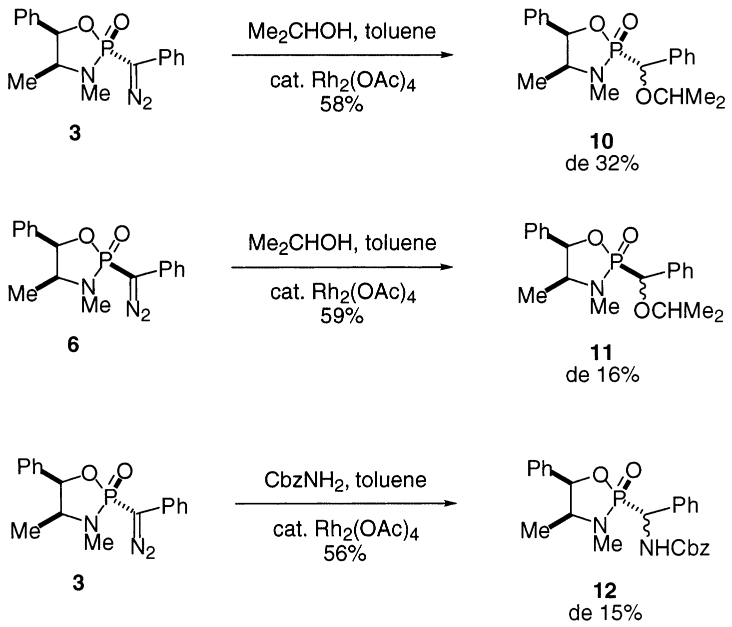
Commercially available reagents were used throughout without further purification; solvents were dried by standard procedures. Light petroleum refers to the



Scheme 3.



Scheme 4.



Scheme 5.

fraction with bp 40–60°C. Analytical TLC was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF_{254}. Plates were visualised under UV light at 254 nm. Flash chromatography was carried out using Merck Kieselgel 60 H or Matrex silica 60. NMR spectra were recorded on a Bruker AM300 or a Bruker Avance DRX 400 spectrometer at the frequencies stated. Mass spectra were obtained using a Kratos Profile HV3 spectrometer or at the EPSRC Mass Spectrometry Service (Swansea).

4.2. (2*R*,4*S*,5*R*)-2-Benzyl-3,4-dimethyl-2-oxo-5-phenyl-1,3,2λ^5-oxazaphospholidine 1 and (2*S*,4*S*,5*R*)-2-benzyl-3,4-dimethyl-2-oxo-5-phenyl-1,3,2λ^5-oxazaphospholidine 2

Prepared from dichlorobenzyl phosphonate and (−)-ephedrine according to the literature procedure.[13] The diastereomers were separated using chromatography (1:19; propan-2-ol:ethyl acetate) to give the (2*R*,4*S*,5*R*)-diastereomer **1** as a solid (31%), mp 134–136°C (lit.,[13] mp 133–134°C) and the (2*S*,4*S*,5*R*)-diastereomer **2** as a solid (40%), mp 171–173°C (lit.,[13] mp 169–171°C).

4.3. (2*R*,4*S*,5*R*)-2-(α-Diazobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-1,3,2λ^5-oxazaphospholidine 3

A solution of (2*R*,4*S*,5*R*)-oxazaphospholidine **1** (389 mg, 1.3 mmol) in THF (10 mL) was cooled to −78°C and treated with a solution of LDA (2 M; 1.4 mL, 2.8 mmol). After 30 min, a solution of 4-nitrobenzenesulfonyl azide[15] (555 mg, 2.4 mmol) in THF (10 mL) was added and the mixture allowed to warm up to room temperature overnight. Phosphate buffer (pH 7; 10 mL) was added, and the mixture extracted with dichloromethane; the organic extracts were dried (sodium sulfate), filtered and concentrated to an oil. This was then chromatographed (40% EtOAc–light petroleum) to give a mixture of the diazophosphonate **3** and the azido phosphonate **4**. After two further chromatographic purifications, the title compound was obtained as an oil (81 mg, 19%), which still contained trace amounts of the azide **4**; data for the diazophosphonate is given below.

4.4. (2*R*,4*S*,5*R*)-2-(α-Diazobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-1,3,2λ^5-oxazaphospholidine 3 and (2*S*,4*S*,5*R*)-2-(α-diazobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-1,3,2λ^5-oxazaphospholidine 6

Diethyl (α-diazo)benzyl phosphonate **5**[17] (5.00 g, 22 mmol) was dissolved in freshly distilled dichloromethane (10 mL) under argon and trimethylsilyl bromide (5.8 mL, 43.9 mmol) was added. The mixture was stirred overnight, concentrated, and the resulting oil was taken up again in dichloromethane (10 mL) under argon. Oxalyl chloride (4.2 mL, 48.4 mmol) and one drop of dry dimethylformamide were added and the mixture stirred for 0.5 h and concentrated. The resulting oil was taken up in anhydrous toluene (10 mL) under argon while in a separate flask (−)-ephedrine (3.6 g, 21.8 mmol) was dissolved in toluene (10 mL) with molecular sieves and triethylamine (6 mL). This was then added dropwise to the phosphonate solution over a 0.5 h period before leaving to stir overnight. Water (20 mL) was added and the solution extracted with dichloromethane (3×50 mL); the combined organic extracts were dried (sodium sulfate), filtered and concentrated to an oil. This oil was chromatographed (2:3 ethyl acetate:light petroleum) to separate the diastereomers and give the (2*R*,4*S*,5*R*)-diastereomer **3** as a yellow oil (126 mg, 1.7%), $[\alpha]_D^{21} = -43.2$ (*c* 1, $CHCl_3$); (Found: M^+, 327.1133. $C_{17}H_{18}N_3O_2P$ requires: 327.1137); ν_{max} (film)/cm^{-1} 2976, 2075, 1660, 1598, 1450, 1290, 1255, 1173, 1052, 980, 888, 853, 751, 726, 700; δ_H (400 MHz; $CDCl_3$) 0.89 (3H, d, $J = 6.6$, MeCH), 2.75 (3H, d, $J = 10.5$, NMe), 3.70 (1H, m, CHN), 5.54 (1H, dd, *J*=6.4, 4.4, CHO), 7.18–7.40 (10H, m, ArH); δ_C (100 MHz; $CDCl_3$) 14.8 (Me, d, *J*=1.2), 28.4 (CH, d, *J*=6.1), 50.5 (CN_2, d, *J*=209.7), 59.2 (Me, d, *J*=11.6), 82.5 (CH), 124.6 (CH, d, *J*=3.8), 125.9 (CH), 126.1 (CH), 127.5 (C, d, *J*=9.5), 128.3 (CH), 128.5 (CH), 129.3 (CH), 135.9 (C, d, *J*=6.0); δ_P (123 MHz; $CDCl_3$) 31.9; *m*/*z* (EI) 327 (M^+, 4%), 210 (2), 194 (27), 77 (46); and the (2*S*,4*S*,5*R*)-diastereomer **6** (99 mg, 1.4%) as a yellow oil, $[\alpha]_D^{21}=-15.6$ (*c* 1, $CHCl_3$); (Found: M^+, 327.1133); ν_{max} (film)/cm^{-1} 3062, 2976, 2931, 2063, 1653, 1598, 1497, 1453, 1331, 1254, 1216, 1185, 1063, 975, 884, 857, 813, 753, 701; δ_H (400 MHz; $CDCl_3$) 0.60 (3H, d, *J*=6.6, $\underline{\text{Me}}$CH), 2.83 (3H, d, *J*=9.9, NMe), 3.77 (1H, m, CHN), 5.87 (1H, d, *J*=6.4, CHO), 7.17–7.47 (10H, m, ArH); δ_C (100 MHz; $CDCl_3$) 14.2 (Me, d, *J*=1.1), 29.2 (CH, d, *J*=6.7), 49.9 (CN_2, d, *J*=212.7), 60.1 (Me, d, *J*=10.6), 80.2 (CH, d, *J*=1.2), 125.5 (CH), 125.6 (C, d, *J*=10.0), 125.7 (CH, d, *J*=4.5), 126.2 (CH), 127.2 (C, d, *J*=10.5), 128.2 (CH), 128.5 (CH), 129.1 (CH); δ_P (123 MHz; $CDCl_3$) 31.1; *m*/*z* (EI) 327 (M^+, 11%), 299 (23), 194 (66), 210 (20), 77 (88).

4.5. (3a*S*,7a*S*)-2-Diazobenzyl-1,3,3a,4,5,6,7,7a-octahydro-1,3-dimethyl-1*H*-1,3,2λ^5-benzodiazaphosphole-2-oxide 8

(3a*S*,7a*S*)-2-Benzyloctahydro-1,3-dimethyl-1*H*-1,3,2λ^5-benzodiazaphosphole-2-oxide **7** (prepared from (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diaminocyclohexane by the literature method for the (*R*,*R*)-isomer[14]) (1.24 g, 4.0 mmol) was dissolved in freshly distilled THF (50 mL) under argon. This solution was cooled to −78°C before the addition of *n*-butyllithium (1.6 M; 3.3 mL, 5 mmol) over a 0.5 h period. The mixture was stirred for a further 0.5 h before the addition of 4-nitrobenzenesulfonyl azide[15] (844 mg, 3.6 mmol) in THF (50 mL). After stirring for 4 h, phosphate buffer (pH 7; 10 mL) was added. The solution was then extracted with dichloromethane; the organic extracts were dried (sodium sulfate), filtered and concentrated. The resulting oil was chromatographed column (2:98; methanol:dichloromethane) to give a mixture of diazophosphonate **8** and azido phosphonate **9**. The mixture was recrystallised twice from *n*-pentane to give the title compound (212 mg, 31%) as a orange solid, mp 86–90°C; $[\alpha]_D^{21}=+7.3$ (*c* 1, $CHCl_3$); (Found: C, 59.7; H, 7.2; N, 18.1. $C_{15}H_{21}N_4OP$ requires: C, 59.2; H, 7.0; N, 18.4%); (Found: M^+, 304.1455. $C_{15}H_{21}N_4OP$ requires: 304.1453); ν_{max} (film)/cm^{-1} 2938, 2865, 2817, 2071, 2054, 1120, 1289, 1255, 1174, 1026, 1010, 958, 805, 750; δ_H (400 MHz; $CDCl_3$) 1.15–1.45 (4H, m), 1.84–2.11 (4H, m), 2.52 (3H, d, *J*=8.8, NMe), 2.60–2.66 (1H, m, NCH), 2.66 (3H, d, *J*=9.0, NMe), 2.90–2.93 (1H, m, NCH), 7.11–7.36 (5H, m, ArH); δ_C (100 MHz, $CDCl_3$) 24.1 (CH_2, d, *J*=1.5), 24.2 (CH_2), 28.1 (Me), 28.3 (CH_2, d, *J*=10.5), 28.4 (CH_2, d, *J*=8.24), 28.4 (Me, d, *J*=2.2), 49.7 (CN_2, d, *J*=180.5), 63.6 (CH, d, *J*=7.5), 65.4 (CH, d, *J*=8.2), 124.2 (CH, d, *J*=3.0), 125.1 (CH), 128.7 (C, d, *J*=9.0), 128.9 (CH); δ_P (162 MHz; $CDCl_3$) 32.5; *m*/*z* (EI) 304 (M^+, 1%), 277 (30), 276 (M^+-N_2, 13), 229 (100), 187 (34), 171 (72), 110 (31), 77 (34),

4.6. (2*R*,4*S*,5*R*)-2-(α-Isopropoxybenzyl)-3,4-dimethyl-2-oxo-5-phenyl-1,3,2λ^5-oxazaphospholidine 10

The diazophosphonate **3** (44.5 mg, 0.12 mmol) was dissolved in toluene (2 mL), and isopropyl alcohol (110 µl, 1.4 mmol) and rhodium acetate (catalytic) were added before heating to 110°C for 1 h. The mixture was concentrated and the resulting oil analysed by ^{31}P NMR; a de of 32% was determined. The oil was chromatographed (3:2; ethyl acetate:light petroleum) to obtain one diastereomer of the title compound (14 mg, 29%) as an oily solid, $[\alpha]_D^{22}=+3$ (*c* 1, $CHCl_3$); (Found: M^+, 359.1651. $C_{20}H_{26}NO_3P$ requires: 359.1650); ν_{max} (film)/cm^{-1} 2970, 2929, 2877, 1452, 1327, 1375, 1255, 1219, 1061, 982, 899, 854, 702; δ_H (400 MHz; $CDCl_3$) 0.75 (3H, d, *J*=6.6, $\underline{\text{Me}}$CH), 1.19 (3H, d, *J*=6.1, CH$\underline{\text{Me}_2}$), 1.21 (3H, d, *J*=6.1, CH$\underline{\text{Me}_2}$), 2.26 (3H, d, *J*=9.1, NMe), 3.66 (1H, m, CHN), 3.77 (1H, heptet, *J*=6.1, C$\underline{\text{H}}$Me$_2$), 5.04 (1H, d, *J*=18.3, PCH), 5.62 (1H, dd, *J*=3.6, 6.4, CHO), 7.26–7.60 (10H, m, ArH); δ_C (100 MHz; $CDCl_3$) 14.2 (Me), 21.6 (Me), 22.9 (Me), 29.5 (Me, d, *J*=4.5), 58.7 (CH, d, *J*=9.0), 72.5 (CH, d, *J*=10.5), 76.9 (CH, d, *J*=148.3), 82.7 (CH, d, *J*=3.0), 126.1 (CH), 127.1 (CH), 127.4 (CH, d, *J*=65.2), 128.0 (CH, d, *J*=58.4), 128.1 (CH, d, *J*=21.0), 128.3 (CH), 136.6 (C), 136.8 (C, d, *J*=5.2); δ_P (123 MHz; $CDCl_3$) 36.6; *m*/*z* (EI) 360 (MH^+, 6%), 316 (2), 301 (10), 149 (93), 77 (61); and the other diastereomer (14 mg, 29%) as an impure oil, (Found: M^+, 359.1650); ν_{max} (film)/cm^{-1} 3062, 3032, 2979, 2931, 1740, 1716, 1645, 1495, 1452, 1373, 1227, 1176, 1059, 995, 748, 690; δ_H (400 MHz; $CDCl_3$) 0.72 (3H, d, *J*=6.6, $\underline{\text{Me}}$CH), 1.21 (3H, d, *J*=6.1, CH$\underline{\text{Me}_2}$), 1.25 (3H, d, *J*=6.1, CH$\underline{\text{Me}_2}$), 2.79 (3H, d, *J*=9.2, NMe), 3.47–3.56 (1H, m, CHN), 3.77 (1H, m, C$\underline{\text{H}}$Me$_2$), 4.95 (1H, dd, *J*=0, 6.6, CHO), 5.05 (1H, d, *J*=14.4, PCH), 7.26–7.37 (10H, m, ArH); δ_C (100 MHz; $CDCl_3$) 15.0 (Me), 21.3 (Me), 23.1 (Me), 29.0 (Me, d, *J*=5.5), 58.7 (CH, d, *J*=9.4), 71.4 (CH, d, *J*=12.1), 76.9 (CH, d, *J*=147.8), 82.4 (CH, d, *J*=2.7), 126.1–128.3 (6×CH), 136.5 (C), 136.7 (C, d, *J*=4.5); δ_P (123 MHz; $CDCl_3$), 36.5; *m*/*z* (EI) 360 (MH^+, 7%), 316 (1), 301 (4), 149 (94), 77 (31).

4.7. (2*S*,4*S*,5*R*)-2-(α-Isopropoxybenzyl)-3,4-dimethyl-2-oxo-5-phenyl-1,3,2λ^5-oxazaphospholidine 11

A mixture of the diazophosphonate **6** (42.0 mg, 0.12 mmol), toluene (2 mL), isopropyl alcohol (20 µl, 1.5 mmol) and rhodium acetate (catalytic) was heated at 80°C for 1 h. The mixture was concentrated and the resulting oil analysed by ^{31}P NMR; a d.e. of 16% was determined. The oil was chromatographed (3:2; ethyl acetate:light petroleum) to obtain one diastereomer of the title compound (14 mg, 30%) as an oil, (Found: M^+, 359.1660. $C_{20}H_{26}NO_3P$ requires: 359.1650); ν_{max} (film)/cm^{-1} 3415, 3062, 3032, 2972, 2929, 1768, 1691, 1647, 1495, 1452, 1381, 1331, 1248, 1215, 1184, 1117, 1090, 1065, 978, 889, 742, 702; δ_H (300 MHz; $CDCl_3$) 0.89 (3H, d, *J*=6.6, $\underline{\text{Me}}$CH), 1.19 (3H, d, *J*=6.1, CH$\underline{\text{Me}_2}$), 1.26 (3H, d, *J*=6.1, CH$\underline{\text{Me}_2}$), 2.45 (3H, d, *J*=8.0, NMe), 3.64 (1H, heptet, *J*=6.1, C$\underline{\text{H}}$Me$_2$), 3.72–3.80 (1H, m, CHN), 5.07 (1H, d, *J*=17.6, PCH), 5.78 (1H, d, *J*=6.3, CHO), 7.28–7.57 (10H, m, ArH); δ_C (100

MHz; $CDCl_3$) 14.6 (Me), 20.9 (Me), 23.2 (Me), 31.2 (Me, d, $J=4.5$), 61.3 (CH, d, $J=9.0$), 70.7 (CH, d, $J=10.5$), 75.1 (CH, d, $J=148.3$), 80.1 (CH, d, $J=3.0$), 126.0 (CH), 127.7 (CH, $J=5.2$)), 128.0 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 136.2 (C), 136.5 (C, d, $J=5.2$); δ_P (123 MHz; $CDCl_3$) 35.1; m/z (EI) 359 (M^+, 0.3%), 118 (17). 91 (13), 77 (14), 58 (15); a mixture of diastereomers (6 mg, 12%), and the other diastereomer (8 mg, 17%) as an oil; (Found: M^+, 359.1650); ν_{max} (film)/cm^{-1} 3406, 3062, 2970, 2926, 1734, 1647, 1454, 1373, 1236, 1066, 1028, 976, 744, 702; δ_H (300 MHz; $CDCl_3$) 0.87 (3H, d, $J=6.6$, $\underline{Me}$CH), 1.20 (3H, d, $J=6.4$, CH$\underline{Me_2}$), 1.28 (3H, d, $J=6.4$, CH$\underline{Me_2}$), 2.43 (3H, d, $J=8.1$, NMe), 3.60–3.74 (2H, m, C$\underline{H}$Me$_2$ and CHN), 5.05 (1H, d, $J=17.6$, PCH), 5.78 (1H, d, $J=6.4$, CHO), 7.28–7.40 (10H, m, ArH); δ_C (100 MHz; $CDCl_3$) 14.2 (Me), 20.9 (Me), 23.1 (Me), 29.5 (Me, d, $J=4.5$), 61.0 (CH, d, $J=9.0$), 70.8 (CH, d, $J=10.5$), 74.5 (CH, d, $J=148.3$), 79.7 (CH, d, $J=3.0$), 126.1 (CH), 127.1 (CH), 127.4 (CH, d, $J=65.2$), 128.0 (CH, d, $J=58.4$), 128.1 (CH, d, $J=21.0$), 128.3 (CH), 136.6 (C), 136.8 (C, d, $J=5.2$); δ_P (123 MHz; $CDCl_3$) 35.6; m/z (EI) 359 (M^+, 0.2%), 122 (66). 91 (49).

4.8. (2*R*,4*S*,5*R*)-2-[(α-Benzyloxycarbonyl)aminobenzyl]-3,4-dimethyl-2-oxo-5-phenyl-1,3,2λ^5-oxazaphospholidine 12

A mixture of the diazophosphonate **3** (46.1 mg, 0.14 mmol), toluene (2 mL), benzyl carbamate (45.7 mg, 0.3 mmol) and rhodium acetate (catalytic) was heated under nitrogen to 80°C for 5 h. The mixture was concentrated and the resulting oil analysed by ^{31}P NMR; a de of 15% was determined. The oil was chromatographed (2:3; ethyl acetate:light petroleum) to give the title compound as an inseparable mixture of diastereoisomers (36 mg, 56%) as an oil, (Found: MH^+, 451.1784. $C_{25}H_{27}N_2O_4P+H$ requires: 451.1787); ν_{max} (film)/cm^{-1} 3216, 3063, 3027, 2914, 1721, 1532, 1448, 1245, 1063, 1023, 979; δ_H (400 MHz; $CDCl_3$) 0.74 (3H, 2×d, $J=6.6$, CH$\underline{Me}$), 2.17 (3H, d, $J=9.3$, NMe), 2.65 (2H, m, 2×CH), 3.38–3.57 (1H, m, PCH), 5.02–5.30 (2H, m, C$\underline{H_2}$Ph), 5.97 (1H, d, $J=5.3$, NH), 7.22–7.52 (15H, m, ArH); δ_C (100 MHz; $CDCl_3$) (major and minor) 14.2 and 14.3 (Me), 28.6 and 29.1 (Me), 54.8 and 53.6 (CH), 59.1 and 58.4 (CH), 67.3 and 67.2 (CH_2), 82.0 and 82.7 (CH), 126.2–128.8 (9×CH, for both diastereomers), 135.71 and 135.68 (C), 135.76 and 135.9 (C), 136.15 and 136.11 (C), δ_P (123 MHz; $CDCl_3$) 35.8 and 36.5; m/z (CI) 451 (MH^+, 20%0, 150 (65), 72 (100).

4.9. Crystal data

Rigaku AFC7S diffractometer with Cu radiation. $T=293$ K, all non-H atoms refined anisotropically.[18]

4.10. (3a*S*,7a*S*)-2-Diazobenzyl-1,3,3a,4,5,6,7,7a-octahydro-1,3-dimethyl-1*H*-1,3,2λ^5-benzodiazaphosphole-2-oxide 8

$C_{15}H_{21}N_4OP$, $M=304.33$, orthorhombic, $P2_12_12_1$, $a=8.8367$ (3), $b=9.9769$ (3), $c=18.3490$ (5) Å, $V=1617.70$ (9) Å^3, ρ_{calcd} 1.250 g/cm^3, $Z=4$, μ(Cu Kα)$=0.175$ mm^{-1}; 7160 reflections measured, 2436 independent, observed with $I>2\sigma(I)$ 2296 to yield $R=0.0597$.

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