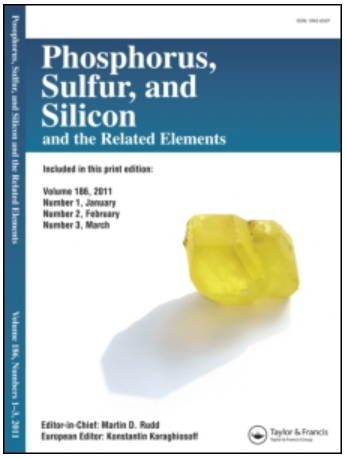

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Formation of Cyclic Phosphonium Salts in Trichlorosilane Reduction of Phosphine Oxides Bearing a Pendant Hydroxyl Group and Their Hydrolysis to Cyclic Phosphine Oxides

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Formation of Cyclic Phosphonium Salts in Trichlorosilane Reduction of Phosphine Oxides Bearing a Pendant Hydroxyl Group and Their Hydrolysis to Cyclic Phosphine Oxides

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An unusual ring closure to cyclic phosphonium salts was observed during trichlorosilane reduction of phosphine oxides with a pendant hydroxylmethyl group. Alkaline hydrolysis of the cyclic phosphonium salts afforded a cyclic phosphine oxide and a ring-fission product.

Keywords Alkaline hydrolysis; phosphine oxide; phosphonium salt; trichlorosilane reduction

INTRODUCTION

Trichlorosilane is an often-used reducing agent for converting phosphine oxides into phosphines.[1] Generally, the P-chirogenic relative configuration is retained when a phosphine oxide is reduced by trichlorosilane alone, while the relative configuration is inverted when trichlorosilane is used in combination with an organic base such as triethylamine.[2] Phosphine oxides can also be reduced by triethoxysilane or a safer alternative, polymethyl-hydrosiloxane (PMHS) with titanium isopropoxide catalysis.[3] It is noteworthy that the phosphine produced by the latter method may be reacted in situ with an alkyl halide to give a quaternary phosphonium salt.[4] Herein, we report the formation of cyclic phosphonium salts in trichlorosilane reduction of phosphine oxides bearing a pendant hydroxyl group. The reaction possibly involved a reduction step

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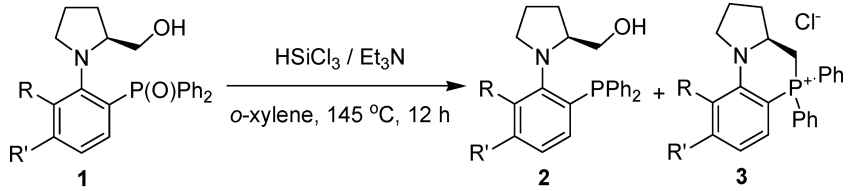
and quaternization of the phosphine intermediate with a neighboring methylene moiety.

RESULTS AND DISCUSSION

As illustrated in Scheme 1, reduction of phosphine oxides **1** with trichlorosilane in the presence of triethylamine afforded phosphines **2**, which were used as chiral P, N-ligands for asymmetric catalysis.[5] We found that when phosphine oxide **1a** containing the pyrrolidinyl group bearing a pendant free hydroxyl group was subject to reduction, an unusual product was isolated and identified as quaternary phosphonium salt **3a**, along with the normal tertiary phophine product **2a**.



a: R = H, R' = H; **b**: R = OMe, R' = H; **c**: R, R' = CH=CH-CH=CH

SCHEME 1

The reaction showed a large tendency to undergo quaternization at elevated temperature and with prolonged reaction time. The ^{31}P NMR signals of the phosphine oxide, phosphine and phosphonium salt were characteristically at about 29, −16, and 10 ppm, respectively. The ^{31}P NMR analysis of samples from different solvents such as xylene, toluene, benzene, or acetonitrile indicated that **3a** was the major product along with the yield of **2a** less than 10%, while less forcing conditions (*m*-xylene, 120°C, and 6 h in Refs. 5a and 5b) gave 90% yield of **2a**. In the absence of triethylamine, the conversions of **1a** to phosphines or phosphonium salts were incomplete, showing the ^{31}P NMR signals corresponding to **1a**, **2a** and **3a** and a peak at -39 ppm (probably indicating the C-P bond-cleavage Ph_2PH).[6]

After quenching the reaction with aqueous sodium hydroxide, **3a** could be extracted into methylene chloride, purified by column chromatography eluting with methylene chloride/methanol, and recrystallized from methylene chloride/petroleum ether. The ^{1}H NMR spectrum of **3a** is somewhat elusive. Signal of one hydrogen atom from four at 3′ and 4′ position on the pyrrolidinyl ring downfield shifts to 4.8 ppm (Figure 1). The structure is confirmed by X-ray analysis of its single crystal (CCDC 245589).[7] The aza-phospha-six-membered ring has a partially half chair conformation with C1 locating at the tip position

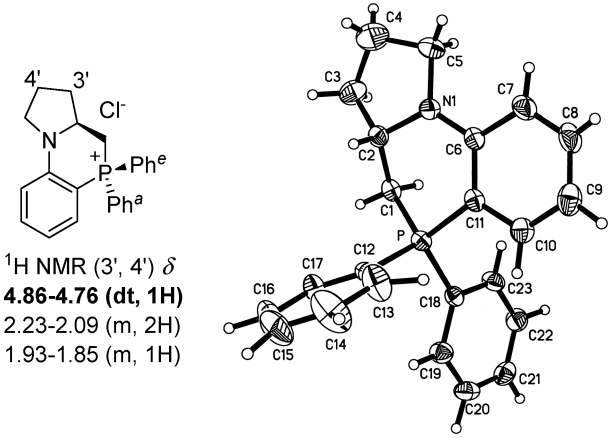
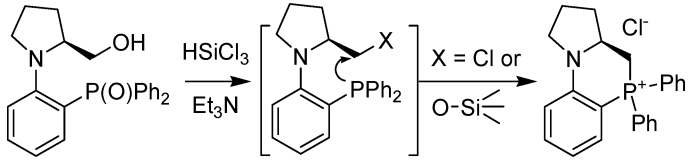


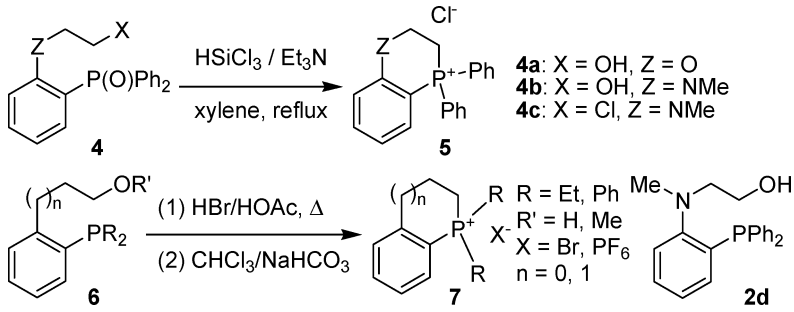
FIGURE 1 Selected ^{1}H NMR Data and X-Ray Structure (Cl^- not Shown) for **3a.**

and the phenyl group (C12–C17) projecting at the axial position. In a mechanistic consideration, though the explicit reaction sequence could not be depicted at this stage, It is obvious that, as shown in Scheme 2, the reaction involved reduction of phosphine oxide into tertiary phosphine and intramolecular quarternization with the neighboring methylene moiety (probably to be a chlorine-displaced one or in the form of a siloxy species).[8]



SCHEME 2

Reduction of **1b** gave tertiary phosphine **2b** in more than 80% yield. The formation of **3b** was not observed, suggesting that the possible axial rotamers might not adopt a suitable conformation to undergo quaternization.[9] As for phosphine oxide **1c**, the tertiary phosphine **2c** was isolated in about 50% yield, while the yield of quaternary phosphonium salt **3c** was less than 30% based on ^{31}P NMR spectrum (δ 12.5–11.5 ppm). However, **3c** could not be purified for satisfactory NMR spectra even when the chlorine anion was exchanged by BF_4 or PF_6 anions. Its cationic component was confirmed by ESI-HRMS to be 394.1715 in accordance with the formula $[C_{27}H_{25}NP]^+$ calcd. for 394.1719.



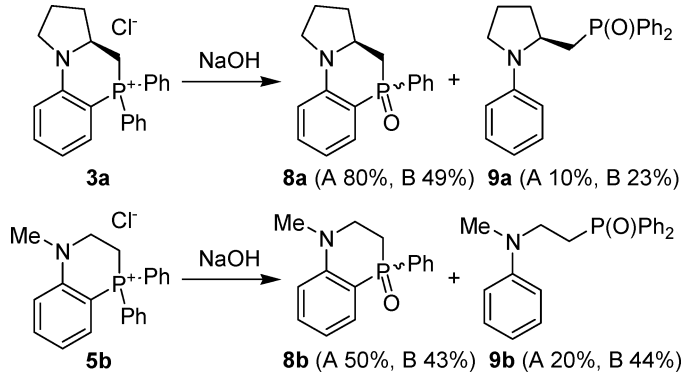
SCHEME 3

Achiral phosphine oxides **4a**, **b** were also prepared according to the literature.[10] Reduction of **4a** did not give any phosphonium product detectable by ^{31}P NMR analysis. Reduction of **4b** afforded phosphonium salt **5b** in 75% yield, the characteristic ^{31}P NMR signal of which was at about +9 ppm (Scheme 3). Beeby and Mann had described the preparation of cyclic phosphonium bromide **7** from tertiary phosphine **6** bearing an alkyloxy side chain through the sequential dealkyloxy bromination, biphasic extraction, neutralization and quaternization process.[11] Hamanaka et al. reported that active alcohol such as allylic or benzylic alcohol and unactivated alcohols (even in the form of esters and lactones) could be heated and reacted with the hydrobromic salt of triphenylphosphine to form quaternary phosphonium salts.[12] Halogenation and cyclization of phosphine **2d** were attempted. Heating of **2d** with reagents such as HCl (concd), $SOCl_2$, $P(O)Cl_3$ or HBr/HOAc, and so on, only resulted in a complex mixture as indicated by ^{31}P NMR analysis. The starting material or its oxide **4b** were recovered, and **4c** with the hydroxyl group displaced by chlorine was also isolated.

The application of phosphonium salts in phase transfer catalysis is of interest. We examined the usage of **3a** and **5b** in reactions such as epoxidation of chalcone with sodium hypochlorite, Darzens reaction, alkylation of benzophenone imine of *tert*-butyl glycine ester and chloroform condensation.[13] The yields were good, but the enantioselectivities were very low (typically less than 10% ee).

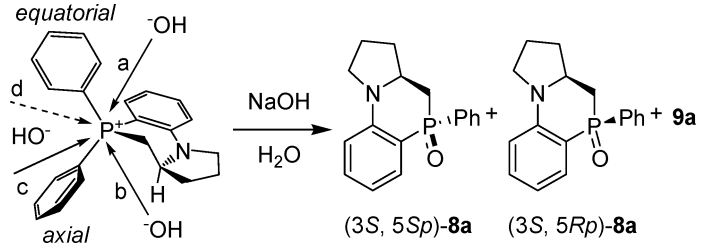
We noticed that in some cases the phosphonium salts as catalysts could not be recovered due to degradation under strong basic conditions. Then the alkaline hydrolysis of **3a** and **5b** by sodium hydroxide was investigated.[14] Heating the solution of **3a** for several hours, by method A (aq. 2 M NaOH, 100°C), cyclic phosphine oxide **8a**, and ring-cleavage product **9a** were formed in 80% and 10% yields according to ^{31}P NMR. Using method B (1 M NaOH in water/methanol, v/v = 1/5, 80°C), **8a** and

9a were isolated in 49% and 23% yields. As for achiral **5b**, the yields and ratios of **8b** and **9b** were 50% to 20% by method A, and 43% to 44% by method B, respectively (Scheme 4).



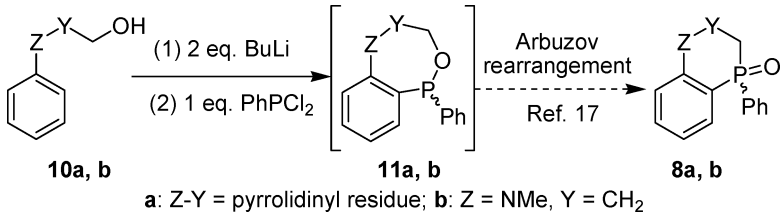
SCHEME 4

The product distribution and stereoselectivity for hydrolysis of **3a** might be attributed to its rigid conformation.[15] The diastereoselectivity was ca. 5/1 to 7/1 regardless of method A or B. However, obtained as waxy solids, the configurations of **8a** could not be fully defined. The mechanism of stereoselectivity is much complicate since the hydrolysis involving trigonal bipyramid phosphorus intermediates could be resulted from facial attacks (via route a, b, c, and d), or attacks from edge sites and subsequent rearrangements.[16] Tentatively, route d would be least likely because of the crowded triaryl surroundings (Scheme 5), and attack by hydroxide ion *anti* to the pseudo axial phenyl group via route a might be more favorable than route b and c, eventually leading to (*S*, *Sp*)-**8a** as the major diastereoisomer.



SCHEME 5

It is worthy to note that attempts to prepare **8a**,**b** in an alternative way were unsuccessful (Scheme 6). Double lithiation of **10a**,**b** by



SCHEME 6

n-BuLi and reaction with benzenephosphonous dichloride were conducted. Subsequently, trimethylsilyl iodide promoted intramolecular Michaelis-Arbuzov rearrangement[17] of phosphite intermediate **11a**,**b** was performed, but there were no formation of phosphine oxides **8a**,**b** as indicated by ^{31}P NMR analysis.

In summary, an unusual ring closure to form cyclic phosphonium salts in reduction of phosphine oxides bearing a pendant hydroxyl group was observed. The molecular structure of phosphonium salt **3a** was determined by X-ray diffraction. The alkaline hydrolysis of the cyclic phosphonium salts were also examined, giving a cyclic phosphine oxide, and a ring-opened product.

EXPERIMENTAL

Melting points were uncorrected. Specific rotation was recorded on a PERKIN-ELMER 341 polarimeter.^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz), and ^{31}P NMR (121 MHz) analyses were performed on a VARIAN MERCURY 300 spectrometer. IR spectra were recorded on a BIO-RAD FTS-185 spectrometer. EI MS and HRMS were obtained on an AGILENT 5973N MSD and an IONSPEC 4.7 TESLA FTMS spectrometer. ESI MS were obtained on an APEXIII 7.0 TESLA FTMS spectrometer.

Reduction of Phosphine Oxide 1a and 4b

Into an ice-water cooled 100-mL tube with Teflon-tipped valve containing a solution of the phosphine oxide (1.5 mmol) and triethylamine (1.1 mL, 8.0 mmol) in dry *o*-xylene (10 mL) trichlorosilane (0.8 mL, 8 mmol) was added slowly. The slurry in the sealed tube was stirred and heated at 150°C overnight. After cooled to 0°C, the mixture was treated with 2 M NaOH (50 mL) with caution and stirred until all solids were dissolved. The mixture was extracted with ether (3×50 mL) and CH_2Cl_2 (3 × 50 mL), and the combined organic layer was dried over Na_2SO_4.

After filtration and evaporation in vacuo, the residue was purified by chromatography on silica gel eluting with CH_2Cl_2/MeOH (v/v = 10/1) to afford a semi-solid, which was recrystallized from CH_2Cl_2/petroleum ether to give the phosphonium salt.

(3a*S*)-5,5-diphenyl-1,2,3,3a,4-pentahydro-9b-aza-cyclopenta-[*c*]phosphinolinium chloride (3a)

95% yield. m.p. 244.4–245.0°C; $[\alpha]_D^{20}$ –74.5° (*c* 0.62, $CHCl_3$); IR (KBr) 3401, 2868, 1599, 1546, 1492, 1475, 1454, 1437, 1354, 1110, 750 cm^{-1}; ^1H NMR: δ 8.20–8.12 (m, 2H), 7.80–7.50 (m, 9H), 7.11–7.03 (m, 1H), 6.78–6.71 (m, 2H), **4.86–4.76** (**dt**, J = **14.5**, **2 Hz**, **1H**), 3.67–3.60 (m, 1H), 3.50–3.46 (m, 2H), 3.09–2.97 (m,1H), 2.81–2.73 (m,1H), **2.23–2.09** (**m**, **2H**), **1.93–1.85** (**m**, **1H**); ^{13}C NMR: δ 150.0 (d, J = 5 Hz), 136.4 (d, J = 2 Hz), 134.7, 134.6 (d, J = 4 Hz), 133.5, 133.4 (d, J = 11 Hz), 133.2 (d, J = 10 Hz), 130.3 (d, J = 14 Hz), 129.9 (d, J = 13 Hz), 120.0 (d, J = 27 Hz), 118.6 (d, J = 27 Hz), 116.4 (d, J = 12 Hz), 114.0 (d, J = 8 Hz), 92.2 (d, J = 92 Hz), 53.2 (d, J = 7 Hz), 47.9, 34.3 (d, J = 15 Hz), 22.6, 22.0 (d, J = 52 Hz); ^{31}P NMR: δ 10.5; ESI MS m/z 344 ([M-Cl]$^+$); HRMS Calcd. for $C_{23}H_{23}NP^+$ 344.1563, Found 344.1558.

1,1-Diphenyl-4-methyl-2,3-dihydro-4-aza-phosphinolinium Chloride (5b)

75% yield. m.p. 250.6–251.1°C; IR (KBr) 3443, 3366, 2920, 1598, 1550, 1505, 1438, 1337, 1109, 1076, 955, 750 cm^{-1}; ^1H NMR: δ 7.84–7.76 (m, 6H), 7.71–7.65 (m, 4H), 7.61–7.55 (m,1H), 7.15–7.07 (m,1H), 6.93–6.81 (m, 2H), 3.99–3.95 (m,1H), 3.92–3.87 (m,1H), 3.83–3.76 (m, 2H), 3.15 (s, 3H); ^{13}C NMR: δ 152.7 (d, J = 4 Hz), 136.5 (d, J = 3 Hz), 134.8 (d, J = 2 Hz), 134.0 (d, J = 7 Hz), 133.4 (d, J = 11 Hz), 130.2 (d, J = 13 Hz), 119.4 (d, J = 88 Hz), 117.5 (d, J = 12 Hz), 114.4 (d, J = 7 Hz), 94.3 (d, J = 90 Hz), 46.8 (d, J = 7 Hz), 40.5, 18.9 (d, J = 53 Hz); ^{31}P NMR: δ 9.3; ESI MS m/z 318 ([M-Cl]$^+$); HRMS Calcd. for $C_{21}H_{21}NP^+$ 318.1406, Found 318.1394.

2-((2-(Diphenylphosphoryl)phenyl)(methyl)amino)ethanol (4b)

m.p.: 158–160°C; IR (film) 3215, 3055, 2934, 1586, 1567, 1440, 1286, 1172, 1113, 1045, 754, 706, 535 cm^{-1}; ^1H NMR: δ 7.75–7.67 (m, 4H), 7.59–7.53 (m, 7H), 7.51–7.36 (m, 1H), 7.19–7.13 (m, 1H), 7.01 (dd, 1H, J = 7.3, 13.0 Hz), 6.23 (t, 1H, J = 5.1 Hz), 3.57 (dd, 2H, J = 4.9, 9.4 Hz), 3.04 (t, 2H, J = 4.5 Hz), 1.97 (s, 3H); ^{13}C NMR: δ 159.2 (d, J = 4.0 Hz),

134.20, 134.04, 133.95, 133.92, 133.30, 131.88, 131.60, 131.46, 131.43, 131.39, 128.44, 128.28, 125.53, 125.52, 125.42, 125.37, 62.0, 59.2, 41.7; ^{31}P NMR: δ +29.8; EIMS: 352 ([M+H]$^+$, 23%), 318 (29%), 242 (100%); Anal. Calcd. for $C_{21}H_{22}NO_2P$: C, 71.78; H, 6.31; N, 3.99. Found: C, 71.79; H, 6.30; N, 3.80.

N-(2-Chloroethyl)-2-(diphenylphosphoryl)-*N*-methylbenzenamine (4c)

m.p.: 154–155°C; IR (film) 2960, 2794, 1584, 1568, 1474, 1435, 1180, 1118, 934, 753, 696, 537 cm^{-1}; ^{1}H NMR: δ 7.68–7.61 (m, 4H), 7.51–7.37 (m, 7H), 7.29–7.24 (m, 1H), 7.10–7.06 (m, 2H), 3.10–3.07 (m, 2H), 3.04–2.98 (m, 2H), 2.42 (s, 3H); ^{13}C NMR: δ 157.96 (d, J = 4.0 Hz), 134.75, 134.59, 134.42, 133.62, 133.59, 133.01, 131.26, 131.21, 131.14, 131.07, 131.04, 130.98, 129.58, 128.22, 128.11, 128.06, 124.85, 124.69, 124.28, 124.18, 59.5, 43.1, 40.6; ^{31}P NMR: δ +26.8; EIMS: 370 ([M+H]$^+$, 22.8%), 372 (7.6%), 334 (7.7%), 318 (23%), 242 (100%); HRMS: [M+H]$^+$ Calcd. for $C_{21}H_{22}ClNOP^+$ 370.1122, Found 370.1122; Anal. Calcd. for $C_{21}H_{21}ClNOP$: C, 68.20; H, 5.72; N, 3.79. Found: C, 68.17; H, 5.75; N, 3.48.

Hydrolysis of Phosphonium Salt 3a and 5b

The phosphonium salt (0.7 mmol) was added into 50 mL of 2 M NaOH or 1 M NaOH in water/MeOH (v/v = 1/5). The mixture was stirred and refluxed gently for 12 h. After cooled to rt and neutralized with 2 M HCl, the mixture was extracted with CH_2Cl_2 (4×50 mL), and the combined organic layer was dried over Na_2SO_4. After filtration and evaporation *in vacuo*, the residue was purified by chromatography on silica gel eluting with acetone to give two phosphine oxide products.

(3a*S*)-5-phenyl-1,2,3,3a,4-pentahydro-9b-aza-cyclopenta-[*c*]phosphinoline Oxide (8a)

$[\alpha]_D^{20}$ −65° (*c* 0.87, $CHCl_3$); IR (film from $CDCl_3$) 3422, 2966, 1710, 1598, 1554, 1477, 1439, 1255, 1328, 1173, 1113, 747, 697 cm^{-1}; ^{1}H NMR: δ 7.72–7.65 (m, 2H), 7.53–7.43 (m, 3H), 7.38–7.29 (m,1H), 7.24–7.17 (m,1H), 6.66–6.60 (m, 2H), 4.00 (m,1H), 3.54 (m,1H), 3.40 (m,1H), 2.49 (m,1H), 2.34 (m,1H), 2.13 (m,1H), 1.99 (m,1H), 1.75 (m, 2H); ^{13}C NMR: δ 149.4, 133.5, 133.03, 132.93, 131.73, 131.68, 131.64, 131.60, 131.4, 131.3, 128.5, 128.4, 128.3, 128.27, 116.3, 116.1, 116.0, 115.8, 112.8, 112.7, 112.0, 111.9, 53.7 (d, J = 6 Hz), 47.8, 34.8, 34.3 (d, J = 66 Hz), 22.8; ^{31}P NMR: δ 21.5 for (3a*S*, 5*Sp*)-**8a** and (3a*S*, 5*Rp*)-**8a** at 23.8 ppm

could not be fully separated. EI MS *m/e* 283 (M^+, 53%); HRMS Calcd. for $C_{17}H_{18}NOP^+$ 283.1126, Found 283.1084.

(*S*)-2-((Diphenylphosphoryl)methyl)-1-phenylpyrrolidine (9a)

m.p. 165.7–165.8°C; $[\alpha]_D^{20}$ −32° (*c* 1.15, $CHCl_3$); IR (KBr) 2925, 1724, 1598, 1506, 1438, 1177, 1118, 744, 692 cm^{-1}; ^1H NMR: δ 7.85–7.70 (m, 4H), 7.61–7.42 (m, 6H), 7.13–7.08 (m, 2H), 6.65–6.60 (m,1H), 6.29–6.25 (m, 2H), 4.07 (m,1H), 3.36 (m,1H), 3.15 (m,1H), 2.70 (m,1H), 2.25 (m,1H), 2.03 (m, 4H); ^{13}C NMR: δ 145.8, 134.2, 133.32, 133.28, 133.12, 132.07, 132.02, 131.9, 131.83, 131.79, 131.1, 130.9, 130.6, 130.5, 129.2, 128.78, 128.73, 128.58, 128.56, 128.4, 115.7, 111.9, 52.7, 47.4, 31.6, 29.6, 23.0; ^{31}P NMR: δ 30.0; EI MS *m/e* 361 (M^+, 10%); HRMS Calcd. for $C_{23}H_{25}NOP^+$ ($[M+H]^+$) 362.1668, Found 362.1668.

1-Phenyl-4-methyl-2,3-dihydro-4-phosphinoline Oxide (8b)

IR (film from $CDCl_3$) 3429, 2833, 1598, 1557, 1497, 1431, 1326, 1173, 1115, 954, 753, 696 cm^{-1}; ^1H NMR: δ 7.71–7.64 (m, 2H), 7.51–7.37 (m, 5H), 6.76 (m, 2H), 3.81–3.66 (m,1H), 3.61–3.45 (m,1H), 3.05 (s, 3H), 2.51–2.37 (m,1H), 2.32–2.20 (m,1H); ^{13}C NMR: δ 151.1 (d, $J = 5$ Hz), 133.7, 132.89, 132.87, 132.3, 132.2, 131.05, 131.0, 130.8, 130.7, 127.8, 127.7, 116.6, 116.4, 113.8, 112.5, 112.4, 112.3, 47.6 (d, $J = 7$ Hz), 39.9, 28.0 (d, $J = 67$ Hz); ^{31}P NMR: δ 21.6; EI MS *m/e* 257 (M^+, 100%); HRMS calcd for $C_{15}H_{17}NOP^+$ ($[M+H]^+$) 258.1042, Found 258.1033.

Methylphenylaminoethyl Diphenylphosphine Oxide (9b)

m.p. 107.7–107.9°C; IR (KBr) 3494, 1598, 1504, 1437, 1355, 1180, 1121, 974, 753, 695; ^1H NMR: δ 7.77–7.70 (m, 4H), 7.57–7.45 (m, 6H), 7.19 (m, 2H), 6.72 (m,1H), 6.56 (m, 2H), 3.72 (m, 2H), 2.84 (s, 3H), 2.54 (m, 2H); ^{13}C NMR: δ 147.9, 133.2, 131.93, 131.89, 131.86, 130.6, 130.54, 130.5, 129.2, 128.75, 128.60, 116.78, 112.57, 45.6, 38.0, 26.0 (d, $J = 68$ Hz); ^{31}P NMR: δ 31.7; EI MS *m/e* 335 (M^+, 18%); HRMS Calcd. for $C_{21}H_{23}NOP^+$ ($[M+H]^+$) 336.1512, Found 336.1507.

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