An Unconventional Synthesis of Dibromophosphines

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Abstract: Dibromophosphines, $RPBr_2$, are obtained by reaction of tetrabromomethane with 7-substituted 7-phosphanorbornenes in toluene at ca. 100 °C. The phosphanorbornenes are obtained in situ by cycloaddition of *N*-phenylmaleimide with 1-substituted 3,4-dimethylphospholes. The overall reaction sequence shows a good compatibility with functional groups.

Key words: phospholes, cycloreversion, dihalophosphines

Dihalophosphines RPX_2 (X = Cl, Br) are certainly among the most versatile synthetic intermediates in organophosphorus chemistry. However, only a restricted number of methods are available in the literature[1] for their preparation and most of them are not compatible with a wide range of functional groups on the R substituent. In two preceding papers,[2,3] we have demonstrated that 7-phosphanorbornenium salts collapse under nucleophilic attack to give the tricoordinated products formally derived from the phosphenium bridging unit. We also demonstrated that the bromide ion was able to perform this nucleophilic attack at 120 °C. Hence, we could forecast that a 7-bromo-7-phosphanorbornenium bromide could be a convenient source of dibromophosphine upon heating.

In order to have an idea of what could be expected, we decided to compute the structure of the 7-bromo-7-methyl-7-phosphanorbornenium bromide (**1**) by DFT at the B3LYP/6-311+G(d,p) level.[4] The results are depicted in Figure 1. One of the two bromine atoms is bonded to phosphorus by a normal covalent bond of 2.26 Å (P–Br: 2.22 Å in PBr_3)[5] and has a weak negative charge (Mulliken charge –0.15). The second P–Br bond is very long at 2.64 Å and is partly ionized (bromine Mulliken charge –0.45).

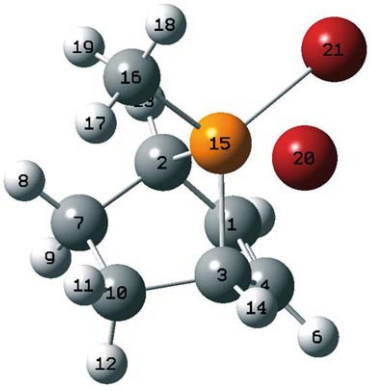
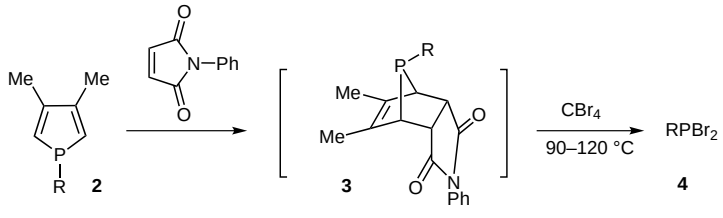


Figure 1 Computed structure of 7-bromo-7-methyl-7-phosphanorbornenium bromide (**1**). Significant distances (Å) and angles (°): P–Br 20 2.639, P–Br 21 2.259, P–Me 1.840, P–C2 1.932, P–C3 1.919; C2–P–C3 78.63°, Br20–P–Br21 89.76°.

The two P–C bridge bonds are very long at 1.92–1.93 Å and indicate that the bridge will dissociate readily.

With bromine being excluded because of its high reactivity toward double bonds and other functional groups, we decided to use tetrabromomethane for the *P*-bromination of 7-phosphanorbornenes. Following the work of Appel[6] on the reaction of triphenylphosphine with carbon tetrachloride, it is known that this type of reactions produces a 1:1 mixture of dihalophosphorane and dihalomethylenephosphorane when using a phosphine/CX_4 ratio of 2:1. This means that half of the phosphanorbornene will be lost for our purpose, but this drawback is compensated by the mildness of the experimental conditions. Our starting 7-phosphanorbornenes were easily obtained by reaction



Scheme 1

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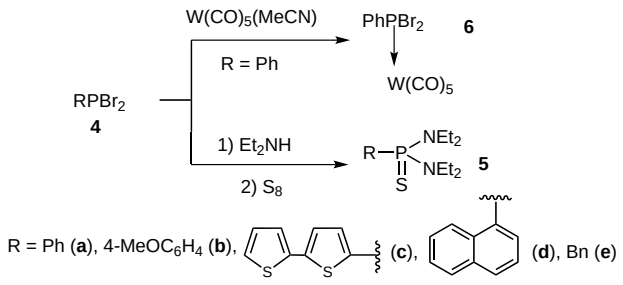
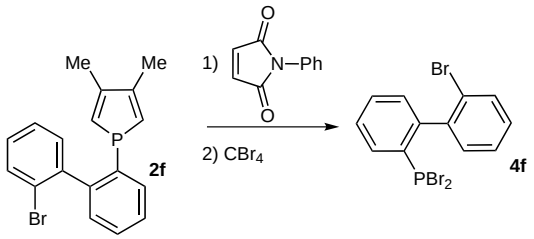


Scheme 2



Scheme 3

of 1-substituted 3,4-dimethylphospholes with *N*-phenylmaleimide.[7] The reaction with tetrabromomethane was carried out at 90–120 °C in toluene and monitored by ^{31}P NMR spectroscopy. The rate of the reaction sharply varied according to the nature of the substituent at phosphorus (completion needed between 10 min and 4 h). The dibromophosphine was characterized by its ^{31}P NMR resonance and by complexation with tungsten pentacarbonyl[8] or by reaction with diethylamine and sulfur (Scheme 1 and Scheme 2).

The yields of **5** from phospholes **2** varied between 13.8% for **5b** to 35% for **5a** but it must be recalled that the maximum theoretical yield is 50%.[9] Even though this one-pot chemistry is easy to perform, it has no practical interest for the synthesis of ordinary dibromophosphines. But it is also possible to apply this scheme to the synthesis of more sophisticated derivatives which are difficult to get using the traditional approaches. An example is given in Scheme 3.

Dibromophosphine **4f** was obtained in reasonable purity by simple extraction with pentane from the crude and analyzed by NMR spectroscopy.[10] The ^{13}C NMR spectrum was interpreted using the data of $PhPBr_2$.[11] It is easy to locate the four C resonances at 124.23 (J_{C-P} = 5.0 Hz, C–Br), 137.50 (J_{C-P} = 62.1 Hz, C–P), 139.41 ($^3J_{C-P}$ = 8.3 Hz, C bridge), 143.15 ($^2J_{C-P}$ = 43.9 Hz, C bridge). The eight other CH resonances are more difficult to assign but all display weak or negligible couplings with phosphorus, including the CH *ortho* to P. Since it is known that $^2J_{C-P}$ is dominated by the proximity of the coupled carbon with the P lone pair,[12] it is clear that the lone pair of PBr_2 is directed toward the bridge. Upon reaction with diethylamine and sulfur, **5f** was obtained in 45% yield.[13] Full experimental details are provided in the supplementary material.

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(8) **Synthesis of 6**: A solution of 3,4-dimethyl-1-phenylphosphole (0.5 mL, 2.65 mmol) and *N*-phenylmaleimide (0.45 g, 2.65 mmol) in toluene was stirred at 100 °C for 3 h (^{31}P NMR: δ = 47.3 ppm). Then CBr_4 (0.44 g, 1.3 mmol) was added to the solution and heated at 100 °C for 1 h (^{31}P NMR: δ = 150.6 ppm). The solution was added to $W(CO)_5(MeCN)$ (2.65 mmol) in THF and the mixture was stirred at 50 °C for 10 h. After evaporation of the solvents, the residue was extracted with hexane and purified by chromatography on silica gel at –10 °C with petroleum ether as the eluent to yield **6** as a yellow liquid (0.23 g, yield: 15%). ^1H NMR ($CDCl_3$): δ = 7.49–7.63 (m, 3 H), 7.97–8.04 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ = 128.69 (d, $^3J_{C-P}$ = 11.1 Hz, 2 × CH), 129.06 (d, $^2J_{C-P}$ = 17.1 Hz, 2 × CH), 132.58 (d, $^4J_{C-P}$ = 1.7 Hz, CH), 141.44 (d, J_{C-P} = 18.8 Hz, P–C), 195.60 (td, J_{C-P} = 7.5 Hz, *cis* CO), 198.37 (d, J_{C-P} = 45.7 Hz, *trans* CO). ^{31}P NMR ($CDCl_3$): δ = 79.4 (t, J_{P-W} = 329.1 Hz).

(9) **General Procedure for 5**: CBr_4 was added to the solution of 7-phosphanorbornenes in toluene and heated at 90–120 °C for 10 min to 4 h. The reactions were monitored by ^{31}P NMR spectroscopy. **4a**: ^{31}P NMR (toluene): δ = 150.6, **4b**: ^{31}P NMR (toluene): δ = 152.1, **4c**: ^{31}P NMR (toluene): δ = 129.0, **4d**: ^{31}P NMR (toluene): δ = 151.1, **4e**: ^{31}P NMR (toluene): δ = 172.4. The solution was cooled to 0 °C, and Et_2NH was added. After the mixture was warmed to r.t. and stirred for 30 min, S_8 was added and reacted for 1 h. The mixture was filtered through silica to remove salts and concentrated. Purification was performed via column chromatography on silica gel. **5a**: ^1H NMR ($CDCl_3$): δ = 1.04 (t, $J_{H–H}$ = 7.1 Hz, 12 H, Me), 3.07–3.20 (m, 8 H, CH_2), 7.38–7.45 (m, 3 H), 7.92–8.00 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ = 13.31 (d, $^3J_{C–P}$ = 4.0 Hz, Me), 39.19 (d, $^2J_{C–P}$ = 4.2 Hz, CH_2), 128.01 (d, $^2J_{C–P}$ = 13.2 Hz, *o*-Ph), 130.81 (d, $^4J_{C–P}$ = 2.9 Hz, *p*-Ph), 131.44 (d, $^3J_{C–P}$ = 10.6 Hz, *m*-Ph), 135.45 (d, $J_{C–P}$ = 124.3 Hz, P–C). ^{31}P NMR ($CDCl_3$): δ = 77.6. HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{25}N_2PSNa$: 307.1374; found: 307.1375. **5b**: ^1H NMR ($CDCl_3$): δ = 1.04 (t, $J_{H–H}$ = 7.2 Hz, 12 H, Me), 3.07–3.19 (m, 8 H, CH_2), 3.84 (s, 3 H, OMe), 6.93 (dd, $^4J_{H–P}$ = 2.7 Hz, $J_{H–H}$ = 9.0 Hz, 2 H, *m*-Ph), 7.88 (dd, $^3J_{H–P}$ = 12.6 Hz, $J_{H–H}$ = 9.0 Hz, 2 H, *o*-Ph). ^{13}C NMR ($CDCl_3$): δ = 13.37 (d, $^3J_{C–P}$ = 4.1 Hz, Me), 39.20 (d, $^2J_{C–P}$ = 4.3 Hz, CH_2), 55.28 (s, OMe), 113.41 (d, $^2J_{C–P}$ = 14.4 Hz, *o*-Ph), 126.68 (d, $J_{C–P}$ = 130.4 Hz, P–C), 133.39 (d, $^3J_{C–P}$ = 12.0 Hz, *m*-Ph), 161.70 (d, $^4J_{C–P}$ = 3.2 Hz, *p*-Ph). ^{31}P NMR ($CDCl_3$): δ = 77.0. HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{27}N_2OPSNa$: 337.1479; found: 337.1483. Anal. Calcd for $C_{15}H_{27}N_2OPS$: C, 57.30; H, 8.66; N, 8.91. Found: C, 58.12; H, 8.65; N, 8.01. **5c**: ^1H NMR ($CDCl_3$): δ = 1.09 (t, $J_{H–H}$ = 7.1 Hz, 12 H, Me), 3.14–3.25 (m, 8 H, CH_2), 7.01 (dd, $J_{H–P}$ = 5.1 Hz, $J_{H–H}$ = 3.6 Hz, 1 H, Th-CH), 7.15 (dd, $J_{H–P}$ = 2.7 Hz, $J_{H–H}$ = 3.8 Hz, 1 H, Th-CH), 7.24 (m, 2 H, Th-CH), 7.46 (dd, $J_{H–P}$ = 8.0 Hz, $J_{H–H}$ = 3.6 Hz, 1 H, Th-CH). ^{13}C NMR ($CDCl_3$): δ = 13.34 (d, $^3J_{C–P}$ = 4.2 Hz, Me), 39.14 (d, $^2J_{C–P}$ = 4.5 Hz, CH_2), 124.07 (d, $^2J_{C–P}$ = 14.2 Hz, Th-CH), 124.60 (s, Th-CH), 125.42 (s, Th-CH), 128.01 (s, Th-CH), 135.34 (d, $^3J_{C–P}$ = 9.4 Hz, Th-CH), 136.45 (s, Th-CH), 137.18 (d, $J_{C–P}$ = 134.0 Hz, P–C), 144.21 (d, $^4J_{C–P}$ = 6.0 Hz, Th-C). ^{31}P NMR ($CDCl_3$): δ = 65.8. HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{25}N_2PS_3Na$: 395.0815; found: 395.0817. Anal. Calcd for $C_{16}H_{25}N_2PS_3$: C, 51.58; H, 6.76; N, 7.52. Found: C, 51.11; H, 6.71; N, 6.57. **5d**: ^1H NMR ($CDCl_3$): δ = 1.16 (t, $J_{H–H}$ = 7.1 Hz, 12 H, Me), 3.15–3.41 (m, 8 H, CH_2), 7.41–7.60 (m, 3 H), 7.70 (ddd, *J* = 1.2, 7.2, 16.5 Hz, 1 H), 7.84 (d, $J_{H–H}$ = 7.8 Hz, 1 H), 7.92 (d, $J_{H–H}$ = 8.4 Hz, 1 H), 9.00 (d, $J_{H–H}$ = 8.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ = 14.15 (d, $^3J_{C–P}$ = 2.4 Hz, Me), 40.64 (d, $^2J_{C–P}$ = 4.8 Hz, CH_2), 124.31 (d, $J_{C–P}$ = 14.8 Hz), 126.21 (s), 126.44 (s), 127.77 (d, $^4J_{C–P}$ = 5.4 Hz), 128.67 (d, $^4J_{C–P}$ = 1.7 Hz), 130.35 (d, $^3J_{C–P}$ = 9.4 Hz), 131.30 (d, $J_{C–P}$ = 124.6 Hz, P–C), 132.35 (d, $^3J_{C–P}$ = 3.4 Hz), 132.70 (d, $^2J_{C–P}$ = 10.9 Hz), 134.39 (d, $^3J_{C–P}$ = 10.4 Hz). ^{31}P NMR ($CDCl_3$): δ = 73.4. HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{27}N_2PSNa$: 357.1530; found: 357.1528. Anal. Calcd for $C_{18}H_{27}N_2PS$: C, 64.64; H, 8.14; N, 8.38. Found: C, 64.61; H, 8.37; N, 7.79. **5e**: ^1H NMR ($CDCl_3$): δ = 1.00 (t, $J_{H–H}$ = 7.2 Hz, 12 H, Me), 2.96–3.18 (m, 8 H, Et), 3.41 (d, $J_{H–P}$ = 14.7 Hz, 2 H, P–CH_2), 7.21–7.31 (m, 3 H), 7.40–7.43 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ = 13.93 (d, $^3J_{C–P}$ = 3.6 Hz, Me), 39.61 (d, $^2J_{C–P}$ = 3.4 Hz, CH_2), 39.66 (d, $J_{C–P}$ = 84.7 Hz, P–CH_2), 126.82 (d, $^5J_{C–P}$ = 3.7 Hz, *p*-Ph), 127.92 (d, $^4J_{C–P}$ = 3.2 Hz, 2 × C, *m*-Ph), 130.67 (d, $^3J_{C–P}$ = 5.7 Hz, 2 × C, *o*-Ph), 132.49 (d, $^2J_{C–P}$ = 6.1 Hz). ^{31}P NMR ($CDCl_3$): δ = 81.9. HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{27}N_2PSNa$: 321.1530; found: 321.1526.

(10) **4f**: ^1H NMR ($CDCl_3$): δ = 7.13–7.69 (m, 7 H), 8.36 (ddd, *J* = 1.5, 3.3, 7.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ = 124.23 (d, $^4J_{C–P}$ = 5.0 Hz, C–Br), 127.43 (s), 129.32 (d, $J_{C–P}$ = 3.2 Hz), 129.53 (s), 130.25 (s), 131.65 (d, $J_{C–P}$ = 5.0 Hz), 132.29 (s), 132.75 (s), 133.74 (d, $J_{C–P}$ = 1.5 Hz), 137.50 (d, $J_{C–P}$ = 62.1 Hz, P–C), 139.41 (d, $^3J_{C–P}$ = 8.3 Hz), 143.15 (d, $^2J_{C–P}$ = 43.9 Hz). ^{31}P NMR ($CDCl_3$): δ = 150.2.

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(13) **5f**: ^1H NMR ($CDCl_3$): δ = 0.96 (t, $J_{H–H}$ = 7.2 Hz, 6 H, Me), 1.09 (t, $J_{H–H}$ = 7.2 Hz, 6 H, Me), 2.78–3.09 (m, 6 H, CH_2), 3.21–3.31 (m, 2 H, CH_2), 7.16–7.30 (m, 4 H), 7.40–7.50 (m, 2 H), 7.58–7.60 (m, 1 H), 7.90 (dd, *J* = 12.4, 7.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ = 13.6 (d, $^3J_{C–P}$ = 5.2 Hz, Me), 13.7 (d, $^3J_{C–P}$ = 2.0 Hz, Me), 39.7 (d, $^2J_{C–P}$ = 4.5 Hz, CH_2), 39.9 (d $^2J_{C–P}$ = 3.8 Hz, CH_2), 124.4 (s, C–Br), 126.0 (s), 127.1 (d, $J_{C–P}$ = 11.5 Hz), 128.7 (s), 130.0 (d, $J_{C–P}$ = 2.8 Hz), 131.4 (s), 131.6 (d, $J_{C–P}$ = 7.2 Hz), 132.2 (s), 133.0 (d, $J_{C–P}$ = 125.5 Hz, P–C), 133.4 (d, $J_{C–P}$ = 11.9 Hz), 142.3 (d, $^3J_{C–P}$ = 3.9 Hz), 144.9 (d, $^2J_{C–P}$ = 11.8 Hz). ^{31}P NMR ($CDCl_3$): δ = 73.1. HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{28}N_2PSBrNa$: 461.0792; found: 461.0792. Anal. Calcd for $C_{20}H_{28}N_2PSBr$: C, 54.67; H, 6.42. Found: C, 55.45; H, 6.34.

