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Preparation and Hydrolysis of Some Sterically Protected 1-Aza-3-phosphaallenes

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Synopsis. Some sterically protected 1-aza-3-phosphaallenes carrying 2,4,6-tri-*t*-butylphenyl group were prepared and the hydrolysis reactions of these azaphosphaallenes were studied.

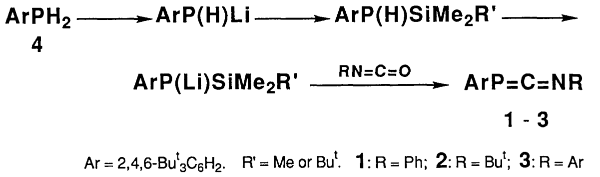
Sterically protected phosphorus containing multiple bonded compounds are currently of interest. There have been several reports on phosphacumulenes including phosphaallenes,[1–4] 1,3-diphosphaallenes,[5,6] as well as 1-aza-3-phosphaallenes[1,7] carrying the 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar) as a kinetically protecting group. These phosphacumulenes contain lowly coordinated phosphorus atom(s) (coordination number 2) and they are interesting molecules because of having a moiety of ambident reactivities.

Carbodiimides are well-known class of compounds and have often been used as dehydrating agents. We have already reported the preparation of 1-phenyl-3-(2,4,6-tri-*t*-butylphenyl)-1-aza-3-phosphaallene (**1**) and the 1-*t*-butyl derivative (**2**) as examples for 1-aza-3-phosphaallene, which is a phosphorus analogue of carbodiimide. We were also able to obtain 1-(2,4,6-tri-*t*-butylphenyl) derivative (**3**) as a stable compound in a similar method by the phospha-Peterson reaction starting from 2,4,6-tri-*t*-butylphenylphosphine (**4**) as shown in Scheme 1.

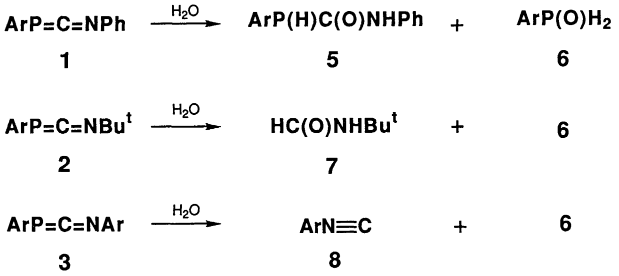
The reaction of the *t*-butyl derivative (**2**) with water in THF (tetrahydrofuran) gave 84% yield of 2,4,6-tri-*t*-butylphenylphosphine oxide (**6**).[8] The formation of *N*-*t*-butylformamide (**7**) was also observed.

The process of the hydrolysis was monitored by ^{31}P NMR, as follows. As the intensity of the peak of the starting material **2** decreased, the intensity of the phosphine oxide **6** increased, while other peaks were not observed. On the other hand, during the hydrolysis of azaphosphaallene **1**, the peak of **1** decreased while the peak of the phosphinoformamide **5**, a phosphorus analogue of urea, appeared after 24 h. The peak due to **6** also appeared after two days. Futhermore, in the case of the Ar derivative **3**, the hydrolysis reaction gave **6** and 2,4,6-tri-*t*-butylphenyl isocyanide **8**[9,10] almost quantitatively, but no peak due to the corresponding phosphinoformamide **9** was observed (Scheme 2).

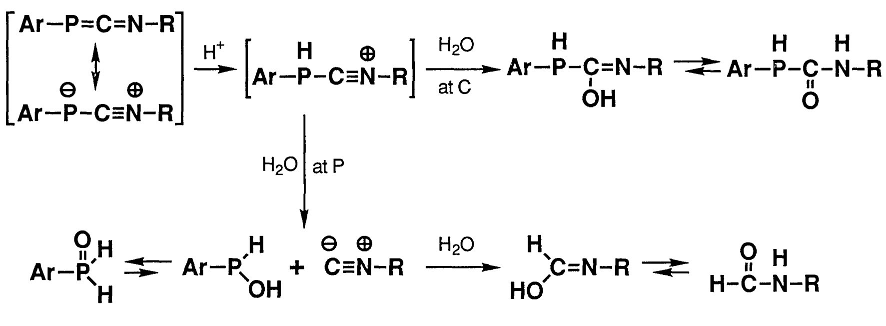
These results are explicable by the mechanism as shown in Scheme 3. The phosphine oxide **6** was the major product as a phosphorus part in each reaction. An attack of a nucleophile might mainly occur on the phosphorus atom after the protonation there. Probably an attack on the carbon atom might also occur in the case of the phenyl derivative **1**, where the substituent on nitrogen is not so bulky enough to prevent nucleophilic attack on carbon. A sterically bulky isocyanide **8**, which is stable toward water, was obtained in the hydrolysis reaction of **3** also indicating



Scheme 1.



Scheme 2.



Scheme 3.

that an initial protonation occurs on the phosphorus atom resulting in the formation of phosphine oxide and isocyanide. A canonical form of ammoniophosphide type might be important in azaphosphaallene from its spectroscopic point of view[1] and its important contribution has also been confirmed by the reactivity in hydrolysis reactions. The results were quite different from those of 1,3-diphosphaallene reported by Karsch.[11]

Experimental

Preparation of 1-Phenyl-3-(2,4,6-tri-*t*-butylphenyl)-1-aza-3-phosphaallene (1): 2,4,6-Tri-*t*-butylphenylphosphine (**4**, 516.0 mg, 1.85 mmol) was lithiated with 2.04 mmol of butyllithium (1.44 M, in hexane, M=mol dm^{-3}) at room temperature in THF (45 ml).[1] The solution was silylated with *t*-butylchlorodimethylsilane (363.1 mg, 2.41 mmol) and then lithiated again with butyllithium (2.41 mmol) at room temperature. The reaction mixture was allowed to react with phenyl isocyanate (2.59 mmol) at −78 °C to give an orange-red homogeneous solution. The solution was concentrated and chromatographed over silica gel using hexane as eluent to give 289.2 mg of yellow crystals and *N*-phenyl-*P*-(2,4,6-tri-*t*-butylphenyl)phosphinoformamide **5** (6%). Recrystallization of the yellow crystals from pentane gave 177.4 mg of azaphosphaallene **1** in 55% yield. **1**: yellow crystals; mp 90—92 °C; ^{1}H NMR (CDCl$_3$) δ=7.43 (2H, d, $^4J_{\mathrm{PH}}$=2.2 Hz, arom-Ar), 7.3—7.1 (5H, m, Ph), 1.67 (18H, s, *o*-Bu^t), 1.30 (9H, s, *p*-Bu^t); ^{31}P NMR (CDCl$_3$) δ=−106.2 (s); ^{13}C NMR (CDCl$_3$) δ=209.4 (d, $^1J_{\mathrm{PC}}$=27.4 Hz, P=C), 156.6 (d, $^2J_{\mathrm{PC}}$=4.6 Hz, *o*-Ar), 129.2 (s, *m*-Ar), 127.4 (s, *p*-Ph), 124.4 (s, *m*-Ph), 122.3 (s, *o*-Ph), 38.3 (s, *o*-$\underline{\mathrm{C}}$Me$_3$), 35.0 (s, *p*-$\underline{\mathrm{C}}$Me$_3$), 33.1 (d, $^4J_{\mathrm{PC}}$=6.4 Hz, *o*-C$\underline{\mathrm{Me}}_3$), 31.3 (s, *p*-C$\underline{\mathrm{Me}}_3$); IR (KBr) 1845 cm^{-1} (vs); UV (hexane) $\lambda_{\max}$ 202 (ε 73500), 257 (45100), 286 (sh 14500), and 412 nm (1410); MS (70 eV) *m/z* 379 (M$^+$); Found: *m/z* 379.2430. Calcd for C$_{25}$H$_{34}$NP: M, 379.2431. **5**: mp 199—200 °C; ^{1}H NMR (CDCl$_3$) δ=7.61 (2H, d, $^4J_{\mathrm{PH}}$=1.5 Hz, *m*-Ar), 7.4—6.9 (5H, m, Ph), 5.99 (1H, brs, NH), 5.89 (1H, d, $^1J_{\mathrm{PH}}$=244.9 Hz, PH), 1.58 (18H, brs, *o*-Bu^t), 1.39 (9H, s, *p*-Bu^t); ^{31}P NMR (CDCl$_3$) δ=−62.1 (d, $^1J_{\mathrm{PH}}$=238.0 Hz); Found: *m/z* 397.2543. Calcd for C$_{25}$H$_{36}$NOP: M, 397.2533.

Preparation of 1-*t*-Butyl-3-(2,4,6-tri-*t*-butylphenyl)-1-aza-3-phosphaallene (2): Lithium phosphide, obtained from the phosphine **4** (505.5 mg, 1.82 mmol) in THF (40 ml) and 2.00 mmol of butyllithium (2.53 M, in hexane) at room temperature, was treated with *t*-butylchlorodimethylsilane (359.2 mg, 2.38 mmol) and stirred for 3 h and then lithiated with 2.55 mmol of butyllithium at room temperature. The solution was stirred for 100 min and then to this was added 2.73 mmol of *t*-butyl isocyanate at −78 °C. The resulting mixture was warmed up to room temperature. The solvent was removed under reduced pressure and the residue was chromatographed over silica gel using pentane as eluent at 0°C to give 508.6 mg (78%) of **2**. **2**: yellow crystals; mp 166—168 °C (decomp); ^{1}H NMR (CDCl$_3$) δ=7.37 (2H, d, $^4J_{\mathrm{PH}}$=2.0 Hz, arom.), 1.64 (18H, s, *o*-Bu^t), 1.30 (9H, s, *p*-Bu^t), 1.16 (9H, s, *N*-Bu^t); ^{31}P NMR (CDCl$_3$) δ=−101.9 (s); ^{13}C NMR (CDCl$_3$) δ=192.2 (d, $^1J_{\mathrm{PC}}$=76.2 Hz, P=C=N), 156.7 (d, $^2J_{\mathrm{PC}}$=3.7 Hz, *o*-arom.), 149.3 (s, *p*-arom.), 123.2 (d, $^1J_{\mathrm{PC}}$=52.0 Hz, *i*-arom.), 121.6 (d, $^3J_{\mathrm{PC}}$=1.5 Hz, *m*-arom.), 61.0 (d, $^3J_{\mathrm{PC}}$=12.5 Hz, *N*-$\underline{\mathrm{C}}$Me$_3$), 38.3 (s, *o*-$\underline{\mathrm{C}}$Me$_3$), 34.9 (s, *p*-$\underline{\mathrm{C}}$Me$_3$), 33.1 (d, $^4J_{\mathrm{PC}}$=7.3 Hz, *o*-C$\underline{\mathrm{Me}}_3$), 31.3 (s, *p*-C$\underline{\mathrm{Me}}_3$), 30.6 (s, *N*-C$\underline{\mathrm{Me}}_3$); IR (KBr) 1885 cm^{-1} (vs); UV (hexane) $\lambda_{\max}$ 203 (ε 49600), 250 (sh 7200), 291 (9600), and 376 nm (490); Found: *m/z* 359.2756. Calcd for C$_{23}$H$_{38}$NP: M, 359.2741.

Preparation of 1,3-Bis(2,4,6-tri-*t*-butylphenyl)-1-aza-3-phosphaallene (3): Lithium phosphide, obtained from the phosphine **4** (147.0 mg, 0.528 mmol) in THF (10 ml) and 0.594 mmol of butyllithium (1.40 M, in hexane) at room temperature was treated with chlorotrimethylsilane (0.632 mmol) and stirred for 15 min and lithiated again with 0.632 mmol of butyllithium at room tempurature. The solution was stirred for 16 min at −78 °C and then to this was added 0.686 mmol (197.1 mg) of 2,4,6-tri-*t*-butylphenyl isocyanate at −78 °C.[10] The resulting mixture was warmed up to room temperature and the solvent was removed by rotary evaporation. The residue was chromatographed over silica gel (using pentane as eluent) at 0 °C to give 180.8 mg (63% yield) of 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1-aza-3-phosphaallene (**3**) and 18.2 mg (6%) of *N*,*P*-bis(2,4,6-tri-*t*-butylphenyl)phosphinoformamide (**9**). **3**: red crystals; mp 82—84 °C (decomp); ^{1}H NMR (CDCl$_3$) δ=7.37 (2H, d, $^4J_{\mathrm{PH}}$=2.2 Hz, *P*-*m*-Ar), 7.20 (2H, s, *N*-*m*-Ar), 1.63 (18H, s, *o*-Bu^t, *P*-Ar), 1.33 (9H, s, *p*-Bu^t, *P*-Ar), 1.26 (9H, s, *p*-Bu^t, *N*-Ar), 1.14 (18H, s, *o*-Bu^t, *N*-Ar); ^{31}P NMR (CDCl$_3$) δ=−135.3 (s); ^{13}C NMR (CDCl$_3$) δ=171.8 (d, $^1J_{\mathrm{PC}}$=91.4 Hz, P=C=N), 158.5 (d, $^2J_{\mathrm{PC}}$=3.9 Hz, *o*-arom., *P*-Ar), 149.3 (s, *p*-arom., *N*-Ar), 146.0 (d, $^4J_{\mathrm{PC}}$=2.6 Hz, *p*-arom., *P*-Ar), 139.7 (d, $^4J_{\mathrm{PC}}$=2.6 Hz, *o*-arom., *N*-Ar), 128.1 (s, *i*-arom., *N*-Ar), 121.5 (s, *m*-arom.), 121.4 (s, *m*′-arom.), 119.3 (d, $^1J_{\mathrm{PC}}$=47.4 Hz, *i*-arom., *P*-Ar), 38.4 (s, *o*-$\underline{\mathrm{C}}$Me$_3$, *P*-Ar), 35.2 (s, *o*-$\underline{\mathrm{C}}$Me$_3$, *N*-Ar), 34.9 (s, *p*,*p*′-$\underline{\mathrm{C}}$Me$_3$), 33.2 (d, $^4J_{\mathrm{PC}}$=7.2 Hz, *o*-C$\underline{\mathrm{Me}}_3$, *P*-Ar), 31.5 (s, *p*-C$\underline{\mathrm{Me}}_3$), 31.4 (s, *p*′-C$\underline{\mathrm{Me}}_3$), 30.5 (s, *o*-C$\underline{\mathrm{Me}}_3$, *N*-Ar); IR (KBr) 2060, 2040, 2020 cm^{-1}; Found: *m/z* 547.4287. Calcd for C$_{37}$H$_{58}$NP: M, 547.4305. **9**: ^{31}P NMR (CDCl$_3$) δ=−43.2 (d, $^1J_{\mathrm{PH}}$=256.5 Hz); ^{1}H NMR (CDCl$_3$) δ=7.46 (2H, d, $^4J_{\mathrm{PH}}$=2.6 Hz, *P*-*m*-Ar), 7.34 (2H, s, *N*-*m*-Ar), 6.85 (1H, brs, NH), 5.94 (1H, d, $^1J_{\mathrm{PH}}$=258.5 Hz, PH), 1.6—0.9 (54H, Bu^t); ^{13}C NMR (CDCl$_3$) δ=176.7 (d, $^1J_{\mathrm{PC}}$=23.2 Hz, P$\underline{\mathrm{C}}$ON); MS *m/z* 567 (M+2), 566 (M+1), 565 (M$^+$), 550 (M−Me), 509 (M−C$_4$H$_8$), 453 (M$^+$−2C$_4$H$_8$); Found: *m/z* 565.4415. Calcd for C$_{37}$H$_{60}$NOP: M, 565.4413.

Hydrolysis of 1-*t*-Butyl-3-(2,4,6-tri-*t*-butylphenyl)-1-aza-3-phosphaallene (2): 1-*t*-Butyl-3-(2,4,6-tri-*t*-butylphenyl)-1-aza-3-phosphaallene (**2**) (8.0 mg, 0.022 mmol) was dissolved in 1.5 ml of THF. To the solution was added 0.01 ml (0.555 mmol) of water at room temperature. The process of hydrolysis was monitored by ^{31}P NMR spectra. When **2** disappeared completely, the solvent was removed under reduced pressure and the residue was chromatographed over silica gel using CH$_2$Cl$_2$ to give 5.4 mg (84%) of 2,4,6-tri-*t*-butylphenylphosphine oxide (**6**). The oxide was identified by comparison of the following data with those of an authentic sample. ^{31}P NMR (CDCl$_3$) δ=−10.6 (t, $^1J_{\mathrm{PH}}$=482.2 Hz); ^{1}H NMR (CDCl$_3$) δ=7.85 (2H, d, $^1J_{\mathrm{PH}}$=481.5 Hz, P$\underline{\mathrm{H}}_2$), 7.49 (2H, d, $^4J_{\mathrm{PH}}$=4.4 Hz, arom.), 1.61 (18H, s, *o*-Bu^t), 1.32 (9H, s, *p*-Bu^t). The formation of *N*-*t*-butylformamide (**7**) was confirmed by VPC analysis using an OV-1 column at 80 °C.

^{31}P NMR Study of Hydrolysis of 1-Phenyl-3-(2,4,6-tri-*t*-butylphenyl)-1-aza-3-phosphaallene (1): 1-Aza-3-phosphaallene **1** (4.9 mg, 0.013 mmol) was dissolved in 1.5 ml of ether in an NMR tube under argon and 0.555 mmol of water was added. The reaction was followed by ^{31}P NMR. After one day a new doublet peak appeared at −62.3 ppm ($^1J_{\mathrm{PH}}$=238.0 Hz) due to **5** with intensity of two thirds of that of **1**. After 2 days a new triplet signal was observed at −13.6 ($^1J_{\mathrm{PH}}$=478.5 Hz) due to **6** with an equal intensity of the azaphosphaallene **1**.

Hydrolysis of 1,3-Bis(2,4,6-tri-*t*-butylphenyl)-1-aza-3-phosphaallene (3): The reaction products of hydrolysis of **3** under similar conditions in THF were phosphine oxide **6** and 2,4,6-tri-*t*-butylphenyl isocyanide **8**[9,10] almost quantitatively. **8**, ^{1}H NMR (CDCl$_3$) δ=7.33 (2H, s, arom.), 1.54 (18H, s, *o*-Bu^t), 1.31 (9H, s, *p*-Bu^t). IR (KBr) 2120, 1595, 1428, and 1368 cm^{-1}; MS *m/z* 271 (M$^+$), 256 (M−Me).

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