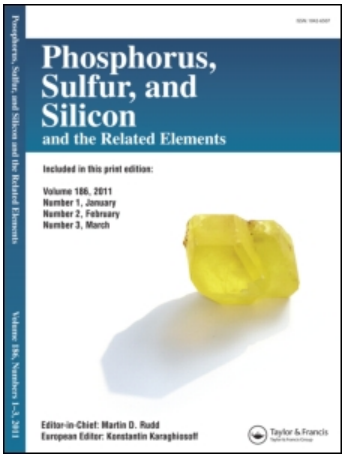

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P-N COMPOUNDS 33. PHOSPHAMINIMIDES 7. N-METHYL-N-PHOSPHINYLAMINO-1,2,5,6- TETRAHYDROPYRIDINIUM INNER SALTS

L. A. Cates[a]; V. -S. Li[a]
[a] Department of Medicinal Chemistry, College of Pharmacy, University of Houston, Houston, Texas

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P-N COMPOUNDS 33. PHOSPHAMINIMIDES 7. N-METHYL-N-PHOSPHINYLAMINO-1,2,5,6-TETRAHYDROPYRIDINIUM INNER SALTS[1]

L. A. CATES* and V.-S. LI
Department of Medicinal Chemistry, College of Pharmacy, University of Houston, Houston, Texas 77204-5511

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Phosphinylaminopyridinium inner salts were reduced and methylated to yield N-methyl-N-phosphinylamino-1,2,5,6-tetrahydropyridinium iodides. Dehydroiodination of these intermediates gave the title compounds.

Key words: Phosphaminimides, reduction/methylation; N-methyl-N-phosphinylamino-1,2,5,6-tetrahydropyridinium inner salts; dehydroiodination.

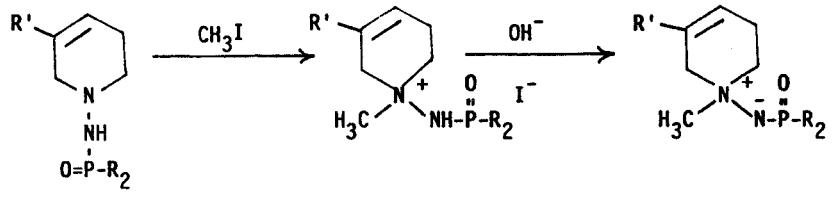
In some previous investigations involving phosphaminimides, reactions and products were shown to occur which differed from those expected when compared to carbaminimides, their carbonyl counterparts. These included resonance stabilization which interfered with dehydrohalogenation of a dimethylamino derivative,[2] and formations of unique monoethoxyphosphaminimide[3] and hydrazinium iodide-hydrazinium inner salts.[4] This present study continues the search for chemical dissimilarities that might occur when a phosphinyl group is introduced in lieu of a carbonyl moiety in hydrazinium inner salts.

RESULTS AND DISCUSSION

Diethoxy (**1**) and diphenyl (**2**) N-phosphinylamino-1,2,5,6-tetrahydropyridines and the 3-methyl derivative of **2** (**3**) were synthesized by reduction of phosphaminimides which were prepared from the phosphorylation of 1-aminopyridinium salts in the presence of potassium hydroxide.[4] The pyridines were reacted with methyl iodide to yield phosphaminimides **4–6** which were dehydroiodinated to provide the title compounds (**7–9**).

For the purpose of comparison the carbaminimide analog of **7**, N-methyl-N-ethoxycarbonylimino-1,2,5,6-tetrahydropyridinium inner salt, was resynthesized using the same scheme.[5]

Both types of reaction, methylation and dehydroiodination, proceeded in a manner similar to that found for carbaminimides. Steric hindrance might be expected to be involved in the former process, however, the high yields found for **4–6**, comparable to almost quantitative ones reported for carbonyl intermediates, indicate that such is not the case. Therefore, no disparity was found between the formation of N-methyl-N-phosphinylamino-1,2,5,6-tetrahydropyridines and their carbonyl analogs. The title compounds are candidates for investigations involving ring contraction reactions.



1 - 3 4 - 6 7 - 9

1, 4, 7 R = OC_2H_5, R' = H

2, 5, 8 R = C_6H_5, R' = H

3, 6, 9 R = C_6H_5, R' = CH_3

EXPERIMENTAL

The ^{1}H-NMR spectra were measured on a Nicolet NT-300 spectrometer using tetramethylsilane as the internal standard and deuterated chloroform as the solvent. Chemical shifts are reported in δ units and coupling constants in Hz. The IR (KBr, neat for **3** and **6**) spectra were obtained with a Perkin-Elmer 283 spectrophotometer and absorbances are reported in cm^{-1}. Elemental analyses were conducted by Atlantic Microlab, Inc., Norcross, GA. Melting points were taken on a Thomas-Hoover apparatus and readings were corrected to reference standards. Silica gel 60 (70-230 mesh) (**2**, **4–6**) or neutral alumina (**7–9**) was used for chromatography. Evaporations and dryings were made under reduced pressure.

3-Methyl-N-[(diphenylphosphinyl)amino]-1,2,5,6-tetrahydropyridine (**2**). According to a previously reported method,[6] a solution of N-[(diphenylphosphinyl)imino]pyridinium inner salt[2] (1.4 g, 4.8 mmole) in EtOH (20 mL) was added dropwise with stirring and under nitrogen to a solution of $NaBH_4$ (0.9 g, 2.4 mmole) in EtOH (20 mL) at 0°C and the mixture maintained at 0°C for 8 h. Water (50 mL) was added and the reaction temperature was slowly increased to 25°C. The mixture was extracted with CH_2Cl_2; the extract was dried with sodium sulfate, filtered and evaporated. The yellow solid residue was chromatographed using $CHCl_3$ and 1% MeOH in $CHCl_3$ and the residue from the evaporation of appropriate elutions was recrystallized from CH_2Cl_2-EtOH to yield 1.4 g (32%) of **2**: mp 195–197°C: IR 3080 (NH), 1190, 1205 (P=O); NMR 2.17 (*m*, 2H, C_5—H), 2.99 (*t*, 2H, C_6—H), 3.42 (*s*, 2H, C_6—H), 4.25 (*d*, J = 17.83, 1H, NH), 5.55 (*d*, J = 10.1, 1H, C_4—H), 5.65 (*d*, J = 10.1, 1H, C_3—H), 7.46 (*m*, 6H, 2Ph), 7.93 (*m*, 4H, 2Ph). Anal. Calc. for $C_{17}H_{19}N_2OP$: C, 68.42; H, 6.42; N, 9.39. Found: C, 68.28; H, 6.48; N, 9.32.

N-Methyl-N-phosphinylamino-1,2,5,6-tetrahydropyridine iodides (**4–6**). A 10-fold excess of iodomethane was added to a solution of **1**,[6] (0.4 g, 1.7 mmole) or suspensions of **2** or **3**[6] in CH_3CN (10 mL) and the mixtures heated at 65°C for 15 h. The yellow solutions were evaporated and dried to yield **5**; **6** and **7** were recrystallized from CH_2Cl_2-Et_2O.

4: Gummy solid ($C_{10}H_{22}IN_2O_3P$, 78% yield); IR 3120 (NH), 1245 (P=O), 955, 1030, 1080 (POEt); NMR 1.38 (*t*, 6H, $2CH_3$), 2.54 (*m*, 1H, C_5—H), 2.76 (*m*, 1H, C_5—H), 3.65 (*s*, 3H, CH_3N), 3.93 (*m*, 1H, C_6—H), 4.14 (*m*, 1H, C_6—H), 4.26 (*m*, 4H, $2CH_2O$), 4.81 (*d*, J = 16.81, 1H, C_2—H), 4.96 (*d*, J = 16.29, 1H, C_2—H), 5.69 (*d*, $J_{4,3}$ = 10.83, C_4—H), 5.93 (*d*, $J_{3,4}$ = 10.25, 1H, C_3—H), 8.18 (*d*, J = 4.24, 1H, NH).

5: Solid ($C_{18}H_{22}IN_2OP$, 93% yield); mp 163–165°C; IR 3050 (NH), 1195, 1215 (P=O); MNR 2.50 (*m*, 1H, C_5—H), 2.62 (*m*, 1H, C_5—H), 3.76 (*s*, 3H, CH_3N), 4.23 (*m*, 1H, C_5—H), 4.48 (*d*, J = 16.28, 1H, C_2—H), 4.63 (*m*, 1H, C_6—H), 5.15 (*d*, J = 16.39, 1H, C_2—H), 5.55 (*d*, $J_{4,3}$ = 10.33, 1H, C_4—H), 5.95 (*d*, $J_{3,4}$ = 10.40, 1H, C_3—H), 7.55 (*m*, 6H, 2Ph), 8.00 (*m*, 4H, 2Ph), 8.97 (*d*, J = 8.62, 1H, NH).

6: Solid ($C_{19}H_{24}IN_2OP$, 94% yield); mp 88–90°C; IR 3050 (NH), 1210 (P=O); NMR 1.49 (*s*, 3H, CH_3), 2.42 (*m*, 1H, C_5—H), 2.76 (*m*, 1H, C_5—H), 3.80 (*s*, 3H, CH_3N), 4.03 (*m*, 1H, C_6—H), 4.28 (*d*, J =

16.24, 1H, C_2—H), 4.65 (*m*, 1H, C_6—H), 4.93 (*d*, J = 15.97, 1H, C_2—H), 5.59 (*s*, 1H, C_4—H), 7.60 (*m*, 6H, 2Ph), 7.96 (*m*, 4H, 2Ph), 8.87 (bs, 1H, NH).

N-Methyl-N-phophinylamino-1,2,5,6-tetrahydropyridinium inner salts (**7–9**). A 5% solution of NaOH (2 mL) was added dropwise to a solution (**4**) or suspension (**5** or **6**) in water (3 mL) and the solution evaporated at 25°C. The residue was extracted with CH_2Cl_2 and the extract was filtered through a size F sintered glass filter. The filtrate was evaporated to yield a yellow oil or gum which was chromatographed twice using $CHCl_3$ and 1% MeOH in $CHCl_3$, successively; then with 2% MeOH in $CHCl_3$ (**7**) or once using 1% MeOH in $CHCl_3$ (**8** and **9**). For the latter two compounds the solid obtained from evaporation of appropriate elutions was recrystallized from CH_2Cl_2-Et_2O.

7: Yellow oil (34% yield); IR 3400 (OH), 1205 (P=O), 940, 1040 (POEt); NMR 1.28 (*t*, 6H, $2CH_3$), 2.40 (*m*, 1H, C_5—H), 2.60 (*m*, 1H, C_5—H), 3.37 (*s*, 3H, CH_3N), 3.69 (*m*, 2H, C_6—H), 3.97 (*m*, 5H, $2CH_2O$, C_2—H), 4.33 (*d*, J = 16.85, 1H, C_2—H), 5.66 (*d*, $J_{4,3}$ = 10.34, 1H, C_4—H), 5.90 (*d*, $J_{3,4}$ = 10.33, 1H, C_3—H). Anal. Calc. for $C_{10}H_{21}N_2O_3P \cdot 1/2H_2O$: C, 46.66; H, 8.62; N, 10.88. Found C, 46.63, H, 8.66; N, 10.87.

8: White solid (82% yield); mp 133–134°C: IR 3430 (OH), 1110, 1140, 1170 (P=O); NMR 2.37 (*m*, 1H, C_5—H), 2.55 (M, 1H, C_5—H), 3.32 (*s*, 3H, CH_3N), 3.72 (*m*, 2H, C_6—H), 3.97 (*d*, J = 16.81, 1H, C_2—H), 4.39 (*d*, J = 16.93, 1H, C_2—H), 5.56 (*d*, $J_{4,3}$ = 10.09, 1H, C_4—H), 5.84 (*d*, $J_{3,4}$ = 9.94, 1H, C_3—H), 7.33 (*m*, 6H, 2Ph), 7.87 (*m*, 4H, 2Ph). Anal. Calc. for $C_{18}H_{21}N_2OP \cdot 1/2H_2O$: C, 67.25; H, 6.90; N, 8.72. Found: C, 67.38; H, 6.91; N, 8.78.

9: White solid (76% yield); mp 110–112°C: IR 1110, 1160 (P=O); NMR 1.52 (*s*, 3H, CH_3), 2.30 (*m*, 1H, C_5—H), 2.49 (*m*, 1H, C_5—H), 3.32 (*s*, 3H, CH_3N), 3.62 (*m*, 2H, C_6—H), 3.82 (*d*, J = 16.65, 1H, C_2—H), 4.30 (*d*, J = 16.44, 1H, C_2—H), 5.49 (*m*, 1H, C_4—H), 7.33 (*m*, 6H, 2Ph), 7.78 (*m*, 4H, 2Ph). Anal. Calc. for $C_{19}H_{23}N_2OP$: C, 69.90; N, 7.11; N, 8.58. Found C 69.67; H, 7.19; N, 8.51.

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