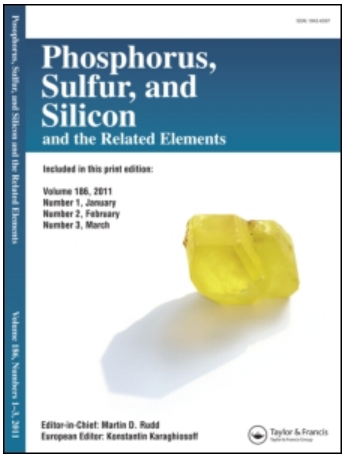

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P-N COMPOUNDS 29. PHOSPHAMINIMIDES 4. SYNTHESIS COMPARISONS WITH CARBONYL AND SULFONYL COMPOUNDS

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P–N COMPOUNDS 29. PHOSPHAMINIMIDES 4. SYNTHESIS COMPARISONS WITH CARBONYL AND SULFONYL COMPOUNDS[1]

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General preparatory methods for carbonyl and sulfonylaminimides were examined for application to phosphaminimides. Three routes to these agents were investigated and one, the reaction between phosphoric or phosphinic chlorides and aminopyridinium salts, was successful. A further anomaly involving the hydrazinium salt dehydrohalogenation procedure was also found.

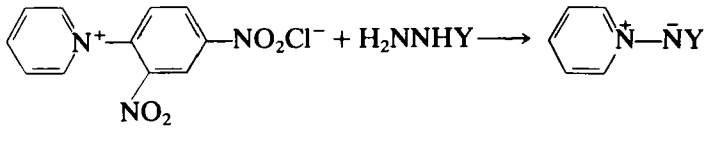
Previous papers in this series reported phosphaminimides (phosphinylhydrizinium inner salts) whose structures differed from those anticipated when routes theretofore applied only to the synthesis of other types of aminimides (carbonyl and sulfonylhydrazinium inner salts) were employed. During the attempted synthesis of phosphinylene (bis)1,1,1-trimethyl hydrizinium) inner salt only the mono-, instead of the expected dihydrazinium compound, was realized.[2] Also, 2-ethyoxyphosphinyl-1,1-dimethyl-1-(4-nitrobenzyl) hydrazinium inner salt, a unique type of phosphaminimide, was obtained instead of the anticipated corresponding diethoxy bromide compound when 2-ethyoxy-1,1-dimethylhydrazide and 4-nitrobenzyl bromide were reacted.[3]

In this present paper we report a further anomaly involving dehydrohalogenation of a hydrazinium salt, two unsuccessful preparations involving an acid azide and a pyridinium chloride and the synthesis of phoshaminimides via a method not previously applied to this type of compound.

RESULTS AND DISCUSSION

There are four general procedures for aminimide synthesis: preparation from hydrazides (method A) which includes dehydrohalogenation of hydrazinium salts (A-1) and reaction of hydrazides with 1-(2,4-dinitrophenyl)pyridinium chlorides (A-2), reaction of acid azides with amines (method B), preparation from tertiary aminimines (method C) and synthesis from hydrazinium salts (method D).[4,5]

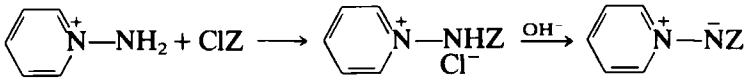
$$ZNH\overset{+}{N}(R')_4X^- \xrightarrow{OH^-} Z\overset{+}{N}\overset{-}{N}(R')_4 \qquad \text{(A-1)}$$



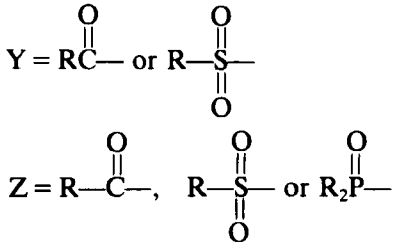
(A-2)

$$R_3N + N_3Y \xrightarrow{h\nu \text{ or } \Delta} R_3\overset{+}{N}\overset{-}{N}Y \qquad (B)$$

$$(CH_3)_3\overset{+}{N}\overset{-}{N}H + ROZ \longrightarrow Z\overset{-}{N}\overset{+}{N}(CH_3)_3 \qquad (C)$$



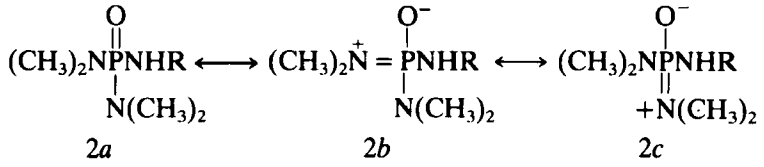
(D)



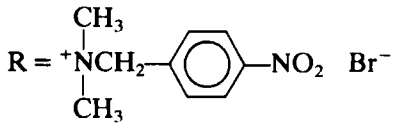
Despite the aforementioned exceptions method A-1 appears to have good applicability. In addition to those phosphaminimides prepared in our laboratory, this procedure was also employed by Kameyama *et al.* to synthesize a single compound, 2-diphenyl-1,1,1-trimethyl hydrizinium inner salt.[5] Prior to this present report the only other procedure successfully applied to phosphaminimides is method C involving the reaction between aminimines and phosphinates.[6]

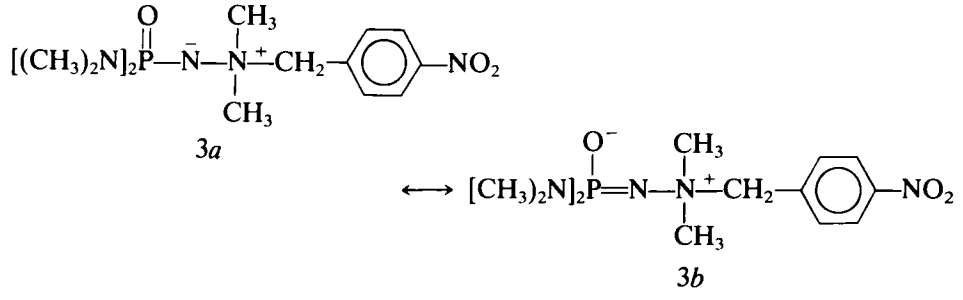
As a portion of a study involving the effect of P-substituents on the thermolysis of phosphaminimides we wished to include the dimethylamino derivative with the previously synthesized diethoxy-, diphenoxy- and diphenyl-1,1-dimethyl-1-(4-nitrobenzyl)hydrazinium inner salts.[3] The reaction of bis(dimethylamino)phosphorochloridate and 1,1-dimethyl hydrazine gave the corresponding hydrazide (**1**) which, when treated with 4-nitrobenzyl bromide, produced 2-bis(dimethylamino)-phosphinyl-1,1-dimethyl-1-(4-nitrobenzyl)hydrazinium bromide (**2**). Several attempts at dehydrobromination of **2** with NaOH and Et_3N at various temperatures followed by chromatography did not yield the corresponding phosphaminimide (**3**).

This failure is attributed to the presence of resonance forms (**2a–2c**) with delocalization of the negative charge from the N^1 atom. Therefore, the formation of **3a** and **3b**, whose resonance would stabilize the aminimide, is not favored.



2a *2b* *2c*



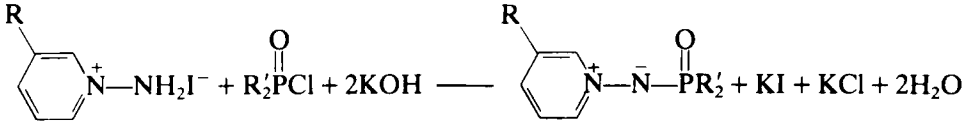


3a ⟷ 3b

A second type of phosphaminimide synthesis which also employs hydrazides was attempted (method A-2). This was patterned after the reaction between N-(2,4-dinitrophenyl)ethylpyridinium chloride (**4**), prepared from 2,4-dinitrochlorobenzene and 3-ethylpyridine, and various carbonyl and sulfonylhydrazines as employed by Tamura *et al.* and Knaus and Redda.[7,8] While we were able to reproduce the synthesis of the benzyl derivative using this method, the reaction between **4** and diphenylphosphinylhydrazide (**5**) did not yield the corresponding phosphaminimide. This lack of success is probably due to the exceptionally high polarity of **5** and its poor solubility in any suitable solvent, including methanol. The synthesis of the diphenyl phosphaminimide and others were, however, achieved by use of method D (q.v. below).

While the reaction between amines and acid azides (method B) yields aminimides with sulfonyl and carbonyl derivatives, this procedure using diphenyl and diethylphosphoryl azides did not succeed as a preparatory route to phosphaminimides. Since unreacted starting materials were recovered from the refluxing of diphenylphosphoryl azide with pyridine (12 hr) and diethylphosphoryl azide[9] with 3-ethylpyridine (8 hr) it appears these agents are too stable, due to electron delocalization,[10] to serve as reactants in this method.

The last of the four general procedures for aminimides involving hydrazinium salts, method D, led to the synthesis of phosphaminimides. 1-Amino- (**6**) or 1-amino-3-ethyl (**7**) pyridinium iodide, from pyridine or 3-ethylpyridine, hydroxylamine-O-sulfonic acid and potassium carbonate followed by hydriodic acid treatment,[11] reacts with acyl or tosyl chlorides and alkali to yield carbonyl or sulfonylaminimides.[12] Similarly, **6** reacts with diethyl or diphenyl phosphorochloridate or diphenyl phosphinic chloride in the presence of potassium hydroxide to give phosphaminimides **8**, **9** and **10**, respectively. The use of these latter reagents and **7**, in lieu of **6**, gave the corresponding diethoxy (**11**), diphenoxy (**12**) and diphenyl (**13**) phosphaminimides.



8, R = H, R′ = OC_2H_5 **11**, R = C_2H_5, R′ = OC_2H_5

9, R = H, R′ = OC_6H_5 **12**, R = C_2H_5, R′ = OC_6H_5

10, R = H, R′ = C_6H_5 **13**, R = C_2H_5, R′ = C_6H_5

Therefore, of the four main routes to aminimides three, with the exception of subtype A-2, have thus far found application in the synthesis of phosphaminimides.

EXPERIMENTAL

The ^{1}H-NMR spectra were measured on a Nicolet NT-300 spectrophotometer 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 **8**, **11** and **12**) spectra were obtaned with a Perkin–Elmer 283 spectrophotometer and absorbances are reported in cm^{-1}. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA. Viscous liquid products **8**, **11** and **12** were unsuitable for elemental analysis and their structural assignments are based on spectrometric data. Melting point were taken on a Thomas–Hoover apparatus and readings were corrected to reference standards. Silica gel 60 (70–230 mesh) was used for chromatography. Evaporation and drying were carried out under reduced pressure unless otherwise indicated.

1-Bis(dimethylamino)(2,2-dimethylhydrazino)phosphine Oxide (**1**). Bis(dimethylamino)phosphorochloridate (8.53 g, 50 mmole) in CH_2Cl_2 (25 mL) was added to 1,1-dimethylhydrazine (9.01 g, 0.15 mole) in CH_2Cl_2 (5 mL) at 24°C, the mixture refluxed for 16 h and the solvent evaporated under a nitrogen stream. Addition of excess of CH_2Cl_2 to the residue gave a white precipitate of 1,1-dimethylhydrazine HCl which was removed by filtration and the filtrate was concentrated by evaporation. The residue was chromatographed using, in sequence, 2%, 5% and 10% MeOH in $CHCl_3$. Appropriate fractions, as determined by TLC (10% MeOH in $CHCl_3$) were distilled through a short path distilling head to yield 5.1 g (52%) of the hygroscopic product: bp 85–88° C/0.1 mm; IR 3160 (NH), 1200 (P═O), 740 (P—N); NMR 2.48 (s, 6H, $2CH_3$), 2.67 (d, $J = 9.45$, 12H, $4CH_3$). Anal. Calc. for $C_6H_{19}N_4OP$; C, 37.08; H, 9.86; N, 28.84. Found: C, 37.14; H, 9.87; N, 28.76.

2-Bis(dimethylamino)phosphinyl-1,1-dimethyl-1-(4-nitrobenzyl)hydrazinium bromide (**2**). To 4-nitrobenzyl bromide (7.8 g, 36 mmole) in CH_3CN (60 mL) was added **1** (7.0 g, 36 mmole). The mixture was heated at 50–52°C for 6 h and the solvent evaporated. The residue was chromatographed using, in sequence, 2, 5, 10 and 20% MeOH in $CHCl_3$ to yield a yellow mass which was recrystallized from CH_2Cl_2-acetone to give 10.33 g (70%) of **2**: mp 158–160°C; IR 3480 (OH), 3100 (NH), 1600, 1625 (C═C), 1350, 1520 (CNO_2), 1180, 1195 (P═O) 740 (PN); NMR 2.63 (d, $J = 9.76$, 12H, $4CH_3$), 3.74 (s, 6H, CH_3NCH_3), 5.68 (s, 2H, CH_2N), 8.14 (d, $J = 8.67$, 2H, arom), 8.25 (d, $J = 8.55$, 2H, arom), 8.50 (bs, 1H, NH). Anal. Calc. for $C_{13}H_{25}BrN_5O_3P \cdot H_2O$: C, 36.44; H, 6.36; N, 16.35; Br, 18.66. Found: C, 36.41; H, 6.35; N, 16.32; Br, 18.73.

N-[(Phosphinyl)imino] ((**8–10**) *and N-[(Phosphinyl)imino]-3-ethyl* (**11–13**) *pyridinium inner salts.* To 1-aminopyridinium iodide[11] or 1-amino-3-ethylpyridinium iodide[11] (15 mmole) suspended in EtOH (100 mL) was added, dropwise and concurrently with stirring at 25°C, a solution of KOH (45 mmole) in EtOH (100 mL) and of diethylphosphorochloridate, diphenylphosphorochloridate or diphenylphosphinic chloride (30 mmole) in CH_2Cl_2 (20 mL) at a rate that maintains a basic condition as indicated by purple coloration in the reaction mixture. After 16 h at 25°C the mixture was evaporated, the residue was dissolved in 10% aqueous Na_2CO_3 (40 mL) and extracted with CH_2Cl_2 (3×). The organic layer was dried over Na_2SO_4, filtered and the filtrate evaporated to yield a residue which was dried and chromatographed using eluants in sequence and further treated, as necessary, to yield the pure products as follows: For **8**: $CHCl_3$, 2, 3, 4, 5 and 10% MeOH in $CHCl_3$ to give the product ($C_9H_{15}N_2O_3P$, 42% yield) as a brown oil: IR 1615 (C═C), 1210 (P═O), 980, 1030 (POEt), 780 (PN); NMR 1.33 (t, 6H, $2CH_3$), 4.12 (quintet, 4H, $2CH_2O$), 7.40 (m, C_{3-5}-H, pyridinium), 8.64 (d, $J = 5.86$, 2H, C_2—H, C_6—H, pyridinium). For **9**: 2 and 5% MeOH in $CHCl_3$ to yield a yellow mass which gave the crystalline product in 68% yield when triturated with ether: mp 74–75°C; IR 1580 (C═C), 1190, 1230, 1260 (P═O), 900 (POPh), 775 (PN); NMR 7.13–7.64 (m, 13H, C_{3-5}, pyridinium and 2Ph), 8.62 (d, $J = 5.76$, 2H, C_2—H, C_6—H, pyridinium). Anal. Calc. for $C_{17}H_{15}N_2O_3P$: C, 62.55; H, 4.63; N, 8.58. Found: C, 62.46; H, 4.65; N, 8.54. For **10**: 2 and 5% MeOH in $CHCl_3$ followed by recrystallization twice from CH_2Cl_2-ether to give the product ($C_{17}H_{15}N_2OP$, 42% yield): mp 208–210°C (dec.); IR 1620 (C═C), 1180, 1190, 1220 (P═O); NMR 7.28 (m, 3H, C_{3-5}-H, pyridinium), 7.40 (m, 6H, Ph), 7.94 (m, 4H, Ph), 8.76 (d, $J = 6.07$, 2H, C_2—H, C_6—H, pyridinium). For **11**: $CHCl_3$, 2 and 5% MeOH in $CHCl_3$ to yield the product as a brown oil ($C_{11}H_{19}N_2O_3P$, 77% yield): IR 1590 (C═C), 1175, 1225, 1260 (P═O), 970, 1020 (POEt); NMR 1.27 (t, 3H, CH_3), 1.32 (t, 6H, $2CH_3$), 2.67 (q, 2H, CH_2), 4.11 (quintet, 4H, $2CH_2O$), 7.32 (m, 2H,

C_4—H, C_5—H, pyridinium), 8.46 (s, 1H, C_2—H, pyridinium), 8.50 (d, $J = 6.77$, C_6—H, pyridinium). For **12**: $CHCl_3$, 2 and 3% MeOH in $CHCl_3$ to give the product as a brown oil ($C_{19}H_{19}N_2O_3P$, 42% yield): IR 1595 (C═C), 1170, 1210, 1220 (P═O), 910 (POPh); NMR 1.24 (t, 3H, CH_3), 2.66 (q, 2H, CH_2), 7.11 (m, 2H, C_4—H, C_5–H, pyridinium), 7.32 (m, 10H, 2PhO) 8.39 (s, 1H, C_2—H, pyridinium), 8.46 (d, $J = 6.11$, 1H, C_6—H, pyridinium). For **12**; $CHCl_3$, 1, 2, and 5% MeOH in $CHCl_3$ followed by trituration of the resulting yellow mass with ether to yield the solid product in 40% yield: mp 127–128°C; IR 1610 (C═C), 1175, 1250 (P═O); NMR 1.17 (t, 3H, CH_3), 2.58 (q, 2H, CH_2), 7.22 (m, 2H, C_4—H, C_5—H, pyridinium), 7.39 (m, 6H, Ph), 7.95 (m, 4H, Ph), 8.58 (s, 1H, C_2—H, pyridinium), 8.62 (d, $J = 6.02$, 1H, C_6—H, pyridinium); Anal. Calc. for $C_{19}H_{19}N_2OP$: C, 70.77; H, 5.94; N, 8.69. Found: C, 70.69; H, 5.97; N, 8.68.

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