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Synthesis of Bis(phosphinoyl)amines and Phosphinoyl–Phosphorylamines by the *N*-Phosphinoylation and *N*-Phosphorylation of 1-Alkylamino-2,5-dihydro-1*H*-phosphole 1-Oxides

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ABSTRACT: *The N-phosphinoylation and N-phosphorylation reaction of 1-alkylamino-2,5-dihydro-1H-phosphole 1-oxides with diphenylphosphinoyl chloride and diethylphosphoryl chloride/diphenylphosphoryl chloride afforded new families of compounds comprising bis(phosphinoyl)amines and phosphinoyl-phosphorylamines, respectively, whose stereostructures were elucidated by B3LYP/6-31G(d,p) and B3LYP/6-31G++(d,p) calculations. The P analogues of the mixed imides may be valuable intermediates in syntheses.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 26:134–141, 2015; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21229

INTRODUCTION

The 2,5-dihydro-1*H*-phosphole 1-oxides are useful starting materials for the synthesis of other P-heterocycles, such as 3-phosphabicyclo[3.1.0]hexane 3-oxides, 1,2-dihydrophosphinine 1-oxides, 1,2,3,6-tetrahydrophosphinine 1-oxides, and 1,2,3,4,5,6-hexahydrophosphinine 1-oxides, along with the phospholes and their derivatives [1–6]. We have developed a simple ring enlargement method that made possible versatile syntheses [7]. The basic starting materials 1-hydroxy-2,3- or 2,5-dihydro-1*H*-phosphole 1-oxides obtained by the hydrolysis of the corresponding McCormack cycloadducts of dienes and P-trihalides [1]. A novel functionalization of the cyclic phosphinic acids involves microwave (MW)-assisted direct derivatizations, such as esterifications [8, 9], thioesterifications [10], and amidations [11]. It is, however, more appropriate to perform the amidations of the hydroxy-2,5-dihydro-1*H*-phosphole-oxides by the traditional methods [12, 13], as, in this case, the MW-assisted derivatizations are not too efficient.

We have, recently, experienced that the preparation of 1-alkylamino-2,5-dihydro-1*H*-phosphole 1-oxides (**3** and **4**) by the reaction of the corresponding cyclic phosphinic chlorides (**1** and **2**) with primary amines was accompanied by the formation of bis(2,5-dihydro-1*H*-phosphol-1-yl)amine P,P′-dioxides **5** and **6**, if 1 equiv of the primary amine was added to a toluene solution of the corresponding phosphinic chloride (**1** and **2**) and triethylamine.

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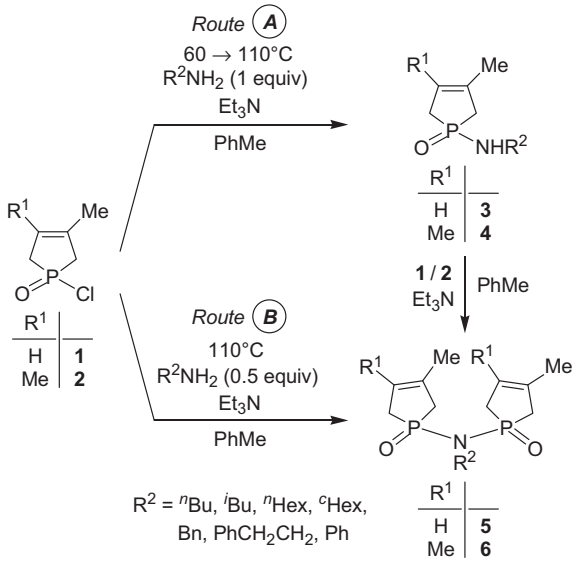
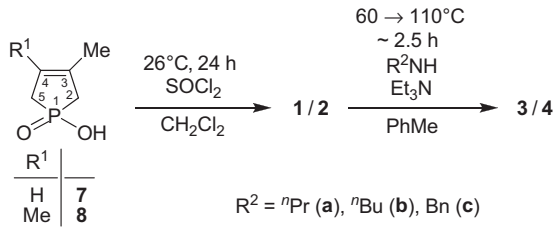


SCHEME 1 Synthesis of 1-alkylamino-2,5-dihydro-1*H*-phosphole oxides **3** and **4** and bis(2,5-dihydro-1*H*-phosphol-1-yl)amine dioxides **5** and **6** [14].

The desired 1-alkylamino-dihydrophosphole oxides **3** and **4** were obtained in only 35–46% yields [14]. However, adding the toluene solution of chlorodihydrophosphole oxides (**1** and **2**) to an equimolar mixture of the primary amine and triethylamine at 60°C, and then increasing the temperature to reflux, the alkylamino-dihydrophosphole oxides (**3** and **4**) were formed as almost exclusive products, and were obtained in yields of 76–88% (Scheme 1, route A) [14]. At the same time, it was also possible to get the bis(2,5-dihydro-1*H*-phosphol-1-yl)amine dioxides (**5** and **6**) as the only products, if the primary amines, used in a 0.5 equiv quantity, was added to the toluene solution of the phosphinic chloride (**1** or **2**) and triethylamine, and the mixture was stirred at the boiling point. In this way, the bisphosphinoyl products (**5** and **6**) were obtained in yields of 72–95% (Scheme 1, route B) [14]. One may conclude that the outcome of the reaction may be "fine-tuned" by the order of addition of the reagents to each other and the molar ratio.

It is also a possibility to convert 1-alkylamino-2,5-dihydro-1*H*-phosphole oxides **3** and **4** to the corresponding bisproducts (**5** and **6**) by the reaction with the chloro-2,5-dihydro-1*H*-phosphole oxides (**1** and **2**) [14]. However, this protocol was not studied in detail and, with a variation, it is also possible to synthesize novel "phosphimides" with two different P-moieties. Unsymmetrical "imides" can be obtained from alkylamino-dihydrophosphole oxides **3** and **4** by the reaction with nonheterocyclic P-chlorides. This new approach has been followed in the present article.



SCHEME 2 Preparation of the 1-alkylamino-2,5-dihydro-1*H*-phosphole oxides (**3** and **4**) as the starting materials.

Not much is known about bisphosphinoylamines. Beside our paper [14], there is only one hint on this kind of compounds, mentioning the preparation of two bis(2,5-dihydro-1*H*-phosphol-1-yl)amine dioxides in a superficial way, and characterizing the products only by melting points and elemental analyses [15]. The imides with two different >P(O)– moieties described in the present paper represent a new and valuable family of compounds.

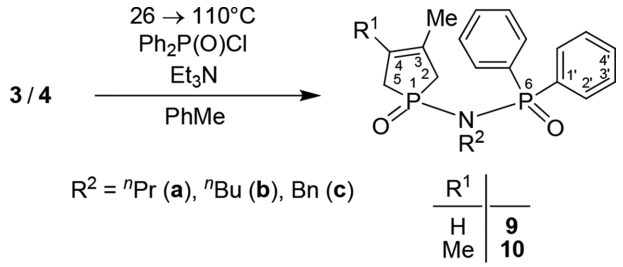
RESULTS AND DISCUSSION

Synthesis of the New >P(O)NR(O)P< Derivatives

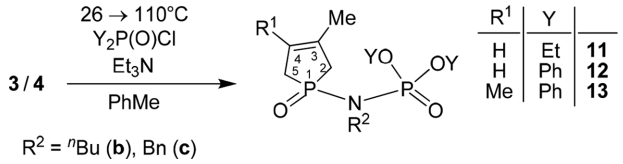
The alkylamino-2,5-dihydro-1*H*-phosphole oxides (**3** and **4**) starting materials were prepared by the procedure outlined above. The 1-chloro-2,5-dihydro-1*H*-phosphole oxides (**1** and **2**) were obtained from the corresponding cyclic phosphinic acids (**7** and **8**) by the reaction with thionyl chloride. It was important that the toluene solution of the chlorodihydrophosphole oxides (**1** and **2**) was added dropwise to the toluene solution of the equimolar mixture of the primary amine and triethylamine at 60°C. Then, the temperature was increased to 110°C. Eventually, 1-alkylamino-2,5-dihydro-1*H*-phosphole oxides **3a–c** and **4a–c** were prepared (Scheme 2). Compounds **3a** and **4a–c** are new that were obtained in yields of 66–82%.

The 1-alkylamino-2,5-dihydro-1*H*-phosphole oxides (**3** and **4**) were then reacted with 1.1 equiv of diphenylphosphinoyl chloride in toluene solution in the presence of 1.1 equiv of triethylamine. The temperature was raised from 26 to 110°C, and the mixture was stirred for 3.5 h. The work-up including purification by column chromatography afforded bisphosphinoylamines **9a–c** and **10a–c** in yields of 62–86% (Scheme 3).

The alkylamino-2,5-dihydro-1*H*-phosphole oxides **3b**, **3c**, and **4b** were also reacted with diethylphosphoryl chloride and/or diphenylphosphoryl chloride in the presence of triethylamine in toluene elevating the temperature from 26°C to



SCHEME 3 *N*-Phosphinoylation of 1-alkylamino-2,5-dihydro-1*H*-phosphole oxides **3** and **4**.



SCHEME 4 *N*-Phosphorylation of 1-alkylamino-2,5-dihydro-1*H*-phosphole oxides **3** and **4**.

the boiling point, and stirring the mixture for 4 h. The work-up comprising chromatography furnished phosphinoyl-phosphorylamines **11b** and **11c** in modest yields of around 30%, whereas products **12b** and **13b** were obtained in more reasonable yields of 68 and 80%, respectively (Scheme 4). The reagent diethylphosphoryl chloride was of lower reactivity than the diphenyl analogue.

Structures of the imide analogue products **9a–c**, **10a–c**, **11b**, **11c**, **12b**, and **13b** were identified by ^{31}P, ^{13}C, and ^{1}H NMR, as well as high-resolution mass spectrometry spectral data. ^{31}P NMR spectra of the >P(O)NR(O)P< derivatives exhibited two doublets for the two different phosphorus atoms. For the bis(phosphinoyl)amines (**9** and **10**) and phosphinoyl-phosphorylamines (**11–13**), the ^{2}J(P,P) couplings fall in the range of 5.5–7.3 and 15.9–17.9 Hz, respectively. With the exception of the α and β carbon atoms of the N-substituent, all carbon atoms within three-bond distances from either of the phosphorus atoms were coupled by the corresponding phosphorus atom in the ^{13}C NMR spectra. It is worth mentioning that in the ^{13}C NMR spectra of compounds **9a–c** and **12b**, the ^{2}J(P,C) or ^{3}J(P,C) doublets of the $C_{2'}$ atoms of the two phenyl rings appeared as a broad signal, or as two distinct signals due to the diastereotopy. The signal for the carbon atom of $C_{1'}$ for compound **12b** was also doubled. In contrast to the NMR spectra of the bis(2,5-dihydro-1*H*-phosphol-1-yl)amine P,P′-dioxides described in the first part of our study [14], those of the newly synthesized species with two different P-moieties were simpler.

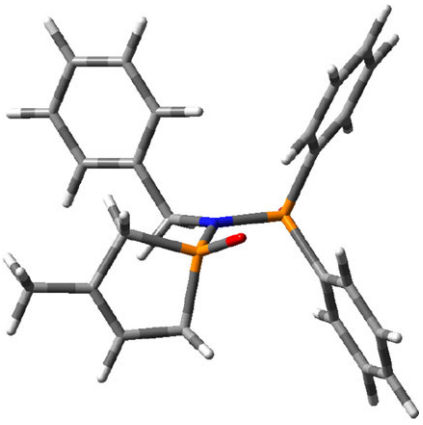


FIGURE 1 Computed three-dimensional structure of phosphinoylamino-dihydrophosphole oxide **9c**.

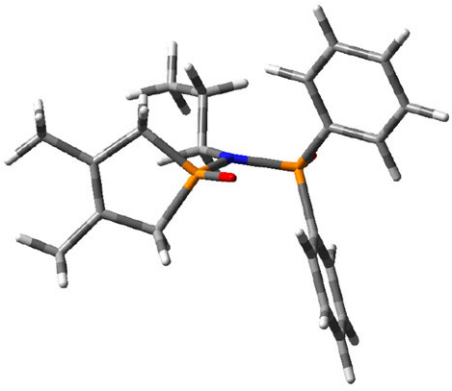


FIGURE 2 Computed three-dimensional structure of phosphinoylamino-dihydrophosphole oxide **10a**.

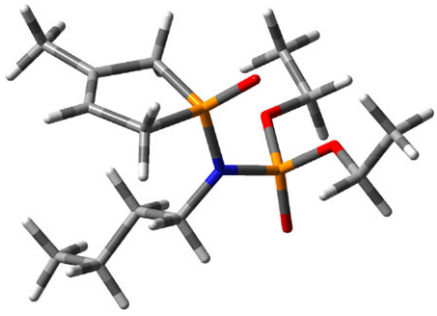


FIGURE 3 Computed three-dimensional structure of phosphorylamino-dihydrophosphole oxide **11b**.

Theoretical Calculations

Structures of three model compounds (**9c**, **10a**, and **11b**) were optimized at both the B3LYP/6-31G++(d,p) and B3LYP/6-31G(d,p) levels of theory [16] using the Gaussian 09 program package [17]. In the case of larger basis set B3LYP/6-31G++(d,p), the implicit solvent model was also used assuming MeOH. The stereostructures are shown in Figs. 1–3,

TABLE 1 Selected Atomic Distances for Compounds **9c**, **10a**, and **11b** Computed at the B3LYP/6-31G++(d,p)//PCM(MeOH) and B3LYP/6-31G(d,p) Levels Of Theory

Bond Lengths	*Compound*		
	9c	**10a**	**11b**
P1–C2	1.856 (1.847)	1.851 (1.844)	1.841 (1.846)
C2–C3	1.512 (1.515)	1.515 (1.517)	1.520 (1.517)
C3–C4	1.341 (1.343)	1.355 (1.350)	1.351 (1.347)
C4–C5	1.501 (1.507)	1.510 (1.516)	1.514 (1.519)
C5–P1	1.867 (1.855)	1.856 (1.848)	1.850 (1.844)
P1–O1	1.511 (1.501)	1.506 (1.498)	1.501 (1.495)
P1–N	1.722 (1.713)	1.716 (1.709)	1.740 (1.732)
P6–N	1.754 (1.749)	1.741 (1.737)	1.708 (1.702)
P6–O6	1.514 (1.502)	1.509 (1.501)	1.491 (1.484)
P6–C1′ or P6–OY	1.833 (1.829)	1.838 (1.831)	1.625 (1.618)
P6–C1″ or P6–OY′	1.830 (1.825)	1.823 (1.819)	1.604 (1.600)
N–C1‴	1.489 (1.486)	1.498 (1.492)	1.499 (1.495)
O1···P6	3.368 (3.366)	3.295 (3.289)	3.361 (3.347)

The results of the latter method are shown in brackets.

TABLE 2 Selected Bond Angles and Torsion Angles for Compounds **9c**, **10a** and **11b** Computed at the B3LYP/6-31G++(d,p)//PCM(MeOH) and B3LYP/6-31G(d,p) Levels of Theory

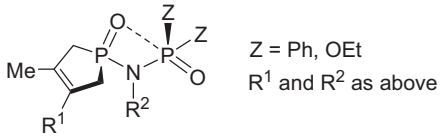
Bond Angles/Torsion Angles	*Compound*		
	9c	**10a**	**11b**
P1–C2–C3	105.22 (105.19)	105.60 (105.57)	105.50 (105.47)
C2–C3–C4	116.41 (116.41)	116.84 (116.81)	116.80 (116.81)
C3–C4–C5	118.73 (118.73)	116.90 (116.87)	118.05 (118.02)
C4–C5–P1	105.11 (105.11)	105.70 (105.63)	105.60 (105.57)
C5–P1–C2	95.55 (95.55)	94.92 (94.88)	95.25 (95.23)
N–P1–O1	112.24 (112.24)	112.30 (112.34)	112.82 (112.81)
N–P6–O6	108.79 (108.79)	108.10 (108.15)	111.59 (111.54)
P1–N–P6	123.66 (123.66)	123.84 (123.88)	120.84 (120.83)
P6–N–C1‴	115.14 (115.14)	115.51 (115.55)	114.35 (114.34)
C1‴–N–P1	118.67 (118.67)	118.40 (118.44)	122.99 (122.94)
Sum of the angles around the N atom	357.48 (357.47)	357.85 (357.87)	358.10 (358.09)
O1–P1–N–C1‴	–163.16 (–163.17)	–175.87 (–175.87)	154.21 (154.20)
O1–P1–N–P6	35.71 (35.76)	21.53 (21.50)	–42.49 (–42.44)
O6–P6–N–C1‴	–5.77 (–5.77)	9.86 (9.83)	–17.16 (–17.14)
O6–P6–N–P1	155.91 (155.89)	172.90 (172.92)	178.26 (178.22)

The results of the latter method are shown in brackets.

whereas selected geometries are listed in Tables 1 and 2. It can be seen that the two P=O groups point to opposite directions. The central N atom is nearly planar, due to the almost 360° of the sum of the three bond angles around it, showing a high conjugation with the adjacent P=O groups. The data listed in Tables 1 and 2 suggest that practically the same geometrical parameters were obtained, no matter if the lower basis set B3LYP/6-31G(d,p) was applied in vacuo, or the higher basis set B3LYP/6-31G++(d,p) was used along with the implicit solvent model.

In structures **9c** and **10a**, a remarkable hydrogen bond can be substantiated between the P1*O1* and one of the aromatic *ortho* H atoms (where the corresponding distance is ca. 2.27 Å for both structures).

The atomic distances between the O1 and P6 atoms in **9c**, **10a**, and **11b** are somewhat larger than the sum of their van der Walls radius, consequently, a weak interaction may be assumed between these atoms as shown below.



In summary, beside the four new 1-alkylamino-2,5-dihydro-1*H*-phosphole oxides, 10 new bis(phosphinoyl)amines/phosphinoyl-phosphorylamines were prepared by a new protocol

utilizing the reaction of 1-alkylamino-2,5-dihydro-1*H*-phosphole oxides with $Y_2P(O)Cl$ (Y = Ph, EtO, PhO) reagents. NMR spectra of the unsymmetrical >P(O)NR(O)P< species were simpler than those of the bis(dihydrophospholyl)amine dioxides. Stereostructure of the imide analogue compounds was elucidated by quantum chemical calculations. The phosphinoyl- and phosphorylamino-dihydro-1*H*-phosphole oxides will be utilized as intermediates in further syntheses including ring enlargement by dichlorocarbene and other related transformations described by us [6, 7].

EXPERIMENTAL

The ^{31}P, ^{13}C, and ^{1}H NMR spectra were taken on a Bruker Avance-300 instrument operating at 121.5, 75.5, and 300 MHz, respectively. The exact mass measurements were performed using a Q-TOF Premier mass spectrometer in a positive electrospray mode.

General Procedure for the Preparation of 1-Alkylamino-2,5-dihydro-1H-phosphole 1-Oxides

To 11.4 mmol of phosphinic acid (3-methyl-1-hydroxy-2,5-dihydro-1*H*-phosphole oxide [1.5 g] or 3,4-dimethyl-1-hydroxy-2,5-dihydro-1*H*-phosphole oxide [1.7 g]) in 5 mL of dry dichloromethane, 1 mL (13.8 mmol) of thionyl chloride was added, and the mixture was stirred at 26°C for 24 h. Then, the solvent was evaporated and the volatile residues were removed in high vacuum. The 1-chloro-2,5-dihydro-1*H*-phosphole 1-oxide obtained quantitatively (**1** [1.7 g] or **2** [1.9 g]) was taken up in 3 mL of dry toluene, and the resulting solution was added dropwise to a mixture of 11.4 mmol of the primary amine (*n*-propylamine [0.94 mL], *n*-butylamine [1.1 mL], and benzylamine [1.3 mL]) and 1.6 mL (11.4 mmol) of triethylamine in 3 mL of toluene at 60°C. The contents of the flask were stirred at 26°C for 30 min. Then, the amine hydrochloride salt was removed by filtration and the filtrate concentrated. The crude product was purified by column chromatography (3% methanol in chloroform, silica gel) to afford phosphinic amides **3** and **4**.

The following new compounds were thus prepared:

*1-(Propylamino)-3-methyl-2,5-dihydro-1H-phosphole 1-Oxide (**3a**)*. Yield: 82%; ^{31}P NMR ($CDCl_3$) δ: 63.2; ^{13}C NMR ($CDCl_3$) δ: 11.2 (CH_2CH_3), 20.6 (d, ^3J = 12.1, C_3–CH_3), 25.2 (d, ^3J = 6.3, NCH_2CH_2), 32.1 (d, ^1J = 82.1, C_5), 35.0 (d, ^1J = 85.6, C_2), 42.4 (d, ^2J = 1.7, NCH_2), 120.7 (d, ^2J = 9.7, C_4), 136.6 (d, ^2J = 15.2, C_3); ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, $^3J_{H,H}$ = 7.4, 3H, CH_2CH_3), 1.42–1.64 (m, 4H, 2×CH_2), 1.77 (s, 3H, C_3–CH_3), 2.19–2.61 (m, total intensity 5H, 2×PCH_2, NH), 2.78–2.98 (m, 2H, NCH_2), 5.49 (d, $^3J_{P,H}$ = 33.8, 1H, CH=); $[M + H]^+_{found}$ = 174.1048, $C_8H_{17}NOP$ requires 174.1048.

*1-(Propylamino)-3,4-dimethyl-2,5-dihydro-1H-phosphole 1-Oxide (**4a**)*. Yield: 78%; ^{31}P NMR ($CDCl_3$) δ: 56.0; ^{13}C NMR ($CDCl_3$) δ: 11.0 (CH_2CH_3), 16.3 (d, ^3J = 14.7, C_3–CH_3), 25.0 (d, ^3J = 6.2, NCH_2CH_2), 37.0 (^1J = 84.4, C_2), 42.2 (NCH_2), 127.5 (^2J = 11.5, C_3); ^{1}H NMR ($CDCl_3$) δ: 0.92 (t, $^3J_{H,H}$ = 7.3, 3H, CH_2CH_3), 1.47–1.60 (m, 2H, CH_2), 1.71 (s, 6H, C_3–CH_3), 2.27–2.60 (m, total intensity 5H, 2×PCH_2, NH), 2.82–2.95 (m, 2H, NCH_2); $[M + H]^+_{found}$ = 188.1208, $C_9H_{19}NOP$ requires 188.1204.

*1-(Butylamino)-3,4-dimethyl-2,5-dihydro-1H-phosphole 1-Oxide (**4b**)*. Yield: 66%; ^{31}P NMR ($CDCl_3$) δ: 56.2; ^{13}C NMR ($CDCl_3$) δ: 13.6 (CH_2CH_3), 16.5 (d, ^3J = 14.7, C_3–CH_3), 19.8 (CH_2CH_3), 34.1 (d, ^3J = 6.2, NCH_2CH_2), 37.2 (^1J = 84.4, C_2), 40.3 (d, ^2J = 1.6, NCH_2), 127.7 (^2J = 11.5, C_3); ^{1}H NMR ($CDCl_3$) δ: 0.91 (t, $^3J_{H,H}$ = 7.2, 3H, CH_2CH_3), 1.27–1.43 (m, 2H, CH_2), 1.43–1.57 (m, 2H, CH_2), 1.71 (s, 6H, C_3–CH_3), 2.22–2.62 (m, total intensity 5H, 2×PCH_2, NH), 2.85–3.01 (m, 2H, NCH_2); $[M + H]^+_{found}$ = 202.1363, $C_{10}H_{21}NOP$ requires 202.1361.

*1-(Benzylamino)-3,4-dimethyl-2,5-dihydro-1H-phosphole 1-Oxide (**4c**)*. Yield: 74%; ^{31}P NMR ($CDCl_3$) δ: 56.6; ^{13}C NMR ($CDCl_3$) δ: 16.4 (d, ^3J = 14.8, C_3–CH_3), 37.2 (^1J = 84.0, C_2), 44.3 (NCH_2), 127.2 ($C_{2'}$*, $C_{4'}$), 127.7 (d, ^2J = 11.5, C_3), 128.5 ($C_{3'}$)*, 139.7 (d, ^3J = 6.0, $C_{1'}$), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 1.70 (s, 6H, C_3–CH_3), 2.26–2.63 (m, 4H, 2×PCH_2), 2.68–2.86 (m, 1H, NH), 4.08–4.22 (m, 2H, $NHCH_2$), 7.21–7.38 (m, 5H, Ar); $[M + H]^+_{found}$ = 236.1207, $C_{13}H_{19}NOP$ requires 236.1204.

Preparation of compounds **3b** and **3c** is summarized in Table 3.

*General Procedure for the Preparation of Phosphinoyl- and Phosphonoyl-alkylamino-3-methyl-2,5-dihydro-1H-phosphole 1-Oxides (**9a–c**, **10a–c**, **11b**, **11c**, **12b**, and **13b**)*

To the solution of 1.6 mmol of 1-amino-3-methyl-2,5-dihydro-1*H*-phosphole 1-oxides (**3a**: 0.28 g, **3b**: 0.30 g, **3c**: 0.35 g, **4a**: 0.30 g, **4b**: 0.32 g, **4c**: 0.38 g) in 3 mL of dry toluene, 1.8 mmol of phosphinic chloride (diphenylphosphinoyl chloride: 0.34 mL,

TABLE 3 ^{31}P NMR and High-Resolution Mass Spectrometry Data for Compounds **3b** and **3c**

Product	*Yield (%)*	δ_P	δ_P *[lit]*	$[M + H]^+_{found}$	$[M + H]^+_{requires}$	*Formula*
3b	58	63.1	63.2 [20]	188.1210	188.1204	$C_9H_{19}NOP$
3c	67	63.5	63.5 [20]	222.1051	222.1048	$C_{12}H_{17}NOP$

diethylphosphoryl chloride: 0.26 mL, and diphenyl phosphorochloridate: 0.37 mL) and 1.8 mmol (0.25 mL) of triethylamine were added. The contents of the flask were stirred at reflux for 3.5–5 h. Then, the amine hydrochloride salt was removed by filtration and the filtrate concentrated. The crude product was purified by column chromatography (3% methanol in chloroform, silica gel) to afford the title derivatives.

The following products were thus prepared:

*Diphenylphosphinoyl-1-n-propylamino-3-methyl-2,5-dihydro-1H-phosphole 1-Oxide (***9a***)*. Yield: 75%; ^{31}P NMR ($CDCl_3$) δ: 32.0 (d, ^2J = 7.2), 65.9 (d, ^2J = 7.2); ^{13}C NMR ($CDCl_3$) δ: 10.9 (CH_2CH_3), 20.5 (d, ^3J = 12.8, C_3–CH_3), 24.2 (CH_2CH_3), 35.6 (^1J = 80.5, C_5), 38.3 (^1J = 84.1, C_2), 47.3 (NCH_2), 120.1 (^2J = 10.4, C_4), 128.6 (d, ^3J = 13.1, $C_{3'}$), 131.4 (d, ^1J = 124.4, $C_{1'}$), 132.0 (bd, ^2J = 10.5, $C_{2'}$), 132.5 (d, ^4J = 2.2, $C_{4'}$), 136.1 (^2J = 16.4, C_3); ^{1}H NMR ($CDCl_3$) δ: 0.51 (t, $^3J_{H,H}$ = 7.3, 3H, CH_3CH_2), 1.18–1.28 (m, 2H, CH_2), 1.78 (s, 3H, C_3–CH_3), 2.23–2.53 (m, 2H, PCH_2), 2.82–2.98 (m, 2H, PCH_2), 3.11–3.28 (m, 2H, NCH_2), 5.52 (d, $^3J_{P,H}$ = 36.1, 1H, CH), 7.43–7.63 and 7.70–7.83 (m, 10H, Ar); $[M + H]^+_{found}$ = 374.1424, $C_{20}H_{25}NO_2P_2$ requires 374.1433.

*Diphenylphosphinoyl-1-n-butylamino-3-methyl-2,5-dihydro-1H-phosphole 1-Oxide (***9b***)*. Yield: 78%; ^{31}P NMR ($CDCl_3$) δ: 32.0 (d, ^2J = 7.3), 65.8 (d, ^2J = 7.3); ^{13}C NMR ($CDCl_3$) δ: 13.1 (CH_2CH_3), 19.6 (CH_2CH_3), 20.4 (d, ^3J = 12.9, C_3–CH_3), 32.7 (NCH_2CH_2), 35.5 (^1J = 80.5, C_5), 38.2 (^1J = 84.2, C_2), 45.4 (NCH_2), 120.0 (^2J = 10.5, C_4), 128.5 (d, ^3J = 13.1, $C_{3'}$), 131.3 (d, ^1J = 124.3, $C_{1'}$), 131.9 (bd, ^2J = 10.5, $C_{2'}$), 132.4 (d, ^4J = 1.8, $C_{4'}$), 135.7 (^2J = 16.3, C_3); ^{1}H NMR ($CDCl_3$) δ: 0.58 (t, $^3J_{H,H}$ = 7.3, 3H, CH_2CH_3), 0.87–0.98 (m, 2H, CH_2), 1.15–1.24 (m, 2H, CH_2), 1.79 (s, 3H, C_3–CH_3), 2.27–2.51 (m, 2H, PCH_2), 2.85–2.97 (m, 2H, PCH_2), 3.18–3.29 (m, 2H, NCH_2), 5.53 (d, $^3J_{P,H}$ = 36.0, 1H, CH =), 7.45–7.63 and 7.72–7.81 (m, 10H, Ar); $[M + H]^+_{found}$ = 388.1599, $C_{21}H_{28}NO_2P_2$ requires 388.1595.

*Diphenylphosphinoyl-1-benzylamino-3-methyl-2,5-dihydro-1H-phosphole 1-Oxide (***9c***)*. Yield: 62%; ^{31}P NMR ($CDCl_3$) δ: 32.6 (d, ^2J = 5.8), 66.7 (d, ^2J = 5.8); ^{13}C NMR ($CDCl_3$) δ: 20.3 (d, ^3J = 12.7, C_3–CH_3), 34.9 (^1J = 80.4, C_5), 37.6 (^1J = 84.0, C_2), 48.5 (NCH_2), 120.0 (^2J = 10.6, C_4), 127.0 ($C_{1''}$), 127.1 ($C_{3''}$)*, 128.1 ($C_{2''}$)*, 128.5 (d, ^3J = 13.2, $C_{3'}$), 130.9 (d, ^1J = 124.6, $C_{1'}$), 132.2 (bd, ^2J = 10.5, $C_{2'}$), 132.4 (d, ^4J = 2.8, $C_{4'}$), 136.0 (^2J = 16.4, C_3), 137.5 ($C_{4''}$), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 1.72 (s, 3H, C_3–CH_3), 2.15–2.43 (m, 2H, PCH_2), 2.72–2.91 (m, 2H, PCH_2), 4.50–4.66 (m, 2H, NCH_2), 5.47 (d, $^3J_{P,H}$ = 36.0, 1H, CH=), 6.98–7.18, 7.38–7.57, and 7.72–7.84 (m, 15H, Ar); $[M + H]^+_{found}$ = 422.1441, $C_{24}H_{26}NO_2P_2$ requires 422.1439.

*Diphenylphosphinoyl-1-n-propylamino-3,4-dimethyl-2,5-dihydro-1H-phosphole 1-Oxide (***10a***)*. Yield: 80%; ^{31}P NMR ($CDCl_3$) δ: 31.8 (d, ^2J = 6.8), 59.2 (d, ^2J = 6.8); ^{13}C NMR ($CDCl_3$) δ: 10.9 (CH_2CH_3), 16.5 (d, ^3J = 15.5, C_3–CH_3), 24.2 (CH_2CH_3), 40.3 (^1J = 82.8, C_2), 47.4 (NCH_2), 127.3 (^2J = 12.2, C_3), 128.6 (d, ^3J = 13.1, $C_{3'}$), 131.5 (d, ^1J = 124.4, $C_{1'}$), 132.1 (d, ^3J = 10.4, $C_{2'}$), 132.5 (d, ^4J = 2.8, $C_{4'}$); ^{1}H NMR ($CDCl_3$) δ: 0.53 (t, $^3J_{H,H}$ = 7.4, 3H, CH_2CH_3), 1.16–1.33 (m, 2H, CH_2), 1.69 (s, 6H, C_3–CH_3), 2.25–2.45 (m, 2H, PCH_2), 2.90–3.04 (m, 2H, PCH_2), 3.10–3.28 (m, 2H, NCH_2), 7.43–7.66 and 7.72–7.85 (m, 10H, Ar); $[M + H]^+_{found}$ = 388.1599, $C_{21}H_{28}NO_2P_2$ requires 388.1595.

*Diphenylphosphinoyl-1-n-butylamino-3,4-dimethyl-2,5-dihydro-1H-phosphole 1-Oxide (***10b***)*. Yield: 80%; ^{31}P NMR ($CDCl_3$) δ: 31.7 (d, ^2J = 6.9), 59.1 (d, ^2J = 7.0); ^{13}C NMR ($CDCl_3$) δ: 13.3 (CH_2CH_3), 16.5 (d, ^3J = 15.5, C_3–CH_3), 19.7 (CH_2CH_3), 32.9 (NCH_2CH_2), 40.3 (^1J = 82.8, C_2), 45.6 (NCH_2), 127.2 (^2J = 12.3, C_3), 128.6 (d, ^3J = 13.1, $C_{3'}$), 131.5 (d, ^1J = 124.5, $C_{1'}$), 132.1 (d, ^3J = 10.4, $C_{2'}$), 132.4 (d, ^4J = 2.8, $C_{4'}$); ^{1}H NMR ($CDCl_3$) δ: 0.58 (t, $^3J_{H,H}$ = 7.4, 3H, CH_2CH_3), 0.88–0.97 (m, 2H, CH_2), 1.17–1.26 (m, 2H, CH_2), 1.69 (s, 6H, C_3–CH_3), 2.30–2.41 (m, 2H, PCH_2), 2.91–3.01 (m, 2H, PCH_2), 3.16–3.27 (m, 2H, NCH_2), 7.47–7.53 and 7.56–7.61 (m, 10H, Ar); $[M + H]^+_{found}$ = 402.1750, $C_{22}H_{29}NO_2P_2$ requires 402.1752.

*Diphenylphosphinoyl-1-benzylamino-3,4-dimethyl-2,5-dihydro-1H-phosphole 1-Oxide (***10c***)*. Yield: 86%; ^{31}P NMR ($CDCl_3$) δ: 32.4 (d, ^2J = 5.5), 60.1 (d, ^2J = 5.5); ^{13}C NMR ($CDCl_3$) δ: 16.3 (d, ^3J = 15.4, C_3–CH_3), 39.6 (^1J = 82.6, C_2), 48.6 (NCH_2), 127.0 ($C_{1''}$), 127.1 ($C_{3''}$)*, 127.2 (^2J = 12.3, C_3), 128.1 ($C_{2''}$)*, 128.5 (d, ^3J = 13.2, $C_{3'}$), 131.0 (d, ^1J = 124.8, $C_{1'}$), 132.3 (d, ^2J = 10.6, $C_{2'}$), 132.4 (d, ^4J = 4.4, $C_{4'}$), 137.6 ($C_{4''}$), *may be reversed; ^{1}H NMR

($CDCl_3$) δ: 1.61 (s, 6H, C_3–CH_3), 2.15–2.37 (m, 2H, PCH_2), 2.76–2.93 (m, 2H, PCH_2), 4.47–4.65 (m, 2H, NCH_2), 6.98–7.21, 7.33–7.64, and 7.71–7.87 (m, 15H, Ar); $[M + H]^+_{found}$ = 436.1598, $C_{25}H_{28}NO_2P_2$ requires 436.1595.

*Diethylphosphoryl-1-n-butylamino-3-methyl-2,5-dihydro-1H-phosphole 1-Oxide (***11b***)*. Yield: 29%; ^{31}P NMR ($CDCl_3$) δ: 3.8 (d, ^2J = 16.4), 65.5 (d, ^2J = 16.4); ^{13}C NMR ($CDCl_3$) δ: 13.7 (CH_2CH_3), 16.0 (d, ^3J = 7.2, OCH_2CH_3), 20.0 (CH_2CH_3), 20.5 (d, ^3J = 12.9, C_3–CH_3), 33.2 (NCH_2CH_2), 34.6 (^1J = 81.7, C_5), 37.2 (^1J = 85.4, C_2), 45.2 (NCH_2), 63.0 (d, ^2J = 5.4, OCH_2), 120.1 (^2J = 10.5, C_4), 136.1 (^2J = 16.6, C_3); ^1H NMR ($CDCl_3$) δ: 0.92 (t, $^3J_{H,H}$ = 7.4, 3H, $CH_2CH_2CH_3$), 1.26–1.36 (m, 8H, CH_2, CH_3), 1.62–1.72 (m, 2H, CH_2), 1.82 (s, 3H, C_3–CH_3), 2.32–2.60 (m, 2H, PCH_2), 2.78–2.92 (m, 2H, PCH_2), 3.26–3.38 (m, 2H, NCH_2), 4.03–4.17 (m, 4H, OCH_2), 5.55 (d, $^3J_{P,H}$ = 36.2, 1H, CH=); $[M + H]^+_{found}$ = 324.1497, $C_{13}H_{28}NO_4P_2$ requires 324.1494.

*Diethylphosphoryl-1-benzylamino-3-methyl-2,5-dihydro-1H-phosphole 1-Oxide (***11c***)*. Yield: 32%; ^{31}P NMR ($CDCl_3$) δ: 3.1 (d, ^2J = 15.9), 66.3 (d, ^2J = 15.9); ^{13}C NMR ($CDCl_3$) δ: 15.8 (d, ^3J = 7.4, OCH_2CH_3), 20.5 (d, ^3J = 13.0, C_3–CH_3), 34.6 (^1J = 81.3, C_5), 37.2 (^1J = 85.0, C_2), 47.6 (NCH_2), 63.1 (d, ^2J = 5.4, OCH_2), 120.2 (^2J = 10.7, C_4), 127.4 ($C_{1'}$), 128.3 ($C_{2'}$, $C_{3'}$), 136.1 (^2J = 16.7, C_3), 138.4 ($C_{4'}$); ^1H NMR ($CDCl_3$) δ: 1.19 (m, 6H, CH_2CH_3), 1.79 (s, 3H, C_3–CH_3), 2.36–2.58 (m, 2H, PCH_2), 2.77–2.92 (m, 2H, PCH_2), 3.73–3.86 (m, 2H, OCH_2), 3.96–4.06 (m, 2H, OCH_2), 4.56–4.63 (m, 2H, NCH_2), 5.54 (d, $^3J_{P,H}$ = 36.4, 1H, CH=), 7.22–7.46 (m, 5H, Ar); $[M + H]^+_{found}$ = 358.1340, $C_{16}H_{26}NO_4P_2$ requires 358.1337.

*Diphenylphosphoryl-1-n-butylamino-3-methyl-2,5-dihydro-1H-phosphole 1-Oxide (***12b***)*. Yield: 68%; ^{31}P NMR ($CDCl_3$) δ: –5.81 (d, ^2J = 17.9), 66.6 (d, ^2J = 17.9); ^{13}C NMR ($CDCl_3$) δ: 13.7 (CH_2CH_3), 20.1 (CH_2CH_3), 20.5 (d, ^3J = 13.2, C_3–CH_3), 33.1 (NCH_2CH_2), 34.9 (^1J = 80.7, C_5), 37.4 (^1J = 84.5, C_2), 45.7 (NCH_2), 120.1 ($^2J \approx$ 10.7, C_4) overlapped by 120.2 (^3J = 4.6) and 120.3 (^3J = 4.6) $C_{2'}$, 125.5 ($C_{4'}$), 129.8 ($C_{3'}$), 136.1 (d, ^2J = 16.9, C_3), 150.1 (d, ^2J = 7.1) and 150.2 (d, ^2J = 7.2) $C_{1'}$; ^1H NMR ($CDCl_3$) δ: 0.95 (t, $^3J_{H,H}$ = 7.3, 3H, CH_2CH_3), 1.29–1.46 (m, 2H, CH_2), 1.73–1.87 (m, CH_2), overlapped by 1.77 (s, C_3–CH_3) total intensity 5H, 2.26–2.56 (m, 2H, PCH_2), 2.64–2.86 (m, 2H, PCH_2), 3.48–3.68 (m, 2H, NCH_2), 5.52 (d, $^3J_{P,H}$ = 35.5, 1H, CH=), 7.15–7.40 (m, 10H, Ar); $[M + H]^+_{found}$ = 420.1497, $C_{21}H_{28}NO_4P_2$ requires 420.1494.

*Diphenylphosphoryl-1-n-butylamino-3,4-dimethyl-2,5-dihydro-1H-phosphole 1-Oxide (***13b***)*. Yield: 80%; ^{31}P NMR ($CDCl_3$) δ: –5.7 (d, ^2J = 17.1), 60.0 (d, ^2J = 17.1); ^{13}C NMR ($CDCl_3$) δ: 13.7 (CH_2CH_3), 16.5 (d, ^3J = 15.9, C_3–CH_3), 20.1 (CH_2CH_3), 33.2 (NCH_2CH_2), 39.5 (^1J = 83.1, C_2), 45.8 (NCH_2), 120.3 (d, ^3J = 4.8, $C_{2'}$), 125.5 ($C_{4'}$), 127.3 (^2J = 12.7, C_4), 129.8 ($C_{3'}$), 150.2 (d, ^2J = 7.0, $C_{1'}$); ^1H NMR ($CDCl_3$) δ: 0.94 (t, $^3J_{H,H}$ = 7.4, 3H, CH_2CH_3), 1.30–1.44 (m, 2H, CH_2), 1.69 (s, 6H, C_3–CH_3), 1.72–1.87 (m, 2H, CH_2), 2.33–2.50 (m, 2H, PCH_2), 2.71–2.90 (m, 2H, PCH_2), 3.48–3.66 (m, 2H, NCH_2), 7.11–7.41 (m, 10H, Ar); $[M + H]^+_{found}$ = 434.1653, $C_{22}H_{30}NO_4P_2$ requires: 434.1650.

Theoretical Calculations

Quantum chemical investigations were carried out with electronic structure computations, using the B3LYP [16] method, employing the 6–31G(d,p) basis set for all atoms, using the Gaussian09 (G09) program package [17].

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