Reaction of *N*-Vinylic Phosphazenes Derived from *β*-Amino Acids with Aldehydes. Azadiene-Mediated Synthesis of Dihydropyridines, Pyridines, and Polycyclic Nitrogen Derivatives

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Enamino phosphonium salts **2** are obtained by 1,2-addition of hydrogen chloride to *N*-vinylic phosphazenes **1** derived from triphenylphosphine. Aza-Wittig reaction of phosphazenes **1** derived from triphenylphosphine and **6** derived from diphenylmethylphosphine with aldehydes **3** leads to the formation of 2-azadienes **7**. Reaction of azadienes **7** with enamines affords dihydropyridines **9** and **11**, pyridines **12**, and bicyclic nitrogen heterocycles **15**−**18** in a regioselective fashion, while heterodiene **20** reacts in the same way with pyrrolidinocyclohexanone giving 1-azaphenanthrene compound **21**. Reaction of enamino phosphonium salts **2** with aldehydes **3** gives symmetrical dihydropyridines **5**.

Introduction

Phosphazenes[1] represent an important class of compounds and have attracted a great deal of attention in recent years because of their broad range of applications. The utility of *N*-vinylic phosphazenes[2] has been demonstrated in the synthesis of functionalized imine compounds, such as electronically neutral[3] and electron-poor 2-azadienes,[4] and as key intermediates in the preparation of heterocycles, such as 1,3-oxazines,[3] pyridine derivatives,[4a,b−7] and bicyclic[8] and polycyclic compounds,[2,9] as well as in elegant routes toward both the preparation of biologically active natural products and the construction of the framework of pharmacologically active alkaloids.[10]

We have been involved in the study of simple and functionalized phosphazenes[1b] as well as in their use in the preparation of acyclic[3,4,11] and heterocyclic compounds.[6,8,12] In some cases the reaction involves the phosphazene group,[3,4,11b,12d] while in other examples it remains unaffected.[4b,11a,12a] In the case of *N*-vinylic phosphazenes, an adjacent double bond in conjugation with the phosphazene moiety introduces the interesting problem of site selectivity: reaction at the nitrogen (1,2-addition) of the phosphazene group[1] versus reactions at the *γ*-C atom (1,4-addition).[2,4b,7a,13] We have reported that the influence of substituents of the phosphorus atom in *N*-vinylic phosphazenes **I** can play an important role in the reactivity pattern observed with carbonyl compounds,[4b] since reaction of phosphazenes derived from triphenylphosphine (**I**, R^1 = Ph) with carbonyl compounds gives the monoadduct **II** (1,4-addition), while phosphazene derived from diphenylmethylphosphine (**I**, R^1 = Me) undergoes aza-Wittig reaction with carbonyl compounds and leads to the formation of 2-azadienes **III** (Scheme 1).

A recent publication[14] has reported that *N*-vinylic phosphazenes **IV** (R^1 = Ph, R^3 = H), with an ethoxycarbonyl group at the *β*-position and prepared by Staudinger reaction of *β*-azido carboxylate[15] with phosphines in a similar way to that described[4a] for **IV** (R^1 = Ph, R^3 = Me), reacted with aldehydes. This reaction was reported as involving an initial nucleophilic attack of the *γ*-C atom (1,4-addition) of the phosphazene on the aldehyde, in contrast to the behavior of conjugated phosphazenes with carbonyl compounds to give 2-azadienes.[4a] These results have prompted us to report our own study on the ambident reactivity (1,2- and 1,4-addition) of phos-

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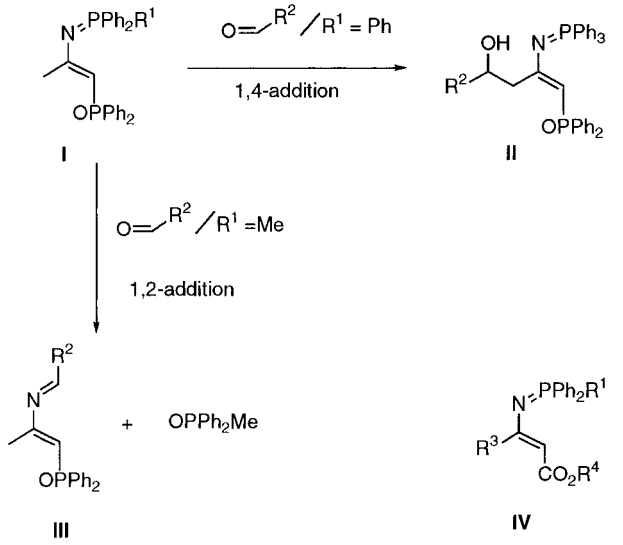
Scheme 1. 1,2-Addition versus 1,4-Addition of *N*-Vinylic Phosphazenes I with Aldehydes



phazenes **IV** (R^1 = Ph) derived from triphenylphosphine with hydrogen chloride. The regioselective aza-Wittig reaction (1,2-addition) of phosphazenes I**V** (R^1 = Me) derived from diphenylmethylphosphine with aldehydes and the isolation of the corresponding 2-azadiene derivative were also studied. This is consistent with the reported behavior not only of these kinds of phosphazenes[4a] derived from *β*-amino acids but also that of *N*-vinylic phosphazenes derived from α-amino acids[4c,d] and that of other *N*-vinylic phosphazenes.[3,4b] Moreover, we report here that 2-azadienes can be used as key intermediates in the synthesis of heterocyclic compounds derived from *β*-amino acids and of polycyclic nitrogen derivatives.

Results and Discussion

Regioselective 1,2-Addition of HCl to Phosphazenes 1 Derived from Triphenylphosphine. Hydrogen chloride was bubbled through a solution of *N*-vinylic phosphazenes **1a** (R^1 = H) in CH_2Cl_2/Et_2O to yield hygroscopic enamino phosphonium salt **2a** in a regioselective fashion. The hygroscopic compound **2a** was not isolated but characterized by its spectroscopic properties. The ^{31}P NMR spectrum of **2a** showed an absorption at δ_P 37.99 ppm. The signal for the **2a** vinylic protons appeared at δ_H 7.02 and 6.40 ppm, respectively, with a coupling constant of $^3J_{HH}$ = 13.6 Hz. This is consistent with the *E*-configuration of the carbon−carbon double bond.[4a,16] The olefinic carbons gave a singlet at δ_C 139.5 and a doublet at 105.1 ppm ($^3J_{PC}$ = 11.1 Hz). The crude **2a** was used without purification. In the case of 3-methyl-substituted *N*-vinylic phosphazenes **1b** (R^1 = Me) the reaction with HCl gave a mixture of both *Z*- and *E*-enamines **2b** in a 1:1 ratio (Scheme 2).

Aza-Wittig Reaction of Phosphazenes 6 Derived from Diphenylmethylphosphine with Aldehydes 3 (1,2-Addition versus 1,4-Addition). A recent report describes the reaction of *N*-vinylic phosphazene **1a** with aromatic aldehydes **3**, in *o*-xylene at 160 °C, in the presence of palladium on charcoal and in a sealed tube, giving 4-aryl-3,5-(diethoxycarbonyl)dihydropyridines **5** in

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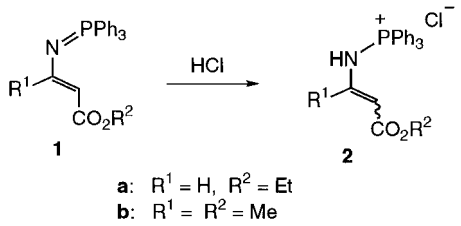
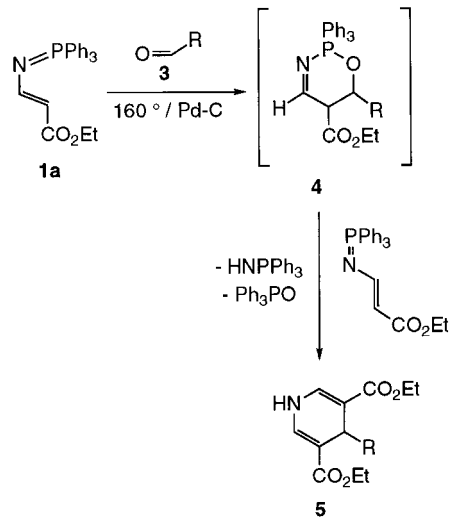
Scheme 2. Phosphonium Salts 2 Formation



Scheme 3. 1,4-Dihydropyridines 5 Formation through Reaction of *N*-Vinylic Phosphazenes 1 and Aldehydes 3



moderate yields.[14] The authors suggest that these heterocycles **5** could be formed by an initial addition of aldehydes **3** on the *β*-carbon atom of the *N*-vinylic phosphazene **1a** (1,4-addition) to give 1,2,5-oxaazaphosphorane **4** followed by regioselective attack of a second molecule of the phosphorane **1a** with loss of triphenylphosphine oxide (Scheme 3).

We found that the room-temperature reaction of *N*-vinylic phosphazene **6a** (containing an ethoxycarbonyl group as substituent in the 4 position) with *p*-nitrobenzaldehyde at room temperature gave the aza-Wittig product (1,2-addition) **7aa** in excellent yield (Scheme 4, Table 1, entry 1). Spectroscopic data and mass spectrometry of compound **7aa** indicate that only the *E*,*Z*-isomer was obtained. The olefinic protons of **7aa** showed absorptions at *δ* 7.88 and 6.23 ppm ($^3J_{HH}$ = 13.0 Hz) as doublets, and the iminic proton appeared at *δ* 8.44 ppm as a singlet. The selective saturation of the singlet at 8.44 ppm afforded positive NOE over the adjacent vinylic proton without interaction with the olefinic proton in the 4 position (Scheme 4). This NOE observation was consistent with the *E* stereochemistry of azadiene **7aa**. Heterodienes **7ab**−**ae** (Table 1, entries 2−5) are unstable during distillation and/or chromatography and were used without purification.[17]

The scope of this aza-Wittig reaction was not limited to the phosphazenes derived from ethyl *β*-azidoacrylate, given that 3-methyl- **6b** (R^1 = Me) and 3-phenyl-substituted *N*-vinylic phosphazenes **6c** (R^1 = Ph) also reacted with aldehydes leading to the formation of

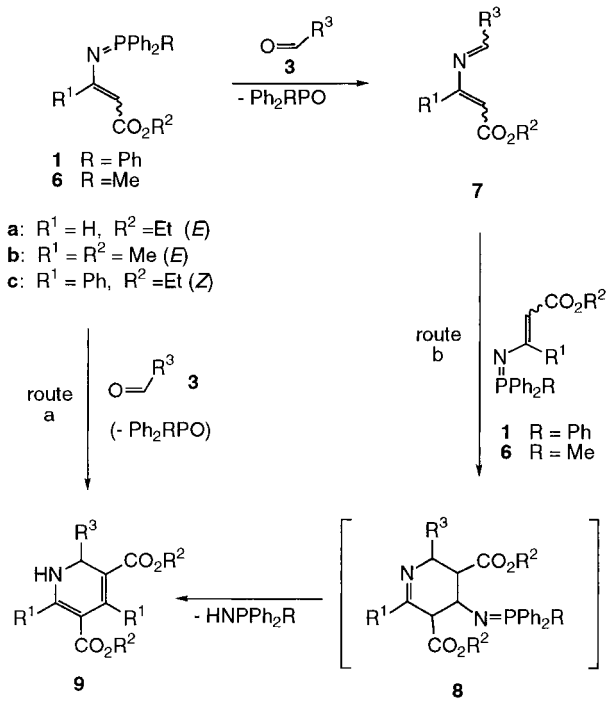
(17) The reaction was monitored by ^{31}P and ^1H NMR showing the disapperance of phosphazene **6** or **19** and the formation of azadiene **7** or **20**.

Table 1. Compounds 7 Obtained

entry	starting material	products	R^1	R^2	R^3	reactn conditions: T (°C)	reactn conditions: time (h)	yield (%)	E/Z ratio[b]
1	**6a**	**7aa**	H	Et	*p*-NO_2-Ph	rt	2	82[a]	100/0
2	**6a**	**7ab**	H	Et	*o*-NO_2-Ph	rt	2	75[d]	100/0
3	**6a**	**7ac**	H	Et	Ph	rt	3	88[d]	100/0
4	**6a**	**7ad**	H	Et	3-Pyr	rt	2	67[d]	100/0
5	**6a**	**7ae**	H	Et	*p*-OMe-Ph	45	24	68[d]	100/0
6	**6b**	**7ba**	Me	Me	*p*-NO_2-Ph	rt	24	80[a]	100/0
7	**1b**	**7ba**	Me	Me	*p*-NO_2-Ph	100[c]	3	61[a]	100/0
8	**6b**	**7bb**	Me	Me	Ph	45	200	80[d]	80/20
9	**1b**	**7bb**	Me	Me	Ph	100[c]	24	45[d]	80/20
10	**6b**	**7bc**	Me	Me	*o*-NO_2-Ph	rt	24	75[d]	80/20
11	**6c**	**7ca**	Ph	Et	*p*-NO_2-Ph	rt	2	71[a]	100/0
12	**1c**	**7ca**	Ph	Et	*p*-NO_2-Ph	100[c]	3	52[a]	100/0
13	**6c**	**7cb**	Ph	Et	*p*-Me-Ph	60	30	75[d]	90/10
14	**1c**	**7cb**	Ph	Et	*p*-Me-Ph	100[c]	30	47[d]	90/10

[a] Purified by chromatography. [b] E/Z ratio (iminic bond) by GC and ^{1}H NMR assignment. [c] The reaction was performed without solvent. [d] Yield calculated by ^{1}H NMR.

Scheme 4. 1,2-Dihydropyridines 9 Formation through [4 + 2] Cycloaddition Reaction of Azadienes 7 and Phosphazenes 1 and 6



azadienes **7ba**,**bc** and **7ca**,**cb**, obtained mainly as *E*-imine isomers (Table 1, entries 6 and 11). In the case of **7bb**, **7bc**, and **7cb** a mixture of *E*- and *Z*-imine isomers (Table 1, entries 8, 10, and 13) was obtained. Azadienes **7ba**, **7bb**, **7ca**, and **7cb** (Table 1, entries 7, 9, 12, and 14) were obtained in moderate yields from *N*-vinylic phosphazenes derived from triphenylphosphine **1b**,**c** when the reaction of **1b**,**c** with aldehydes **3** was performed at 100 °C without solvent. Treatment of 2 equiv of phosphazenes **6b** and **1b,c** derived from both diphenylmethylphosphine and triphenylphosphine respectively with 1 equiv of aromatic aldehydes **3** gave 2-aryl-3,4-(dialkoxycarbonyl)dihydropyridines **9** (Scheme 4, route a) in good yields and in a regioselective fashion (Table 2, entries 1−5). The process could start with an aza-Wittig reaction of the phosphazenes **1** or **6** and aldehydes **3** to give azadienes **7,** which then undergo a regioselective [4 + 2] cycloaddition reaction with a second molecule of phosphazenes **1** or **6**, which act as dienophile. Thermal elimination of the iminophosphorane from the cycloadduct **8** could give dihydropyridines **9** (Scheme 4).

Cycloaddition Reaction of Azadienes 7 with Enamines. To test the synthetic usefulness of the new azadienes **7** as reagents for heterocyclic synthesis[18] we explore cycloaddition reactions of electron deficient 2-azadienes **7** (Scheme 4). At first, the reaction of azadienes **7** with conjugated phosphazenes **6** was studied. Treatment of azadienes **7aa**,**ae** with a second molecule of phosphazene **6a** also led to dihydropyridines **9af**,**ag** (Scheme 4, route b, Table 2, entries 6 and 7). This behavior suggests that, in the reaction of 2 equiv of phosphazenes **6** and **1** with aldehydes to obtain dihydropyridines **9** (Scheme 4, route a), azadienes **7** are involved. Dihydropyridines **9** (R^1 = H, R^2 = R^4) may alternatively be obtained through reaction of azadienes **7** with β-enamino esters **10** (Scheme 5). Reaction of azadienes **7** with enamines **10** led to the formation of dihydropyridines **9** (R^1 = H, R^2 = R^4 = Et) (Table 2, entries 8 and 9). Likewise, dihydropyridines **11** ($R^2 \neq R^4$) can be obtained when azadienes **7** react with enamines **10** derived from other carboxylic esters ($R^2 \neq R^4$, Table 2, entries 10−15). Calcium channel antagonist action of 1,2-dihydropyridines derived from β-amino acids has been reported.[19] Dihydropyridines **11** underwent aromatization to give functionalized pyridines **12** by means of oxidation with quinone (Table 2, entries 16 and 17). Nevertheless pyridines **12ac**,**bd** were directly obtained when azadienes **7ab**,**bc** were used (Table 2, entries 18 and 19). The reduction of 2-*o*-nitrophenyl-substituted pyridines **12ac,-bd** with Fe/HOAc affords benzonaphthyridinones **13a**,**b** (Scheme 6).

The reaction of heterodienes **7** with more reactive enamines was also performed. Pyrrolidinecyclohexanone **14a** (n = 2) reacts with azadienes **7aa**,**ad** (R^1 = H) at

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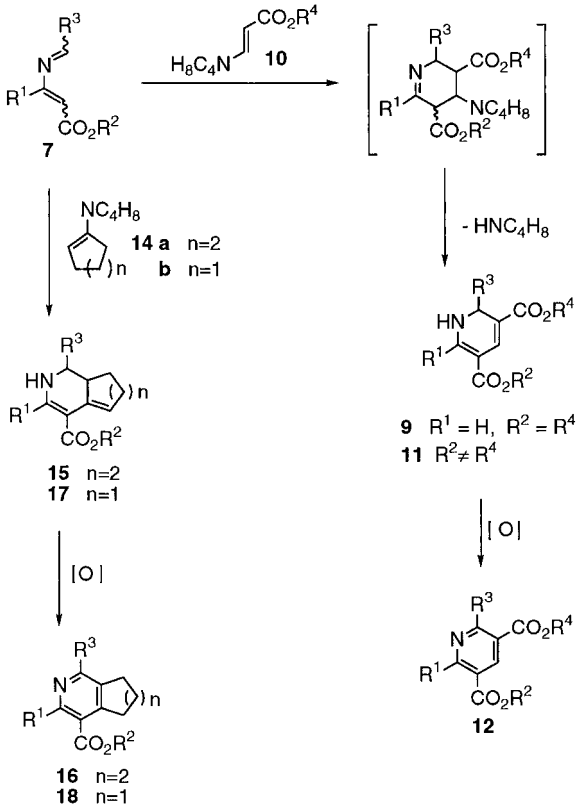
Table 2. Compounds 9, 11, and 12 Obtained

						reactn conditions		
entry	products	R^1	R^2	R^3	R^4	*T* (°C)	time (h)	yield (%)[a]
1	**9ba**[b]	Me	Me	*p*-NO_2-Ph		60	72	44
2	**9bb**[b]	Me	Me	Ph		100[c]	165	43
3	**9bc**[b]	Me	Me	*p*-OMe-Ph		60	280	65
4	**9bd**[b]	Me	Me	*p* -Me_2N-Ph		60	300	44
5	**9ce**[b]	Ph	Et	*p*-Me-Ph		100[c]	48	55
6	**9af**[d]	H	Et	*p*-NO_2-Ph		60	4	39
7	**9ag**[d]	H	Et	*p*-OMe-Ph		60	48	72
8	**9af**[e]	H	Et	*p*-NO_2-Ph	Et	rt	112	55
9	**9ag**[e]	H	Et	*p*-OMe-Ph	Et	75	70	45
10	**11aa**[e]	H	Et	*p*-NO_2-Ph	Me	rt	160	62
11	**11ab**[e]	H	Et	Ph	Me	60	17	43
12	**11ac**[e]	H	Et	*p*-OMe-Ph	Me	60	68	42
13	**11bd**[e]	Me	Me	*p*-NO_2-Ph	Et	100	15	61
14	**11be**[e]	Me	Me	Ph	Et	60	120	44
15	**11cf**[e]	Ph	Et	*p*-NO_2-Ph	Me	100	48	51
16	**12aa**[f]	H	Et	*p*-OMe-Ph	Me	100	24	95
17	**12cb**[f]	Ph	Et	*p*-NO_2-Ph	Me	100	90	87
18	**12ac**[e]	H	Et	*o*-NO_2-Ph	Me	60	48	52
19	**12bd**[e]	Me	Me	*o*-NO_2-Ph	Me	60	48	50

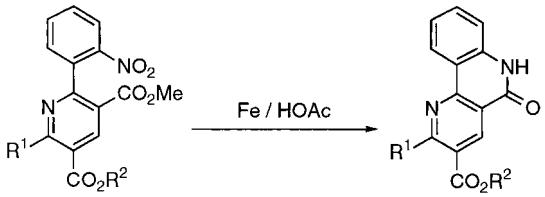
[a] Purified by chromatography. [b] Obtained by reaction of 2 equiv of phosphazenes **6** or **1** and 1 equiv of aldehydes. [c] The reaction was performed without solvent. [d] Obtained from 1 equiv of phosphazenes **6** and azadienes **7**. [e] Obtained from azadienes **7** and enamines **10**. [f] Obtained by oxidation of dihydropyridines **11**.

Scheme 5. Reaction of Azadienes 7 with Enamines 10 and 14



room temperature affording 1,2,6,7,8,8a-hexahydroisoquinoline compounds derived from *β*-amino acids **15aa**,**ab** (Table 3, entries 1 and 2). Spectral data were in agreement with the enamine structure of a bicyclic heterocycle. In the ^{1}H NMR spectrum of **15aa** (R^1 = H) the signal for 3-H appeared at δ_H 7.59 as a doublet with a coupling constant of 6.3 Hz, while 1-H and 5-H showed absorptions at δ_H 3.95 ($^3J_{HH}$ = 10.8 Hz) and 6.62 ppm ($^3J_{HH}$ = 1.8 Hz) as doublets. Oxidation of bicyclic heterocycles **15aa,ab** with quinone led to the formation of 5,6,7,8-tetrahydroisoquinoline **16aa,ab** derived from *β*-amino acids (Table 3, entries 3 and 4). Pyrrolidinecyclopentanone **14b** (*n* = 1) reacted similarly with azadienes **7aa**,**ad** (R^1 = H) to give bicyclic compounds **17aa,ab** (Table 3, entries 8 and 9). Aromatization of these nitrogen heterocycles **17** provided bicyclic pyridine compounds **18aa,ab** in excellent yields (Table 3, entries 10 and 11). 3-Methyl-**7ba**,**bb** (R^1 = Me) and 3-phenyl-substituted azadienes **7ca** (R^1 = Ph) also reacted with pyrrolidinecyclohexanone **14a** (*n* = 2) to yield 5,6,7,8-tetrahydroisoquinoline compounds **16** (see Table 2, entries 5−7).

Scheme 6. Formation of Benzo[*h*][1,6]naphthyridin-5-ones 13



Aza-Wittig Reaction of Phosphazenes 19 with Aldehydes (1,2-Addition) and Preparation of Phenantridin-1-one Derivative 21. Aza-Wittig reaction of phosphazenes **6** and aldehydes **3** was extended to conjugated phosphazenes **19**. *N*-vinylic phosphazene derived from cyclic ketones **19a** (R^1 = Me) was prepared by Staudinger reaction[1b] of diphenylmethylphosphine and 3-azidocyclohex-2-enone.[20] Compound **19a** reacts with *p*-nitrobenzaldehyde at 45 °C and gave the aza-Wittig reaction (1,2-addition). Azadiene **20** was not isolated and was used "in situ" without isolation in a [4 + 2] cycloaddition reaction with pyrrolidinecyclohexanone enamine **14a** leading to the formation of the tricyclic phenantridin-1-one derivative **21**. These findings are in contrast with the reported reaction of phosphazenes derived from triphenylphosphine **19b** (R^1 = Ph) with aldehydes in *o*-xylene at 160 °C in a sealed tube, to afford 9-azaantracene compounds **22**[14] (Scheme 7).

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Table 3. Compounds 15−18 Obtained

entry	starting material	products	R^1	R^2	R^3	reactn conditions: T (°C)	reactn conditions: time (h)	yield (%)[a]
1	**7aa**	**15aa**	H	Et	*p*-NO_2-Ph	rt	1	95
2	**7ad**	**15ab**	H	Et	3-Pyr	rt	24	96
3	**15aa**	**16aa**	H	Et	*p*-NO_2-Ph	100	14	90
4	**15ab**	**16ab**	H	Et	3-Pyr	100	24	90
5	**7ba**	**16bc**	Me	Me	*p*-NO_2-Ph	rt	14	76
6	**7bb**	**16bd**	Me	Me	Ph	rt	24	44
7	**7ca**	**16ce**	Ph	Et	*p*-NO_2-Ph	rt	14	46
8	**7aa**	**17aa**	H	Et	*p*-NO_2-Ph	rt	1	98
9	**7ad**	**17ab**	H	Et	3-Pyr	rt	24	97
10	**17aa**	**18aa**	H	Et	*p*-NO_2-Ph	100	12	93
11	**17ab**	**18ab**	H	Et	3-Pyr	100	120	95

[a] Purified by chromatography.

Scheme 7. Aza-Wittig Reaction of Phosphazene 19 with *p*-Nitrobenzaldehyde

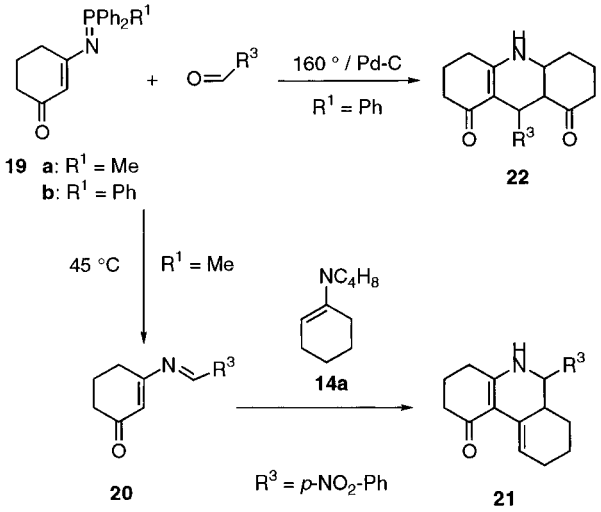


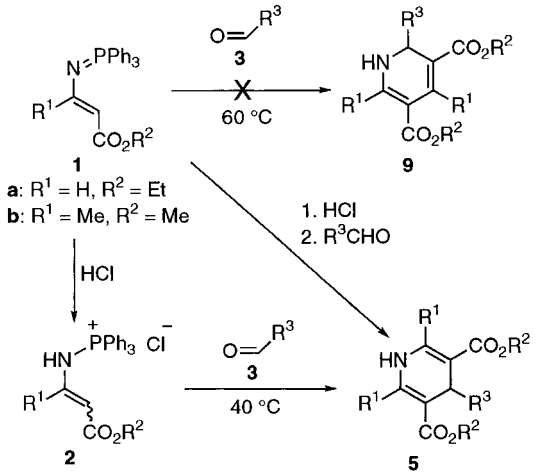
Table 4. Compounds 5 Obtained

entry	starting material	products	R^1	R^2	R^3	time (h)	yield (%)[a]
1	**1a**	**5aa**	H	Et	3-Pyr	24	52
2	**1a**	**5ab**	H	Et	*p*-OMe-Ph	24	66
3	**1b**	**5bc**	Me	Me	Ph	5	61
4	**1b**	**5bd**	Me	Me	*p*-OMe-Ph	5	71
5	**1b**	**5be**	Me	Me	*p*-Me-Ph	5	71
6	**1b**	**5bf**	Me	Me	*o*-NO_2-Ph	5	65

[a] Purified by chromatography.

Reaction of Enamino Phosphonium Salts 2 Derived from Phosphazenes 1 with Aldehydes 3. Preparation of Symmetrical Dihydropyridines 5. To test the 1,4 addition versus the 1,2-addition reaction of conjugated phosphazenes derived from triphenylphosphine **1**, we explored the reactivity of phosphazene **1** and their derivatives **2** with aldehydes **3**. Neither symmetric 1,4-dihydropyridines **5** nor asymmetric 1,4-dihydropyridines **9** were obtained by the reaction of phosphazene **1a** (R^1 = H) with aromatic aldehydes at 60 °C, and the starting phosphazene **1a** was recovered. However, the reaction of enamino phosphonium salts **2a**, prepared by acid treatment of *N*-vinylic phosphazene **1a** (R^1 = H), with aromatic and heteroaromatic aldehydes in refluxing CH_2Cl_2 led to the formation of 4-aryl-3,5-diethoxycarbonyl-1,4-dihydropyridines **5aa,ab** (Table 4, entries 1 and 2). The formation of dihydropyridines **5aa**,**ab** could be explained by an initial 1,4-addition of the aldehyde to the γ-carbon atom of the phosphonium salt **2a** to give 1,2,5-oxaazaphosphorane **4** followed by regioselective

Scheme 8. Preparation of Symmetrical 1,4-Dihydropyridines 5



attack[2,14] of a second molecule of the phosphonium salt **2a** (Scheme 8). Dihydropyridines **5aa,ab** were characterized and their structures were consistent with reported symmetrical heterocycles.[14] This reaction can also be extended to 3-methyl-substituted phosphonium salt **2b** (R^1 = CH_3), to give 3-methyl-substituted symmetrical dihydropyridines **5ba**−**bd** (Table 4, entries 3−6). This methodology has been also used in the preparation (Table 4, entry 6) of the biologically active nifedipine **5bd** used for the treatment of coronary diseases.[21] The synthesis of dihydropyridines **5** does not require the isolation and purification of phosphonium salts **2**, and they can also be obtained when phosphazenes **1** are directly treated with acid with subsequent addition of aldehydes. Therefore, this strategy offers a new approach to the synthesis of symmetrical dihydropyridines **5** under mild reaction conditions. 1,4-Dihydropyridines are compounds with interesting therapeutic[22] and biorganic[23] applications.

We conclude that *N*-vinylic phosphazenes **1** derived from triphenylphosphine are ambident nucleophilic reagents. They are suitable for 1,2-addition with hydrogen chloride. The nucleophilic character of the nitrogen atom of *N*-vinylic phosphazenes can be increased when they are derived from diphenylmethylphosphine **6,** and these undergo aza-Wittig reaction (1,2-addition) with aldehydes

(21) Bossert, F.; Vater, W. *Med. Res. Rev.* **1989**, *9*, 291.
(22) For reviews see: Triggle, D. J. In *Comprehensive Medicinal Chemistry*; Hansch, C., Ed.; Pergamon: Oxford, U.K., 1990; Vol. 3, p 1070.
(23) (a) Bennasar, M. L.; Juan, C.; Bosch, J. *Tetrahedron Lett.* **1998**, *39*, 9275. (b) Almarsson, O.; Bruice, T. C. *J. Am. Chem. Soc.* **1993,** *115*, 2125. (c) Wu, Y. D.; Haunk, K. N. *J. Org. Chem.* **1993**, *58*, 2043.

in a regioselective fashion. Isolated azadienes **7** are intermediates in the preparation not only of monocyclic 1,2-dihydropyridines **9** and pyridines **12** but also of bicyclic nitrogen heterocycles **15**−**18** derived from *β*-amino acids, as well as of phenanthridin-1-one **21** and benzonaphthyridinone derivatives **13**. The efficient synthesis of symmetrical dihydropyridines **5** here described provides an easy approach to the preparation of these kinds of compounds, avoiding the use of high temperatures (160 °C).[14] It is worth noting that pyridine compounds derived from *β*-amino acids are useful heterocycles not only for their biological activities[24] but also because the pyridine nucleus is a structural unit appearing in many natural products.[25]

Experimental Section

General Methods. All reactions were carried under nitrogen. Dioxane and diethyl ether were distilled from benzophenone ketyl and sodium, while $CHCl_3$ and CH_2Cl_2 were distilled from P_2O_5. Phosphazenes **1** and **6** were synthesized according to literature procedures.[4a,15] For new phosphazenes **1a**,**c** and **6c**, see the Supporting Information.

General Procedure for the Preparation of Phosphonium Salts 2. Hydrogen chloride was bubbled through a 0−10 °C solution of phosphazene **1** (1.13 g, 3 mmol) in CH_2Cl_2 (10 mL)/Et_2O (20 mL), and the mixture was stirred at 0−10 °C for 30 min. Evaporation of solvent under reduced pressure afforded to the enamino phosphonium salt **2**.

((2-(Ethoxycarbonyl)-1-ethenyl)amino)triphenylphosphonium Chloride (2a). The general procedure was followed using phosphazene **1a** to give **2a(*E*)**. The reaction product is unstable to recrystalation or chromatography and therefore was not isolated and used for the following reactions: ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.51 (s, 1H), 7.89−7.47 (m, 15H), 7.02 (dd, $^3J_{HH}$ = 13.6 Hz, $^3J_{PH}$ = 24.1 Hz, 1H), 6.40 (d, $^3J_{HH}$ = 13.6 Hz, 1H), 4.04 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 1.17 (t, $^3J_{HH}$ = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 139.5, 135.0−128.0 (m), 118.5 (d, $^1J_{PC}$ = 100 Hz), 105.1 (d, $^3J_{PC}$ = 11.1 Hz), 59.1, 13.5; ^{31}P NMR ($CDCl_3$, 120 MHz) δ 37.99.

General Procedure for the Preparation of Dihydropyridines 5. Aldehyde **3** (1.5 mmol) was added to a 0−10 °C solution of phosphonium salt **2** (1.234 g, 3 mmol) in CH_2Cl_2 (8 mL) under N_2, and the mixture was stirred and warmed at 40 °C until TLC indicated the disappearance of aldehyde **3**. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the compounds **5**.

Diethyl 4-(3-Pyridyl)-1,4-dihydro-3,5-pyridinedicarboxylate (5aa). The general procedure was followed using phosphonium salt **2a** and 0.142 mL (1.5 mmol) of 3-pyridinecarboxaldehyde (24 h). Evaporation of solvent under reduced pressure afforded a oil which was chromatographed on silica gel (1/2 hexane/AcOEt) to give 0.236 g (52%) of **5aa** as a yellow oil (R_f = 0.21 in AcOEt): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 8.35 (d, $^3J_{HH}$ = 4.8 Hz, 1H), 7.68 (d, $^3J_{HH}$ = 10.5 Hz, 1H), 7.44 (s, 1H), 7.37 (d, $^3J_{HH}$ = 5.1 Hz, 2H), 7.20−7.16 (m, 1H), 4.91 (s, 1H), 4.10−4.00 (m, 4H), 1.19−1.14 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 149.7, 147.3, 142.5, 136.1, 134.2, 123.1, 107.5, 60.2, 35.7, 14.2; IR (film) 3216, 3153, 3088, 2982, 2937, 1697, 1497, 1289, 1176; M/S (EI) *m*/*z* 302 (M^+, 8). Anal. Calcd for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.89; H, 6.05; N, 9.29.

General Procedure A for the Preparation of 2-Azadienes 7. Aldehyde **3** (4 mmol) was added to a 0−10 °C solution of phosphazene **6** (4 mmol) in $CHCl_3$ (15 mL) under N_2, and the mixture was stirred at room temperature or warmed at 45 °C or 60 °C until TLC indicated the disappearance of phosphazene.

General Procedure B for the Preparation of 2-Azadienes 7. Aldehyde **3** (4 mmol) was added to phosphazene **1** (4 mmol) under N_2, and the mixture was warmed at 100 °C until TLC indicated the disappearance of phosphazene.

4-(Ethoxycarbonyl)-1-(4-nitrophenyl)-3-phenyl-2-azabuta-1,3-diene (7ca). The general procedure A was followed using phosphazene **6c** (1.558 g, 4 mmol) and 0.604 g (4 mmol) of *p*-nitrobenzaldehyde (room temperature/2 h). Evaporation of solvent under reduced pressure afforded an oil which was chromatographed on silica gel (1/10 AcOEt/hexane) to give 0.92 g (71%) of **7ca** as a brown oil. Following the general procedure B 1.806 g (4 mmol) of phosphazene **1c** and 0.604 g (4 mmol) of *p*-nitrobenzaldehyde were used for 3 h, and the crude oil was chromatographed on silica gel (1/10 AcOEt/hexane) to give 0.674 g (52%) of **7ca** as a brown oil (R_f = 0.52, AcOEt): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.23 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 8.02 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.55−7.28 (m, 5H), 5.76 (s, 1H), 4.02 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 1.27 (t, $^3J_{HH}$ = 7.2 Hz, 3H). Anal. Calcd for $C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.99; H, 4.91; N, 8.67.

General Procedure A for the Preparation of Dihydropyridines 9. Aldehyde **3** (3 mmol) was added to a 0−10 °C solution of phosphazene (6 mmol) in $CHCl_3$ (8 mL) under N_2, and the mixture was stirred at 60 °C until TLC indicated the disappearance of phosphazene. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the commpounds **9**.

Dimethyl 4,6-Dimethyl-2-(4-nitrophenyl)-1,2-dihydro-3,5-pyridinedicarboxylate (9ba). The general procedure A was followed using phosphazene **6b** (1.88 g, 6 mmol) and 0.453 g (3 mmol) of *p*-nitrobenzaldehyde for 72 h. The crude oil was chromatographed on silica gel (5/1 hexane/AcOEt) to give 0.455 g (44%) of **9ba** as an orange oil (R_f = 0.25, AcOEt): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.36 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 5.99 (s, 1H), 5.64 (d, $^3J_{HH}$ = 4.5 Hz, 1H), 3.63 (s, 3H), 3.62 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 166.9, 154.7, 149.7, 147.7, 145.2, 127.0, 123.8, 108.5, 104.3, 53.9, 51.3, 50.8, 20.9, 19.3; IR (film) 3326, 3081, 2952, 2930, 2853, 1696, 1595, 1518, 1345, 1214; M/S (EI) *m*/*z* 346 (M^+, 3). Anal. Calcd for $C_{17}H_{18}N_2O_6$: C, 59.93; H, 5.24; N, 8.12. Found: C, 59.00; H, 5.29; N, 8.10.

General Procedure B for the Preparation of Dihydropyridines 9. Aldehyde **3** (3 mmol) was added to phosphazene (6 mmol) under N_2, and the mixture was warmed at 100 °C until TLC indicated the disappearance of phosphazene. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the commpounds **9**.

General Procedure C for the Preparation of Dihydropyridines 9. Phosphazene **6** (3 mmol) was added to a 0−10 °C solution of 2-azadiene **7** (3 mmol) in $CHCl_3$ (10 mL) under N_2, and the mixture was warmed to 60 °C until TLC indicated the disappearance of phosphazene. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the commpounds **9**.

General Procedure D for the Preparation of Dihydropyridines 9 and 11. To a solution of 2-azadiene **7** (3 mmol) in $CHCl_3$ or toluene (10 mL) was added enamine **10** (3 mmol), and the mixture was stirred to adequate temperature until TLC indicated the disappearance of phosphazene. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the commpounds **9** or **11**.

Diethyl 2-(4-Nitrophenyl)-1,2-dihydro-3,5-pyridinedicarboxylate (9af). The general procedure C was followed using azadiene **7aa** (0.74 g, 3 mmol) and 0.939 g (3 mmol) of phosphazene **6a** for 4 h. The crude oil was chromatographed on silica gel (5/1 hexane/AcOEt) to give 0.41 g (39%) of **9af** as an orange oil. Following the general procedure D azadiene **7aa** (0.74 g, 3 mmol) and 0.51 g (3 mmol) of ethyl *trans*-2-

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(25) For recent reviews, see: (a) Schneider, M. J. In *Alkaloids. Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 10, pp 155−299. (b) Shipman, M. *Contemp. Org. Synth.* **1995**, *2*, 1.

pyrrolydineacrylate in $CHCl_3$ were used (room temperature/112 h), and the crude oil was chromatographed on silica gel (5/1 hexane/AcOEt) to give 0.578 g (55%) of **9af** as an orange oil (R_f = 0.54 in AcOEt): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.68 (s, 1H), 7.67 (s, 1H), 7.51 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.80 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 5.74 (d, $^3J_{HH}$ = 2.4 Hz, 1H), 4.16−4.00 (m, 4H), 1.26−1.15 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 165.6, 149.7, 147.4, 146.8, 133.4, 127.6, 123.9, 111.7, 97.5, 60.5, 59.9, 54.5, 14.4, 14.1; IR (film) 3302, 3075, 2982, 2928, 2850, 1677, 1620, 1524, 1347, 1223; M/S (EI) *m/z* 346 (M^+, 2). Anal. Calcd for $C_{17}H_{18}N_2O_6$: C, 58.96; H, 5.24; N, 8.09. Found: C, 59.00; H, 5.27; N, 8.10.

General Procedure for the Preparation of Benzo[*h*]-[1,6]naphthyridin-5-one 13. A mixture of pyridine **12** (1.5 mmol), acetone (10 mL), acetic acid (1 mL), water (1 mL), and powdered iron (0.36 g) was refluxed for 5 h, and then dichloromethane (10 mL) was added. The resultant suspension was filtered, and a saturated solution of sodium carbonate (5 mL) was added to the filtrate. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was recrystallized from acetonitrile to give **13**.

3-(Ethoxycarbonyl)-benzo[*h*][1,6]naphthyridin-5-one (13a). It was prepared according to the general procedure using pyridine **12ac** (0.494 g) to give 0.285 g (71%) of **13a** as a white solid: mp 291−292 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.04 (s, 1H), 9.45 (s, 1H), 8.98 (s, 1H), 8.63 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.66 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.41 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.34 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 4.41 (q, $^3J_{HH}$ = 7.0 Hz, 2H), 1.38 (t, $^3J_{HH}$ = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.0, 160.4, 153.7, 153.5, 138.8, 136.7, 132.5, 124.8, 124.7, 122.8, 120.7, 118.2, 116.2, 61.5, 14.1; IR (KBr) 3433, 3177, 3033, 2962, 2905, 1708, 1666, 1275, 1250; M/S (EI) *m/z* 268 (M^+, 100). Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.05; H, 4.50; N, 10.42. Found: C, 67.11; H, 4.55; N, 10.40.

General Procedure for [4 + 2] Cycloaddition Reaction of 2-Azadienes 7 with Cyclic Enamines 14. Cyclic enamine (4 mmol) was added to a 0−10 °C solution of 2-azadiene **7** (4 mmol) in $CHCl_3$ (15 mL) under N_2, and the mixture was stirred at room temperature until TLC indicated the disappearance of 2-azadiene. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the compounds **15**, **16**, or **17**.

Ethyl 1,2,6,7,8,8a-Hexahydro-1-(4-nitrophenyl)-4-isoquinolinecarboxylate (15aa). The general procedure was following using azadiene **7aa** (0.992 g, 4 mmol) and 1-pyrrolidine-1-cyclohexene **14a** (0.605 g, 4 mmol) for 1 h. The crude oil was chromatographed on silica gel (10/1 hexane/AcOEt) to give 1.25 g (95%) of **15aa** as an orange solid: mp 110−111 °C (recrystallized from Et_2O/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.59 (d, $^3J_{HH}$ = 6.3 Hz, 1H), 7.51 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.62 (d, $^3J_{HH}$ = 1.8 Hz, 1H), 4.61 (d, $^3J_{HH}$ = 6.3 Hz, 1H), 4.26−4.15 (m, 2H), 4.05 (d, $^3J_{HH}$ = 10.8 Hz, 1H), 2.54−1.42 (m, 6H), 1.30 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 1.09−1.01 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 148.0, 147.9, 142.0, 128.7, 127.6, 124.0, 121.6, 98.5, 62.1, 59.3, 40.2, 26.7, 25.9, 21.6, 14.5; IR (KBr) 3283, 2931, 2866, 1655, 1592, 1519, 1342; M/S (EI) *m/z* 328 (M^+, 24). Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.65; H, 6.18; N, 8.50.

Methyl 3-Methyl-1-(4-nitrophenyl)-5,6,7,8-tetrahydro-4-isoquinolinecarboxylate (16bc). The general procedure was following using azadiene **7ba** (0.996 g, 4 mmol) and 1-pyrrolidine-1-cyclohexene **14a** (0.605 g, 4 mmol) for 14 h. The crude oil was chromatographed on silica gel (10/1 hexane/AcOEt) to give 0.996 g (76%) of **16bc** as an orange solid: mp 114−115 °C (recrystallized from AcOEt/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.63 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.97 (s, 3H), 2.80 (t, $^3J_{HH}$ = 6.3 Hz, 2H), 2.60 (t, $^3J_{HH}$ = 6.3 Hz, 2H), 2.52 (s, 3H), 1.84−1.78 (m, 2H), 1.73−1.70 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 156.5, 151.3 147.0, 146.7, 144.6, 129.9, 128.8, 128.1, 123.4, 52.4, 27.4, 26.8, 22.4, 22.3, 21.7; IR (KBr) 3433, 3077, 2923, 2854, 1727, 1521, 1348, 1255; M/S (EI) *m/z* 326 (M^+, 41). Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.11; H, 5.60; N, 8.59.

Ethyl 6-(4-Nitrophenyl)-4,5-(1-propanyl-3-yliden)-1,4,5,6-tetrahydro-3-pyridinecarboxylate (17aa). The general procedure was following using azadiene **7aa** (0.992 g, 4 mmol) and 1-pyrrolidine-1-cyclopentene **14b** (0.496 g, 4 mmol) for 1 h. The crude oil was chromatographed on silica gel (10/1 hexane/AcOEt) to give 1.232 g (98%) of **17aa** as a yellow solid: mp 118−119 °C (recrystallized from AcOEt/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.59 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 7.50 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.12 (d, $^3J_{HH}$ = 2.4 Hz, 1H), 4.76 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 4.24−4.19 (m, 2H), 4.08 (d, $^3J_{HH}$ = 9.9 Hz, 1H), 2.87−2.84 (m, 1H), 2.42−2.40 (m, 2H), 1.79−1.70 (m, 1H), 1.44−1.21 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 147.9, 147.7, 143.6, 133.1, 128.0, 124.1, 121.8, 98.5, 63.0, 59.4, 50.7, 31.5, 28.3, 14.5; IR (KBr) 3296, 3070, 2975, 2929, 2848, 1657, 1578, 1514, 1346, 1232; M/S (EI) *m/z* 314 (M^+, 2). Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.96; H, 5.77; N, 8.91. Found: C, 64.75; H, 5.80; N, 8.86.

General Procedure for Aromatization of Compounds 15 and 17. To a solution of bicyclic compound (2 mmol) in dioxane (5 mL) was added 0.212 g (2 mmol) of *p*-benzoquinone, and the mixture was stirred at 100 °C under N_2. The solvent was evaporated under reduced pressure, and the resulting oil was purified by silica gel column chromatography.

Ethyl 6-(4-Nitrophenyl)-4,5-trimethylene-3-pyridinecarboxylate (18aa). The general procedure was following using 0.63 g (2 mmol) of compound **17aa** for 12 h. The crude oil was chromatographed on silica gel (10/1 hexane/AcOEt) to give 0.58 g (93%) of **18aa** as a brown solid: mp 110−111 °C (recrystallized from AcOEt/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.31 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.59 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 4.40 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 3.36 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 3.11 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 2.15−2.13 (m, 2H), 1.41 (t, $^3J_{HH}$ = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 158.0, 154.3, 149.5, 145.5, 138.9, 129.6, 123.5, 122.5, 61.2, 33.9, 32.5, 25.2, 14.3; IR (KBr) 3423, 2980, 2925, 2851, 1706, 1516, 1346, 1281; M/S (EI) *m/z* 312 (M^+, 100). Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 65.29; H, 5.14; N, 8.98.

1,1-Diphenyl-1-methyl-3,4-(tetramethylen-4-one)-2-aza-1λ^5-phosphabuta-1,3-diene (19a). A solution of 0.686 g (5 mmol) of 3-azidocyclohex-2-enone[21] in anhydrous CH_2Cl_2 (3 mL) was added dropwise to a 0−10 °C solution of 1.001 g (5 mmol) of methyldiphenylphospine in anhydrous CH_2Cl_2 (8 mL) under N_2, and the mixture was stirred for 30 min at room temperature. The reaction product is unstable to distillation or chromatography and therefore was not isolated and used for the following reactions: ^{1}H NMR (300 MHz, $CDCl_3$) of crude reaction mixture (**19a** + Ph_2CH_3PO) δ 7.66−7.40 (m, 10H), 4.87 (s, 1H), 2.45 (t, $^3J_{HH}$ = 6.0 Hz, 2H), 2.21−2.16 (m, 2H), 2.09 (d, $^2J_{PH}$ = 13.0 Hz, 3H), 1.90−1.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.0, 176.0 (d, $^2J_{PC}$ = 6.3 Hz), 132.4−128.1 (m), 108.5 (d, $^3J_{PC}$ = 15.5 Hz), 36.3, 35.7 (d, $^3J_{PC}$ = 24.7 Hz), 22.2, 13.3 (d, $^1J_{PC}$ = 67.9 Hz); ^{31}P NMR ($CDCl_3$, 120 MHz) δ 5.91.

1-(4-Nitrophenyl)-3,4-(tetramethylen-4-one)-2-azabuta-1,3-diene (20). *p*-Nitrobenzaldehyde (0.604 g, 4 mmol) was added to a 0−10 °C solution of phosphazene **19a** (4 mmol) in $CHCl_3$ (15 mL) under N_2, and the mixture was stirred at 45 °C until TLC indicated the disappearance of phosphazene. The reaction product is unstable to distillation or chomatography and therefore was not isolated and used for the following reactions: ^{1}H NMR (300 MHz, $CDCl_3$) of crude reaction mixture (**20** + Ph_2CH_3PO) δ 8.23 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.96 (s, 1H), 7.94 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.61−7.30 (m, 10H), 5.53 (s, 1H), 2.53 (t, $^3J_{HH}$ = 6.1 Hz, 2H), 2.36 (t, $^3J_{HH}$ = 6.6 Hz, 2H), 1.98−2.06 (m, 2H), 1.83 (d, $^2J_{PH}$ = 13.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.6, 170.8, 155.9, 150.9, 139.9, 134.3−122.9 (m), 113.0, 36.8, 28.4, 21.7, 16.1 (d, $^1J_{PC}$ = 74.0 Hz).

6-(4-Nitrophenyl)-2,3,4,6,7,8,9-heptahydrophenanthridin-1(5*H*)-one (21). 1-Pyrrolidine-1-cyclohexene **14a** (0.605 g, 4 mmol) was added to a 0−10 °C solution of 2-azadiene **20** (4 mmol) in $CHCl_3$ (15 mL) under N_2, and the mixture was stirred at room temperature for 17 h. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel (1/2 hexane/AcOEt) to give 0.675 g (52%)

of **21** as an orange solid: mp 109−110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.45 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 6.97 (d, $^3J_{HH}$ = 2.4 Hz, 1H), 4.71 (s, 1H), 4.03 (d, $^3J_{HH}$ = 10.5 Hz, 1H), 2.56−0.77 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 157.9, 148.0, 147.8, 128.7, 126.9, 124.0, 123.6, 106.4, 62.4, 39.9, 38.7, 30.0, 29.7, 26.9, 26.0, 21.2; IR (film) 3350, 3215, 2926, 2858, 1513, 1345; M/S (EI) *m*/*z* 324 (M^+, 2). Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.36; H, 6.22; N, 8.64. Found: C, 70.56; H, 6.20; N, 8.65.

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Supporting Information Available: Text providing preparation, elemental analysis, and spectral data (^{1}H NMR, ^{13}C NMR, ^{31}P NMR, IR, and MS) for compounds **1a**,**c, 6c**, **2b**, **5ab**−**5bf**, **7aa**−**7bc**, **7cb**, **9bb**−**9ce**, **9ag**, **11aa**−**11cf**, **12aa**−**12bd**, **13b**, **15ab**, **16bd**−**16ce**, **17ab**, **16aa**−**16ab**, and **18ab**. This material is available free of charge via the Internet at http://pubs.acs.org.

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