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Umpolung Reactivity of Allylic Phosphonates. A Simple Route to 3-Aminoalkane- and 3-Amino-1-alkenylphosphonates (Phosphinates and Phosphine Oxides)

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ABSTRACT

Dibutyl allylphosphonate can react with palladium chloride to give the dibutyl phosphorylated π-allyl palladium chloride complex which was found to be able to react with a nucleophile, such as sodium dimethyl malonate, to give a functionalized 1-alkenylphosphonate. A 1-acetoxyallylic phosphonate can be regarded as the precursor of a phosphorylated π-allylic palladium complex in a palladium(0) catalyzed reaction, and the latter reacts with nucleophiles to yield 3-substituted 1-alkenylphosphonates. The reaction is regioselective. Using this methodology, 3-aminoalkane- and 3-aminoalkenylphosphonates were synthesized from 1-acetoxyallylic phosphonates regioselectively.

INTRODUCTION

Reactions of carbanions stabilized by a connected P=O bond with electrophiles are widely used in organic synthesis [1]. Recently, the regioselectivity of the alkylation reaction of allylic phosphonate anions has received considerable attention [2,3], and the reactions with electrophiles, such as aldehydes and ketones, to give dienes have been widely studied [4]. However, to the best of our knowledge, there is no report concerning the chemistry of allylic phosphonate cations. Should the allylic phosphonate cations exist, they would react with nucleophiles to form the functionized phosphonates and would be rich in interesting chemistry. Although it is difficult to prepare the allylic phosphonate cation which is strongly destabilized by the connected P=O bond, on the basis of the study of the chemistry of π-allylic palladium complexes, it occurred to us that the palladium complex could make the π-allylic phosphonate cation stable enough to exist. Herein, we wish to report our results of the studies on the umpolung reactivity of allylic phosphonates in the form of a palladium(0) complex and the regioselective synthesis of 3-amino alkane phosphonates and 3-amino-1-alkenylphosphonates from 1-acetoxyallylic phosphonates.

RESULTS AND DISCUSSION

Synthesis and Umpolung Reactivity of Dibutyl Phosphorylated π-Allyl Palladium Chloride Complex (2)

It is well-known that a π-allylic palladium complex can easily be obtained by the reaction of an alkene with palladium chloride [5], but there is no report concerning the synthesis and reaction of a phosphorylated π-allyl palladium complex. We re-

Dedicated to Prof. Yao-Zeng Huang on the occasion of his eightieth birthday.

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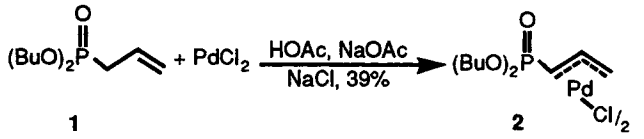
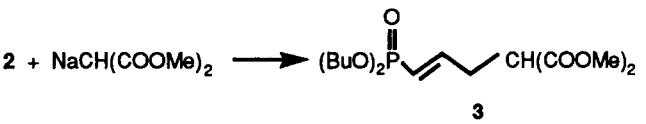
cently found that dibutyl allylphosphonate could react with palladium chloride to give the dibutyl phosphorylated π-allyl palladium chloride complex (**2**) in moderate yield.



1 2

When **2** was treated with sodium dimethyl malonate in THF at room temperature, the reaction proceeded smoothly to provide a 3-substituted 1-alkenylphosphonate (**3**) regioselectively in 58% yield.



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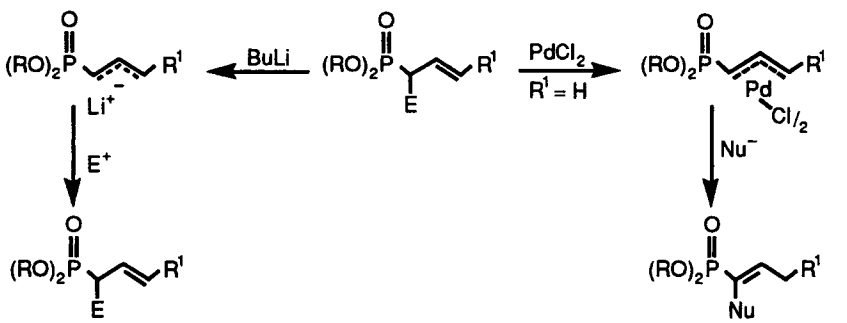
As opposed to the reaction of an allylphosphonate anion, which can react with an electrophile, this new reaction could introduce a nucleophile into the 3-position of an allylphosphonate. Thus, an umpolung effect of the reactivity is established, as shown in the following scheme:



The reaction is highly regioselective and yields the 1-alkenyl phosphonate as the only product. Therefore, this reaction provides a novel method for preparing functionalized 1-alkenylphosphonates.

Reactions of 1-Acetoxyallylic Phosphonates with Nucleophiles under Palladium(0) Catalysis

Owing to the fact that the acetoxy group is a good leaving group in Pd catalyzed reactions in allylic systems [6,7], a 1-acetoxyallylic phosphonate might be considered as the precursor of an allylic phosphonate cation. Thus, the reactions of 1-acetoxyallylic phosphonates with nucleophiles, such as carbanions [8], amines [9], and phosphites [10], under Pd(0) or Ni(0) catalysis have been investigated and some of the results have been reported as communications. It is clear that the electron-withdrawing phosphoryl group exerted a decisive influence on the regioselectivity of this reaction, and the attack by nucleophiles occurred at the electron deficient side, i.e., at the 3-position of the 1-alkenylphosphonates.

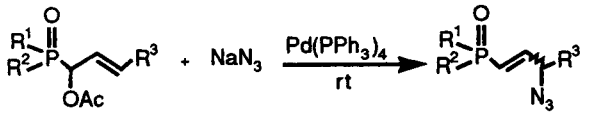
Synthesis of 3-Aminoalkanephosphonates from 1-Acetoxyallylic Phosphonates

Aminophosphonic acids H_2N-R-PO_3H_2 may be considered as analogs of aminocarboxylic acids. The synthesis of a group of microbial metabolites [11,12] or enzyme inhibitors [13] containing γ-amino phosphonic acid functions, especially γ-amino-α,β-unsaturated phosphonates, has attracted increasing interest because of the unique biological properties of these substances [14]. We have reported the synthesis of γ-amino-substituted-α,β-unsaturated phosphonates by Pd catalyzed reactions of 1-acetoxyallylic phosphonates [9]. In general, primary and secondary amines react nicely with the π-allylic palladium intermediate but ammonia fails to do so [15]. For the synthesis of allylic amines, Murahashi et al. reported the reaction of sodium azide with allylic acetates under catalysis by Pd (0), followed by hydrolysis to afford allylic amines [16,17]. Trost and Keinan used a synthon for ammonia, *p,p'*-dimethoxybenzhydrylamine, as the nucleophile to react with allylic acetates, followed by hydrogenolysis to yield the allylic amines [18]. These two procedures seem to offer a possible method for the synthesis of 3-amino-1-alkenylphosphonates from 1-acetoxyallylic phosphonates.

The reaction of 1-acetoxyallylic phosphonates (**4**) with sodium azide in THF-H_2O took place smoothly at room temperature to yield the corresponding 3-azido-1-alkenylphosphonates (**5**) in high yield. This method could also be applied to phosphinates and phosphine oxides. The results are shown in Table 1.

From Table 1, it is apparent that the phosphoryl group has a decisive influence on the regioselectivity of the reaction, and only the corresponding 3-azido-1-alkenylphosphonates were

TABLE 1 Synthesis of (3-Azido-1-alkenyl)phosphorus Derivatives (**5**) from 1-Acetoxyallylic Phosphorus Derivatives (**4**)[a]



4 5

Entry	4 R^1	4 R^2	4 R^3	*t* (hours)	Product	*Isolated Yield* (%)
1	EtO	EtO	H (**4a**)	4	**5a**	78
2	BuO	BuO	H (**4b**)	6	**5b**	82
3	Ph	EtO	H (**4c**)	10	**5c**	83
4	Ph	Ph	H (**4d**)	10	**5d**	81
5	EtO	EtO	Me (**4e**)	20	**6**[b]	76
6	EtO	EtO	Ph (**4f**)	20	—	0[c]

[a]The reaction was carried out at room temperature in THF-H_2O (5:2) from **4** (1 mmol), NaN_3 (3 mmol), and Pd $(PPh_3)_4$ (0.02 mmol).
[b]Diethyl phosphorylbutadiene (**6**) was obtained.
[c]The reaction was carried out at 65°C, and only **4f** was recovered.

isolated. The substituent groups on the phosphorus atom have no apparent influence on the reaction. When diethyl 1-acetoxy-2-butenylphosphonate (**4e**) was used (entry 5), 1-(O,O-diethylphosphorylbutadiene) (**6**) was unexpectedly isolated in moderate yield. This may be due to the basicity of sodium azide which enables a β-elimination reaction to occur easily. No reaction occurred when diethyl 1-acetoxycinnamylphosphonate (**4f**) was used (entry 6).

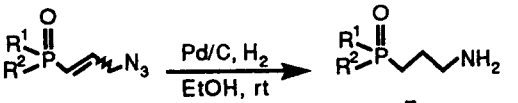
Surprisingly, the azide **5** did not undergo hydrolysis in the presence of Ph_3P and 2N NaOH according to Murahashi's procedure [17]. Consequently, the azides **5** were hydrogenated using Pd on charcoal as the catalyst, and 3-aminopropylphosphonates (**7**) were obtained in high yield (Table 2).

Synthesis of 3-Aminoalkenylphosphonates from 1-Acetoxyallylic Phosphonates

The failure of the synthesis of 3-aminoalkenylphosphonates (phosphinates and phosphine oxides) from 1-acetoxy allylic phosphonates using Murahashi's procedure forced us to try Trost's procedure [18]. 1-Acetoxyallylic phosphonates reacted readily with *p,p'*-dimethoxybenzhydrylamine (DMB-NH_2) in the presence of a catalytic amount of Pd $(PPh_3)_4$ to give 3-DMB-amino substituted alkenylphosphonates (phosphinates and phosphine oxides) (**8**) regioselectively in high yield (Table 3).

When the compounds **8** were treated with formic acid for several hours, the corresponding 3-amino-1-alkenylphosphonates (phosphinates and phosphine oxides) (**9**) were obtained in good yield (Table 4).

TABLE 2 Hydrogenation of (3-Azido-1-alkenyl)phosphorus Derivatives (**5**)



5 7

5	*t* (hours)	Product	*Isolated Yield* (%)
5a	5	**7a**	90
5b	8	**7b**	91
5c	10	**7c**	94
5d	10	**7d**	91

This method could also be applied to allylic compounds with substituted groups and might be useful in the synthesis of the respective new classes of compounds.

EXPERIMENTAL

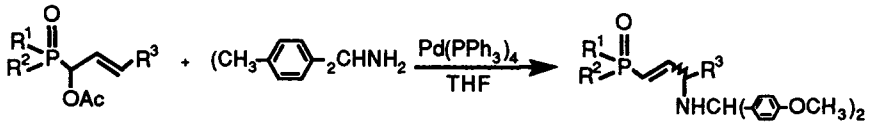
All reactions were carried out under a prepurified nitrogen atmosphere. All solvents and starting materials were distilled under nitrogen before use. ^1H NMR spectra were recorded on a Varian EM-360, FX-90Q, or Varian XL-200 spectrometer. Infrared spectra were taken using a Shimadzu IR 440 or 983G-7500 spectrometer. Mass spectra were obtained on a Finnigan 4021 GC/MS/DC instrument.

Diethyl (1-acetoxyallyl)phosphonate (**4a**) [19], dibutyl (1-acetoxyallyl)phosphonate (**4b**) [20], ethyl (1-acetoxyallyl)phenylphosphinate (**4c**) [10], (1-acetoxyallyl)diphenylphosphine oxide (**4d**) [10], diethyl (1-acetoxybuten-2-yl)phosphonate (**4e**) [21], diethyl (1-acetoxycinnamyl)phosphonate (**4f**) [21], and dibutyl (1-acetoxybuten-2-yl)phosphonate (**4g**) [21] were prepared according to the literature.

Preparation of the Dibutyl Phosphorylated π-Allyl Palladium Chloride Complex (2)

Palladium chloride (0.63 g, 3.55 mmol), sodium acetate (0.58 g, 7.1 mmol), and sodium chloride (0.42 g, 7.1 mmol) were added to a 50 mL flask containing acetic acid (17 mL). The mixture was heated at 80°C for 14 minutes. After the reaction mixture had been allowed to cool to 50°C, a solution of dibutyl allylphosphonate (**1**) (2.4 g, 10.3 mmol) in acetic acid (3 mL) was added by use of a syringe. The mixture was stirred at 20°C for 41 hours, and the color of the reaction mixture turned from deep red to orange red. The mixture was poured into water (20 mL) and extracted with ether (20 mL). The ether layer was washed with sodium bicarbonate solution and water and dried with anhydrous magnesium sulfate. After removal of solvent under vacuum, the product was crystallized from

TABLE 3 Synthesis of 3-(*p,p'*-Dimethoxybenzhydrylamino)-1-alkenylphosphorus Derivatives (**8**)

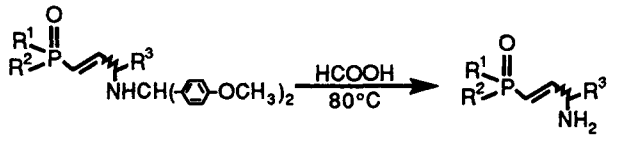


4 **8**

4	*T* (°C)	*t* (hours)	*Product*	*Isolated Yield (%)*
4a	RT	10	**8a**	80
4b	RT	10	**8b**	83
4c	RT	10	**8c**	86
4d	RT	10	**8d**	81
4e	65	5	**8e**	81
4g[a]	65	6	**8g**	80

[a]Compound **4g** is dibutyl (1-acetoxy-2-butenyl)phosphonate ($R^1=R^2=BuO$, $R^3=Me$).

TABLE 4 Synthesis of (3-Amino-1-alkenyl)phosphorus Derivatives (**9**)



8 **9**

8	*t* (hours)	*Product*	*Isolated Yield (%)*
8a	1	**9a**	69
8b	1	**9b**	80
8c	2	**9c**	74
8d	2	**9d**	78
8e	2	**9e**	81
8g	2	**9g**[a]	76

[a]Compound **9g** is dibutyl 3-amino-1-butenylphosphonate.

hexane and ethyl acetate to give yellow crystals (**2**), 520 mg, 39%, mp 140–144°C. ^{1}H NMR ($CDCl_3$): δ 0.90–0.99 (m, 6H), 1.31–1.73 (m, 8H), 3.20–3.32 (m, 1H), 3.94–4.42 (m, 6H), 5.57–5.86 (m, 1H). IR (KCl): 1240, 1020 cm^{-1}. MS *m/e* 748 (M^+). Anal.: Calcd for $C_{11}H_{22}O_3ClPPd$: C, 35.22; H, 5.91; Cl, 9.45; P, 8.26; Found: C, 35.22; H, 5.82; Cl, 8.94; P, 7.92.

Reaction of **2** *with Sodium Dimethyl Malonate*

A solution of sodium dimethyl malonate (2 mmol) in THF (prepared from sodium hydride and dimethyl malonate) was added to a solution of **2** (300 mg, 0.8 mmol) in THF (5 mL). The mixture was stirred at room temperature for 24 hours. After the solvent had been removed under vacuum, the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1/1) as the eluent to give the product dibutyl 4,4-bis(methoxycarbonyl)-1-butenylphosphonate, 170 mg, 58% [8]. ^{1}H NMR ($CDCl_3$): δ 0.80–1.78 (m, 14H), 2.77–3.18 (m, 2H), 3.29–4.10 (m, 5H), 3.70 (s, 6H), 5.20–7.19 (m, 2H). IR (neat): 1755, 1740, 1630, 1240, 1020 cm^{-1}. MS *m/e*: 365 (M^+ +1), 364 (M^+), 333, 305, 277, 252, 219, 193.

*3-Azido-1-Alkenylphosphonates (***5***). Typical Procedure. O,O-Diethyl 3-Azido-1-propenylphosphonate (***5a***)*

A mixture of $Pd(PPh_3)_4$ (50 mg, 0.04 mmol), THF (5 mL), H_2O (2 mL), sodium azide (400 mg, 6.15 mmol), and **4a** (470 mg, 1.99 mmol) was stirred at room temperature for 4 hours, the reaction being monitored by TLC. After the reaction was complete, the reaction mixture was poured into water (5 mL), extracted with ether (3 × 15 mL), and dried with anhydrous sodium sulfate. After removal of the ether, **5a** was obtained by column chromatography on silica gel using petroleum ether/ethyl acetate (1/2) as the eluent. Yield; 340 mg (78%). Oil; ^{1}H NMR (CCl_4): δ 1.46 (t, *J* = 7 Hz, 6H), 3.90–4.38 (m, 6H), 5.7–7.2 (m, 2H). IR (neat): 2100, 1640, 1245, 1010 cm^{-1}. MS *m/e*: 220 (M^+ +1), 219 (M^+), 179, 109. Anal.: Calcd for $C_7H_{14}O_3N_3P$: C, 38.36; H, 6.44; P, 14.13; Found: C, 38.41; H, 6.72; P, 13.70.

The following compounds were prepared similarly. All compounds gave low nitrogen analytical data.

*O,O-Dibutyl (3-Azido-1-propenyl)phosphonate (***5b***).* Oil; ^{1}H NMR (CCl_4): δ 1.1 (t, *J* = 7 Hz, 6H), 1.6–1.7 (m, 8H), 4.0–4.3 (m, 6H), 5.8–7.0 (m, 2H). IR (neat): 2100, 1640, 1245, 1010 cm^{-1}; MS *m/e*: 276 (M^+ +1), 275 (M^+), 248, 234, 193, 82. Anal.: Calcd for $C_{11}H_{18}O_3N_3P$: C, 47.98; H, 8.06, P, 11.25; Found: C, 47.90; H, 8.30; P, 10.84.

*O-Ethyl (3-Azido-1-propenyl)phenylphosphinate (***5c***).* Oil; ^{1}H NMR (CCl_4): δ 1.4 (t, *J* = 7 Hz, 3H),

4.1–4.3 (m, 4H), 6.0–7.1 (m, 2H), 7.5–7.7 (m, 5H). IR (neat): 2100, 1630, 1210, 1010 cm^{-1}. MS *m/e*: 252 (M^+ +1), 251 (M^+), 209, 195, 169, 77. Anal.: Calcd for $C_{11}H_{14}O_2N_3P$: C, 52.59; H, 5.62; P, 12.33; Found: C, 52.23; H, 5.33; P, 11.84.

(3-Azido-1-propenyl)diphenylphosphine Oxide (**5d**). Oil; ^1H NMR (CCl_4): δ 4.0–4.2 (m, 2H), 6.4–6.8 (m, 2H), 7.5–7.9 (m, 10H). IR (neat): 2100, 1620, 1180. MS *m/e*: 284 (M^+ +1), 283 (M^+), 241, 227, 201, 77. Anal.: Calcd for $C_{15}H_{14}ON_3P$: C, 63.60; H, 4.98; P, 10.93; Found: C, 63.83; H, 5.07; P, 10.58.

3-Aminopropylphosphonates. Typical Procedure. Diethyl 3-Aminopropylphosphonates (**7a**)

A solution of **5a** (73 mg, 0.3 mmol) in ethanol (3 mL) was stirred with Pd/charcoal (5%) at room temperature under 1 atm of hydrogen atmosphere. After 5 hours, the reaction mixture was filtered and the solvent was removed to give **7a**. Yield: 60 mg (92%).

The following compounds were prepared similarly. The analytical samples were purified by short bath distillation at the specified oil bath temperature.

Diethyl 3-Aminopropylphosphonate (**7a**). bp 100°C/0.5 mm (Ref. [22]: 77–78°C/0.5 mm). ^1H NMR (CCl_4): δ 1.23 (t, *J* = 7 Hz, 6H), 1.55–2.67 (m, 8H), 3.80–4.27 (m, 4H). IR (neat): 3400, 1650, 1250, 1212 cm^{-1}. MS *m/e*: 196 (M^+ +1), 195 (M^+), 179, 152, 138.

Dibutyl 3-Aminopropylphosphonate (**7b**). bp 110°C/0.5 mm. ^1H NMR (CCl_4): δ 0.83–1.97 (m, 18H), 2.53–3.50 (m, 4H), 3.80–4.10 (m, 4H). IR (neat): 3350, 1650, 1240, 1215 cm^{-1}. MS *m/e*: 252 (M^+ +1), 251 (M^+), 235, 193. Anal.: Calcd for $C_{11}H_{26}O_3NP$: C, 52.57; H, 10.43; N, 5.57; P, 12.33; Found: C, 52.16; H, 10.21; N, 5.01; P, 11.84.

Ethyl (3-Aminopropyl)phenylphosphinate (**7c**). bp 110°C/0.5 mm. ^1H NMR (CCl_4): δ 1.15–2.75 (m, 11H), 3.37–4.27 (m, 2H), 7.3–7.95 (m, 5H). IR (neat): 3400, 1640, 1220, 1215 cm^{-1}. MS *m/e*: 228 (M^+ +1), 227 (M^+), 211, 169. Anal.: Calcd for $C_{11}H_{18}O_2NP$: C, 58.14; H, 7.98; N, 6.17; P, 13.63; Found: C, 57.73; H, 7.61; N, 5.68; P, 13.90.

(3-Aminopropyl)diphenylphosphine Oxide (**7d**). bp 120°C/0.5 mm. ^1H NMR (CCl_4): δ 0.80–3.10 (m, 8H), 7.15–7.90 (m, 10H). IR (neat): 3450, 1650, 1215, 1180 cm^{-1}. MS *m/e*: 260 (M^+ +1), 259 (M^+), 243, 215, 201, 105, 77. Anal.: Calcd for $C_{15}H_{18}ONP$: C, 69.48; H, 7.00; N, 5.40; P, 11.95; Found: C, 69.50; H, 6.71; N, 4.90; P, 11.46.

3-(p,p'-Dimethoxybenzhydrylamino)alkenyl Phosphonates (**8**). *Typical Procedure. Diethyl 3-(p,p'-Dimethoxybenzhydrylamino)-1-propenylphosphonate* (**8a**)

A mixture of **4a** (236 mg, 1 mmol), $Pd(PPh_3)_4$ (50 mg, 0.04 mmol), and *p,p'*-dimethoxybenzhydrylamine (DMB-NH_2) (486 mg, 2 mmol) in THF (4 mL) was stirred at room temperature for 10 hours. After removal of the solvent, **8a** was isolated after purification by chromatography on silica gel using petroleum ether/ethyl acetate (1/2) as eluent. Yield: 335 mg (80%).

The following compounds were prepared similarly. All compounds are colorless oils. The samples for analysis were further purified by short path distillation at the specified oil bath temperature.

Diethyl 3-(p,p'-Dimethoxybenzhydrylamino)-1-propenylphosphonate (**8a**). Oil; bp 140°C/0.001 mm. ^1H NMR (CCl_4): δ 1.35 (t, *J* = 7 Hz, 6H), 1.95 (s, 1H), 3.2–3.4 (m, 2H), 3.8 (s, 6H), 3.9–4.1 (m, 4H), 4.7 (s, 1H), 5.5–6.1 (m, 2H), 6.8 (d, *J* = 8 Hz, 4H), 7.3 (d, *J* = 8 Hz, 4H). IR (neat): 3400, 1610, 1260, 1250 cm^{-1}. MS *m/e*: 419 (M^+), 418 (M^+ −1), 242, 227, 190, 175. Anal.: Calcd for $C_{22}H_{30}O_5NP$: C, 62.99; H, 7.21; N, 3.34; P, 7.38; Found: C, 62.64; H, 6.90; N, 2.93; P, 7.10.

Dibutyl 3-(p,p'-Dimethoxybenzhydrylamino)-1-propenylphosphonate (**8b**). Oil; bp 140°C/0.001 mm. ^1H NMR (CCl_4): δ 0.95–1.95 (m, 14H), 2.0 (s, 1H), 3.3 (br, 2H), 3.7 (s, 6H), 3.9 (br, 4H), 4.7 (s, 1H), 5.5–6.4 (m, 2H), 6.7 (d, *J* = 8 Hz, 4H), 7.3 (d, *J* = 8 Hz, 4H). IR (neat): 3400, 1610, 1260, 1250 cm^{-1}. MS *m/e*: 475 (M^+), 474 (M^+ −1), 248, 242, 227. Anal.: Calcd for $C_{26}H_{38}O_5NP$: C, 65.66; H, 8.06; N, 2.95; P, 6.51; Found: C, 65.71; H, 7.78; N, 2.94; P, 6.90.

Ethyl 3-(p,p'-Dimethoxybenzhydrylamino)-(1-propenyl)phenylphosphinate (**8c**). Oil; bp 150°C/0.001 mm. ^1H NMR (CCl_4): δ 1.3 (t, *J* = 7 Hz, 3H), 1.9 (s, 1H), 3.2 (br, 2H), 3.7 (s, 6H), 3.9–4.1 (m, 2H), 4.7 (s, 1H), 5.4–6.2 (m, 2H), 6.7 (d, *J* = 8 Hz, 4H), 7.2 (d, *J* = 8 Hz, 4H), 7.3–7.9 (m, 5H). IR (neat): 3400, 1610, 1250, 1220 cm^{-1}. MS *m/e*: 451 (M^+), 450 (M^+ −1), 227, 224, 169. Anal.: Calcd for $C_{26}H_{30}O_4NP$: C, 69.16; H, 6.70; N, 3.10; P, 6.86. Found: C, 68.80; H, 6.50; N, 3.01; P, 6.51.

3-(p,p'-Dimethoxybenzhydrylamino)-(1-pro-penyl) diphenylphosphine Oxide (**8d**). Oil; bp 150°C/0.001 mm. ^1H NMR (CCl_4): δ 1.9 (s, 1H), 3.1–3.4 (m, 2H), 3.7 (s, 1H), 4.6 (s, 1H), 5.5–6.3 (m, 2H), 6.6 (d, *J* = 8 Hz, 4H), 7.1 (d, *J* = 8 Hz, 4H), 7.3–7.8 (m, 10H). IR (neat): 3400, 1610, 1250, 1200 cm^{-1}. MS *m/e*: 483 (M^+), 482 (M^+ −1), 256, 241. Anal.: Calcd for $C_{30}H_{30}O_3NP$: C, 74.52; H, 6.25; N, 2.90; P, 6.41; Found: C, 74.14; H, 6.13; N, 2.70; P, 6.80.

Diethyl 3-(p,p'-Dimethoxybenzhydrylamino)-1-butenylphosphonate (**8e**). Oil; bp 140°C/0.001 mm. ^1H NMR (CCl_4): δ 1.2–1.6 (m, 9H), 1.9–2.0 (m, 1H),

3.7 (s, 6H), 3.8–4.2 (m, 5H), 4.7 (s, 1H), 5.2–6.2 (m, 2H), 6.7 (d, J = 8 Hz, 4H), 7.3 (d, J = 8 Hz, 4H). IR (neat): 3400, 1610, 1260, 1250 cm^{-1}. MS m/e: 433 (M^+), 432 ($M^+ - 1$), 242, 227, 206. Anal.: Calcd for $C_{23}H_{32}O_5NP$: C, 63.74; H, 7.44; N, 3.23; P, 7.15; Found: C, 63.39; H, 7.10; N, 3.01; P, 7.61.

*Dibutyl 3-(p,p'-Dimethoxybenzhydrylamino)-1-butenylphosphonate (**8g**).* Oil; bp 150°C/0.001 mm. ^1H NMR (CCl_4): δ 1.0–1.8 (m, 17H), 2.1 (s, 1H), 3.1–3.4 (m, 1H), 3.7 (s, 6H), 4.0–4.2 (m, 4H), 4.8 (s, 1H), 5.2–6.2 (m, 2H), 6.9 (d, J = 8 Hz, 4H), 7.3 (d, J = 8 Hz, 4H); IR (neat): 3400, 1610, 1260, 1250 cm^{-1}. MS m/e: 489 (M^+), 488 ($M^+ - 1$), 262, 247, 227. Anal.: Calcd for $C_{27}H_{40}O_5NP$: C, 66.24; H, 8.24; N, 2.86; P, 6.33; Found: C, 65.98; H, 8.03; N, 2.54; P, 6.80.

*(3-Amino-1-alkenyl)phosphonates (**9**): Typical Procedure*

*Diethyl (3-Amino-1-propenyl)phosphonate (**9a**).* A solution of **8a** (126 mg, 0.3 mmol) in formic acid (88%, 1.5 mL) was heated at 80°C for 40 minutes. After distillation off the formic acid in vacuum, the residue was extracted with water. The water solution was vacuum distilled to dryness and extracted with chloroform (4 mL). The chloroform solution was stirred with few drops of ammonium hydroxide solution for 2 hours and dried ($NaHCO_3$). After removal of the solvent, **9a** was purified by preparative TLC on silica gel using ethyl acetate:methanol:diethylamine (80:20:5) as solvent. Yield 40 mg (69%).

The following compounds were prepared similarly. All compounds were obtained as colorless oil. The samples for analysis were further purified by short path distillation at the specified oil bath temperature.

*Diethyl (3-Amino-1-propenyl)phosphonate (**9a**) [23].* Oil; bp 110°C/0.5 mm. ^1H NMR (CCl_4): δ 1.3 (t, J = 7 Hz, 6H), 1.7 (br, 2H), 3.3–3.5 (m, 2H), 3.7–4.1 (m, 4H), 5.4–6.4 (m, 2H). IR (neat): 3400, 1650, 1260, 1020 cm^{-1}. MS m/e: 194 ($M^+ + 1$), 193 (M^+), 177, 137.

*Dibutyl (3-Amino-1-propenyl)phosphonate (**9b**) [23].* Oil; bp 120°C/0.5 mm. ^1H NMR (CCl_4): δ 0.9–1.7 (m, 16H), 3.6–4.2 (m, 6H), 5.8–6.8 (m, 2H). IR (neat): 3400, 1650, 1260, 1020 cm^{-1}. MS m/e: 250 ($M^+ + 1$), 249 (M^+), 233, 193.

*Ethyl (3-amino-1-propenyl)phenylphosphinate (**9c**).* Oil; bp 130°C/0.5 mm. ^1H NMR (CCl_4): δ 1.2 (br, t, 3H), 1.7 (s, 2H), 3.2–3.3 (m, 2H), 3.4–3.9 (m, 2H), 5.9–6.9 (m, 2H), 7.3–7.9 (m, 5H). IR (neat): 3400, 1650, 1220, 1010 cm^{-1}. MS m/e: 226 ($M^+ + 1$), 225 (M^+), 209, 169. Anal.: Calcd for $C_{11}H_{16}O_2NP$: C, 58.66; H, 7.16; N, 6.22; P, 13.75; Found: C, 58.28; H, 6.97; N, 5.71; P, 13.40.

*(3-Amino-1-propenyl)diphenylphosphine Oxide (**9d**).* Oil; bp 130°C/0.5 mm. ^1H NMR (CCl_4): δ 3.8–4.2 (m, 4H), 6.3–6.9 (m, 2H), 7.3–7.8 (m, 10H). IR (neat): 3400, 1650, 1200 cm^{-1}. MS m/e: 258 ($M^+ + 1$), 257 (M^+), 241, 201. Anal.: Calcd for $C_{15}H_{16}ONP$: C, 70.03; H, 6.27; N, 5.45; P, 12.03; Found: C, 70.41; H, 5.95; N, 4.97; P, 11.60.

*Diethyl (3-Amino-1-butenyl)phosphonate (**9e**) [13].* Oil; bp 120°C/0.5 mm. ^1H NMR (CCl_4): δ 1.2 (d, J = 7 Hz, 3H), 1.3 (t, J = 7 Hz, 6H), 1.9 (br, s, 2H), 3.4–3.6 (br, m, 1H), 3.9–4.2 (m, 2H), 5.3–6.7 (m, 2H). IR (neat): 3400, 1650, 1260, 1010 cm^{-1}. MS m/e: 208 ($M^+ + 1$), 207 (M^+), 191, 137, 70.

*Dibutyl (3-Amino-1-butenyl)phosphonate (**9g**).* Oil; bp 120°C/0.5 mm. ^1H NMR (CCl_4): δ 1.1 (d, J = 7 Hz, 3H), 1.3–1.9 (m, 14H), 2.1–2.4 (m, 2H), 3.4 (br, s, 1H), 3.7–4.2 (m, 4H), 5.3–6.8 (m, 2H). IR (neat): 3400, 1650, 1260, 1010 cm^{-1}. MS m/e: 264 ($M^+ + 1$), 263 (M^+), 247, 193. Anal.: Calcd for $C_{12}H_{26}O_3NP$: C, 54.73; H, 9.95; N, 5.32; P, 11.76; Found: C, 54.46; H, 9.70; N, 5.04; P, 11.70.

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