Dialkyl (1-Hydroxyiminoalkyl)phosphonates from 1-Bromo-1-nitroalkanes and Trialkyl Phosphites

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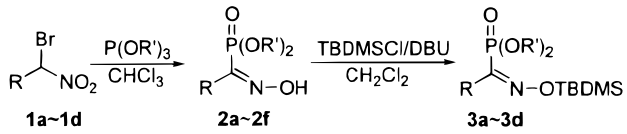
α-Aminophosphonic acids may be considered as phosphorus analogues of naturally occurring α-amino acids and have recently received a great deal of attention owing to their interesting biological activities and their potential in important biological functions.[1] Various synthetic methods for α-aminophosphonic acids and α-aminophosphonates have therefore been reported.[2] We envisaged a new method for the synthesis of α-aminophosphonates that comprises the Arbuzov reaction[3] of 1-halo-1-nitroalkanes with trialkyl phosphites and reduction of the resulting α-nitroalkylphosphonates. There have been reports on the reaction of 1-halo-1-nitroalkanes with trialkyl phosphites;[4−6] however, the results are neither conclusive nor consistent. Thus, Allen reported that 1-halo-1-nitroalkanes reacted with trialkyl phosphites to form alkyl halides and oxime esters of the corresponding pentavalent phosphorus acids,[4] whereas Stirling et al. reported that the reaction of bromonitromethane with triethyl phosphite gave triethyl phosphate and hydrogen cyanide.[5] On the other hand, Donnelly et al. found that 1-bromo-1-phenylnitromethane reacted with 2 molar equiv of triethyl phosphite to afford benzonitrile as the major product, together with phenylnitromethane, ethyl bromide, and triethyl phosphate.[6] These earlier results also indicated that the halonitromethanes, which are the first members of the homologous series, have a reactivity different from that of the others. We, therefore, reinvestigated the reaction of 1-bromo-1-nitroalkanes, with the exception of bromonitromethane, with trialkyl phosphites and found that the products of the reaction were unexpected dialkyl (1-hydroxyiminoalkyl)phosphonates.[7]

1-Halo-1-nitroalkanes **1a**−**d** were prepared by the reaction of the potassium salt of 1-nitroalkanes with bromine.[8] Reaction of compounds **1a**−**d** with 2.2 molar equiv of trimethyl phosphite in chloroform afforded a mixture of *E*- and *Z*-isomers of dimethyl (1-hydroxyiminoalkyl)phosphonates **2a**−**d**, respectively, along with 1 equiv of trimethyl phosphate (Scheme 1).

Scheme 1



1a~1d **2a~2f** **3a~3d**

Table 1. Reaction of 1-Bromo-1-nitroalkanes with Trialkyl Phosphites[a] and Subsequent Silylation of the Resultant Oximes[b]

bromide	phosphite	oxime yield %[c,d]	silyl oxime yield %[c] (ratio, *E*/*Z*)[d]
1a R = Me	R′ = Me	**2a** 52 (84)	**3a** 88 (4.3:1)
1b R = Et	R′ = Me	**2b** 62 (88)	**3b** 92 (3.2:1)
1c R = *i*-Pr	R′ = Me	**2c** 50 (84)	**3c** 86 (1.8:1)
1d R = Bu	R′ = Me	**2d** 58 (87)	**3d** 86 (1.5:1)
1a R = Me	R′ = Et	**2e** 54 (85)	
1b R = Et	R′ = Et	**2f** 56 (85)	

[a] Reaction conditions: bromide (2.0 mmol) and phosphite (4.4 mmol), room temperature in $CHCl_3$ (4 mL). [b] Reaction conditions: oxime (1.5 mmol), DBU (1.7 mmol), and TBDMSCl (1.6 mmol), 0 °C in CH_2Cl_2 (5 mL). [c] Yields refer to isolated pure product. [d] The yields and *E*/*Z* ratios in parentheses were determined by HPLC before purification.

Reaction of **1a** and **1b** with triethyl phosphite also gave a mixture of *E*- and *Z*-isomers of the corresponding diethyl derivatives **2e** and **2f**, respectively, as shown in Table 1. Although several methods have been known for the preparation of dialkyl (1-hydroxyiminoalkyl)phosphonates,[9−11] their rigorous identification has not been performed except in a few cases.[9,10] Thus, their complete spectral and physical data have not been available, maybe because of their instability and difficulty in separation of their *E*- and *Z*-isomers. In fact, we had difficulty in the separation of the *E*- and *Z*-isomers because of the decomposition and *E*- and *Z*-isomerization of the products during purification. The *Z*-isomer was the major product right after reaction, but the *E*-isomer became predominant after flash column chromatography. Nevertheless, we could obtain the pure *E*-isomers **2bE** and **2dE** and *Z*-isomer **2bZ** after careful repeated chromatography. The NMR and IR spectral and microanalytical data indicated that the products were neither 1-(dialkylphosphonyl)-1-nitroalkanes nor 1-(dialkylphosphonyl)alkanenitronic acids. IR spectrum of compound **2a**, for example, showed a broad intense OH absorption near 3200 cm^{-1} and a weak C=N absorption at 1610 $cm.^{-1}$ The ^1H NMR spectrum of **2a** showed the three bond couplings between the phosphorus and methoxy protons ($J_{P,H}$ = 11.1 Hz for *E*-isomer **2aE** and 11.5 Hz for

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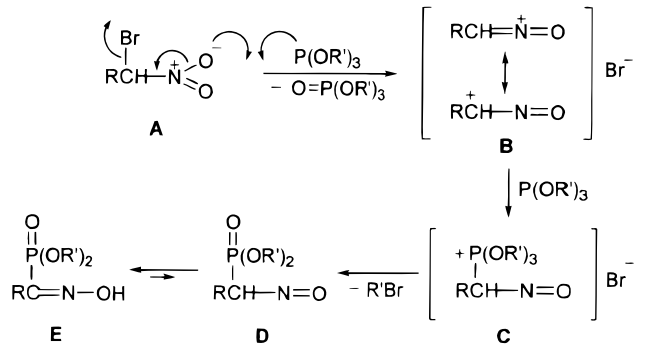
Z-isomer **2aZ**) and between the phosphorus and methyl protons ($J_{P,H}$ =11.0 Hz for **2aE** and 11.1 Hz for **2aZ**). The ^{13}C NMR spectrum of **2a** showed a doublet at 151.6 ppm ($J_{P,C}$ = 217.1 Hz) for **2aE** and at 148.6 ppm ($J_{P,C}$ = 156.8 Hz) for **2aZ** attributable to the C=N carbon.

Hydroxyiminophosphonates **2a**−**d** were transformed to silylated derivatives **3a**−**d**, respectively (Table 1). For example, silylation of compound **2a** with TBDMS chloride in the presence of DBU at 0 °C in methylene chloride gave a stable *O*-silyl oxime **3a** in 90% yield. ^1H and ^{13}C NMR spectra of **3a** clearly showed that it was a mixture of *E*-isomer **3aE** and *Z*-isomer **3aZ** in the ratio of about 5:1.[12] The *E*-isomers were consistently the major products in other silylated oximes **3b**−**d**. Although no appreciable isomerization between the two isomers occurred in solution or neat at room temperature, isolation of the two isomers was difficult because of slow isomerization of the *Z*-isomer to the *E*-isomer during flash column chromatography. Isolation of pure *E*-isomer **3bE** and *Z*-isomers **3bZ** and **3cZ**, nevertheless, was possible by careful repeated flash column chromatography. The silylation did not occur with pyridine or with DMAP−triethylamine, and the yield was very low with triethylamine alone at 0 °C or room temperature. LDA in THF at −78 °C gave almost same result as DBU at 0 °C. The existence of *E*- and *Z*-isomerism of **3b** further confirmed that the product of the reaction between **1b** and trimethyl phosphite is oxime **2b** but not the nitronic acid, because it has been well established that the silyl nitronate does not show *E*- and *Z*-isomerism.[13]

Assignment of *E*- and *Z*-isomers **3bE** and **3bZ** was made on the basis of $^1H-^1H$ 2D NOESY NMR spectra. NOEs were observed between methyl protons of the TBDMS group and C-3 methyl protons in **3bE** and between *tert*-butyl protons of the TBDMS group and methoxy protons of the phosphonyl group in **3bZ**. NOE interaction also existed between *tert*-butyl protons of the TBS group and methoxy protons of the phosphonyl group in **3cZ**. The most characteristic feature in the spectral data for *E*- and *Z*-isomers of the silyl oximes **3b** and **3c** was the $J_{P,C}$ value for the C=N carbon, larger than 200 Hz for the *E*-isomer and around 150 Hz for the *Z*-isomer. It was also noteworthy that the methoxy proton signal of the phosphonyl group in **3bZ** and **3cZ** consistently resonated at slightly higher field than that of **3bE** and **3cE** and that the $J_{P,H}$ value for the methoxy proton in **3bZ** and **3cZ** was larger than that in the corresponding *E*-isomers. The assignment of *E*- and *Z*-isomers for the other silyl oximes **3a** and **3d** and oximes **2a**−**f** was, therefore, made on the basis of these spectral characteristics.

The plausible mechanism for the present reaction can be suggested as shown in Scheme 2. Deoxygenation of the nitro group by an trialkyl phosphite and concurrent elimination of the bromide in compound **A** in the first step would produce an intermediate **B** and the trialkyl phosphate. Addition of the second trialkyl phosphite to **B** and the subsequent displacement of the alkyl group in the resultant phosphonium salt **C** by the bromide

Scheme 2



would give the α-phosphonylnitroso compound **D**, which would readily tautomerize to the more stable conjugate oxime **E**. The fact that 1 equiv of trialkyl phosphate was generated in this reaction and the reaction proceeded only one-third with 1 equiv of trialkyl phosphite supports the mechanism presented in Scheme 2. However, one might still argue that an Arbuzov reaction occurs in the first step to displace the bromide in **A** by the trialkyl phosphite and the resulting α-phosphonylnitroalkane is deoxygenated by the second trialkyl phosphite, or that the deoxygenation of the nitro group in **A** by the trialkyl phosphite occurs in the first step without elimination of bromide and the Arbuzov reaction follows in the second step. Diisopropyl 1-nitropropanephosphonate, which we prepared by the known procedure,[10] was not deoxygenated with trialkyl phosphites. In fact, the deoxygenation of simple aliphatic nitro compounds to the corresponding oximes by trialkyl phosphites is unprecedented.[14]

Because various methods are available for the reduction of dialkyl (1-hydroxyiminoalkyl)phosphonates to dialkyl (1-aminoalkyl)phosphonates,[11,15] the present reaction can be utilized for the synthesis of α-aminophosphonic acids. We are currently pursuing the asymmetric reduction of the dialkyl (1-hydroxyiminoalkyl)phosphonates and their TBS ethers to prepare optically pure α-aminophosphonic acids.

Experimental Section

General. All reactions were run under a nitrogen atmosphere. NMR spectra were recorded at 300 or 250 MHz for protons, at 75.5 or 62.9 MHz for carbons, and at 121.4 MHz for phosphorus, respectively, in $CDCl_3$. Tetramethylsilane was employed as the internal standard for ^1H and ^{13}C NMR spectra, and H_3PO_4 was the external standard for ^{31}P spectra. Microanalyses were carried out by Organic Chemistry Research Center, Korea. High-resolution mass spectrometry was performed by Korea Basic Science Institute. Solvents were dried and distilled prior to use.

General Procedure for the Preparation of Dialkyl (1-Hydroxyiminoalkyl)phosphonates 2a−**f.** To a solution of a 1-bromo-1-nitroalkane (2 mmol) in chloroform (4 mL) was added dropwise a trialkyl phosphite (4.4 mmol) at 0 °C. After the reaction mixture was allowed to reach room temperature, it was further stirred for 24 h. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with saturated sodium bicarbonate solution and then with water. The dried ($MgSO_4$) organic solution was evaporated in vacuo, and then the trialkyl phosphate, generated during the reaction, was collected in high vacuum and identified. The residual crude product was purified

(12) Before purification with flash column chromatography, the *E*/*Z* ratio of **3a** determined by HPLC was 4.3:1.

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by flash chromatography (silica gel, ethyl acetate). A mixture of the *E*- and *Z*-isomers of oximes **2a**−**f** was obtained as a colorless oil. Repeated chromatography provided pure *E*-isomers **2bE** and **2dE** and a pure *Z*-isomer **2bZ**.

(*E*)- and (*Z*)-Dimethyl (1-Hydroxyiminoethyl)phosphonate (2aE and 2aZ). ^{1}H NMR of **2aE** (250 MHz, from the mixture): δ 9.06 (brs, 1H), 3.82 (d, J = 11.1 Hz, 6H), 2.06 (d, J = 11.0 Hz, 3H). ^{13}C NMR of **2aE** (62.9 MHz): δ 151.6 (d, $J_{P,C}$ = 217.1 Hz), 53.8 (d, $J_{P,C}$ = 6.1 Hz), 12.2 (d, $J_{P,C}$ = 16.0 Hz). ^{31}P NMR of **2aE** (121.4 MHz): δ 12.9. ^{1}H NMR of **2aZ** (250 MHz): δ 9.58 (brs, 1H), 3.84 (d, J = 11.5 Hz, 6H), 2.07 (d, J = 11.1 Hz, 3H). ^{13}C NMR of **2aZ** (62.9 MHz, from the mixture): δ 148.6 (d, $J_{P,C}$ = 156.8 Hz), 53.5 (d, $J_{P,C}$ = 5.6 Hz), 19.2 (d, $J_{P,C}$ = 18.2 Hz). ^{31}P NMR of **2aZ** (121.4 MHz, from the mixture): δ 6.9. IR of the mixture (neat): 3200, 3030, 2960, 1610, 1460, 1240 cm.$^{-1}$ HRMS of the mixture: calcd for $C_4H_{10}O_4NP$ (M^+) 167.0347, found 167.0335.

(*E*)- and (*Z*)-Dimethyl (1-Hydroxyiminopropyl)phosphonate (2bE and 2bZ). ^{1}H NMR of **2bE** (250 MHz): δ 9.45 (brs, 1H), 3.83 (d, J = 11.1 Hz, 6H), 2.61−2.47 (m, 2H), 1.16 (t, J = 7.8 Hz, 3H). ^{13}C NMR of **2bE** (62.9 MHz): δ 153.2 (d, $J_{P,C}$ = 213.4 Hz), 52.6 (d, $J_{P,C}$ = 6.1 Hz), 19.0 (d, $J_{P,C}$ = 16.5 Hz), 9.5 (d, $J_{P,C}$ = 1.8 Hz). ^{31}P NMR of **2bE** (121.4 MHz): δ 13.2. ^{1}H NMR of **2bZ** (250 MHz): δ 9.45 (brs, 1H), 3.81 (d, J = 11.1 Hz, 6H), 2.61−2.47 (m, 2H), 1.16 (t, J = 7.6 Hz, 3H). ^{13}C NMR of **2bZ** (62.9 MHz): δ 151.1 (d, $J_{P,C}$ = 150.8 Hz), 52.3 (d, $J_{P,C}$ = 5.9 Hz), 25.9 (d, $J_{P,C}$ = 18.7 Hz), 11.2 (d, $J_{P,C}$ = 3.2 Hz). ^{31}P NMR of **2bZ** (121.4 MHz): δ 8.1. IR of the mixture (neat): 3185, 3030, 2957, 1650, 1456, 1260 cm.$^{-1}$ HRMS of the mixture: calcd for $C_5H_{12}O_4NP$ (M^+) 181.0504, found 181.0505.

(*E*)- and (*Z*)-Dimethyl (1-Hydroxyiminoisobutyl)phosphonate (2cE and 2cZ). ^{1}H NMR of **2cE** (300 MHz, from the mixture): δ 9.36 (brs, 1H), 3.78 (d, J = 11.1 Hz, 6H), 2.86−2.79 (m, 2H), 1.24 (d, J = 6.9 Hz, 6H). ^{13}C NMR of **2cE** (75.5 MHz, from the mixture): δ 159.6 (d, $J_{P,C}$ = 206.9 Hz), 53.4 (d, $J_{P,C}$ = 5.9 Hz), 27.3 (d, $J_{P,C}$ = 16.5 Hz), 18.7 (d, $J_{P,C}$ = 1.8 Hz). ^{1}H NMR of **2cZ** (300 MHz, from the mixture): δ 9.36 (brs, 1H), 3.79 (d, J = 11.4 Hz, 6H), 2.86−2.79 (m, 1H), 1.18 (d, J = 6.9 Hz, 6H). ^{13}C NMR of **2cZ** (75.5 MHz, from the mixture): δ 151.7 (d, $J_{P,C}$ = 167.0 Hz), 53.1 (d, $J_{P,C}$ = 5.4 Hz), 32.5 (d, $J_{P,C}$ = 17.1 Hz), 20.7 (d, $J_{P,C}$ = 3.0 Hz). IR of the mixture (neat): 3245, 2962, 2853, 1605, 1454, 1249 cm.$^{-1}$ HRMS of the mixture: calcd for $C_6H_{14}O_4NP$ (M^+) 195.0660, found 195.0664.

(*E*)- and (*Z*)-Dimethyl (1-Hydroxyiminopentyl)phosphonate (2dE and 2dZ). ^{1}H NMR of **2dE** (300 MHz): δ 9.84 (brs, 1H), 3.85 (d, J = 11.1 Hz, 6H), 2.46−2.35 (m, 2H), 1.58−1.49 (m, 2H), 1.39−1.30 (m, 2H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C NMR of **2dE** (75.5 MHz): δ 154.5 (d, $J_{P,C}$ = 212.0 Hz), 53.2 (d, $J_{P,C}$ = 6.0 Hz), 27.5, 26.0 (d, $J_{P,C}$ = 15.9 Hz), 22.6, 13.4. ^{1}H NMR of **2dZ** (250 MHz, from the mixture): δ 9.28 (brs, 1H), 3.83 (d, J = 11.4 Hz, 6H), 2.46−2.35 (m, 2H), 1.58−1.49 (m, 2H), 1.39−1.30 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). IR of the mixture (neat): 3140, 2992, 2843, 1600, 1430, 1239 cm.$^{-1}$ HRMS of the mixture: calcd for $C_7H_{16}O_4NP$ (M^+) 209.0817, found 209.0812.

(*E*)- and (*Z*)-Diethyl (1-Hydroxyiminoethyl)phosphonate (2eE and 2eZ). ^{1}H NMR of a mixture of **2eE** and **2eZ** (250 MHz): δ 11.16 (brs, 1H), 4.12−3.96 (m, 4H), 1.93 (d, J = 11.0 Hz, 3H), 1.24 (dt, J = 7.1 Hz, J = 0.9 Hz, 6H). ^{13}C NMR of **2eE** (62.9 MHz, from the mixture): δ 150.1 (d, $J_{P,C}$ = 218.3 Hz), 63.5 (d, $J_{P,C}$ = 5.8 Hz), 15.9 (d, $J_{P,C}$ = 6.7 Hz), 11.5 (d, $J_{P,C}$ = 16.9 Hz). HRMS of the mixture: calcd for $C_6H_{14}O_4NP$ (M^+) 195.0660, found 195.0665.

(*E*)- and (*Z*)-Diethyl (1-Hydroxyiminopropyl)phosphonate (2fE and 2fZ). ^{1}H NMR of a mixture of **2fE** and **2fZ** (250 MHz): δ 11.13 (brs, 1H), 4.21−4.05 (m, 4H), 2.61−2.46 (m, 2H), 1.34 (t, J = 7.1 Hz, 6H), 1.15 (t, J = 7.5 Hz, 3H).^{13}C NMR of **2fE** (62.9 MHz, from the mixture): δ 154.9 (d, $J_{P,C}$ = 211.5 Hz), 63.5 (d, $J_{P,C}$ = 5.8 Hz), 19.7 (d, $J_{P,C}$ = 16.4 Hz), 15.9 (d, $J_{P,C}$ = 6.7 Hz), 10.1 (d, $J_{P,C}$ = 1.5 Hz). HRMS of the mixture: calcd for $C_7H_{16}O_4NP$ (M^+) 209.0817, found 209.0825.

General Procedure for Preparation of Dimethyl (1-*tert*-Butyldimethlysilyloxyimino alkyl)phosphonates 3a−d. To a solution of oxime (1.5 mmol) in CH_2Cl_2 (5 mL) were added DBU (1.7 mmol) and TBDMSCl (1.6 mmol) at 0 °C. After 30 min of stirring at 0 °C, the reaction mixture was diluted with ethyl acetate (30 mL) and washed with saturated sodium bicarbonate solution and then with water. The dried ($MgSO_4$) organic solution was evaporated in vacuo. The crude product was purified by flash chromatography (silica gel, hexanes−ethyl acetate, 1:1). A mixture of the *E*- and *Z*-isomers of silyloximes **3a**−**d** was obtained as a colorless oil. Repeated chromatography provided a pure *E*-isomer **3bE** and pure *Z*-isomers **3bZ** and **3cZ**.

(*E*)- and (*Z*)-Dimethyl (1-*tert*-Butyldimethlysilyloxyiminoethyl)phosphonate (3aE and 3aZ).^{1}H NMR of **3aE** (300 MHz, from the mixture): δ 3.81 (d, J = 11.0 Hz, 6H), 2.06 (d, J = 10.9 Hz, 3H), 0.93 (s, 9H), 0.20 (s, 6H). ^{13}C NMR of **3aE** (62.9 MHz, from the mixture): δ 155.2 (d, $J_{P,C}$ = 208.9 Hz), 53.5 (d, $J_{P,C}$ = 6.4 Hz), 25.9, 18.1, 12.5 (d, $J_{P,C}$ = 16.8 Hz), −4.4. ^{1}H NMR of **3aZ** (300 MHz, from the mixture): δ 3.79 (d, J = 11.5 Hz, 6H), 2.09 (d, J = 11.8 Hz, 3H), 0.94 (s, 9H), 0.21 (s, 6H). IR of the mixture (neat): 2967, 2869, 1640, 1597, 1497 cm.$^{-1}$ Anal. Calcd for $C_{10}H_{24}O_4NPSi$: C, 42.68; H, 8.60; N, 4.98. Found: C, 42.26; H, 8.69; N, 4.90.

(*E*)-Dimethyl (1-*tert*-Butyldimethlysilyloxyiminopropyl)-phosphonate (3bE). ^{1}H NMR (300 MHz): δ 3.80 (d, J = 11.1 Hz, 6H), 2.62−2.48 (m, 2H), 1.13 (t, J = 7.6 Hz, 3H), 0.94 (s, 9H), 0.19 (s, 6H). ^{13}C NMR (75.5 MHz): δ 160.4 (d, $J_{P,C}$ = 205.7 Hz), 53.3 (d, $J_{P,C}$ = 6.3 Hz), 25.7, 20.2 (d, $J_{P,C}$ = 16.2 Hz), 17.9, 10.1, −5.6. IR (neat): 2920, 2840, 1636, 1590, 1445 cm.$^{-1}$ Anal. Calcd for $C_{11}H_{26}NO_5PSi$: C, 42.44; H, 8.36; N, 4.50. Found: C, 42.89; H, 8.67; N, 4.48.

(*Z*)-Dimethyl (1-*tert*-Butyldimethlysilyloxyiminopropyl)-phosphonate (3bZ). ^{1}H NMR (300 MHz): δ 3.78 (d, J = 11.5 Hz, 6H), 2.58−2.42 (m, 2H), 1.14 (t, J = 7.3 Hz, 3H), 0.95 (s, 9H), 0.21 (s, 6H). ^{13}C NMR (75.5 MHz): δ 157.6 (d, $J_{P,C}$ = 152.9 Hz), 52.4 (d, $J_{P,C}$ = 6.0 Hz), 26.5 (d, $J_{P,C}$ = 18.0 Hz), 25.7, 18.0, 11.2 (d, $J_{P,C}$ = 4.1 Hz), −5.7. IR (neat): 2930, 2845, 1640, 1594, 1450 cm.$^{-1}$ Anal. Calcd for $C_{11}H_{26}NO_5PSi$: C, 42.44; H, 8.36; N, 4.50. Found: C, 42.25; H, 8.56; N, 4.63.

(*E*)- and (*Z*)-Dimethyl (1-*tert*-Butyldimethlysilyloxyiminoisobutyl)phosphonate (3cE and 3cZ). ^{1}H NMR of **3cE** (300 MHz, from the mixture): δ 3.79 (d, J = 11.1 Hz, 6H), 2.92−2.80 (m, 1H), 1.23 (d, J = 7.1 Hz, 6H), 0.97 (s, 9H), 0.22 (s, 6H). ^{1}H NMR of **3cZ** (300 MHz): δ 3.77 (d, J = 11.5 Hz, 6H), 2.92−2.80 (m, 1H), 1.18 (d, J = 6.8 Hz, 6H), 0.96 (s, 9H), 0.20 (s, 6H). ^{13}C NMR of **3cZ** (75.5 MHz, from the mixture): δ 160.9 (d, $J_{P,C}$ = 149.0 Hz), 52.4 (d, $J_{P,C}$ = 5.9 Hz), 32.5 (d, $J_{P,C}$ = 17.6 Hz), 25.8, 20.5 (d, $J_{P,C}$ = 3.4 Hz), 18.1, −5.6. IR of the mixture (neat): 2969, 2865, 1650, 1595, 1472 cm.$^{-1}$ HRMS of the mixture: calcd for $C_{12}H_{28}NO_4PSi$ (M^+) 309.1525, found 309.1532.

(*E*)- and (*Z*)-Dimethyl (1-*tert*-Butyldimethlysilyloxyiminopentyl)phosphonate (3dE and 3dZ). ^{1}H NMR of **3dE** (300 MHz, from the mixture): δ 3.80 (d, J = 11.0 Hz, 6H), 2.58−2.40 (m, 2H), 1.59−1.50 (m, 2H), 1.42−1.26 (m, 2H), 0.95 (s, 9H), 0.92 (t, J = 7.4 Hz, 6H), 0.19 (s, 6H). ^{13}C NMR of **3dE** (75.5 MHz, from the mixture): δ 159.7 (d, $J_{P,C}$ = 205.4 Hz), 53.2 (d, $J_{P,C}$ = 6.2 Hz), 27.8, 26.4 (d, $J_{P,C}$ = 16.0 Hz), 25.6, 22.5, 17.8, 13.4, −5.6. ^{1}H NMR of **3dZ** (300 MHz, from the mixture): δ 3.78 (d, J = 11.5 Hz, 6H), 2.58−2.40 (m, 2H), 1.59−1.50 (m, 2H), 1.42−1.26 (m, 2H), 0.96 (s, 9H), 0.92 (t, J = 7.4 Hz, 6H), 0.20 (s, 6H).^{13}C NMR of **3dZ** (75.5 MHz, from the mixture): δ 156.8 (d, $J_{P,C}$ = 152.2 Hz), 52.4 (d, $J_{P,C}$ = 6.1 Hz), 32.4 (d, $J_{P,C}$ = 17.2 Hz), 28.7 (d, $J_{P,C}$ = 3.0 Hz), 25.7, 21.9, 18.0, 13.4, −5.7. IR of the mixture (neat): 2918, 2850, 1600, 1570, 1450, 1248 cm.$^{-1}$ HRMS of the mixture: calcd for $C_{13}H_{30}NO_4PSi$ (M^+) 323.1682, found 323.1678.

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