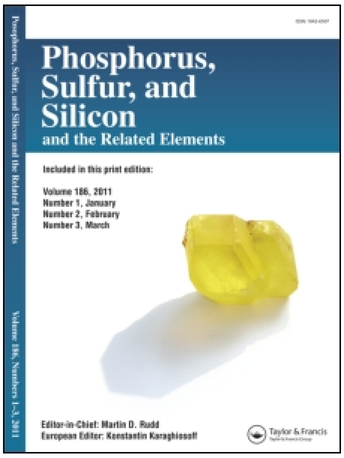

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Aminophosphinic Acids in a Pyridine Series: Cleavage of Pyridine-2- and Pyridine-4-methyl(amino)phosphinic Acids in Acidic Solutions

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Aminophosphinic Acids in a Pyridine Series: Cleavage of Pyridine-2- and Pyridine-4-methyl(amino)phosphinic Acids in Acidic Solutions

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The synthesis of a series of new pyridine aminomethylphosphinic acids is described. These compounds were obtained in the reaction of the corresponding pyridine aldehydes with primary amines and with ethyl phenylphosphinate, or methylphosphinate, in the presence of bromotrimethylsilane. In aqueous, strong acid solutions, pyridine aminophosphinic acids were split, forming the phenyl-, or methylphosphonic, acid and the corresponding secondary pyridyl-alkylamines. The kinetics of some observed cleavages were measured, and a mechanism of the cleavage has been proposed.

Keywords Aminophosphinic acids; bromotrimethylsilane; cleavage reactions; phosphonic acids; pyridine aminophosphinic acids; pyridyl amines

INTRODUCTION

Pyridine aminophosphinic acids are compounds of great importance due to potential biological activity.[1] Some of parent compounds, i.e., the peptidyl pyridine aminophosphonates, were tested as enzyme inhibitors for serine proteases.[2] Also some of pyridine aminophosphonic acids were used as powerful binding agents for transition metals.[3] There is an expectancy that the pyridine aminophosphinic acids will be products with valuable biological and chemical properties, like the parent aminophosphonic acids.

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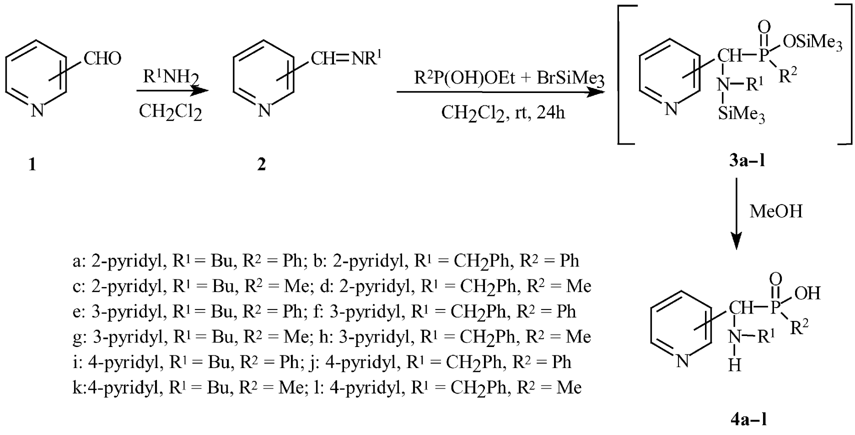
A few years ago, we described a new, convenient procedure for the synthesis of pyridine aminophosphonic acids by the use of a mixture composed of trimethyl phosphite and bromotrimethylsilane for the addition to aldimines.[4] We found that such a procedure can be applied for the synthesis of aminophosphinic acids, with a slight modification. When H-phenyl- and H-methylphosphinate ethyl esters are treated with bromotrimethylsilane, the corresponding trimethylsilyl esters are formed. The obtained mixture, comprising mainly of the phosphinite trimethylsilyl esters, could be used directly for additional reactions to the aldimines.

RESULTS AND DISCUSSION

The title pyridine aminophosphinic acids were synthesized by a sequence of reactions from the corresponding pyridine aldehydes, primary amines, appropriate phosphinic esters, and bromotrimethylsilane, according to Scheme 1.



a: 2-pyridyl, R^1 = Bu, R^2 = Ph; b: 2-pyridyl, R^1 = CH_2Ph, R^2 = Ph
c: 2-pyridyl, R^1 = Bu, R^2 = Me; d: 2-pyridyl, R^1 = CH_2Ph, R^2 = Me
e: 3-pyridyl, R^1 = Bu, R^2 = Ph; f: 3-pyridyl, R^1 = CH_2Ph, R^2 = Ph
g: 3-pyridyl, R^1 = Bu, R^2 = Me; h: 3-pyridyl, R^1 = CH_2Ph, R^2 = Me
i: 4-pyridyl, R^1 = Bu, R^2 = Ph; j: 4-pyridyl, R^1 = CH_2Ph, R^2 = Ph
k:4-pyridyl, R^1 = Bu, R^2 = Me; l: 4-pyridyl, R^1 = CH_2Ph, R^2 = Me

SCHEME 1

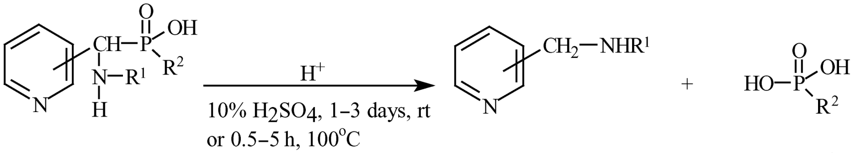
The procedure was as follows: the pyridine aldehydes **1** were mixed with butyl- or benzylamine to form the corresponding pyridine aldimines **2**, which were treated with a mixture composed of phenyl- or methylphosphinic acid ethyl ester and bromotrimethylsilane. Intermediates, i.e., the silylated phosphinates **3**, were easily formed in this case, and they were then transformed to the final pyridyl aminophosphinic acids **4** by hydrolysis with methanol. Hydrolysis of the silyl phosphonate esters to free phosphonic acids by use of methanol, was previously utilized by Boduszek[4] and Zoń.[5]

The present method of synthesis of the pyridine aminophosphinic acids is a one-pot convenient and simple procedure leading directly to the products **4** with a high yield and purity.

All the synthesized products were characterized by means of ^{1}H NMR and ^{31}P NMR spectroscopy. Analytical data of the obtained aminophosphinic acids **4** are given in Table I.

The synthesis of some obtained compounds (**4b**, **4f**, and **4j**) already has been published in a preliminary communication.[10]

The prepared aminophosphinic acids **4a–d** and **4i–l** underwent interesting transformations in aqueous solutions of mineral acids. Under the influence of strong acids, the aminophosphinic acids were split to form the secondary amines and aryl(alkyl)phosphonic acids. A similar way of splitting was found for 2- and 4-pyridylmethyl(amino)phosphonic acids,[6] and other heterocyclic phosphonate compounds.[8,9] Thus, for example, a solution of **4b** in 10% aq. sulfuric acid at r.t. decomposed gradually to form the amine **5b** and phenylphosphonic acid (Scheme 2). After about 20 h, the cleavage of **4b** was complete. Likewise, the 4-pyridyl phosphinic acid **4j** was cleaved in the same manner, however much slower, than the corresponding 2-pyridyl derivatives. Cleavage of the aminophosphinic acids can be considerably accelerated at elevated temperature; thus, boiling a 10% H_2SO_4 solution of **4a–d** or **4i–l** caused complete decomposition of the aminophosphinic acids during one hour. As a result, formation of a mixture of secondary amines **5a–d** and phenyl- (**6**), or methylphosphonic acid (**7**) was obtained (Scheme 2).



4a-d, i-l

5a-d

a: 2-pirydyl, R^1 = Bu
b: 2-pyridyl, R^1 = CH_2Ph
c: 4-pyridyl, R^1 = Bu
d: 4-pyridyl, R^1 = CH_2Ph

6, R^2 = Ph
7, R^2 = Me

SCHEME 2

Phosphinic 3-pyridyl derivatives **4e–h** were not affected by strong mineral acids at these conditions.

^{31}P NMR spectroscopy allowed measurement of some kinetics of the cleavages. The measurement of kinetic rates for selected compounds was executed likewise as it was done for the corresponding phosphonic acids.[7] Obtained pseudo-first-order rate constants (k_{obs}) for

TABLE I Analytical Data of Pyridylmethyl(amino)phosphinic Acids 4

Compound no.	Yield %	M.p. °C	^{1}H NMR (D_2O) δ, ppm	^{31}P NMR (D_2O) δ, ppm
4a	34	179–180	8.34 (d, 1H, $J = 4.6$ Hz, py-6), 7.85 (t, 1H, $J = 7.8$ Hz, py-4), 7.45–7.28 (m, 7H, arom.), 4.70 (d, 1H, CH-P, $J = 12.0$ Hz), 2.92–2.90 (m, 2H, CH_2N), 1.50 (m, 2H), 1.15 (m, 2H), 0.70 (t, 3H, CH_3, $J = 7.6$ Hz)	20.48 (s)
4b	81	185–187	8.41–8.37 (m, 2H, py-4,6), 7.85–7.79 (m, 2H. py-3,5), 7.41–7.15 (m, 10H, 2xPh), 4.78–4.74 (d, 1H, $J = 11.8$ Hz, CH-P), 4.40–4.20 (m, 2H, CH_2N)	20.03 (s)
4c	54	159–163	8.68 (d, 1H, $J = 5.41$ Hz, py-6), 8.30 (t, 1H, $J = 7.95$ Hz, py-4), 7.87 (d, 1H, $J = 7.99$ Hz, py-3), 7.77 (t, 1H, $J = 6.63$ Hz, py-5), 4.70 (d, 1H, $J = 20.27$ Hz, CH-P), 3.01 (m, 2H, CH_2N), 1.59 (m, 2H, CH_2), 1.25 (d, 3H, $J = 14.32$ Hz, P-CH_3), 1.20 (m, 2H, CH_2), 0.76 (t, 3H, $J = 7.32$ Hz, CH_3)	30.68 (s)
4d	79	217–218	8.51 (d, 1H, $J = 4.84$ Hz, py-6), 7.77 (t, 1H, $J = 7.80$ Hz, py-4), 7.36–7.23 (m, 7H, arom.), 4.30 (d, 1H, $J = 13.99$ Hz, CH-P), 4.16 (dd, 2H, $J = 13.17$ Hz, CH_2Ph), 1.06 (d, 3H, $J = 14.17$ Hz, P-CH_3)	32.54 (s)
4e	51	242–243	8.37 (bs, 1H, py-6), 8.15 (s, 1H, py-2), 7.69 (d, 1H, py-4, $J = 7.85$ Hz), 7.44–7.32 (m, 6H, arom.), 4.70 (d, 1H, CH-P, $J = 12$ Hz), 2.87 (m, 2H, CH_2N), 1.49 (m, 2H), 1.13 (m, 2H), 0.70 (t, 3H, CH_3, $J = 7.6$ Hz)	21.49 (s)
4f	84	225–227	8.56 (d, 1H, $J = 5.7$ Hz, py-6.), 8.29 (s, 1H. py-2.), 8.18 (d, 1H, py-4.), 7.42 (m, 1H, py-5), 7.32–7.10 (m, 10H, 2xPh), 4.57 (d, 1H, $J = 11.1$ Hz, CH-P), 4.20 (bs, 2H, CH_2N)	21.18 (s)
4g	49	168–169	8.87 (s, 1H, py-2), 8.81 (d, 1H, $J = 5.73$ Hz, py-6), 8.65 (d, 1H, $J = 8.28$ Hz, py-4), 8.09 (m, 1H, py-5), 4.82 (d, 1H, $J = 18.6$ Hz, CH-P), 2.97 (m, 2H, CH_2N), 1.58 (m, 2H), 1.29 (d, 3H, $J = 8.32$ Hz, P-CH_3), 1.20 (m, 2H), 0.77 (t, 3H, $J = 7.34$ Hz, CH_3)	30.05 (s)
4h	78	235–236	8.37 (d, 1H, py-6, $J = 5.77$ Hz), 8.32 (s, 1H, py-2), 8.19 (d, 1H, py-4, $J = 8.27$ Hz), 7.67 (m, 1H, py-5), 6.92 (m., 5H, Ph), 4.42 (d, 1H, $J = 10.45$ Hz, CH-P), 3.94 (m., 2H, CH_2N), 1.01 (d, 3H, $J = 14.44$ Hz, P-CH_3), (in 1M D_2SO_4 in D_2O)	35.55 (s)

TABLE I Analytical Data of Pyridylmethyl(amino)phosphinic Acids 4 *(Continued)*

Compound no.	Yield %	M.p. °C	^{1}H NMR (D_2O) δ, ppm	^{31}P NMR (D_2O) δ, ppm
4i	47	208–210	8.32 (d, 2H, py-2,6, $J = 4.9$ Hz), 7.44–7.31 (m, 5H, arom.), 7.15 (d, 2H, py-3,5, $J = 4.9$ Hz), 4.75 (d, 1H, CH-P $J = 12$ Hz), 2.84 (m, 2H, CH_2N), 1.47 (m, 2 H), 1.11 (m, 2H), 0.69 (t, 3H, CH_3, $J = 7.1$ Hz).	20.99(s)
4j	80	171–173	8.44 (d, 2 H, $J = 6.5$ Hz, py-2,6.), 7.53 (d, 2H, $J = 5.7$ Hz, py-3,5.), 7.45–7.12 (m, 10H, 2xPh), 4.69–4.65 (d, 1H, $J = 11.2$ Hz, CH-P), 4.24 (d, 2H, $J = 3.1$ Hz, CH_2N).	20.52(s)
4k	48	205–208	8.79(d, 2H, $J = 6.71$ Hz, py-2,6), 8.06(d, 2H, $J = 5.56$ Hz, py-3,5), 4.80(d, 1H, $J = 10.96$ Hz, CH-P), 3.02(m., 2H, CH_2N), 1.59(m, 2H), 1.29(d, 3H, $J = 14.28$ Hz, P-CH_3), 1.22(m, 2H), 0.78(t, 3H, $J = 7.36$ Hz, CH_3)	29.37(s)
4l	62	197–198	8.28(d, 2H, py-2,4, $J = 6.13$ Hz), 7.53(d, 2H, py-3,5, $J = 6.44$ Hz), 6.91(m, 5 H, Ph), 4.43(d, 1H, $J = 11.65$ Hz, CH-P), 3.93(m, 2H, CH_2N), 0.98(d, 3H, $J = 14.49$ Hz, P-CH_3) (in 1M D_2SO_4 in D_2O)	34.37(s)

cleavages of the aminophosphinic acids **4** are given in Table II. According to the obtained results, constant rates (k_{obs}) were strongly depended on the concentration of sulfuric acid. For example, the rates for aminophosphinic acids (**4b**,**4c**, and **4j**) increased faster than could be expected from direct proportionality to the concentration of sulfuric acid (Table II).

A small kinetic isotope effect (k_H/k_D) was observed in the cleavage. An existence of the $k_H/k_D > 1$ shows that protons are involved in a rate-determining step. However, the k_H/k_D was somewhat less than unity for the measured pyridine aminomethylphosphinic acids (**4c**, and **4d**, Table II). All the kinetic data indicate that the observed cleavages are a kind of an electrophilic substitution observed at α-carbon in the aminophosphinic acids. In this case, an electrophile (H^+) replaces a phosphinic moiety in the aminophosphinic acid giving as a result the secondary amine. The metaphosphate-like moiety reacts with the solvent (water) to form the phenyl- or methylphosphonic acid (Scheme 2).

Kinetic measurements for the cleavage of **4b** were additionally carried out at 35°C and 45°C in order to calculate the activation parameters (Ea, $\Delta H^{\neq}$, and $\Delta S^{\neq}$, Table II). Low activation energy (Ea) calculated

TABLE II Kinetics for the Cleavage of Pyridylmethyl(amino)-Phosphinic Acids

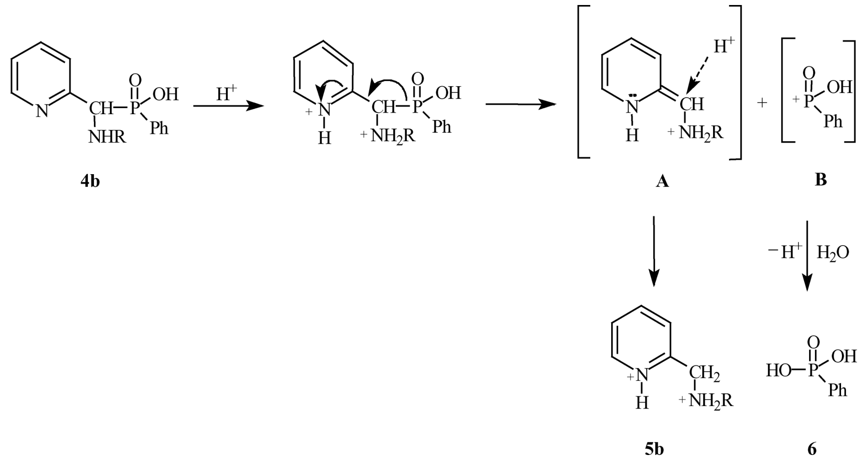
Compound	Conc. of compd. mol L^{-1}	Conc. of acid mol L^{-1}	Temp. °C	Kinetic and thermodynamic parameters	
				k_{obs} h^{-1}	$t_{1/2^a}$ k_H/k_D
4b	0.06	0.5 (H_2SO_4)	25	0.038	$t_{1/2} = 5.5$ h
	0.08	1.0 (H_2SO_4)		0.126	$k_H/k_D = 1.17$
	0.08	1.0 (D_2SO_4)		0.108	
	0.06	2.0 (H_2SO_4)		0.356	$E_a = 73.7$ kJ/mol
	0.08	1.0 (H_2SO_4)	35	0.265	$\Delta H^{\neq} = 71.2$ kJ/mol
	0.08	1.0 (H_2SO_4)	45	0.634	$\Delta S^{\neq} = -91.7$ J/mol·st
4c	0.21	0.5 (H_2SO_4)	25	0.001^b	
	0.21	1.0 (H_2SO_4)		0.006^b	$t_{1/2} = 119$ h
	0.21	2.0 (H_2SO_4)		0.013^b	$k_H/k_D = 0.86$
	0.21	1.0 (D_2SO_4)		0.007^b	
4d	0.18	0.5 (H_2SO_4)	25	0.002^b	
	0.18	1.0 (H_2SO_4)		0.012^b	$t_{1/2} = 73.7$h
	0.18	2.0 (H_2SO_4)		0.031^b	$k_H/k_D = 0.80$
	0.18	1.0 (D_2SO_4)		0.015^b	
	0.18	1.0 (H_2SO_4)	45	0.053^b	
4j	0.07	0.5 (H_2SO_4)	25	0.007	
	0.08	1.0 (H_2SO_4)		0.020	$t_{1/2} = 34.3$ h
	0.08	1.0 (D_2SO_4)		0.018	$k_H/k_D = 1.10$
	0.07	2.0 (H_2SO_4)		0.049	
4l	0.18	0.5 (H_2SO_4)	25	0.001^b	
	0.18	1.0 (H_2SO_4)		0.002^b	$t_{1/2} = 315$ h
	0.18	2.0 (H_2SO_4)		0.004^b	$k_H/k_D = 1.0$
	0.18	1.0 (D_2SO_4)		0.002^b	

[a] Kinetic data for 1M H_2SO_4 solutions.
[b] Kinetics measured in 50% aqueous methanol.

for the cleavage of **4b** is significant, and it confirms the observed facility of the splitting of the aminophosphinic acid.

Taking the obtained data into account, a mechanism for the cleavage of pyridyl aminophosphinic acids in acidic conditions is proposed and shown in Scheme 3, for example, of the cleavage of 2-pyridylmethyl(amino)phenylphosphinic acid **4b**. A similar mechanism was postulated previously for pyridine aminophosphonic acids.[7]

Protonation of the nitrogen atoms in the aminophoshinic acid molecule set up an inductive effect additionally backed up by a resonance effect in the pyridine ring (Scheme 3). It causes, in consequence, a rupture of a C-P bond and the leaving of a positively charged metaphosphate-like moiety **B**. The introduction of a proton to the α-methine group in the moiety **A** leads to the amine **5b**.



SCHEME 3

The metaphosphate-like moiety **B** can react with water to give the phenylphosphonic acid **6** (Scheme 3).

EXPERIMENTAL

^{1}H NMR and ^{31}P NMR spectra were measured on a Bruker Avance 300 MHz spectrometer using TMS as an internal standard. Melting points were determined using an Electrothermal 9200 apparatus and a Boetius hot-stage apparatus and were uncorrected. Elemental analyses were done in the Laboratory of Instrumental Analysis in the Institute. Reagents used were obtained from the Sigma-Aldrich Company (Poznaò, Poland). Solvents were of commercial quality and purchased from a local supplier (POCH Gliwice, Poland).

Ethyl methylphosphinate was prepared from methyldichlorophosphine according to the procedure published in.[11]

General Procedure for the Preparation of the Pyridine Aminophosphinic Acids 4a–l

The procedure for the synthesis of pyridine *N*-benzylaminophosphinic acids[10] was followed with some modifications. Thus, a mixture of the corresponding pyridinecarboxaldehyde **1** (1.07 g, 10 mmol) and benzyl, or butylamine (11 mmol) in methylene chloride (25 mL) was prepared. The mixture was kept at r.t. for 24 h; anhydrous sodium sulfate was added (5.0 g), stirred, and filtered. The filtrate was mixed with ethyl phenylphosphinate, or ethyl methylphosphinate (10 mmol), followed by bromotrimethylsilane (4.6 g, 30 mmol), and left for the next 24 h at r.t. After this, the mixture was evaporated to dryness; and the resulting oily product was kept at 70°C for 1 h and treated with methanol (10 mL). The mixture was refrigerated for several hours until crystals of the aminophosphinic acid **4** separated. If necessary, diethyl ether (20 mL) was added to the mixture to cause precipitation of the products. The products **4a–l** were collected by filtration, washed with diethyl ether, and dried. Yields and analytical data of the **4** are given in the Table I. Elemental anal. for **4a**, calc.: N, 9.21; P, 10.18. Found: N, 9.21; P, 10.27%. For **4b**, calc.: N, 8.28; P, 9.15. Found: N, 8.21; P, 9.11%. Lit.[10]. For **4c**, calc.: N, 11.56; P, 12.79. Found: N, 11.44; P, 12.81%. For **4d**, calc.: N, 10.14; P, 11.21. Found: N, 10.09; P, 11.22%. For **4e**, calc.: N, 9.21; P, 10.18. Found: N, 9.20; P, 10.21%. For **4f**, calc.; N, 8.28; P, 9.15. Found: N, 8.19; P, 9.10%. Lit.[10]. For **4g**, calc.: N, 11.56; P, 12.79. Found: N, 11.48; P, 12.78%. For **4h**, calc.: N, 10.14; P, 11.21. Found: N, 10.09; P, 11.14. For **4i**, calc.: N, 9.21; P, 10.18. Found: N, 9.11; P, 10.13. For **4j**, calc.: N, 8.28; P, 9.15. Found: N, 8.17; P, 9.14%. Lit.[10]. For **4k**, calc.: N, 11.56; P, 12.79. Found: N, 11.44; P, 12.76%. For **4l**, calc.: N, 10.14; P, 11.21. Found: N, 10.05; P, 11.16%.

Cleavage of 4a–d and 4i–l and Isolation of the Products

A sample of pyridine-2-yl aminophosphinic acid **4a–d** (1.0 mmol) was dissolved in aqueous 10% sulfuric acid (10 mL), and the solution was kept for 1–3 days at r.t. In the case of pyridine-4-yl aminophosphinic acids, the solution of the **4i–l** in 10% aq. H_2SO_4 was left for 7–10 days at r.t. After this, the solution was alkalized with sodium carbonate (1.6 g, 15 mmol) and extracted with methylene chloride (25 mL). The extract was dried (anh. Na_2SO_4), filtered, and evaporated to give the amines **5a–d**, as thick oils. Yield: 70–90%. The amines **5a–d** are known compounds and were characterized as oxalate salts and by comparison with the literature data.[6]

The remaining aqueous layer was acidified with 10% aq. H_2SO_4(5 mL) and evaporated to dryness. The residue was treated with absolute ethanol (25 mL), warmed to70°C, and filtered; the filtrate evaporated to give the phosphonic acids, **6** and **7**, respectively.

Phenylphosphonic acid **6**, (0.12–0.15 g, 76–95%). Methylphosphonic acid **7** (0.075–0.09 g, 78–94%).

The phosphonic acids **6** and **7** are known, commercial compounds and their analytical data are given elsewhere.[12]

Procedure for Kinetic Runs

Stock aqueous, or stock 50% aq. methanol solutions of sulfuric acid, with the concentration of H_2SO_4; $c = 0.5$, 1.0, and 2.0 mol·L^{-1}, were prepared. Similarly, a solution of deuterated sulfuric acid was prepared with a conc. of D_2SO_4 $c = 1.0$ mol·L^{-1}. Samples of aminophosphinic acids **4** (10–20 mg) and sulfuric acid solutions (0.5 mL) were mixed in NMR tubes and thermostated at 25°C, 35°C, or 45°C for a specified period of time (1, 2, 4, 8, and 16 h), and the ^{31}P NMR spectra were recorded. The pseudo-first-order rate constants (k_{obs}) were determined from ^{31}P NMR spectra by plotting the dependence of *log(a-x)* on time (where the "$a - x$" represents concentration of unreacted (**4**). In most cases, a dependence of *log(a-x)* on time was obeyed very well.

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