An Efficient and Convenient Procedure for the One-Pot Synthesis of α-Aminophosphonates from Aryl Azides under Solvent-Free Conditions

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Abstract: A novel and simple approach to the multicomponent one-pot reaction of aldehydes, diethyl phosphite, and azides to form α-aminophosphonates under solvent-free conditions at room temperature has been developed. In the presence of iodine and iron, aryl azides were, for the first time, used as substrates for the synthesis of α-aminophosphonates. The reactions were completed within 5 minutes to 12 hours and afforded the corresponding products in good yields.

Key words: α-aminophosphonates, azides, multicomponent reactions, solvent-free conditions, iodine

Multicomponent reactions (MCRs) are highly important reactions because of their wide range of applications in pharmaceutical chemistry for the production of structural scaffolds and combinatorial libraries for drug discovery.[1] Multicomponent reactions are convergent; they often produce a remarkably high increase of molecular complexity in just one step.[2] α-Aminophosphonates, which are structural analogues of α-amino acids, have attracted much attention due to their wide range of applications in biological and medicinal chemistry as enzyme inhibitors,[3,4] peptide mimics,[5] antibiotics,[6] herbicides and fungicides,[7,8] plant growth regulators,[9] and pharmacological agents.[10] As a result, various synthetic methods have been developed for the synthesis of α-aminophosphonates. Of these methods, multicomponent reactions catalyzed by various acids catalysts, heterogeneous catalysts, and nano catalysts have been reported.[11–13] However, all of these methods used aldehydes, dialkyl phosphites, and amines, as the substrates; only primary or secondary amines were used as the amine component in this transformation. Therefore, the development other substrates as the amine component will extend the scope of the synthesis of α-aminophosphonates. To the best of our knowledge, there are no reports on the use of azides as the amine component in the synthesis of α-aminophosphonates. Herein, we report a simple and mild procedure for the one-pot synthesis of α-aminophosphonates via a multicomponent reaction between arylaldehydes, azides, and diethyl phosphite in the presence of iodine and iron as catalysts.

As our interests are in green chemistry,[14] we wish to perform this multicomponent one-pot reaction in water or under neat conditions. However, the use of solvent, including both water and organic solvents, retarded the rate of the reaction and it required a much longer reaction time than under neat conditions (see Supplementary Information). Hence solvent-free was chosen as the reaction conditions. The multicomponent reaction between 4-chlorophenyl azide (**1a**, 1 mmol), benzaldehyde (**2a**, 1 mmol), and diethyl phosphite (**3**, 2 mmol) in the presence of 10 mol% iodine was chosen as the model reaction. Optimization of the reaction conditions results are summarized in Table 1. The product **4a** was obtained in low yield in 10 hours when iron was not added (entry 1). Product **4a** was obtained in better yields within shorter times when the amount of iron was increased (entries 2–5). The best result was obtained with 84% yield of **4a** in 8 minutes when 100 mol% of iron was added (entry 5). Then we changed the amount of iodine used in the reaction. The reaction was complete in 5 minutes in the presence of 20 mol% iodine; the yield of **4a** was 75% yield (entry 6). When iodine was not added, product **4a** was not obtained (entry 7). The yields of the product were not enhanced when the reactions were carried out at higher temperatures, such as 40 °C, 50 °C, and 80 °C (entries 8–10). Other metals, such as magnesium and zinc, were also employed in the reaction, but only poor yields of **4a** were obtained (entries 11 and 12).

Having established the standard reaction conditions for the multicomponent reactions of 4-chlorophenyl azide (**1a**), benzaldehyde (**2a**), and diethyl phosphite (**3**), we extended our protocol to the synthesis α-aminophosphonate derivatives using various substituted aryl azides **1** and carbonyl compounds **2** under the optimized conditions. The results are shown in Table 2. Both aryl azides and aromatic aldehydes with electron-withdrawing or electron-donating groups were converted into the corresponding α-aminophosphonates **4a**–**p** in good to excellent yields (65–86%) within 12 hours under solvent-free conditions at room temperature (entries 1–16). But when aliphatic aldehydes and cyclohexanone were used, the reaction resulted in lower yields of **4q**,**r** (entries 17 and 18). The product α-aminophosphonates **4a**,**g**,**m** were always obtained in high yields when aromatic aldehydes with electron-donating groups were employed in the reaction (entries 1, 7, and 13). When the aromatic aldehydes with strong electron-withdrawing groups (NO_2) were employed, α-aminophosphonates **4d**–**f**,**j**–**l**,**o** were often synthesized in lower yields under the same conditions (entries 4–6, 10–12, and 15). When the aromatic aldehydes have the same substituents, the reaction of *para*-substituted substrates needed

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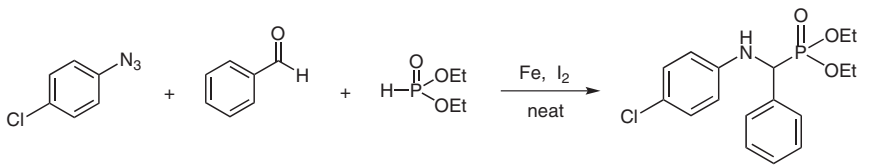
Table 1 Optimization of the Reaction Conditions for the Synthesis of α-Aminophosphonate[a]



1a 2a 3 4a

Entry	M (equiv)	Temp (°C)	Time	Yield[b] (%)
1	Fe (0)	20	10 h	42
2	Fe (0.1)	20	3 h	62
3	Fe (0.2)	20	1.5 h	66
4	Fe (0.5)	20	15 min	75
5	Fe (1.0)	20	8 min	84
6[c]	Fe (1.0)	20	5 min	75
7[d]	Fe (1.0)	20	3 h	0
8	Fe (1.0)	40	12 min	82
9	Fe (1.0)	50	8 min	83
10	Fe (1.0)	80	10 min	84
11	Mg (1.0)	20	5 h	31
12	Zn (1.0)	20	5 h	27

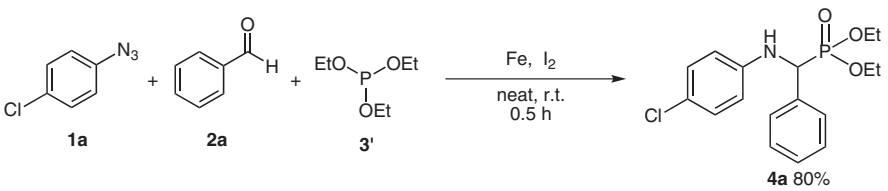
[a] Reaction conditions: 4-chlorophenyl azide (**1a**; 154 mg, 1.0 mmol), benzaldehyde (**2a**, 106 mg, 1.0 mmol), diethyl phosphite (**3**, 276 mg, 2.0 mmol), I_2 (25 mg, 10 mol%), solvent-free.
[b] Isolated yield.
[c] Iodine (20 mol%, 50 mg) was used.
[d] Iodine was not added.

shorter reaction times, and afforded the α-aminophosphonates in higher yields than the substrates with *ortho* or *meta* substituents (entry 4 vs. entries 5 and 6, entry 10 vs. entries 11 and 12). When both *para*-substituted aryl azides and benzaldehyde (**2a**) were employed in the reaction, the α-aminophosphonates **4a** and **4g** were obtained in good yields within a very short time (entries 1 and 7).

We also attempted this reaction out on a gram scale; compound **4b** was chosen as the target compound. The reaction was carried out with 4-chlorophenyl azide (1.54 g, 10 mmol), 4-chlorobenzaldehyde (1.4 g, 10 mmol), and diethyl phosphate (**3**, 2.76 g, 20 mmol) under the optimal reaction conditions. Product **4b** was obtained in 84% yield (3.26 g).

Next, triethyl phosphite was employed instead of diethyl phosphite to carry out the reaction with 4-chlorophenyl azide (**1a**), and benzaldehyde (**2a**) in the presence of iodine and iron. As shown in Scheme 1, both the yield of **4a** and the reaction time were influenced by the phosphorus compounds.

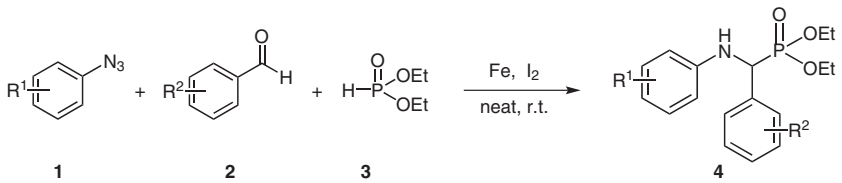
The mechanism of the reaction was also studied. From Table 1, entry 1, the result showed that the product **4a** was obtained with a low yield in ten hours when iron was not added. This means that iron is essential for the high yield of the reaction. In order to study the mechanism of the reaction, further research was performed. First, the substrate 4-chlorophenyl azide (**1a**) was treated under standard reaction conditions. After four hours, we found that 4-chlo-



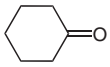
1a 2a 3' **4a** 80%

Scheme 1 Synthesis of α-aminophosphonates from triethyl phosphite

Table 2 Iodine- and Iron-Catalyzed Multicomponent Reactions for Synthesis of α-Aminophosphonates from Azides[a]



1 2 3 4

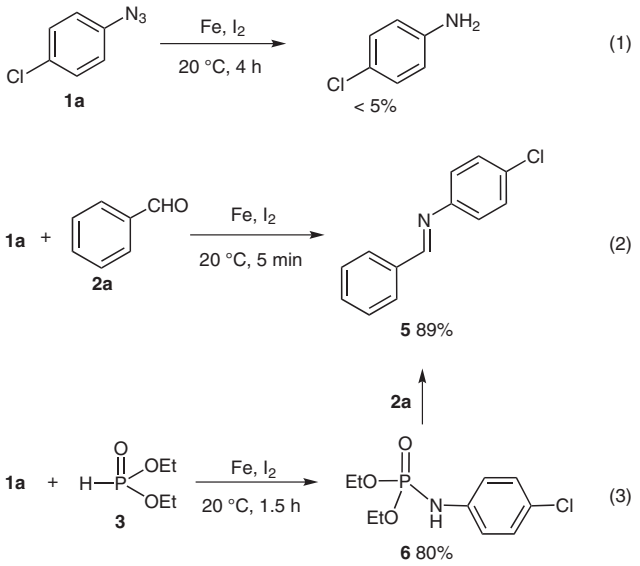
Entry	Azide **1** R^1	Aldehyde **2**	Product	Time	Yield[b] (%)
1	4-Cl	PhCHO	**4a**	8 min	84
2	4-Cl	4-ClC_6H_4CHO	**4b**	4 h	85
3	4-Cl	4-$MeOC_6H_4CHO$	**4c**	12 h	73
4	4-Cl	4-$O_2NC_6H_4CHO$	**4d**	4 h	79
5	4-Cl	2-$O_2NC_6H_4CHO$	**4e**	5 h	70
6	4-Cl	3-$O_2NC_6H_4CHO$	**4f**	10 h	75
7	4-Me	PhCHO	**4g**	5 min	85
8	4-Me	4-ClC_6H_4CHO	**4h**	10 h	69
9	4-Me	4-$MeOC_6H_4CHO$	**4i**	12 h	70
10	4-Me	4-$O_2NC_6H_4CHO$	**4j**	5 h	69
11	4-Me	2-$O_2NC_6H_4CHO$	**4k**	8 h	65
12	4-Me	3-$O_2NC_6H_4CHO$	**4l**	10 h	67
13	H	PhCHO	**4m**	6 h	86
14	H	4-ClC_6H_4CHO	**4n**	12 h	83
15	H	4-$O_2NC_6H_4CHO$	**4o**	4 h	80
16	H	4-$MeOC_6H_4CHO$	**4p**	8 h	83
17	4-Cl	Me_2CHCHO	**4q**	6 h	48
18	4-Cl		**4r**	5 h	43

[a] Reaction conditions: aryl azides **1** (1.0 mmol), aromatic aldehydes **2** (1.0 mmol), diethyl phosphate (**3**, 2.0 mmol), I_2 (25 mg, 10 mol%), Fe (56 mg, 1 equiv), solvent-free.
[b] Isolated yield.

roaniline was obtained in very low yield [Scheme 2, (1)], which indicates that 4-chlorophenyl azide (**1a**) could not be reduced to the corresponding amine under the conditions. But when benzaldehyde was added, the imine was obtained in 89% yield [Scheme 2, (2)]. Thus, in the absence of the formation of 4-chloroaniline, this probably represents a reaction in which both 4-chlorophenyl azide and benzaldehyde are simultaneously involved in imine formation.[15] We also found that when we treated phosphoramide **6**, which was formed from 6-chlorophenyl azide and diethyl phosphite [Scheme 2, (3)],[16] with benzaldehyde under the same conditions, the imine was finally formed. The above results are in accord with the reported literature that the imine is the key intermediate in the product-forming pathway.[11n,o,17] As can be see in Scheme 2, reaction (2) is faster than reaction (3), so the intermediate imine was synthesized by reaction (2) in this multicomponent reaction.

Iodine played the main role as the catalyst in the next step. On the basis of the experimental results and the literature,[18] possible mechanisms for the formation of α-aminophosphonates are presented in Scheme 3.

In summary, it was demonstrated that readily available iodine and iron could behave as efficient catalysts for multicomponent one-pot reaction of aldehydes, diethyl phosphite, and azides, giving α-aminophosphonates with excellent yields in short times. The reactions, performed under solvent-free conditions at room temperature, allowed a very simple, clean synthesis of α-aminophosphonates. In the multicomponent reactions, aryl azides were used for the first time as the amine component in the syn-



Scheme 2

thesis of α-aminophosphonates. We also proposed a possible mechanism based on the experiments. Further investigations on enantioselective multicomponent reactions for the synthesis of α-aminophosphonates are in progress.

Melting points were determined with an X-4 apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian 400-MHz spectrometers with $CDCl_3$ as the solvent relative to TMS as internal standard. IR spectra were obtained as KBr pellet samples on a Bruker-EQUINOX 55 spectrophotometer. Elemental analyses were conducted with a vario EL CUBE analyzer. Mass spectra (ESI) were recorded on a LCQ Advantage mass spectrometer. Flash column chromatography was performed on silica gel (200–300 mesh). Solvents for column chromatography were dried and freshly distilled before use.

4-Chlorophenyl Azide (1a); Typical Procedure[19]

An soln of $NaNO_2$ (3.11 g, 45 mmol) dissolved in H_2O (60 mL) was added dropwise to a cooled (0–5 °C) soln of 4-chloroaniline (3.83 g, 30 mmol) in 6 M HCl (30 mL) with stirring. The mixture was stirred at 0–5 °C for an additional 0.7 h, and to it was added dropwise a soln of NaN_3 (3.90 g, 60 mmol) dissolved in H_2O (60 mL). The mixture was stirred for 1 h, and then it was extracted with Et_2O (3 × 50 mL). The combined Et_2O extracts were washed with brine, aq $NaHCO_3$, and brine, and dried (Na_2SO_4). Evaporation of the solvent furnished the crude azide, which was filtered through a short column (silica gel) to produce pure 4-chlorophenyl azide (4.12 g, 89%).

Diethyl (4-Chlorophenylamino)(phenyl)methylphosphonate (4a); Typical Procedure

4-Chlorophenyl azide (**1a**, 154 mg, 1.0 mmol), benzaldehyde (**2a**, 106 mg, 1.0 mmol), diethyl phosphate (**3**, 276 mg, 2.0 mmol), I_2 (25 mg, 10 mol%), and Fe (56 mg, 1.0 mmol) were placed in a 25-mL flask under solvent-free conditions at r.t. The mixture was stirred at r.t. (TLC monitoring). After completion of the reaction, a mixture of H_2O–EtOAc (1:1, 10 mL) was added. The mixture was filtrated and extracted with EtOAc (3 × 5 mL); the combined extracts were washed with aq $Na_2S_2O_3$ and brine, dried (anhyd Na_2SO_4), and concentrated in vacuo. The resulting residue was purified by column chromatography (silica gel, petroleum ether–EtOAc, 1:2) to afford pure **4a** (297 mg, 84%).

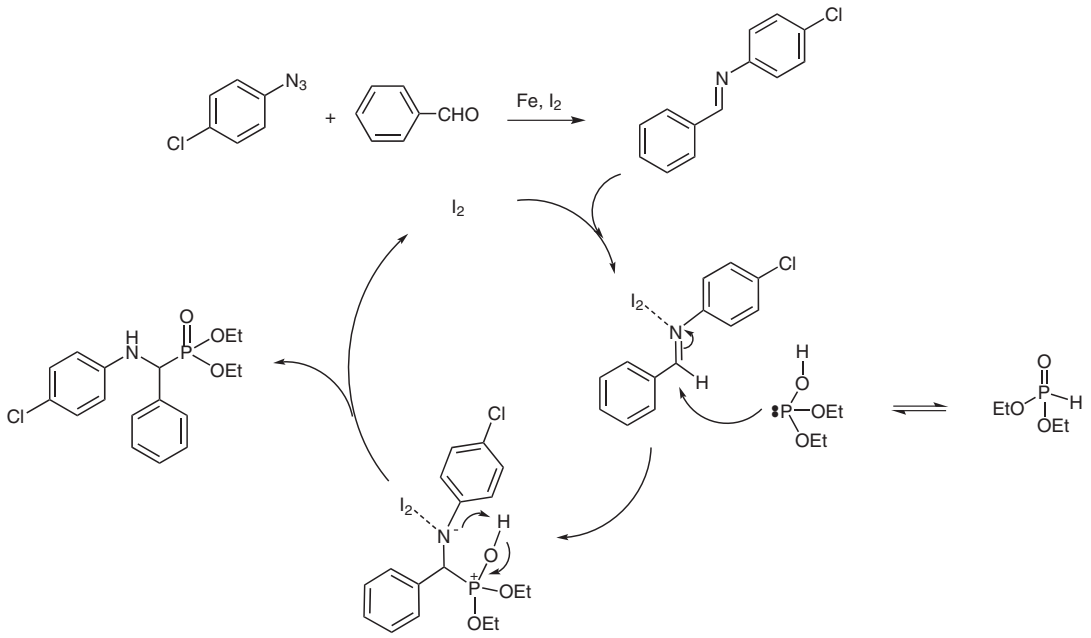
All products were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, IR, and mass spectral data. Known compounds were found to be identical with those described in the literature and only NMR data are given (see Supporting Information); complete spectroscopic data are given for new compounds.

Diethyl (4-Nitrophenyl)(4-tolylamino)methylphosphonate (4j)

Yellow solid; yield: 261 mg (69%); mp 157–158 °C.

IR (KBr): 3308 (NH), 2986, 1613, 1518, 1344, 1297, 1243 (P=O), 1210, 1059, 1032 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, J = 7.2 Hz, 3 H, CH_3), 1.29 (t, J = 7.2 Hz, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 3.87–4.16 (m, 4 H,



Scheme 3 Plausible mechanism

CH_2), 4.83 (d, J = 25.2 Hz, 1 H, CH), 6.44 (d, J = 8.4 Hz, 2 H, H_{Ar}), 6.91 (d, J = 8.0 Hz, 2 H, H_{Ar}), 7.63–7.66 (m, 2 H, H_{Ar}), 8.18 (d, J = 8.4 Hz, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.45, 16.62, 20.56, 56.53, 63.63, 63.95, 114.17, 123.95, 128.89, 130.06, 143.39, 143.53, 144.42, 147.80.

^{31}P NMR (200 MHz, $CDCl_3$): δ = 22.00.

MS: m/z = 397.2 (M^+).

Anal. Calcd for $C_{18}H_{23}N_2O_5P$: C, 57.14; H, 6.13; N, 7.40. Found: C, 57.21; H, 6.02; N, 7.49.

Diethyl 1-(4-Chlorophenylamino)-2-methylpropylphosphonate (4q)
White solid; yield: 154 mg (48%); mp 89–90 °C.

IR (KBr): 3312 (NH), 2985, 2934, 2906, 1601, 1530, 1494, 1325, 1287, 1227 (P=O), 1047, 1012 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06–1.32 (m, 12 H, CH_3), 2.23–2.30 (m, 1 H, $CHCH_3$), 3.58 (d, J = 9.1 Hz, 1 H, P-CH), 4.08–4.14 (m, 4 H, CH_2), 6.58 (d, J = 8.7 Hz, 2 H, H_{Ar}), 7.10 (d, J = 8.7 Hz, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.44, 17.97, 20.68, 29.85, 56.50, 61.86, 62.60, 114.33, 122.34, 129.07, 146.53.

^{31}P NMR (200 MHz, $CDCl_3$): δ = 25.18.

MS: m/z = 320.9 (M^+).

Anal. Calcd for $C_{14}H_{23}ClNO_3P$: C, 52.59; H, 7.25; N, 4.38. Found: C, 52.71; H, 7.31; N, 4.23.

Diethyl 1-(4-Chlorophenylamino)cyclohexylphosphonate (4r)
White solid; yield: 149 mg (43%); mp 136–137 °C.

IR (KBr): 3311 (NH), 2985, 2943, 1617, 1539, 1513, 1455, 1396, 1322, 1220 (P=O), 1021 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, J = 6.9 Hz, 6 H, CH_3), 1.43–1.60 (m, 6 H, CH_2), 2.14–2.19 (m, 4 H, CCH_2), 4.02–4.09 (m, 4 H, OCH_2), 6.99 (d, J = 8.7 Hz, 2 H, H_{Ar}), 7.11 (d, J = 8.7 Hz, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.60, 19.87, 20.15, 25.26, 30.11, 30.33, 56.95, 62.31, 119.62, 124.26, 128.60, 144.64.

^{31}P NMR (200 MHz, $CDCl_3$): δ = 27.45.

MS: m/z = 347.4 (M^+).

Anal. Calcd for $C_{16}H_{25}ClNO_3P$: C, 55.57; H, 7.29; N, 4.05. Found: C, 55.64; H, 7.10; N, 4.11.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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