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α-Aminophosphonates and α-Aminophosphine Oxides by the Microwave-Assisted Kabachnik–Fields Reactions of 3-Amino-6-methyl-2 *H*-pyran-2-ones

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ABSTRACT: *The microwave-assisted Kabachnik–Fields reaction of a series of 3-amino-6-methyl-2H-pyran-2-ones, paraformaldehyde, and dialkyl phosphites or diphenylphosphine oxide led to α-aminophosphonates or α-aminophosphine oxides, respectively. The α–aminophosphonates were obtained under solvent-free conditions, whereas the α–aminophosphine oxides in acetonitrile. The novel products were characterized by NMR and mass spectral data.* © 2013 Wiley Periodicals, Inc. Heteroatom Chem. 24:221–225, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21086

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INTRODUCTION

The most convenient and widespread method for the synthesis of α-aminophosphonates involves the condensation of a primary or secondary amine with an aldehyde or ketone and a dialkyl phosphite [1–5]. This evergreen reaction leads to α-aminophosphonates that are of real or potential bioactivity [6–8].

The senior author of this article suggested that, under microwave (MW) conditions, there is no need to use environmentally unfriendly catalysts [9]. The Kabachnik–Fields (phospha-Mannich) condensation was extended to heterocyclic amines [10] and heterocyclic >P(O)H species [11]. Bis Kabachnik–Fields reactions were also elaborated [12, 13], and

the resulting bis(phosphinoxidomethyl)amines were used in the synthesis of ring platinum complexes after double deoxygenation [13, 14].

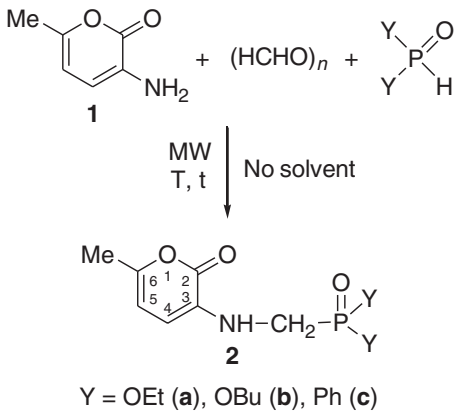
In the continuation, we wished to use 3-amino-6-methyl-2*H*-pyran-2-ones as the starting materials in the phospha-Mannich condensations. 2*H*-Pyran-2-ones and their fused derivatives represent structural units of a wider range of natural products, their synthetic analogues, and many other compounds [15–19]. Furthermore, they are also very important synthons and building blocks in organic synthesis and have found a variety of synthetic applications: in reactions with electrophiles and nucleophiles, as diene components in the Diels–Alder reactions, in photochemical reactions, etc. [20–29].

RESULTS AND DISCUSSION

The starting materials **1** [30], **3**, and **4** [31] were prepared as described earlier.

Kabachnik–Fields Reaction of 3-Amino-6-methyl-2H-pyran-2-one Formaldehyde and >P(O)H Reactants under MW Conditions

In the first approach, the 5-unsubstituted 3-amino-6-methyl-2*H*-pyran-2-one (**1**) was reacted with an equivalent amount of paraformaldehyde and dialkyl (diethyl or dibutyl) phosphites or diphenylphosphine oxide to afford the phosphonomethyl- or phosphinoylmethyl derivatives **2a**/**2b** and **2c**, respectively (Scheme 1 and Table 1). The phosphinoylmethylation required somewhat milder conditions, although it had to be carried out in acetonitrile as the solvent due to the heterogenity. The other reactions did not require the use of solvent. Products **2a–c** were obtained in 74–98% yields after chromatography.

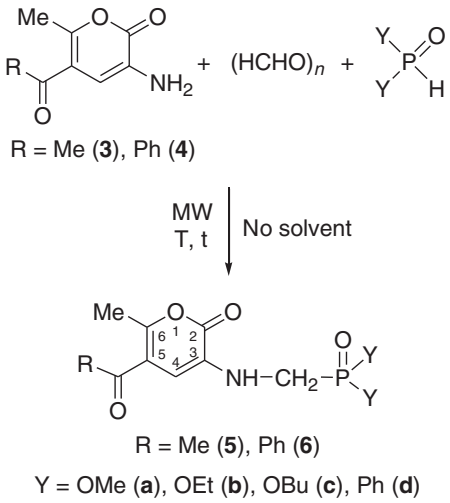


SCHEME 1

TABLE 1 Condensations with 3-Amino-6-methyl-2*H*-pyran-2-one (**1**)

Entry	*Y*	*T (°C)*	*t (h)*	*Yield (%)*
1	OEt	120	2.5	74 (**2a**)
2	OBu	120	2.5	88 (**2b**)
3[a]	Ph	100	3	98 (**2c**)

[a]In acetonitrile.



SCHEME 2

Kabachnik–Fields Reaction of 5-Acetyl-3-amino-6-methyl-2H-pyran-2-one and 3-Amino-5-benzoyl-6-methyl-2H-pyran-2-one Under MW Conditions

The Kabachnik–Fields condensations were extended to the 5-acyl-substituted 3-amino-2*H*-pyran-2-ones (**3** and **4**), as well. Reactions of the 5-acetyl starting material (**3**) with paraformaldehyde and dialkyl phosphites or diphenylphosphine oxide provided products **5a–-c** and **5d**, respectively. The similar reaction of the 5-benzoyl starting material furnished products **6a** and **6d** (Scheme 2 and Table 2). The phosphonomethyl products (**5a–c** and **6a**) were obtained without the use of any solvent, whereas the phosphinoxidomethyl derivatives (**5d** and **6d**) had

TABLE 2 Condensations with 5-Keto-3-amino-6-methyl-2*H*-pyran-2-ones **3** and **4**

Entry	*R*	*Y*	*T (°C)*	*t (h)*	*Yield (%)*
1	Me	OMe	120	1.5	90 (**5a**)
2	Me	OEt	120	2	74 (**5b**)
3	Me	OBu	120	2	91 (**5c**)
4[a]	Me	Ph	100	2	98 (**5d**)
5	Ph	OEt	120	4	61 (**6a**)
6[a]	Ph	Ph	100	2	97 (**6d**)

[a]In acetonitrile.

to be prepared in acetonitrile solution. After chromatography, the yields remain within the range of 61–98%.

Products **2a–c**, **5a–d**, **6a**, **6d**, **7**, and **8** were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as high-resolution mass spectral data.

We tried to prepare bis(phospha-Mannich adducts) by applying the formaldehyde and the >P(O)H species in twofold quantities, but we failed. When α-aminophosphonate **2a** was further attempted to react in the Kabachnik–Fields reaction, it also remained unsuccessful.

Comparative Thermal Experiments

To evaluate the potential of MW irradiation, comparative thermal experiments were also carried out in a few cases. Hence, the experiments presented in Table 1, entry 1, Table 2, entry 2, and Table 2, entry 5 were repeated under conventional heating at 120°C for 2.5, 2 and 4 h, respectively. The corresponding products **2a**, **5b**, and **6a** were obtained in yields of 49%, 51%, and 38%, respectively. The 23–25% lower yields of the thermal control experiments indicate the advantage of the MW technique regarding efficiency.

In summary, nine new *N*-(2*H*-pyranonyl)-α-aminophosphonates or -α-aminophosphine oxides were synthesized under MW conditions, in most cases under solvent-free conditions.

EXPERIMENTAL

General

^{31}P, ^{13}C, and ^{1}H NMR spectra were obtained in $CDCl_3$ solution on a Bruker AV-300 spectrometer operating at 121.5, 75.5, and 300 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 and TMS. Mass spectra were obtained using a Q-TOF Premier mass spectrometer in positive electrospray mode. The reactions were carried out in a 300 W CEM Discover (CEM Microwave Technology Ltd., Buckingham, UK) focused microwave reactor equipped with a pressure controller applying 50–80 W under isothermal conditions.

General Procedure for the Preparation of Dialkyl [(2-Oxo-2H-pyran-3-yl)amino]-methylphosphonates and 3-[(Diphenylphosphinoyl)methylamino]-2H-pyran-2-ones

A mixture of 0.25 mmol of the pyran-2-one derivative (0.031 g of **1**, 0.042 g of **3** or 0.057 g of **4**), 0.25 mmol (0.0075 g) of paraformaldehyde, and 0.25 mmol of the >P(O)H species (0.023 mL of dimethyl phosphite, 0.0325 mL of diethyl phosphite, 0.0488 mL of dibutyl phosphite, or 0.05 g of diphenylphosphine oxide) was heated at 120°C in a closed vial in a CEM Discover microwave reactor equipped with a pressure controller for 1.5–2 h. The reaction with diphenylphosphine oxide was carried out in 1.5 mL of acetonitrile. The water formed was removed in vacuum. Column chromatography (silica gel, 3% methanol in dichloromethane) of the residue afforded the products (**2a–c**, **5a–d**, and **6a**, **6d**) as oils. The following products were thus prepared.

*Diethyl [(6-Methyl-2-oxo-2H-pyran-3-yl)amino] methylphosphonate (**2a**).* Yield 74%; ^{31}P NMR δ: ($CDCl_3$) 22.5; ^{13}C NMR ($CDCl_3$) δ: 16.5 (J = 5.6, CH_2CH_3), 18.8 (C_6—CH_3), 39.6 (J = 158.8, CH_2P), 62.6 (J = 6.8, OCH_2), 103.6 (C_5), 108.4 (J = 1.8, C_4), 131.7 (J = 7.7, C_3), 148.9 (C_6), 160.9 (C=O); ^{1}H NMR ($CDCl_3$) δ: 1.33 (t, J = 7.1, 6H, CH_2CH_3), 2.17 (s, 1H, NH), 2.17 (s, 3H, C_6—CH_3), 3.39 (d, J = 6.0) and 3.43 (d, J = 6.0) (2H, CH_2), 4.07–4.23 (m, 4H, OCH_2), 5.89 (d, J = 7.1, 1H, C_5H),* 6.11 (d, J = 7.1, 1H, C_4H),* *may be reversed; $[M + H]^+_{found}$ = 276.1004, $C_{11}H_{19}NO_5P$ requires 276.1001; $[M + Na]^+_{found}$ = 298.0824, $C_{11}H_{18}NO_5NaP$ requires 298.0820.

*Dibutyl [(6-Methyl-2-oxo-2H-pyran-3-yl)amino] methylphosphonate (**2b**).* Yield 88%; ^{31}P NMR δ: ($CDCl_3$) 22.5; ^{13}C NMR ($CDCl_3$) δ: 13.6 ($CH_3(CH_2)_3$), 18.7 ($CH_3CH_2CH_2$), 18.8 (C_6—CH_3), 32.5 (J = 5.7, CH_2CH_2O), 39.5 (J = 158.6, CH_2P), 66.3 (J = 7.0, OCH_2), 103.6 (C_5), 108.3 (J = 1.8, C_4), 131.7 (J = 7.3, C_3), 148.9 (C_6), 160.9 (C=O); ^{1}H NMR ($CDCl_3$) δ: 0.92 (t, J = 7.3, 6H, $CH_3(CH_2)_3$), 1.30–1.46 (m, 4H, CH_2), 1.55–1.72 (m, 4H, CH_2), 2.17 (s, 3H, C_6—CH_3), 2.19 (s, 1H, NH), 3.39 (d, J = 6.0) and 3.43 (d, J = 6.0) (2H, CH_2P), 3.99–4.17 (m, 4H, OCH_2), 5.89 (d, J = 7.1, 1H, C_5H),* 6.10 (d, J = 7.1, 1H, C_4H),* *may be reversed; $[M + H]^+_{found}$ = 332.1633, $C_{15}H_{27}NO_5P$ requires 332.1627; $[M + Na]^+_{found}$ = 354.1451, $C_{15}H_{26}NO_5NaP$ requires 354.1446.

*3-[(Diphenylphosphinoyl)methylamino]-6-methyl-2H-pyran-2-one (**2c**).* Yield 98%; ^{31}P NMR δ: ($CDCl_3$) 30.0; ^{13}C NMR ($CDCl_3$) δ: 18.9 (C_6—CH_3), 44.2 (J = 79.4, CH_2P), 103.8 (C_5), 109.3 (C_4), 129.0 (J = 11.8, $C_{2'}$),* 130.7 (J = 99.1, $C_{1'}$), 131.3 (J = 9.3, $C_{3'}$),* 131.9 (J = 6.5, C_3), 132.6 (J = 2.7, $C_{4'}$), 149.2 (C_6), 160.9 (C=O), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 1.95 (s, 1H, NH), 2.09 (s, 3H, C_6—CH_3), 3.88 (d, J = 7.5, 2H, PCH_2), 5.78 (d, J = 7.2, 1H, C_5H),* 6.13 (d, J = 7.2, 1H, C_4H),* 7.39–7.81 (m, 10H, ArH), *may be reversed; $[M + H]^+_{found}$ = 340.1107,

$C_{19}H_{19}NO_3P$ requires 340.1103; $[M + Na]^+_{found}$ = 362.0926, $C_{19}H_{18}NO_3NaP$ requires 362.0922.

*Dimethyl [(5-Acetyl-6-methyl-2-oxo-2H-pyran-3-yl)amino]methylphosphonate (***5a***).* Yield 90%; ^{31}P NMR δ: ($CDCl_3$) 22.3; ^{13}C NMR ($CDCl_3$) δ: 19.6 (C_6—*C*H_3), 29.9 (*C*H_3C=O), 39.2 (J = 159.9, CH_2), 53.5 (J = 6.8, OCH_3), 107.7 (J = 2.0, C_4), 117.6 (C_5), 131.1 (J = 6.5, C_3), 155.8 (C_2=O),* 159.3 (C_6),* 196.5 (C=O), *may be reversed; ^1H NMR ($CDCl_3$) δ: 1.25 (s, 1H, NH), 2.47 (s, 3H, CH_3C=O),* 2.51 (s, 3H, C_6—CH_3),* 3.50 (d, J = 6.1) and 3.54 (d, J = 6.1) (2H, CH_2), 3.81 (d, J = 6.1, 6H, OCH_3), 6.55 (s, 1H, C_4H), *may be reversed; $[M + Na]^+_{found}$ = 312.0612, $C_{11}H_{16}NO_6NaP$ requires 312.0613.

*Diethyl [(5-Acetyl-6-methyl-2-oxo-2H-pyran-3-yl)amino]methylphosphonate (***5b***).* Yield 74%; ^{31}P NMR δ: ($CDCl_3$) 20.9; ^{13}C NMR ($CDCl_3$) δ: 16.6 (J = 5.6, CH_2*C*H_3), 19.4 (C_6=*C*H_3), 29.7 (*C*H_3C=O), 39.7 (J = 159.0, CH_2), 62.8 (J = 6.7, OCH_2), 107.4 (J = 1.9, C_4), 117.4 (C_5), 131.1 (J = 6.5, C_3), 155.5 (C_2=O),* 159.1 (C_6),* 196.4 (C=O), *may be reversed; ^1H NMR ($CDCl_3$) δ: 1.26 (s, 1H, NH), 1.35 (t, J = 7.0, 6H, CH_2C*H*$_3$), 2.48 (s, 3H, CH_3C=O),* 2.52 (s, 3H, C_6—CH_3),* 3.48 (d, J = 5.0) and 3.50 (d, J = 5.1) (2H, CH_2), 4.08–4.24 (m, 4H, OCH_2), 6.58 (s, 1H, C_4H), *may be reversed; $[M + H]^+_{found}$ = 318.1111, $C_{13}H_{21}NO_6P$ requires 318.1107; $[M + Na]^+_{found}$ = 340.0930, $C_{13}H_{20}NO_6NaP$ requires 340.0926.

*Dibutyl [(5-Acetyl-6-methyl-2-oxo-2H-pyran-3-yl)amino]methylphosphonate (***5c***).* Yield 91%; ^{31}P NMR δ: ($CDCl_3$) 22.1; ^{13}C NMR ($CDCl_3$) δ: 13.6 (*C*H_3(CH_2)$_3$), 18.7 (CH_3*C*H_2CH_2), 19.4 (C_6—*C*H_3), 29.6 (*C*H_3C=O), 32.6 (J = 5.7, *C*H_2CH_2O), 39.5 (J = 159.4, CH_2), 66.5 (J = 6.9, OCH_2), 107.3 (J = 1.9, C_4), 117.3 (C_5), 131.0 (J = 7.1, C_3), 155.4 (C_2=O),* 159.1 (C_6),* 196.3 (C=O), *may be reversed; ^1H NMR ($CDCl_3$) δ: 0.93 (t, J = 7.3, 6H, C*H*$_3$(CH_2)$_3$), 1.32–1.47 (m, 4H, CH_2), 1.55–1.72 (m, 4H, CH_2), 2.17 (s, 1H, NH), 2.47 (s, 3H, CH_3C=O),* 2.52 (s, 3H, C_6—CH_3),* 3.46 (d, J = 6.2) and 3.51 (d, J = 6.2) (2H, CH_2P), 4.05–-4.15 (m, 4H, OCH_2), 6.54 (s, 1H, C_4H), *may be reversed; $[M + H]^+_{found}$ = 374.1734, $C_{17}H_{29}NO_6P$ requires 374.1733; $[M + Na]^+_{found}$ = 396.1550, $C_{17}H_{28}NO_6NaP$ requires 396.1552.

*5-Acetyl-3-[(diphenylphosphinoyl)methylamino]-6-methyl-2H-pyran-2-one (***5d***).* Yield 98%; ^{31}P NMR δ: ($CDCl_3$) 28.2; ^{13}C NMR ($CDCl_3$) δ: 19.4 (C_6—CH_3), 29.7 (*C*H_3C=O), 44.2 (J = 78.6, CH_2), 108.0 (C_4), 117.4 (C_5), 129.0 (J = 11.8, $C_{2'}$),[a] 130.6 (J = 99.3, $C_{1'}$), 131.2 (J = 9.4, $C_{3'}$),[a] 132.67 ($C_{4'}$), 132.70 (C_3), 155.7 (C_2=O),[b] 159.0 (C_6),[b] 196.4 (C=O), [a,b]may be reversed; ^1H NMR ($CDCl_3$) δ: 1.78 (s, 1H, NH), 2.43 (s, 3H, CH_3C=O),* 2.48 (s, 3H, C_6—CH_3),* 3.96 (d, J = 6.6) and 3.98 (d, J = 6.5) (2H, CH_2), 6.60 (s, 1H, C_4H), 7.45–7.84 (m, 10H, ArH), *may be reversed; $[M + H]^+_{found}$ = 382.1219, $C_{21}H_{21}NO_4P$ requires 382.1208; $[M + Na]^+_{found}$ = 404.1039, $C_{21}H_{20}NO_4NaP$ requires 404.1028.

*Diethyl [(5-Benzoyl-6-methyl-2-oxo-2H-pyran-3-yl)amino]methylphosphonate (***6a***).* Yield 61%; ^{31}P NMR δ: ($CDCl_3$) 22.1; ^{13}C NMR ($CDCl_3$) δ: 16.5 (J = 5.8, CH_2*C*H_3), 18.5 (C_6—*C*H_3), 39.6 (J = 158.7, CH_2), 62.7 (J = 6.9, OCH_2), 107.9 (J = 1.9, C_4), 117.3 (C_5), 128.8 ($C_{2''}$),[a] 129.6 ($C_{3''}$),[a] 133.0 (C_3), 133.5 ($C_{4''}$), 152.4 (C_2=O),[b] 159.4 (C_6),[b] 194.0 (C=O), [a,b]may be reversed; ^1H NMR ($CDCl_3$) δ: 1.33 (t, J = 7.0, 6H, CH_2C*H*$_3$), 1.71 (s, 1H, NH), 2.17 (s, 3H, C_6—CH_3), 3.36 (d, J = 6.0) and 3.41 (d, J = 6.0) (2H, CH_2), 4.09–4.21 (m, 4H, OCH_2), 6.20 (s, 1H, C_4H), 7.44–7.85 (m, 5H, ArH); $[M + H]^+_{found}$ = 380.1266, $C_{18}H_{23}NO_6P$ requires 380.1263; $[M + Na]^+_{found}$ = 402.1088, $C_{18}H_{22}NO_6NaP$ requires 402.1082.

*5-Benzoyl-3-[(diphenylphosphinoyl)methylamino]-6-methyl-2H-pyran-2-one (***6d***).* Yield 97%; ^{31}P NMR δ: ($CDCl_3$) 27.6; ^{13}C NMR ($CDCl_3$) δ: 18.6 (C_6—*C*H_3), 43.5 (J = 77.8, CH_2), 108.3 (C_4), 117.3 (C_5), 128.9 ($C_{2''}$),[a] 129.0 (J = 11.8, $C_{2'}$),[b] 129.6 ($C_{3''}$),[a] 131.2 (J = 9.3, $C_{3'}$)[b], 132.66 ($C_{4'}$), 132.70 (C_3), 133.5 ($C_{4''}$), 152.7 (C_2=O),[c] 159.3 (C_6),[c] 194.0 (C=O), [a–c]may be reversed; ^1H NMR ($CDCl_3$) δ: 1.71 (s, 1H, NH), 2.16 (s, 3H, C_6—CH_3), 3.83 (d, J = 6.9) and 3.85 (d, J = 7.0) (2H, CH_2), 6.16 (s, 1H, C_4H), 7.43–7.82 (m, 15H, ArH); $[M + H]^+_{found}$ = 444.1366, $C_{26}H_{23}NO_4P$ requires 444.1365; $[M + Na]^+_{found}$ = 466.1184, $C_{26}H_{22}NO_4NaP$ requires 466.1184.

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