Potassium Phosphate Promoted Aza-Markovnikov Addition of N-Heterocycles to Vinyl Esters

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Abstract: Anhydrous potassium phosphate promoted the aza-Markovnikov addition of a variety of N-heterocycles to vinyl esters in DMF at room temperature in moderate to excellent yields.

Key words: aza-Markovnikov addition, anhydrous K_3PO_4, N-heterocycles, vinyl esters, 1-[*N*-(N-heterocycle)]alkyl esters

As a subset of heterocyclic compounds, 1-[*N*-(N-heterocycle)]alkyl esters possess valuable biological activities and can act as, amongst others, acaricides (A),[1a,b] antimicrobials (B),[1c] antitumor drugs (C)[1d] and (H^+-K^+)-ATPase inhibitors (D)[1e] (Figure 1). Their preparation is usually through the nucleophilic substitution of N-heterocycles to 1-haloalkyl esters and acetals,[1c–e,2] acylation of *N*-hydroxyalkyl heterocycles,[1e,2b,3] reaction of *N*-acyl heterocycles with aldehydes,[4] and aza-Markovnikov addition of N-heterocycles to vinyl esters.[5] Among these approaches, aza-Markovnikov addition of N-heterocycles to vinyl esters has recently received much attention. Such aza-Markovnikov additions were traditionally performed under harsh reaction conditions in which bases, acids and strong heating were usually used to promote the reaction. In order to avoid these disadvantages, Lin and co-workers developed two effective methods, one was the use of ionic liquid as a catalyst and reaction medium,[6] and the second was the use of acylases as biocatalysts.[7] Nevertheless, a mild and more general method for performing such aza-Markovnikov additions was still desirable.

Over the past few years, anhydrous potassium phosphate (K_3PO_4) has been widely used as mild base in reactions such as Suzuki cross-coupling,[8] transition metal catalyzed C–N coupling[9] and oxidative coupling of thiols to disulfides.[10] Using anhydrous K_3PO_4 as base, our group has successfully carried out the syntheses of tetra-*O*-acetylglycosides,[11] dithiocarbamates,[12] thiazolidines[13,14] and 1,3,4-thiadiazoles.[14] Here, as an extension of this work, we would like to report a mild and efficient anhydrous K_3PO_4-promoted aza-Markovnikov addition of N-heterocycles to vinyl esters.

Initially, we evaluated the feasibility of aza-Markovnikov addition of 2-methyl-5-nitroimidazole (**1a**, 1 mmol) to vinyl acetate (**2a**, 4 mmol), in the presence of anhydrous K_3PO_4 (0.3 mmol), in acetone as solvent, at room temperature, and found that the expected compound **3a** was formed in 84% yield.

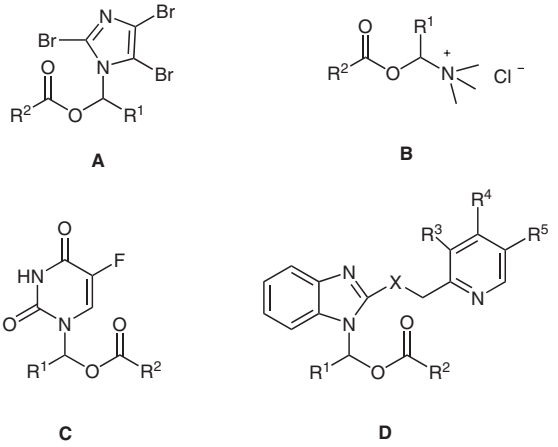
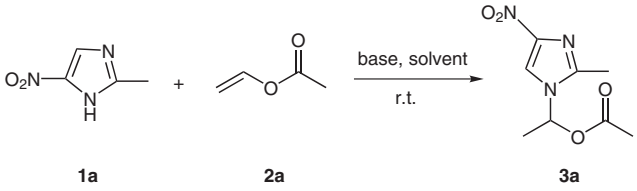


Figure 1



Scheme 1

Encouraged by this result, we then employed this reaction as a template with which to optimize the reaction conditions (Scheme 1). Firstly, the reaction was performed in a range of solvents such as acetone, methanol, chloroform and dimethylformamide (Table 1, entries 1–4), with the latter being found to be best in terms of both yield and reaction time (95%, 10 h). Six weak bases were then examined using DMF as solvent (Table 1, entries 4–9). Comparing the results, anhydrous K_3PO_4 was found to be the most efficient base, giving the product **3a** in 95% yield. Other weak inorganic bases, such as K_2HPO_4, K_2CO_3, $KHCO_3$, afforded lower yields even with longer reaction times, while KH_2PO_4 and the organic base Et_3N, gave only a trace of product. Upon examining the influence of the amount of anhydrous K_3PO_4 on the reaction, it

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Table 1 Markovnikov Addition of 2-Methyl-5-nitroimidazole (**1a**) to Vinyl Acetate (**2a**)[a]

Entry	Solvent	Base	Time (h)	**1a**:**2a**:base (equiv)	Yield (%)[b]
1	Acetone	K_3PO_4	72	1:4:0.3	84
2	MeOH	K_3PO_4	30	1:4:0.3	56
3	$CHCl_3$	K_3PO_4	30	1:4:0.3	38
4	DMF	K_3PO_4	10	1:4:0.3	95
5	DMF	K_2HPO_4	48	1:4:0.3	78
6	DMF	KH_2PO_4	48	1:4:0.3	trace
7	DMF	K_2CO_3	36	1:4:0.3	94
8	DMF	$KHCO_3$	48	1:4:0.3	80
9	DMF	Et_3N	48	1:4:0.3	trace
10	DMF	K_3PO_4	30	1:4:0.2	85
11	DMF	K_3PO_4	10	1:4:0.5	94
12	DMF	K_3PO_4	10	1:4:1	91
13	DMF	K_3PO_4	20	1:3:0.3	89
14	DMF	K_3PO_4	48	1:2:0.3	84
15	DMF	K_3PO_4	60	1:1:0.3	75

[a] All reactions were run at r.t. using **1a** (1.0 mmol) in the indicated solvent (2 mL).
[b] Isolated yields.

was found that 0.3 equivalent of anhydrous K_3PO_4 was sufficient to promote the reaction. In the presence of less than this amount, the yield dropped dramatically, even if longer reaction times were used (Table 1, entry 10). When the amount of anhydrous K_3PO_4 was increased over 0.3 equivalent, however, neither the yield nor the reaction time was improved (Table 1, entries 11 and 12). Finally, the influence of the amount of vinyl acetate relative to 2-methyl-5-nitroimidazole was investigated. The best result was obtained when a 4:1 equivalent of the former to the latter was used (Table 1, entries 13–15 vs. entry 4).

With optimized experimental conditions in hand, we proceeded to investigate the substrate generality of the reaction system; the results are summarized in Table 2. A variety of N-heterocycles, such as imidazoles, pyrrole, 1,2,4-triazole, benzotriazole and benzimidazole, reacted smoothly with vinyl acetate at room temperature, to afford the corresponding Markovnikov adducts in good to excellent yields. Even 1*H*-imidazole-4-carbaldehyde, with an oxidant-sensitive formyl group (entry 5, 90%) and methyl 3-(1*H*-imidazol-4-yl) acrylate, with both a base/acid-sensitive ester group and an oxidant-sensitive C=C bond, gave excellent yields of product (entry 6, 94%). Benzotriazole provided the N-1 adduct (**3i-1**, 78%) and the N-2 adduct (**3i-2**, 17%) with a total yield of 95%. It is noteworthy that this is the first time benzotriazole has been successfully used as a donor in Markovnikov addition to vinyl esters.[15] Furthermore, 5-fluorouracil acted as a novel donor for Markovnikov addition, to give a moderate yield (51%) of **3k** at 50 °C in 24 hours (Table 2, entry 11), which constitutes a significant improvement over the best literature results, i.e. using the ionic liquid method[6a] (35% yield) or the biocatalytic method (24%).[7c] In addition to the various heterocycle donors, we also investigated the Markovnikov additions of 2-methyl-5-nitroimidazole to representative vinyl esters. Compared with vinyl acetate, excellent yields were also obtained for vinyl butyrate (entry 12, 94%, 30 h) and vinyl benzoate (entry 13, 93%, 30 h) by prolonging the reaction time and/or raising the reaction temperature, though their reactivity was lower than that of vinyl acetate.

On the basis of the experimental results, a possible mechanism for the formation of compounds **3** is proposed in Scheme 2. The N-heterocycle anion (Nu^-), formed from N-heterocycle **1** through the action of K_3PO_4, could react with vinyl ester **2**, affording the *N*-acyl heterocycle **4** and acetaldehyde (**5**). Acetaldehyde (**5**) would then be attacked by Nu^- to form the hemiaminal **6**. The target products **3** would be generated from the reaction of **6** with the formerly formed *N*-acyl heterocycle **4**.

Table 2 Markovnikov Addition of N-Heterocycles to Vinyl Esters Promoted by Anhydrous K_3PO_4 in DMF[a]

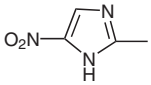
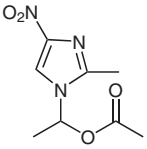
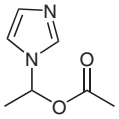
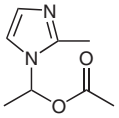
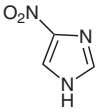
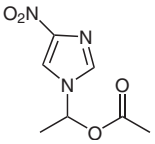
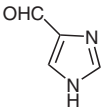
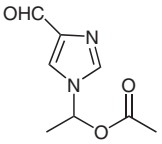
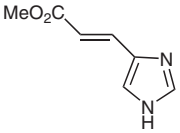
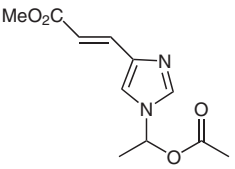
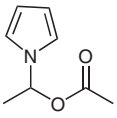
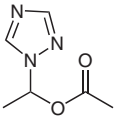
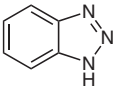
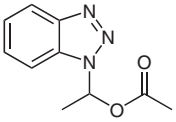
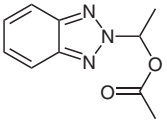
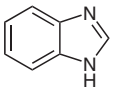
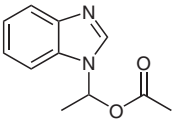
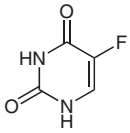
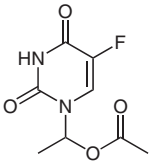
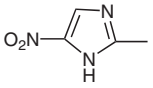
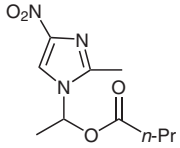
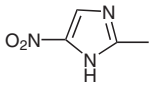
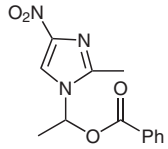
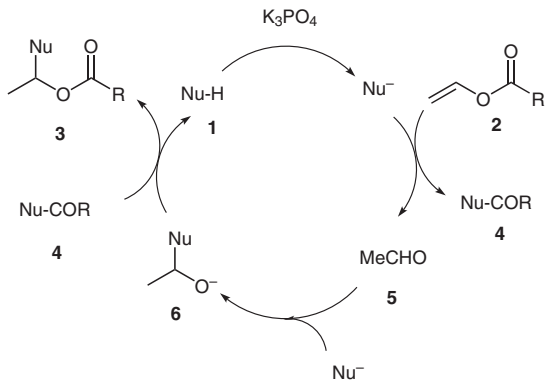
Entry	Nu-H	R	Product		Time (h)	Yield (%)[b]
1		Me		**3a**	10	95
2		Me		**3b**	24	88
3		Me		**3c**	24	82
4		Me		**3d**	10	97
5		Me		**3e**	10	90
6		Me		**3f**	10	94
7		Me		**3g**	24	78
8		Me		**3h**	10	97
9[c]		Me	 	**3i-1** **3i-2**	10	78 17
10		Me		**3j**	10	79
11[d]		Me		**3k**	24	51

Table 2 Markovnikov Addition of N-Heterocycles to Vinyl Esters Promoted by Anhydrous K_3PO_4 in DMF[a] (continued)

Entry	Nu-H	R	Product		Time (h)	Yield (%)[b]
12		*n*-Pr		**3l**	30	94
13[d]		Ph		**3m**	30	93

[a] Reactions were carried out at r.t. on 1.0 mmol scale of N-heterocycles with vinyl esters (4 equiv) and anhyd K_3PO_4 (0.3 equiv) in DMF (2 mL).
[b] Isolated yields.
[c] **3i-1** was the N-1 adduct formed with a yield of 78%, while **3i-2** was the N-2 adduct formed with a yield of 17%.
[d] Reaction was performed at 50 °C.

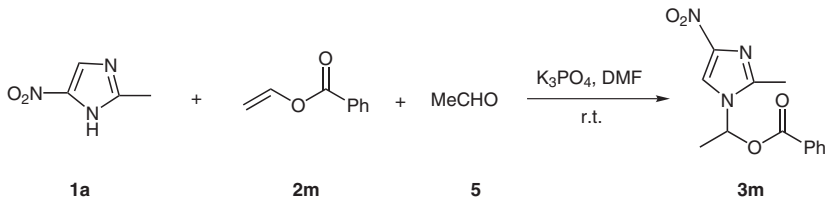


Scheme 2

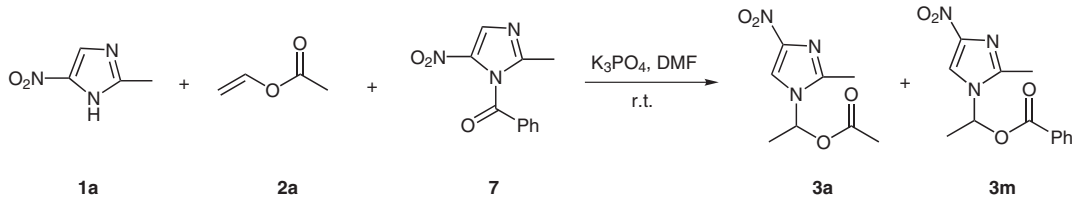
If this mechanism were reasonable, addition of excess acetaldehyde would be expected to accelerate the rate of reaction. Hence, we selected the reaction of 2-methyl-5-nitroimidazole with vinyl benzoate at room temperature in order to examine the influence of acetaldehyde on the reaction rate and yield (Scheme 3). It was found that **3m** was obtained with yields of 59% (48 h), 93% (48 h) and 92% (20 h) in the presence of 1, 2 and 4 equivalents of acetaldehyde, respectively. These results demonstrate that acetaldehyde must form as an intermediate during the reaction.

In addition, in order to clarify whether the hemiaminal intermediate **6** preferentially attacked the *N*-acyl heterocycle **4** in the process of reaction, we mixed **1a**, **2a** and **7** with an equivalent ratio of 1:4:1 in DMF at room temperature and monitored the reaction by TLC (Scheme 4). It was found that **3m** was the major product, with only a trace of **3a** being detected before 10 hours. After about 10 hours, the amount of reagent **7** began to decrease and the amount of **3a** began to increase. These results indicate that the acyl group of product **3** comes from the *N*-acyl heterocycle **4**, rather than from the vinyl ester.

In summary, we have developed an anhydrous K_3PO_4-promoted aza-Markovnikov addition of a variety of N-heterocycles to vinyl esters. This procedure offers several advantages including mild condition, high yields, inexpensive catalyst, wide scope of substrates and operational simplicity.



Scheme 3



Scheme 4

All reagents and solvents were obtained from commercial sources. Melting points were determined on a X4 microscope. IR spectra were recorded on a NEXUS-470 FTIR spectrophotometer. ^{1}H NMR was performed on a VXR 300 (300 MHz) instrument. Elemental analyses were performed on a Vario EL III (Germany).

aza-Markovnikov Addition; General Procedure

A mixture of N-heterocycle (1 mmol), vinyl ester (4 mmol) and anhyd K_3PO_4 (64 mg, 0.3 mmol) in DMF (2 mL) was stirred at r.t. for the time indicated in Table 2. H_2O (20 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with sat. NaCl (20 mL), dried over anhyd $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography [silica gel; EtOAc–PE (60–90 °C)] to provide the desired product **3** (Table 2).

1-(2-Methyl-4-nitro-1*H*-imidazol-1-yl)ethyl Acetate (3a)

Colorless solid; mp 138–139 °C.

IR (KBr): 3144, 1754, 1546, 1501 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.76 (d, *J* = 6.3 Hz, 3 H), 2.10 (s, 3 H), 2.53 (s, 3 H), 6.63 (q, *J* = 6.3 Hz, 1 H), 7.84 (s, 1 H).

Anal. Calcd for $C_8H_{11}N_3O_4$: C, 45.07; H, 5.20; N, 19.71. Found: C, 45.24; H, 5.37; N, 19.74.

1-(Imidazol-1-yl)ethyl Acetate (3b)[6a]

Yellow oil.

IR (film): 3116, 1746, 1495 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75 (d, *J* = 6.3 Hz, 3 H), 2.03 (s, 3 H), 6.69 (q, *J* = 6.3 Hz, 1 H), 7.06 (d, *J* = 1.5 Hz, 1 H), 7.11 (d, *J* = 1.5 Hz, 1 H), 7.72 (s, 1 H).

1-(2-Methyl-1*H*-imidazol-1-yl)ethyl Acetate (3c)[6a]

Yellow oil.

IR (film): 3111, 1744, 1535, 1500 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 (d, *J* = 6.3 Hz, 3 H), 2.06 (s, 3 H), 2.47 (s, 3 H), 6.66 (q, *J* = 6.3 Hz, 1 H), 6.94 (d, *J* = 1.5 Hz, 1 H), 7.02 (d, *J* = 1.5 Hz, 1 H).

1-(4-Nitro-1*H*-imidazol-1-yl)ethyl Acetate (3d)[6a]

Colorless solid; mp 83–84 °C (Lit.[6a] 82–83 °C).

IR (KBr): 3135, 1741, 1547, 1514 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86 (d, *J* = 6.3 Hz, 3 H), 2.11 (s, 3 H), 6.70 (q, *J* = 6.3 Hz, 1 H), 7.69 (d, *J* = 1.5 Hz, 1 H), 7.95 (d, *J* = 1.5 Hz, 1 H).

1-(4-Formyl-1*H*-imidazol-1-yl)ethyl Acetate (3e)

Yellow oil.

IR (film): 3121, 2830, 2755, 1750, 1691, 1538, 1498 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83 (d, *J* = 6.3 Hz, 3 H), 2.09 (s, 3 H), 6.72 (q, *J* = 6.3 Hz, 1 H), 7.83 (s, 2 H), 9.90 (s, 1 H).

Anal. Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.50; H, 5.57; N, 15.43.

Methyl 1-(1-Acetoxyethyl)-4-urocanoate (3f)

Yellow oil.

IR (film): 3127, 1747, 1711, 1642, 1535, 1496 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.80 (d, *J* = 6.3 Hz, 3 H), 2.06 (s, 3 H), 3.78 (s, 3 H), 6.58 (d, *J* = 15.6 Hz, 1 H), 6.67 (q, *J* = 6.3 Hz, 1 H), 7.30 (s, 1 H), 7.54 (d, *J* = 15.6 Hz, 1 H), 7.74 (s, 1 H).

Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.69; H, 5.88; N, 11.53.

1-(Pyrrol-1-yl)ethyl Acetate (3g)[6a]

Colorless oil.

IR (film): 3105, 1741, 1565, 1520 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.76 (d, *J* = 6.3 Hz, 3 H), 2.06 (s, 3 H), 6.19 (d, *J* = 2.3 Hz, 2 H), 6.66 (q, *J* = 6.3 Hz, 1 H), 6.89 (d, *J* = 2.3 Hz, 2 H).

1-(1,2,4-Triazol-1-yl)ethyl Acetate (3h)[6a]

Colorless oil.

IR (film): 3124, 3001, 1753, 1508 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.89 (d, *J* = 6.3 Hz, 3 H), 2.08 (s, 3 H), 6.86 (q, *J* = 6.3 Hz, 1 H), 7.98 (s, 1 H), 8.33 (s, 1 H).

1-(Benzotriazol-1-yl)ethyl Acetate (3i-1)

Colorless oil.

IR (film): 3091, 3029, 1753, 1610, 1590 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3 H), 2.12 (d, *J* = 6.3 Hz, 3 H), 7.40 (m, 2 H), 7.54 (m, 1 H), 7.75 (d, *J* = 8.1 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H).

Anal. Calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.48; H, 5.30; N, 20.28.

1-(Benzotriazol-2-yl)ethyl Acetate (3i-2)

Colorless oil.

IR (film): 3067, 3000, 1757, 1563, 1501 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04 (d, *J* = 6.2 Hz, 3 H), 2.12 (s, 3 H), 7.40 (m, 3 H), 7.89 (m, 2 H).

Anal. Calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.57; H, 5.60; N, 20.21.

1-(Benzimidazol-1-yl)ethyl Acetate (3j)

Colorless oil.

IR (film): 3090, 1748, 1614, 1495 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95 (d, *J* = 6.3 Hz, 3 H), 2.06 (s, 3 H), 7.04 (q, *J* = 6.3 Hz, 1 H), 7.32 (m, 2 H), 7.60 (m, 1 H), 7.81 (m, 1 H), 8.12 (s, 1 H).

Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.45; H, 5.88; N, 13.47.

1-(5-Fluorouracil-1-yl)ethyl Acetate (3k)[6a]

Colorless solid; mp 172–174 °C (Lit.[6a] 171–172 °C).

IR (KBr): 3734, 3170, 3086, 3049, 1752, 1730, 1702, 1662, 1225 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.54 (d, *J* = 6.3 Hz, 3 H), 2.05 (s, 3 H), 6.76 (q, *J* = 6.3 Hz, 1 H), 8.20 (d, J_{H-F} = 7.2 Hz, 1 H), 11.90 (s, 1 H).

1-(2-Methyl-4-nitro-1*H*-imidazol-1-yl)ethyl Butyrate (3l)

Light-yellow oil.

IR (film): 3164, 3114, 1745, 1547, 1504 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.5 Hz, 3 H), 1.66 (m, 2 H), 1.77 (d, *J* = 6.3 Hz, 3 H), 2.33 (t, *J* = 7.8 Hz, 2 H), 2.56 (s, 3 H), 6.65 (q, *J* = 6.3 Hz, 1 H), 7.85 (s, 1 H).

Anal. Calcd for $C_{10}H_{15}N_3O_4$: C, 49.79; H, 6.27; N, 17.42. Found: C, 49.88; H, 6.28; N, 17.18.

1-(2-Methyl-4-nitro-1*H*-imidazol-1-yl)ethyl Benzoate (3m)

Colorless solid; mp 149–150 °C.

IR (KBr): 3143, 3089, 3017, 1725, 1603, 1547, 1504, 1451 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93 (d, *J* = 6.3 Hz, 3 H), 2.63 (s, 3 H), 6.91 (q, *J* = 6.3 Hz, 1 H), 7.49 (m, 2 H), 7.64 (m, 1 H), 7.96 (s, 1 H), 8.02 (m, 2 H).

Anal. Calcd for $C_{13}H_{13}N_3O_4$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.63; H, 5.02; N, 15.20.

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References

(1) (a) Yano, T.; Tomioka, H.; Ishiwatari, T.; Hirata, N. Jpn. Kokai Tokkyo Koho JP 03232805, **1991**; *Chem. Abstr.* **1992**, *116*, 146174. (b) Tomioka, H.; Yano, T.; Ishiwatari, T.; Hirata, N. Jpn. Kokai Tokkyo Koho JP 03232862, **1991**; *Chem. Abstr.* **1992**, *116*, 101146. (c) Bodor, N.; Kaminski, J. J.; Selk, S. *J. Med. Chem.* **1980**, *23*, 469. (d) Ozaki, S.; Watanabe, Y.; Hoshiko, T.; Mizuno, H.; Ishikawa, K.; Mori, H. *Chem. Pharm. Bull.* **1984**, *32*, 733. (e) Sih, J. C.; Im, W. B.; Robert, A.; Graber, D. R.; Blakeman, D. P. *J. Med. Chem.* **1991**, *34*, 1049.

(2) (a) Katritzky, A. R.; Rachwal, S.; Rachwal, B. *Synthesis* **1991**, 69. (b) Katritzky, A. R.; Rachwal, S.; Rachwal, B. *J. Chem. Soc., Perkin Trans. 1* **1987**, 791.

(3) Katritzky, A. R.; Fan, W.-Q. *J. Heterocycl. Chem.* **1990**, *27*, 1543.

(4) (a) Banfi, A.; Benedini, F.; Sala, A. *J. Heterocycl. Chem.* **1990**, *27*, 813. (b) Katritzky, A. R.; Pastor, A.; Voronkov, M. V. *J. Heterocycl. Chem.* **1999**, *36*, 777.

(5) (a) Belousov, A. M.; Gareev, G. A.; Kirillova, L. P.; Vereshchagin, L. I. *Zh. Org. Khim.* **1980**, *16*, 2622. (b) Attaryan, O. S.; Asratyan, G. V.; Darbinyan, E. G.; Matsoyan, S. G. *Zh. Org. Khim.* **1988**, *24*, 1339.

(6) (a) Xu, J.-M.; Liu, B.-K.; Wu, W.-B.; Qian, C.; Wu, Q.; Lin, X.-F. *J. Org. Chem.* **2006**, *71*, 3991. (b) Xu, J.-M.; Wu, W.-B.; Qian, C.; Liu, B.-K.; Lin, X.-F. *Tetrahedron Lett.* **2006**, *47*, 1555.

(7) (a) Wu, W.-B.; Wang, N.; Xu, J.-M.; Wu, Q.; Lin, X.-F. *Chem. Commun.* **2005**, *18*, 2348. (b) Wu, W.-B.; Xu, J.-M.; Wu, Q.; Lv, D.-S.; Lin, X.-F. *Synlett* **2005**, 2433. (c) Wu, W.-B.; Xu, J.-M.; Wu, Q.; Lv, D.-S.; Lin, X.-F. *Adv. Synth. Catal.* **2006**, *348*, 487.

(8) Coudret, C.; Mazenc, V. *Tetrahedron Lett.* **1997**, *38*, 5293.

(9) Holmes, D.; Chotana, G. A.; Maleczka, R. E. Jr.; Smith, M. R. III *Org. Lett.* **2006**, *8*, 1407.

(10) Joshi, A. V.; Bhusare, S.; Baidossi, M.; Qafisheh, N.; Sasson, Y. *Tetrahedron Lett.* **2005**, *46*, 3583.

(11) Li, R.-T.; Zhu, Q.; Cai, M.-S. *Synth. Commun.* **1997**, *27*, 1351.

(12) (a) Li, R.-T.; Ding, P.-Y.; Han, M.; Cai, M.-S. *Synth. Commun.* **1998**, *28*, 295. (b) Li, R.-T.; Ge, Z.-M.; Cheng, T.-M.; Cai, M.-S. *Gaodeng Xuexiao Huaxue Xuebao* **1999**, *20*, 1897; *Chem. Abstr.* **2000**, *132*, 12258. (c) Wang, Y.-Q.; Ge, Z.-M.; Hou, X.-L.; Cheng, T.-M.; Li, R.-T. *Synthesis* **2004**, 675.

(13) Ge, Z.-M.; Li, Q.; Zheng, S.-J.; Cheng, T.-M.; Cui, Y.-X.; Li, R.-T. *Chin. J. Chem.* **2006**, *24*, 381.

(14) Ge, Z.-M.; Cui, J.-L.; Wang, Y.-L.; Cheng, T.-M.; Li, R.-T. *Synthesis* **2004**, 1257.

(15) Katritzky, A. R.; Rachwal, S.; Rachwal, B. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1717.