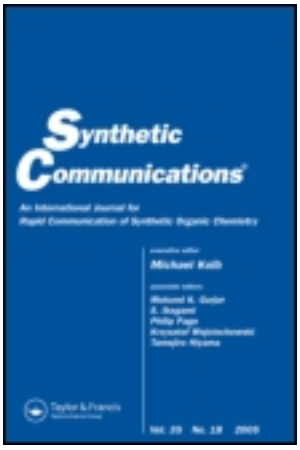

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Efficient Synthesis of 2-Ethoxycarbonyl Indoles

A. Sudhakara [a], H. Jayadevappa [b], K. M. Mahadevan [a] & Vijaykumar Hulikal [c]

[a] Department of Postgraduate Studies and Research Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, Karnataka, India

[b] Department of Chemistry, Sahyadri Science College, Shimoga, Karnataka, India

[c] Bioorganics and Applied Materials Pvt. Ltd., Bangalore, India

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Efficient Synthesis of 2-Ethoxycarbonyl Indoles

A. Sudhakara,[1] H. Jayadevappa,[2] K. M. Mahadevan,[1] and Vijaykumar Hulikal[3]

[1]Department of Postgraduate Studies and Research Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, Karnataka, India
[2]Department of Chemistry, Sahyadri Science College, Shimoga, Karnataka, India
[3]Bioorganics and Applied Materials Pvt. Ltd., Bangalore, India

Abstract: An efficient one-pot procedure for the synthesis of 2-ethoxycarbonyl indoles from commercially available materials has been developed. The one-step procedure involves in situ formation of the hydrazones from phenylhydrazine hydrochloride and ethyl pyruvate in the presence of bismuth nitrate followed by Fischer cyclization in polyphosphoric acid and ethanol. This method is efficient and simple.

Keywords: Bismuth nitrate, ethyl pyruvate, Fisher indole synthesis, one pot, phenylhydrazine hydrochloride

In many natural products and biologically active compounds, the indole scaffold is a privileged substructure.[1] Esters of indole-2-carboxylic acids may serve as glycine site antagonists and hence aid in the treatment of human brain injuries.[2] Meanwhile, 2-ethoxycarbonyl indole and its derivatives, which are considered attractive substrates, have been reported to possess anti-inflammatory activity.[3] In spite of several methods already available for the synthesis of indoles,[4] there is continuous interest in the development of new syntheses of the indole ring. As a result, a large

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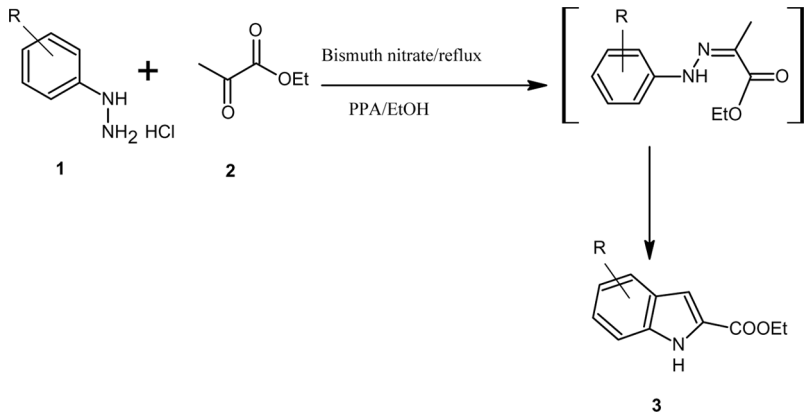
Address correspondence to K. M. Mahadevan, Department of Postgraduate Studies and Research Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, Karnataka, 577 451, India. E-mail: mady_kmm@yahoo.co.uk

number of new syntheses or modifications and applications of known methods countinue to be reported.[5] The most famous synthesis is the Fischer indole synthesis.[6] Several 2-ethoxycarbonyl indoles have been prepared by Fischer indole synthesis using polyphosphoric acid (PPA)[7] from corresponding hydrazones. Usually PPA is required in large amounts, 8- to 9-fold excess by weight, and PPA-catalyzed cyclization reactions often result in poor yield. In spite of these drawbacks, PPA is still used in industry and academia to prepare various indole derivatives.

One-pot approaches to the indole scaffold are attracting considerable attention because of their significance from both economical and ecological points of view.[8] These methods usually start directly from a single, commercially available precursor, which obviates the preparation or isolation of the unstable arylhydrazones (Scheme 1). Hence, here we report a simple, convenient, one-pot synthesis of 2-ethoxycarbonyl indoles (**3**) from commercially available starting materials.

In our initial study, the reaction of 4-nitrophenylhydrazine hydrochloride and ethyl pyruvate was carried out in the presence of bismuth nitrate in methanol to afford the corresponding hydrazone. This has been isolated in good yield in the presence of bismuth nitrate rather than without catalyst. The hydrozones were normally cyclized in hot polyphosphoric acid into 2-ethoxycarbonyl indoles in poor yields.[9] The product is isolated by addition to water followed by filtration of the product, and disposal of the phosphoric acid residue can have a considerable environment impact. Hence, to circumvent these difficulties in isolation, poor yield, and use of 7- to 9-fold excess of PPA, we used ethanol as cosolvent in this



Scheme 1. Synthesis of 2-ethoxycarbonyl indoles catalyzed by bismuth nitrate/PPA in EtOH.

Table 1. Effect of solvent and amount of catalyst in the synthesis of 2-ethoxycarbonyl indoles

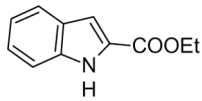
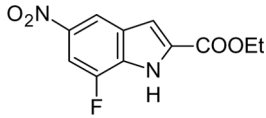
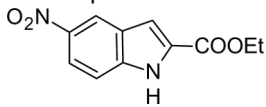
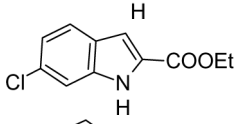
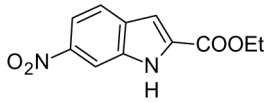
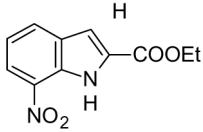
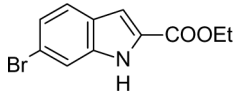
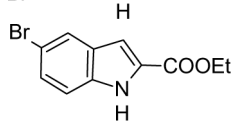
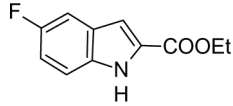
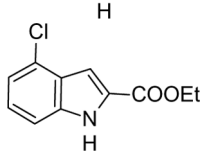
Entry	Solvent	$BiNO_3$ (mol%)	PPA (%)	Time (h)	Yield (%)
1	EtOH	—	—	>5	00
2	EtOH	10	—	>5	00
3	EtOH	10	3	2.5	75
4	MeOH	20	3	0.50	90–95
5	EtOH	30	4	0.40	90–95
6	EtOH	20	3	1.2	90–95
7	CH_3CN	20	3	4	70

one-pot process. Surprisingly, addition of ethanol in the reaction along with PPA during cyclization of hydrozones at reflux temperature (70–80 °C) greatly increased the yield (>90%) of the products and significantly reduced the reaction time (Table 1). Since the development of one-pot approaches to the indole scaffold is attracting considerable attention because of their significance from both economical and ecological points of view, now we thought to carry out the reaction in one pot by mixing molar equivalent of 4-nitrophenylhydrazine hydrochloride, ethyl pyruvate, and catalytic amounts of bismuth nitrate and PPA in MeOH. This method avoids the preparation or isolation of the arylhydrazones. This one-pot procedure gave satisfactory results in terms of easy isolation, improved yield, and reduced reaction time. Thus, it was obvious that the bismuth nitrate catalyzed initial hydrazone formation and subsequent cyclization of hydrazones by PPA in MeOH, afforded various indoles.

Hence, the experiments were carried out to establish the optimal amounts of bismuth nitrate and PPA in a one-pot synthesis. The reaction with 10 mol% of bismuth nitrate in PPA gave 75% yield after 2.5 h (Table 1) in one pot. However, the best result (95%) was achieved when 20 mol% of catalyst was used (Table 2), and the reaction time was also reduced. Increasing the amount of the catalyst and PPA did not change the isolated yield, but reaction time was reduced in ethanol media (Table 2). The reaction of phenyl hydrazine hydrochloride, ethyl pyruvate, and catalytic amounts of bismuth nitrate and PPA was separately performed without using MeOH as cosolvent. This failed to complete the reaction and resulted in poor yield even with longer reaction times.

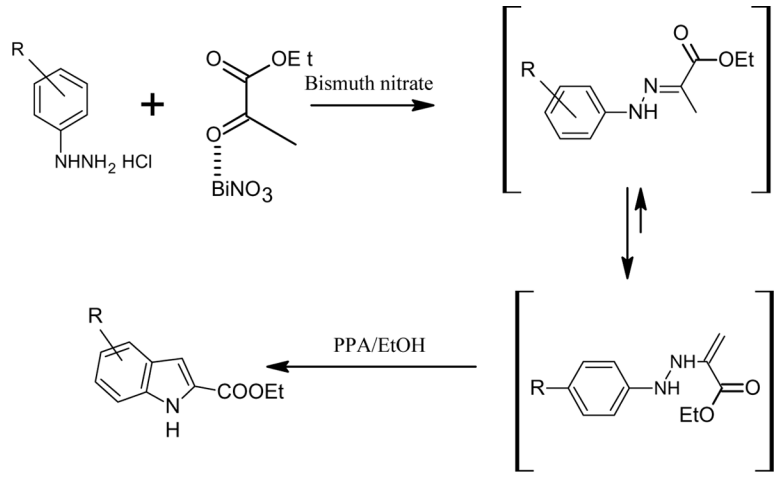
Further, the effect of solvent on this reaction was also studied, and EtOH and MeOH gave the best results. Apart from good yields and shorter reaction times, the other advantage in the use of ethanol and methanol was their solubility in water, which makes the isolation of the product from the reaction mixture easy and reduces the amount

Table 2. Synthesis of 2-ethoxycarbonyl indoles[a]

Entry	Product	Time (h)	Yield (%)[b]	Mp (°C)
1		0.4	90	102–105
2		3	80	171–172
3		2.5	80	142–144
4		2	85	169–171
5		2.5	80	145–147
6		2.5	80	92–94
7		2.5	85	178–180
8		2.5	85	167–169
9		2	85	158–160
10		2	80	168–170

[a]Reaction was carried out at reflux temperature in alcohol + PPA in presence of 20 mol% of $BiNO_3$.

[b]Isolated yields.



Scheme 2. Mechanism for the synthesis of 2-ethoxycarbonyl indoles.

of PPA used (8- to 9-fold excess to 3-fold) in this reaction, with possible assistance by ethanol as cosolvent. Similarly, by adopting optimized reaction conditions, the various 2-ethoxycarbonyl indoles were prepared with various phenylhydrazine hydrochlorides and ethyl pyruvate in the presence of 20 mol% of bismuth nitrate and PPA (3-fold) in MeOH (Scheme 1).

The synthesis requires only a single step: the synthesis of the ethyl-2-[(4-nitrophenyl) hydrazono] propanoate. Subsequent cyclization occurred in one pot with two steps as shown in Scheme 2. The characterization data of all the prepared compounds are given in the experimental section.

In conclusion, the reported protocol is a mild and facile approach to the synthesis of 2-ethoxy carbonyl indoles by [3,3]-sigmatropic rearrangement by in situ generated hydrazones. The scope appears to be presently restricted to hydrazones of ethyl pyruvate, and further investigation on other ketonic hydrazones is under way. Most products can be easily and directly purified by column chromatography. The procedure is amicable for scale-up.

EXPERIMENTAL

General

Products were identified by their physical and spectroscopic data, all the melting points were recorded in open capillaries. The purity of the

compounds was checked by thin-layer chromatography (TLC) on silica gel. ^{1}H NMR spectra were recorded on a Bruker 400-Hz spectrometer using dimethyl sulfoxide (DMSO)-d6 and $CDCl_3$ as an internal standard. Infrared (IR) spectra were obtained using a FTS-135 spectrometer instrument. Mass spectra (MS) were recorded on a Jeol SX102 = DA-6000 (10 kV) fast atom bombardment (FAB) mass spectrometer. Solvents, chemicals, and reagents were purchased from Merck Chemical Company in high-grade quality.

General Procedure for the Synthesis of Ethyl-2-[(4-nitrophenyl) hydrazono] Propanoate

The 4-nitrophenylhydrazine hydrochloride (1 g, 0.0069 mol) and ethyl pyruvate (0.80 g, 0.0068 mol) were dissolved in 20 ml MeOH and 20 mol% of bismuth nitrate (0.67 g). The reaction mixture was refluxed on a water bath for the appropriate time. After completion, the reaction mixture was poured into water (100 ml), and the crude hydrazone was extracted with ethyl acetate (2×50 ml). The combined ethyl acetate extracts were washed with brine followed by water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to provide a crude solid hydrazone. The solid thus obtained was further purified by column chromatography using silica gel (60–120 mesh) and eluted with petroleum ether–ethyl acetate to afford ethyl-2-[(4-nitrophenyl)hydrazono] propanoate.

General Procedure for the Synthesis of 2-Ethoxycarbonyl Indole

The 4-nitro phenylhydrazine hydrochloride (1 g, 0.0069 mol) and ethyl pyruvate (0.80 g, 0.0068 mol) were dissolved in 20 ml MeOH, then 20 mol% of bismuth nitrate (0.67 g) and 3 g of PPA were added. The reaction mixture was refluxed on a water bath for the appropriate time. The completion of the reaction was monitored by TLC (petroleum ether and ethyle acetate). The reaction mixture was poured into water (100 ml), and the crude product was extracted with ethyl acetate (2×50 ml). The combined ethyl acetate extracts were washed with brine followed by water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to provide a crude solid. The solid thus obtained was further purified by column chromatography using silica gel (60–120 mesh) and eluted with petroleum ether–ethyle acetate to afford 2-ethoxycarbonyl indoles.

Data

Ethyl (2*Z*)-2-[(4-nitrophenyl) hydrazono] propanoate ($C_{11}H_{13}N_3O_4$)

Mp: 94–96°C. IR (KBr): 3399 (NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10.98 (br, s, NH), 8.2 (1H, d, $J = 3.2$ Hz), 8.19 (1H, t, $J = 9.2$), 7.6 (1H, t, 7.2 Hz), 7.01 (1H, d, $J = 1.2$), 4.41 (2H, q, $J = 7.2$), 2.25 (3H, t, $J = 2.8$), 1.57 (3H, s). ^{13}C NMR: δ 11, 13.3, 59, 116, 116, 124, 138, 152, 154, 161. MS (EI, eV 70): m/z (%): (M^+) 251. Anal. calcd. (%): C, 52.59; H, 5.22; N, 16.72. Found (%): C, 54.58; H, 5.92; N, 17.72.

Ethyl 1*H*-indole-2-carboxylate **1**: $C_{10}H_{11}NO_2$

IR (KBr): 3381 (NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (br, s, NH), 7.46 (1H, d, $J = 8.05$ Hz), 7.24 (1H, d, $J = 4$ Hz), 7.11 (2H, m, $J = 8$ Hz), 4.5 (q, 2H, $J = 7.2$), 1.47 (3H, t, $J = 7.15$). ^{13}C NMR: δ 15, 65, 111, 115, 121, 128, 134, 135, 140, 154, 161. MS (EI eV 70): m/z (%): (M^+) 177. Anal. calcd. (%): C, 67.68; H, 6.26; N, 7.09. Found (%): C, 66.18; H, 6.06; N, 6.86.

Ethyl 5-nitro-7-fluoro-1*H*-indole-2-carboxylate **2**: $C_{11}H_9FN_2O_4$

IR (KBr): 3391 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.7 (br, s, NH), 8.2 (1H, d, $J = 4.05$ Hz), 7.9 (1H, d, $J = 3.6$ Hz), 7.2 (1H, t, $J = 9.8$ Hz), 4.5 (q, 2H, $J = 7.2$), 1.47 (3H, t, $J = 7.15$). ^{13}C NMR: δ 14, 61, 108, 111, 121, 128, 134, 135, 140, 154, 161. MS (EI eV 70): m/z (%): (M^+) 253. Anal. calcd. (%): C, 55.39; H, 3.60; N, 11.11. Found (%): C, 54.96; H, 3.12; N, 11.01.

Ethyl 5-nitro-1*H*-indole-2-carboxylate **3**: $C_{11}H_{10}N_2O_4$

IR (KBr): 3389 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.3 (br, s, NH), 8.68 (1H, d, $J = 2.04$), 8.3 (dd, 1H, $J = 9.16$ Hz), 7.5 (1H, s), 4.47 (q, 2H, $J = 10.7$), 1.4 (2H, t, $J = 7.12$). ^{13}C NMR: δ 14, 61, 87, 108, 115, 122, 131, 132, 140, 145, 161. MS (EI eV 70): m/z (%): (M^+) 235. Anal. calcd. (%): C, 56.41; H, 4.30; N, 11.96. Found (%) C, 55.81; H, 4.12; N, 11.01.

Ethyl 6-chloro-1*H*-indole-2-carboxylate **4**: $C_{11}H_{10}ClNO_2$

IR (KBr): 3387 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.13 (br, s, NH), 7.6 (1H, d, $J = 8.56$ Hz), 7.42 (s, 1H), 7.2 (1H, S), 7.1 (1H, d, $J = 6.8$ Hz),

4.6 (q, 2H, $J = 7.12$ Hz), 1.4 (3H, t, $J = 6.04$ Hz) Hz. ^{13}C NMR: δ 14, 63, 97, 106, 108, 111, 117, 134, 143, 153, 161. MS (EI, eV 70): m/z (%): (M^+) 224. Anal. calcd. (%): C, 59.07; H, 4.51; N, 6.26. Found (%): C, 59.01; H, 4.11; N, 5.97.

Ethyl 6-nitro-1*H*-indole-2-carboxylate **5**: $C_{11}H_{10}N_2O_4$

IR (KBr): 3381 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.27 (br, s, NH), 8.68 (1H, d, $J = 2.04$ Hz), 8.24 (1H, dd, $J = 3.76$ Hz), 7.5 (1H, d, $J = 9.1$ Hz), 4.47 (q, 2H, $J = 7.16$ Hz), 1.4 (3H, t, $J = 7.14$ Hz). ^{13}C NMR: δ 13.8, 61, 87, 106, 116, 124, 132, 133, 141, 147, 161. MS (EI, eV 70): m/z (%): (M^+) 235. Anal. calcd (%): C, 56.41; H, 4.30; N, 11.96. Found (%): C, 55.23; H, 4.21; N, 11.57.

Ethyl 7-nitro-1*H*-indole-2-carboxylate **6**: $C_{11}H_{10}N_2O_4$

IR (KBr): 3385 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.4 (br, s, NH), 8.2 (1H, d, $J = 7.89$), 7.9 (s, 1H), 7.8 (1H, d, $J = 8.25$ Hz), 7.4 (1H, t, $J = 8.04$ Hz), 4.5 (q, 2H, $J = 10.68$ Hz) 1.4 (3H, t, $J = 7.12$ Hz). ^{13}C NMR: δ 14, 59, 88, 108, 115, 124, 130, 133, 141, 145, 161. MS (EI, eV 70): m/z (%): (M^+) 235. Anal. calcd (%): C, 56.41; H, 4.30; N, 11.96. Found (%): C, 55.43; H, 4.11; N, 11.87.

Ethyl 6-bromo-1*H*-indole-2-carboxylate **7**: $C_{11}H_{10}BrNO_2$

IR (KBr): 3378 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.27 (br, s, NH), 8.68 (1H, d, $J = 2.04$ Hz), 8.24 (1H, dd, $J = 3.76$ Hz), 7.5 (1H, d, $J = 9.1$ Hz), 4.47 (q, 2H, $J = 7.16$ Hz), 1.4 (3H, t, $J = 7.14$ Hz). ^{13}C NMR: δ 13.8, 61, 87, 106, 116, 124, 132, 133, 141, 147, 161. MS (EI, eV 70): m/z (%): (M^+) 268. Anal. calcd (%): C, 49.28; H, 3.76; N, 5.22. Found (%): C, 49.43; H, 4.01; N, 5.37.

Ethyl 5-bromo-1*H*-indole-2-carboxylate **8**: $C_{11}H_{10}BrNO_2$

IR (KBr): 3392 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.27 (br, s, NH), 8.68 (1H, d, $J = 2.04$ Hz), 8.24 (1H, dd, $J = 3.76$ Hz), 7.5 (1H, d, $J = 9.1$ Hz), 4.47 (q, 2H, $J = 7.16$ Hz), 1.4 (3H, t, $J = 7.14$ Hz). ^{13}C NMR: δ 13.8, 61, 87, 106, 116, 124, 132, 133, 141, 147, 161. MS (EI, eV 70): m/z (%): (M^+) 268. Anal. calcd. (%): C, 49.28; H, 3.76; N, 5.22. Found (%): C, 49.43; H, 4.01; N, 5.37.

Ethyl 5-fluoro-1*H*-indole-2-carboxylate **9**: $C_{11}H_{10}FNO_2$

IR (KBr): 3378 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.9 (br, s, NH), 7.3 (2H, t, $J = 5.91$ Hz), 7.1 (1H, d, $J = 1.26$ Hz), 7.07 (1H, t, $J = 2.49$ Hz), 4.4 (q, 2H, $J = 10.69$ Hz), 1.4 (3H, t, $J = 10.69$ Hz). ^{13}C NMR: δ 14, 60, 98, 105, 106, 109, 113, 134, 142, 151, 160. MS (EI, eV 70): m/z (%): (M^+) 208. Anal. calcd. (%): C, 63.76; H, 4.86; N, 6.76. Found (%): C, 64.43; H, 4.31; N, 5.87.

Ethyl 4-chloro-1*H*-indole-2-carboxylate **10**: $C_{11}H_{10}ClNO_2$

IR (KBr): 3391 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.1 (br, s, NH), 7.6 (1H, d, $J = 8.58$ Hz), 7.4 (s, 1H), 7.2 (1H, d, $J = 6.97$ Hz), 7.1 (1H, d, $J = 8.58$), 4.4 (q, 2H, $J = 10.70$ Hz), 1.45 (t, 3H, $J = 7.91$ Hz). ^{13}C NMR: δ 14, 61, 89, 90, 108, 15, 121, 135, 136, 143, 161. MS (EI, eV 70): m/z (%): (M^+) 224. Anal. calcd. (%) C, 59.07; H, 4.30; N, 6.26. Found (%): C, 58.43; H, 4.41; N, 6.17.

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