Synthesis of 3-Substituted Indoles Promoted by Pulverization-Activation Method Catalyzed by Bi(NO₃)₃·5H₂O

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A new, facile, efficient, "green" and chemoselective procedure for the synthesis of indole derivatives has been developed with pulverization-activation method catalyzed by $Bi(NO_3)_3 \cdot 5H_2O$ (PAMC- $Bi(NO_3)_3 \cdot 5H_2O$) through grinding of indoles with aldehydes or Michael acceptors in the presence of catalytic amounts of $Bi(NO_3)_3 \cdot 5H_2O$ under solvent-free conditions.

J. Heterocyclic Chem., 45, 377 (2008).

INTRODUCTION

Indole derivatives are widely distributed in nature and are known to possess broad spectrum of biological and pharmaceutical activities [1]. In particular, 3-substituted indoles have received much attention in previous years [2]. Such compounds are prone to develop interesting bioactivity and could be used as antibacterial [3] and antitumor agents [4]. Moreover, some alkaloids containing indole unit have been isolated from marine sources like Hapalosiphon fontinalis (a blue-green algae) [5]. The scope of this has been further increased by the identification of the tri- or tetracyclic skeleton derivatives called hapalindole, as a biogenetic precursor [6]. Thus, the development of facile and environmentally friendly synthetic methods for the preparation of these compounds constitutes an active area of investigation in pharmaceutical and organic synthesis. The principal approach for the synthesis of these 3-substituted indoles involve, condensation reaction of indoles with various aldehydes or ketones or Friedel-Craftstype conjugated additions of indoles with α , β -unsaturated compounds in the presence of protic or Lewis acids [7,8]. Although a variety of different catalytic systems for the synthesis of 3-substitued indoles has been developed, there is a growing interest in the search for new efficient catalysts for this concern. However, some of these methods are associated with certain drawbacks such as the use of expensive catalyst [9-14] or less easily available reagents [15-17] use of toxic solvents [18,19] prolonged reaction times [20] (e.g. 10 days), tedious manipulations in the isolation of the pure products [21], unsatisfactory yields [3], low selectivity [17] or applicable only for aryl aldehydes [22]. Furthermore, some of these methods require strictly anhydrous conditions [23,24]. Consequently, there is a need for a greener catalytically efficient method for these transformations, which might work under mild and more economical conditions. As a part of our ongoing research program to develop new synthetic methodologies [25-27], we found that $Bi(NO_3)_3$. $5H_2O$ as a non-toxic, inexpensive and readily available Lewis acid, catalyzes bis(indolyl)-methanes synthesis, efficiently with grinding of indole with aldehydes (Scheme I).



RESULTS AND DISCUSSION

First, we investigated the influence of the different catalysts in this transformation. 4-Chlorobenzaldehyde was employed as a model compound and various catalysts were tested under pulverization-activation method. As shown in Table 1, the best conversion was observed when the reaction performed in the presence of 1 mol% of Bi(NO₃)₃·5H₂O for 5 min. Therefore, a series of aromatic and aliphatic aldehydes reacted with indole smoothly to afford the corresponding bis(indolyl)methanes in good to excellent yields (Table 2).

Synthesis of 3,3'-bis(indolyl)-4-chlorophenylmethane with grinding of 4-chlorobenzaldehyde with indole in the presence of various catalysts under solid-state conditions.

Table 1

Catalyst ^a	Time	Yield
	(min)	(%) ^b
ZrCl ₄	5	55
BiCl ₃	5	60
Ce(NO ₃) ₃ ·6H ₂ O	5	25
FeCl ₃	5	45
p-TSOH	5	50
Bi(NO ₃) ₃ ·5H ₂ O	5	87

[a]1 mol%. [b] Isolated yield.

The presence of electron-donating and electronwithdrawing groups on the aromatic ring of aldehydes, irrespective to their positions in the ring, did not make any obvious difference in this condensation reaction (Table 2, entries 1-16). Interestingly we found that under the reaction conditions, only one of the carbonyl groups of terephthalaldehyde participated in this reaction (Table 2, entry 8).

 Table 2

 Synthesis of bis(indolyl)methanes catalyzed with Bi(NO₃)₃5H₂O under solid-state conditions at room temperature.

Entry	R	Time (min)	Yield (%) ^{a,b}	References for Known Compounds	
1	C ₆ H ₅	5	85	15a	
2	$4-NO_2C_6H_4$	7	92	10e	
3	$3-NO_2C_6H_4$	4	91	10e	
4	4-ClC ₆ H ₄	5	87	15b	
5	$2-ClC_6H_4$	4	88	10a	
6	4-BrC ₆ H ₄	5	90	10e	
7	3-BrC ₆ H ₄	4	89	29	
8	4-CHOC ₆ H ₄	7	92	29	
9	4-CNC ₆ H ₄	5	89	29	
10	$4-CH_3C_6H_4$	5	85	10d	
11	$4-PhC_6H_4$	9	86	29	
12°	2,4-(CH ₃) ₂ C ₆ H ₃	8	75	10e	
13	2-CH ₃ OC ₆ H ₄	6	90	10b	

Table 2 (continued)

Entry	R	Time (min)	Yield (%) ^{a,b}	References for Known Compounds	
14°	2,4-(CH ₃ O) ₂ C ₆ H ₃	4	84	29	
15	2,5-(CH ₃ O) ₂ C ₆ H ₃	6	85	29	
16	2-furyl	3	94	10e	
17	2-OHC ₆ H ₄	8	56	22	
18	3-CH ₃ O-4-OHC ₆ H ₃	10	50	10d	
19	C ₆ H ₅ CH=CH	6	83	10b	
20^{d}	C ₆ H ₅ CH ₂ CH ₂	6	80	30	
21 ^d	CH ₃ CH=CH	10	70	22	
22 ^e	CH ₃ (CH ₃)CHCH ₂	13	79	29	
23 ^f	H ₃ C H ₃ C	15	62	29	

[a] Products were characterized by ¹H NMR, ¹³C NMR, IR and comparison with reported data; [b] Isolated yields; [c] In the presence of 2 mol% of Bi(NO₃)₃:5H₂O; [d] In the presence of 5 mol% of Bi(NO₃)₃:5H₂O; [e] In the presence of 3 mol% of Bi(NO₃)₃:5H₂O; [f] In the presence of 4 mol% of Bi(NO₃)₃:5H₂O.

Phenolic aldehydes such as salicylaldehyde and vaniline (Table 2, entries 17,18) afforded the corresponding products in 56 and 50% yields respectively. Aliphatic aldehydes as well as α , β -unsaturated ones, also gave the corresponding bis(indolyl)methanes in good to high yields under similar reaction conditions (Table 2, entries 19-23). However, aliphatic or aromatic ketones were unaffected even the reaction mixtures were ground for 15 min, and the starting materials were quantitatively recovered.

The reaction conditions are mild enough not to induce any isomerization for furfural and conjugated aldeydes (Table 2, entries 16 and 19) or damage to moieties such as methoxy, which often undergo cleavage in strongly acidic reaction media (Table 2, entries 13-15 and 18). On the other hand, no side products were observed in the course of the reactions we studied. The chemoselectivity of the present method is also demonstrated by competitive



reactions of indole with arylaldehydes in the presence of aliphatic ones and ketones. For example, when a mixture of 4-nitrobenzaldeyde and 3-methylbutyraldehyde was allowed to react with two equivalents of indole in the presence of 1 mol% of $Bi(NO_3)_3$ · $5H_2O$ for 8 min, the arylaldehyde was chemoselectively converted to the corresponding bis(indolyl)methane but the aliphatic ones converted slightly (Scheme II). Also in an equimolar mixture of arylaldehyde and ketone, only arylaldehyde converted to the corresponding bis(indolyl)methane, whereas, ketone remained intact (Scheme II).

In continuation of our investigation, we also found that PAMC-Bi(NO₃)₃·5H₂O can also act as an efficient procedure for the Michael addition of indoles. Recently, Srivastava, *et. al.* carried out these conjugate addition reactions in the presence of Bi(NO₃)₃·5H₂O in solvent at prolonged reaction times (10-15h) [30]. In preliminary investigation on this transformation with PAMC-Bi(NO₃)₃·5H₂O, we found that the reaction time reduced surprisingly (3-10 min). Then we decided to expand this protocol to carry out this transformation (Scheme III).

Scheme III



First, we investigated the influence of the amount of catalyst on the reaction using indole and β -nitrostyrene as a model system. As shown in Table 3, 5 mol% of Bi(NO₃)₃ ·5H₂O was the optimum amount for this transformation.

 Table 3

 Effect of Bi(NO₃)₃·5H₂O amount on the reaction of indole with β-nitrostyrene.

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Entry	Mole % of catalyst	Time (min)	Yield (%)		
1	1	20	35		
2	3	13	65		
3	5	7	93		
4	10	7	93		
5	20	7	93		

The reaction is fairly general, clean, rapid and efficient. Unlike previously reported methods, the present method does not require toxic or anhydrous organic solvents. All the products were characterized by NMR, IR and mass spectroscopy and also by comparison with authentic samples. Under the optimized reaction conditions, a wide range of structurally divers Michael acceptors reacted with indoles to afford the corresponding products in good to excellent yields (Table 4). As presented in Table 4, the yields of Michael addition for 1-methylindole in the reaction conditions were less than 30% (Table 4, entries 13-15). To increase the yields, 50 mg of silica gel was added to the reaction mixture. In this case the yields were 60-95%. As a control the same amount of silica gel was used in the reaction of indole and β -nitrostyrene and it was found that silica gel addition didn't have any catalytic influence on the time and yield of the reaction. The promoting role, although not well understood, could be explained through the absorption of 1-methylindole with Michael acceptors that come into closer contact with each other on silica surface. We also examined the chemoselectivity of the present method in this transformation. It is noteworthy that Michael acceptors are transformed to their corresponding 3-substituated indoles in the presence

Scheme IV



of acid sensitive groups such as acetals, THP and TMS ethers with excellent chemoselectivity (Scheme IV).

It is also observed that only one of the unsaturated groups of bis(benzylidene)acetone participated in the Michael addition reaction with indole and the amounts of indole and catalyst did not affect the result (Scheme V). analyses were carried out using a Perkin-Elmer elemental analyzer 2400CHN. All the chemicals were purchased from Aldrich or Merck chemical companies and used without further purification.

Typical Procedure for the Preparation of Bis(indoly)methanes. A mixture of indole (117 mg, 2.1 mmol), terephthaldialdehyde (134 mg, 1 mmol) and Bi(NO₃)₃:5H₂O (4.85 mg,

Scheme V



In conclusion, in this study a new, simple, efficient and eco-friendly procedure is described for the chemoselective synthesis of bis(indolyl)methanes and 3substituated indole derivatives using catalytic amounts of $Bi(NO_3)_3$ ·5H₂O as a cheap and non-toxic catalyst with pulverization-activation method. In addition, efficiency, simplicity and chemoselectivity of this protocol provide a very fast, "green" and low cost procedure for the synthesis of these products.

EXPERIMENTAL

General. All products were identified by comparison of their physical and spectral data with those of authentic samples. Melting points were determined using a Stuart Scientific apparatus and are uncorrected. IR spectra were run on a Shimadzu IR-435 spectrophotometer. ¹H NMR spectra were recorded in CDCl₃ solvent on a Brucker 500 or 200 MHz spectrometer. Mass spectra were obtained on Platform II spectrometer from Micromass; EI mode at 70 eV. Elemental

0.01 mmol) was ground with a pestle in a mortar for 7 min. After completion of the reaction as indicated by TLC, EtOH (5 ml) was added and filtered. The solvent was evaporated under reduced pressure. Column chromatography of the crude residue on silica gel using *n*-heptane/ethyl acetate (4/1) as eluent gave the pure product in 92% yield. (Table 2, Entry 8) Pink colored solid, mp 190-192 °; ir (KBr): 3400, 2900, 1680, 1600, 1200, 740 cm⁻¹; ¹H nmr (200 MHz, CDCl₃): δ 10 (s, 1H), 8.21 (br, s 2H), 7.85-6.95 (m, 12H), 6.7 (s, 2H), 6.06 (s, 1H); $\delta_{\rm C}$ (50 MHz, CDCl₃) 40.9, 111.6, 118.9, 119.9, 120, 122.6, 124.1, 127, 129.8, 130.4, 200.8. *Anal.* Calcd. for C₂₄H₁₈N₂O: C, 82.26; H, 5.18; N, 7.99. Found: C, 82.23; H, 5.19; N, 8.01.

Typical Procedure for the Preparation of Michael Adduct. A mixture of ethyl indole-2-carboxylate (208 mg, 1.1 mmol), methyl vinyl ketone (70 mg, 1 mmol) and Bi(NO₃)₃·5H₂O (26 mg, 0.05 mmol) was ground with pestle in a mortar for 15 min. After completion of the reaction monitored by TLC, the residue was diluted with water (10 ml), extracted with ethyl acetate (3×10 ml) and then dried over MgSO₄. The crude product was purified by chromatography on silica gel using *n*-hexane/ethyl acetate (9/1) as eluent to afford pure product in 85% yield. (Table 4, entry 7) Pale yellow solid; mp 116-117 °; ir

 Table 4

 Condensation reaction of indoles with Michael acceptors in the presence of 5 mol% of Bi(NO₃)₃·5H₂O under solid phase conditions at room temperature.

Entry	R^1	R^2	R ³	R^4	Time (min)	Yield (%) ^a	References for Known Compounds
1	Н	Н	Н	CH ₃ CO	3	96	12
2	Н	Н	C ₆ H ₅	NO_2	7	93	11
3	Н	Н	C ₆ H ₅	CH ₃ CO	10	85	11
4	Н	Н	C ₆ H ₅	C ₆ H ₅ CO	10	86	26c
5	Н	Н	C ₆ H ₅	C ₆ H ₅ CH=CHCO	7	95	14
6	Н	Н	Н	CN	35	80	31
7	Н	CO ₂ Et	Н	CH ₃ CO	15	85	-
8	Н	CH ₃	Н	CH ₃ CO	5	97	26b
9	Н	CH_3	C ₆ H ₅	NO_2	10	97	32
10	Н	CH_3	C ₆ H ₅	CH ₃ CO	10	92	18
11	Н	CH ₃	C ₆ H ₅	C ₆ H ₅ CO	8	95	10b
12	Н	CH_3	C ₆ H ₅	C ₆ H ₅ CH=CHCO	10	95	-
13 ^b	CH_3	Н	Н	CH ₃ CO	8	95	11
14 ^b	CH ₃	Н	C ₆ H ₅	NO_2	20	60	32
15 ^b	CH_3	Н	C ₆ H ₅	CH ₃ CO	40	75	11

[a] Isolated yields. [b] 50 % of silica gel is added; in the absence of silica gel the yields are very low (less than 30%).

(KBr): 3291, 2979, 1689, 1544, 1254, 1023, 738 cm⁻¹; ¹H nmr (500 MHz, CDCl₃): δ 1.39 (t, J = 7.12 Hz, 3H), 2.13 (s, 3H), 2.79 (t, J = 7.86 Hz, 2H), 3.34 (t, J = 7.83 Hz, 2H), 4.40 (q, J = 7.01 Hz, 2H), 7.13 (t, J = 7.47 Hz, 1H), 7.30 (t, J = 7.07 Hz, 1H), 7.35 (d, J = 8.26 Hz, 1H), 7.68 (d, J = 8.16 Hz, 1H), 8.81 (br, s 1H); ms: m/z 259 (M⁺), 216, 202, 189, 186.

(Table 4, entry 12) white solid; mp 104-105 °C; ir (KBr): 3409, 3022, 2902, 1606, 1461, 1300, 1093, 733 cm⁻¹; ¹H nmr (500 MHz, CDCl₃): δ 2.45 (s, 3H), 3.56 (dd, J = 15.35, 8.70 Hz 6.61 (d, J = 16.19 Hz, 1H), 7.06 (t, J = 7.48 Hz, 1H), 7.13 (t, J = 7.51 Hz, 1H), 7.21 (t, J = 7.28 Hz, 2H), 7.28 (d, J = 11.32 Hz, 1H), 7.31-7.44 (m, 8H), 7.52 (d, J = 7.83 Hz, 2H), 7.87 (br, s 1H); ms: m/z 365 (M⁺), 234, 220, 204, 145, 131.

Acknowledgement. We are thankful to Center of Excellence of Chemistry (Catalyst and Fuel Cell), University of Isfahan" (CECUI), Research Council of University of Isfahan and also Razi University Research Councils for their financial support.

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