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RESEARCH LETTER

A green synthesis of symmetrical bis(indol-3-yl)methanes using phosphate-impregnated titania catalyst under solvent free grinding conditions

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An efficient, chemoselective method for the preparation of bis(indol-3-yl)methanes from aldehydes and indoles using phosphate-impregnated titania as the reusable catalyst under solvent-free grinding conditions is reported. The desired products were obtained in excellent yields with tolerability to functional groups such as $-$OMe, $-$Me, $-$Cl, $-$NO$_2$, and $-$OH in a simple and environmentally benign procedure.

Keywords: bis(indol-3-yl)methanes; aldehydes; green chemistry; phosphate-impregnated titania; solvent free; grinding

Introduction

Indole is one of the most profoundly studied, ubiquitous, and π-electron excessive nitrogen heterocyclic systems (*1*) having interesting biological properties that received particular interest in the mid-1950s, when alkaloid reserpine (*2*) was introduced as one of the first drugs for the treatment of central nervous system (CNS) disorders such as anxiety and mental disorder. Substituted indoles are referred to as "privileged structures" since they are capable of binding to many receptors with high affinity. Indole-containing compounds have been reported to exhibit anti-apoptotic properties (*3*). Compared to benzene, indole shows enhanced reactivity in the electrophilic aromatic substitution reaction. C-3 position of Indole is about 1013 times more reactive than benzene (*4,5*).

Unsubstituted indoles respond to electrophilic substitution reaction with aldehyde or ketone in the presence of Lewis or Brønsted acids (*6,7*) via reactive C-3 position resulting bis(indol-3-yl)methanes (BIMs). Various catalysts, e.g. FeF$_3$ (*8*), ZrCl$_4$ (*9*), InCl$_3$ (*10*), In(OTf)$_3$ (*11*), poly(vinyl sulfonic acid) (*12*), [bimim][MeSO$_4$] (*13*), Cu$_{1.5}$PMo$_{12}$O40 (*14*), SiO$_2$–AlCl$_3$ (*15*), NH$_4$Cl (*16*), Zn(OTf)$_2$ (*17*), ultrasound (*18*), cellulose sulfuric acid (*19*), supported-SO$_3$H (*20*), etc. have been reported for the synthesis of BIMs. There are reports describing the preparation of BIMs in water (*21*). Very recently, new β-lactam compounds containing a bis(indolyl) framework were synthesized (*22*).

Naturally occurring or synthetic BIMs and its privileged structures are important intermediates in organic synthesis (*23*) and are particularly important in pharmaceutical chemistry as they exhibit various pharmacological activities and are important metabolites (*24–27*). BIM derivatives as highly selective colorimetric and fluorescent molecular chemosensors for Cu^{2+} cation has been reported (*28*). Although a number of different methods have been reported for the preparation of BIMs, these methods have their merits in some way as claimed, but, on the other way, they suffer from certain drawbacks; e.g. longer reaction time, harsh reaction conditions, expensive use of reagent/catalyst, sensitivity to moisture and air, incompatibility of functional groups, environmental incompatibility, many Lewis acids are prone to undergo decomposition in the presence of nitrogen containing reactants and this requires the use of excess and sometimes stoichiometric amount of Lewis acid catalyst (*29*). Hence, there is still a need to search for better catalysts in terms of toxicity, handling, availability, economic viability, and operational simplicity. In view of the recent trend in catalytic process which comes under the purview of green chemistry, investigations for new and less hazardous catalysts have become a priority in synthetic organic chemistry. Previously, our collaborator, Chaudhari et al. reported the synthesis of phosphate-impregnated titania solid acid catalyst and its use in the nitration (*30*), sulfoxidation (*31*), and aza-Michael reaction (*32*). Inspired by those works, in this communication, we want to report an efficient green synthesis of BIMs

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3 (Scheme 1) from indole **1** and aldehydes **2** catalyzed by solid acid, phosphate-impregnated titania catalyst. To mention, in recent years, the use of solid acid catalysts has received paramount attention and interest in different areas of organic synthesis because of their several inherent useful properties such as environmental compatibility, reusability, greater selectivity, simplicity of handling, lesser toxicity, non-corrosiveness, cheap, and ease of isolation. Also, generation of wastes and byproducts can be minimized or avoided by using solid acid catalyst, thereby developing cleaner synthetic routes (*33, 34*).

Results and discussion

First, 4-chlorobenzaldehyde (**2b**) was chosen as a model substrate for the reaction with indole **1**. Compound **2b** (1 mmol, 0.140 g) and indole **1** (2 mmol, 0.234 g) were mixed and grounded in a mortar with a pestle in the presence of 5 wt% (0.0187 g) of the catalyst at room temperature for 1 min without any solvent. It is our mandates in the laboratory that whenever, we start a new reaction, we always first check it in the absence of a solvent following green chemistry practice. When we checked the TLC after 1 min for monitoring the progress of the reaction, interestingly, we were surprised to observe that the reaction was indeed over by that time providing BIM **3b**. It has been observed that by increasing the catalyst amount from 1 to 5 wt%, the yield of the product also increased from 20 to 99% within 1 min. Further increasing the amount of catalyst did not have any observable effect on the yield of the product. However, using less than 5 wt% of the catalyst and for longer time (beyond 10 min) there was an enhancement of 2–4% only in the overall yield of the product (Table 1). Hence, 5 wt% was chosen as the optimum catalyst amount for this reaction. Having established the optimum reaction conditions, structurally diversed carbonyl compounds were treated with indole **1** under the same reaction conditions in order to investigate the reaction scope and generality, and the results are summarized in Table 2 (entries **2a–t**). The methodology is found to be quite general as variety of substituted aromatic aldehydes, aliphatic aldehydes, and heterocyclic aldehydes (entries **2a–p**, Table 2)

reacted efficiently with indole **1** to give the BIMs **3a–p** in excellent yields quickly than any other reported methods. Many of the pharmacologically relevant substitution patterns on the aromatic ring could be introduced with high efficiency using this procedure. Furthermore, unsaturated aldehyde, cinnamaldehyde (entry **2g**, Table 2) gave the corresponding BIM **3g** without polymerization under the above reaction conditions in 98% yield within 1.5 min. The heterocyclic aldehydes like 2-furaldehyde, which was known as acid-sensitive species, was proved to be applicable under the reaction conditions (entry **2i,** Table 2), indicating the usefulness of our methodology. Furthermore, thiophene-2-carboxaldehyde (entry **2h**, Table 2) also worked well without forming any side products. Notably, the reaction conditions are mild enough and work nicely without damaging moieties such as $-OMe$, $-Me$, $-Cl$, $-NO_2$, and $-OH$. No solvent was used for the reaction and it was carried out at room temperature under grinding conditions. In absence of the catalyst the reaction did not proceed, thereby indicating the necessity of a catalyst.

Interestingly, indol-3-carbaldehyde (entry **2j**, Table 2) reacting with two equivalents of indole **1** under similar conditions afforded tri-indolylmethane **3j** in 93% yield (Scheme 2).

To note, aliphatic aldehydes (entries **2k–n**, Table 2) took some what longer time than the aromatic ones. However, ketones (entries **2q–t**, Table 2) did not react at all with indole **1** under the reaction conditions, demonstrating the chemoselective nature of the methodology. For example, when an equimolar mixture of benzaldehyde (entry **2a**, Table 2) and acetophenone (entry **2q**, Table 2) were allowed to react with indole **1** in the presence of the catalyst, only phenyl-3,3′-bis(indolyl)methane was obtained, while acetophenone **1q** remained as such and was recovered. When we carried out the reaction with 6-oxo-6-phenylhexanal (entry **2p**, Table 2) only the aldehydic part of the molecule reacted leaving aside the ketonic group intact, hence demonstrated the chemoselective nature of the method further. As expected, the electron-rich aldehydes should react faster than the aldehydes with electron withdrawing group. However, we did not observe any such difference; this may be due to the short reaction time with the
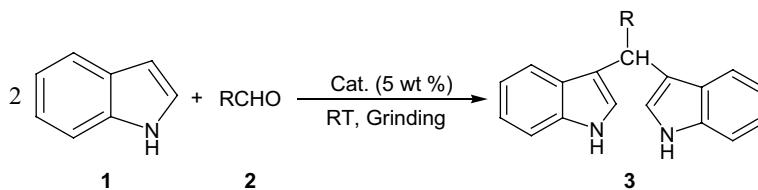
Scheme 1. General scheme for the synthesis of BIMs using phosphate-impregnated titania catalyst.

Table 1. Effect of the catalyst amount investigated for the Scheme 1.

Entry	Wt% of the catalyst	Yield (%) after 1 min	Yield (%) after 10 min
1	1	20	22
2	2	40	43
3	3	75	79
4	4	88	90
5	5	99	99
6	6	99	99
7	7	99	99

exception, *p*-hydroxybenzaldehyde (entry **2f**, Table 2) that required longer time (9.5 min).

Encouraged by this result, we extended the reaction to dialdehyde. Accordingly, the reaction of terephthaldehyde (entry **2o**, Table 2) with indole **1** was investigated under similar conditions (Scheme 3). To our delight, terephthaldehyde **2o** (1 mmol) reacted smoothly with indole **1** (4 mmol) to provide 1,4-bis(di(1*H*-indol-3-yl)methyl)benzene **3o** in 93% yield, which indicated that both the two aldehydic groups of terephthaldehyde reacted. Formation of 4-bis((1*H*-indol-3-yl)methyl)benzene-1-carbaldehyde **4** (Scheme 3) was not observed.

The generality of the reaction is also investigated for the substituted indole. Indole derivatives also react with the aldehyde to give the corresponding bis-indolyl methane (Table 3) supporting the generality of the methodology.

The IR spectra of BIMs **3** show characteristic IR absorptions within 3437–3480 cm^{-1} (N–H). In addition, the ^{1}H NMR spectrum of **3b** displays characteristic signals within δ 7–8 ppm (br s, NH, exchangeable with D$_2$O).

To compare our catalyst with the reported one, the efficiency of the various reported catalysts for the condensation of indole with benzaldehyde is shown in Table 4. Among those catalysts, our catalyst is found to be superior in terms of yield and reaction time.

The reusability of the catalyst was examined for the reaction of 4-chlorobenzaldehyde **2b** and indole **1** as model substrates vide Scheme 1. The result showed that the solid catalyst, phosphate-impregnated titania could be reused for at least four times without reducing the catalytic property of the catalyst appreciably (Table 5); thereafter, the yield started decreasing because of the leaching of the catalyst.

A plausible mechanism for the reaction is shown in Scheme 4. The interaction of the external surface of the solid catalyst, phosphate-impregnated titania with the aldehyde probably occurs, that increases the electrophilicity of the carbonyl carbon and which in turn facilitates the participation of indole molecules. The interaction may also occur via the external acidic sites of the catalyst.

In conclusion, we have developed a highly efficient electrophilic substitution reaction of indole with various aromatic, aliphatic as well as heterocyclic aldehydes using phosphate-impregnated titania as a

Table 2. Synthesis of BIMs **3** using phosphate-impregnated titania catalyst.

Entry	Aldehyde **2**/ketones	Product **3**	Time	Yield (%)[a]
a	C$_6$H$_5$CHO	3a	1 min	99
b	*p*-ClC$_6$H$_4$CHO	3b	1 min	99
c	*p*-MeOC$_6$H$_4$CHO	3c	1 min	98
d	*p*-MeC$_6$H$_4$CHO	3d	1 min	95
e	*m*-NO$_2$C$_6$H$_4$CHO	3e	9.5 min	95
f	*p*-HOC$_6$H$_4$CHO	3f	1.5 min	80
g	C$_6$H$_5$CH = CHCHO	3g	1.5 min	98
h	Thiophene-2-carboxaldehyde	3h	1.5 min	95
i	2-Furaldehyde	3i	1 min	97
j	Indol-3-carbaldehyde	3j	4 min	93
k	Acetaldehyde	3k	5.5 min	90
l	Pentanal	3l	6 min	88
m	Hexanal	3m	6 min	88
n	Cyclohexanecarboxaldehyde	3n	2 min	89
o	Terephthaldehyde	3o	1 min	93
p	6-oxo-6-phenylhexanal	3p	8 min	45
q	Acetophenone	–	3 hr	–
r	Benzophenone	–	3 hr	–
s	Cyclopentanone	–	3 hr	–
t	Cyclohexanone	–	3 hr	–

[a]Isolated yields.
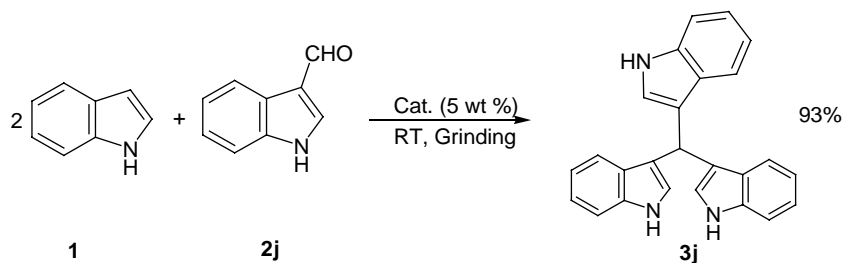
Scheme 2. Synthesis of tris(indolyl)methane using phosphate-impregnated titania catalyst.

recyclable catalyst. The procedure offers several advantages including improved yield of products with no by-products formation, simple experimental procedure with an economic and environmentally friendly solvent-free conditions, cleaner reaction profile, short reaction time, and use of inexpensive catalyst; hence, it is a useful addition to the existing methods for the synthesis of BIMs. Interestingly, the experimental procedure for these reactions is remarkably simple without requiring dry solvents, inert atmosphere, and reflux conditions, which makes it a useful and attractive process for the rapid synthesis of substituted BIMs.

Experimental

Melting points were determined on a Büchi 504 apparatus and are uncorrected and were compared with the literature value and gave good resemblance. IR spectra were recorded in KBr pallets on a Nicolet (Impact 410) FT-IR spectrophotometer. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on an ECS 400 MHz NMR (JEOL) spectro-

photometer. TMS served as the internal standard. GC–MS was carried out on gas chromatograph (Perkin Elmer, Claurus 600) with Thermal Conductivity Detector (TCD) detector, Elite wax column. The progress of the reactions was followed by TLC, using silica gel 60 F254 plates (Merck).

Typical procedure for the synthesis of BIM 3b

A mixture of indole **1** (2 mmol, 0.234 g), 4-chlorobenzaldehyde **2a** (1 mmol, 0.140 g), and catalyst, phosphate-impregnated titania (0.0167 g, 5 wt% based on **1**) under solvent-free conditions was grounded in a mortar with pestle at room temperature for an appropriate time (1 min). After completion of the reaction, as indicated by TLC, the reaction mixture was extracted with ethyl acetate (2×10 mL) and filtered to separate the catalyst. The combined organic layers were dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure in a rotary evaporator to furnish a crude product that was further purified by column chromatography on silica
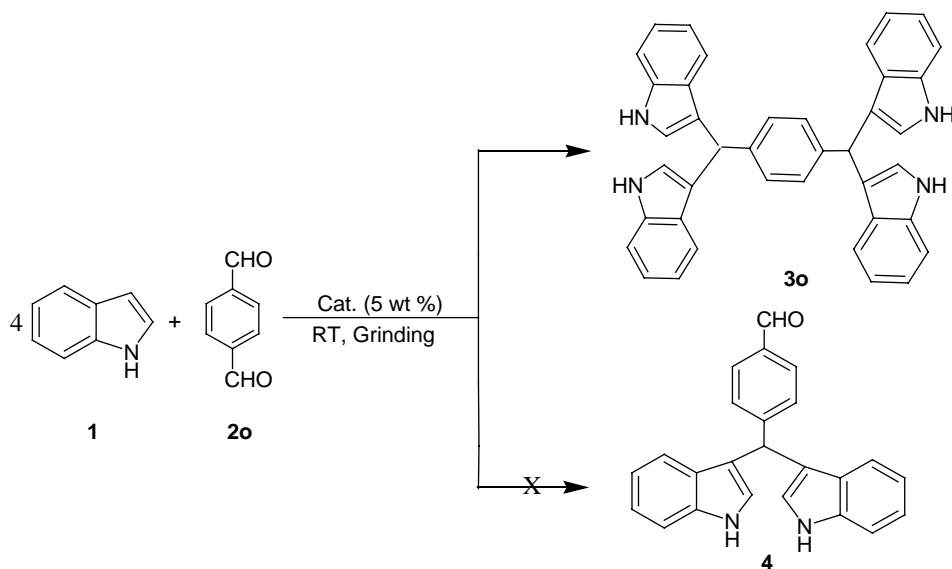
Scheme 3. Reaction of indole with dialdehyde in presence of phosphate-impregnated titania catalyst.

Table 3. Reaction between 4-chlorobenzaldehyde and indole derivatives.

Entry	Indole derivatives	Product	Time (min)	Yield (%)
1	2-Methylindole	3q	1	94
2	5-Hydroxyindole	3r	3	90
3	5-Bromoindole	3s	2	96
4	*N*-Phenylindole	3t	6	60

gel [Eluent: EtOAc/Pet. Ether (1:2)] to give the pure product (99% yield).

Typical procedure for the synthesis of tetra-indolyl(terephthalyl)dimethane 3o

A mixture of indole **1** (4 mmol, 0.468 g), terephthaldehyde 2o (1 mmol, 0.134 g), and the catalyst (0.0234 g, 5 wt% based on **1**) under solvent-free conditions was grounded in a mortar with pestle at room temperature for an appropriate time (1 min). After completion of the reaction, as indicated by TLC, the reaction mixture was extracted with ethyl acetate (2×10 mL) and filtered to separate the catalyst. The combined organic layers were dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure in a rotary evaporator to furnish a crude product that was further purified by column chromatography on silica gel (Eluent: EtOAc/Pet. Ether [1:2]) to give the pure product (93% yield).

All products were identified and characterized by ^1H NMR, ^{13}C NMR, IR, LCMS, GC–MS, and melting point determination to be consistent with the literature result. The yields of the products reported here are isolated yields.

Physical and spectral data for 3b

Yield 99%, solid, melting point 104–105 °C; IR (KBr) (υ_{max}/cm^{-1}) 3402, 3050, 2986, 1615, 1600, 1455,

Table 4. Comparison of catalytic condensation of indole with benzaldehyde.

Catalyst	Solvent	Time [h] $\{T(°C)\}$	Yield [%] (references)
CuBr$_2$	CH$_3$CN	0.4 (RT)	95 (*1*)
Amberlyst	CH$_3$CN	12 (RT)	99 (*1*)
La(PFO)$_3$	EtOH	1.5 (RT)	96 (*1*)
[hmim][HSO$_4$]	EtOH	1 (RT)	97 (*1*)
[bimim][MeSO$_4$]	–	0.4 (RT)	92 (*1*)
NH$_4$Cl	–	2 (RT)	96 (*1*)
Cellulose sulfuric acid	–	0.1 (RT)	92 (*15*)
Impregnated titania	–	0.01 (RT)	99 (*this work*)

1112. ^1H NMR (400 MHz, CDCl$_3$) δ_H 5.83 (s, 1*H*), 6.68 (d, $J = 2.24$ Hz, 2*H*), 7.10–7.45 (m, ArH, 12*H*), 7.81 (br s, 2*H*, NH, exchangeable with D$_2$O); ^{13}C NMR (100 MHz, CDCl$_3$) δ_c 31.6, 110.9, 111.9, 118.4, 119.5, 121.2, 124.0, 126.3, 127.1, 128.5, 128.6, 137.0, 145.2 ppm. MS, *m/z* 322 (M$^+$). Elemental analyses: Calculated, C, 85.72; H, 5.89; N, 8.72%. Found: C, 85.73; H, 5.90; N, 8.74%.

Physical and spectral data for 3r

Yield 90%, solid, melting point 122–124 °C; IR (KBr) (υ_{max}/cm^{-1}) 3410, 2927, 1624, 1466, 1176, 1088. ^1H NMR (400 MHz, DMSO-d_6) δ_H 5.58 (s, 1*H*), 6.66 (d, $J = 2.28$ Hz, 2*H*), 7.1–7.3 (m, 10*H*), 8.51 (s, 2*H*), 10.4 (s, 2*H*); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 30.3, 103.6, 111.7, 112.2, 117.1, 124.5, 127.6, 128.4, 130.62, 130.69, 131.6, 144.4, 150.47 ppm. MS, m/z 386 (M$^+$). Elemental analyses: Calculated C, 54.76; H, 40.47; N, 4.76%. Found C, 54.74; H, 40.48; N, 4.78%.

Physical and spectral data for 3s

Yield 96%, solid, melting point 191–192°C; IR (KBr) (υ_{max}/cm^{-1}) 3423, 2926, 1448, 1089. ^1H NMR (400 MHz, DMSO-d_6) δ_H 5.73 (s, 1*H*), 6.62 (s, 2*H*), 7.24–7.25 (m, 10*H*), 8.11 (s, 2*H*). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 39.38, 112.74, 112.85, 118.6, 122.21, 124.84, 125.18, 128.56, 128.66, 129.95, 132.29, 135.44, 141.73 ppm. MS m/z 514 (M$^+$). Elemental analyses: Calculated, C, 57.5; N, 5; H, 37.5%. Found: C, 57.6; N, 5.04; H, 37.8%.

Synthesis and characterization of the catalyst

Synthesis of the phosphate-impregnated titania catalyst was carried out as per report (*28*). Here, we have followed the same procedure for the preparation of the catalyst as reported: titania and phosphoric acid (88%) were mixed in the molar ratio of 1:1 in a silica boat followed by heating at 200–220 °C on a hot sand bath under stirring until the mass solidified. Heating was then withdrawn and temperature was allowed to come down to approximately 100 °C, then the catalyst was transferred to a vacuum desiccator.

Table 5. Efficacy of recycled catalyst.

Run	Time (min)	Yield (%)
1	1	99
2	4.5	94
3	10	88
4	15	80
5	20	60
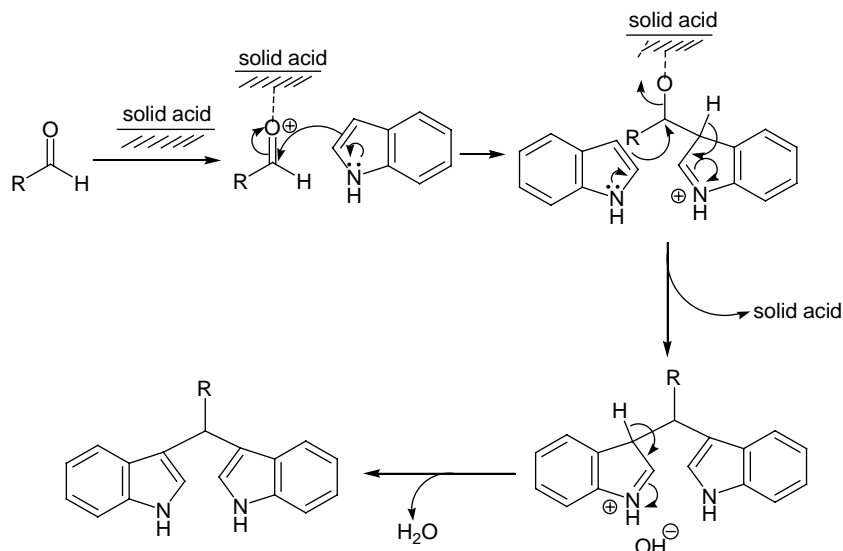
Scheme 4. Plausible mechanism of the reaction.

Finally the catalyst was properly stored in an airtight sample vial. After preparation, the catalyst was characterized (28) by IR, XRD technique and was compared with the reported data.

Reusability of the catalyst

After filtration, the catalyst was recharged by heating at 200–220 °C for 30 min. which was reused for the reaction.

Acknowledgements

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