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## RESEARCH LETTER

### A convenient, eco-friendly, and efficient method for synthesis of bis(3-indolyl)methanes “on-water”

Asok K. Mallik<sup>a\*</sup>, Rammohan Pal<sup>a</sup>, Chayan Guha<sup>a</sup> and Haimanti Mallik<sup>b</sup>

<sup>a</sup>Department of Chemistry, Jadavpur University, 188, Raja S. C. Mullick Road, Kolkata 700 032, India; <sup>b</sup>Department of Chemistry, Lady Brabourne College, P-1/2, Suhrawardy Avenue, Kolkata 700 017, India

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A convenient, eco-friendly, and efficient method for synthesis of bis(3-indolyl)methanes by the reaction of indoles with various aromatic aldehydes “on-water” has been developed. The attractive features of this method are that in cases of aldehydes which are easily oxidized to acids, no external catalyst is necessary while in other cases a trace amount (*ca.* 5 mol%) of commercially available and inexpensive catalyst benzoic acid is sufficient to give good to excellent yield of products.

**Keywords:** bis(3-indolyl)methanes; synthesis; indoles; aromatic aldehydes; “on-water”

#### Introduction

A good number of indole derivatives find important applications in the fields of pharmaceuticals, agro-chemicals, and material sciences (1–3), which have made synthesis of indole derivatives an important research area for organic chemists. Among the indole derivatives, bis(3-indolyl)methanes (BIMs) exhibit a wide range of biological activities such as antimicrobial and antifungal (4), antibacterial (5), analgesic (6), cytotoxic (7), and anti-inflammatory (6) activities. Cancer chemotherapy with BIMs has recently been reviewed (8). BIMs inhibit bladder cancer growth (9), mammary tumor growth (10), and the proliferation process of breast tumor cells (11). Due to the versatile possibilities of application of BIMs, there is a continuous quest for more efficient, economic, and environment-friendly methods for their synthesis.

Indole can readily undergo electrophilic substitution reaction with carbonyl compounds to form BIMs. Different protic acids, such as HCl, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, HCOOH, amberlyst, silica sulfuric acid (SSA), and *p*-TsOH, and Lewis acids, such as InCl<sub>3</sub>, In(OTf)<sub>3</sub>, Ln(OTf)<sub>3</sub>, LiClO<sub>4</sub>, VCl<sub>3</sub>, CuBr<sub>2</sub>, montmorillonite K10, and I<sub>2</sub>, have been used to catalyze the reaction. Most of such methods developed up to the middle of 2009 have been enumerated in a recent elaborate review done by Shiri *et al.* (12). However, in spite of their potential utility, some of the reported methods suffer from drawbacks such as long reaction time, expensive catalyst, low yield, and cumbersome

product isolation procedures. In order to alleviate such drawbacks, development of newer catalytic conditions has become necessary. It is worthwhile to point out here that even after publication of the above-mentioned review, a sizable number of methods have been reported in the literature through use of newer catalysts, mainly with a view to decreasing the reaction time and making the process more and more simple and eco-friendly. Thus, mention may be made of at least 12 very recent methods, seven of which were performed under solvent-free condition using catalysts such as alum [KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O] (13), LaCl<sub>3</sub>·7H<sub>2</sub>O (14), boric acid (15), 3-methyl-1-sulfonic acid imidazolium chloride (16), combination of *N,N,N,N*-tetrabromobenzene-1,3-disulfonamide (TBBDA) and poly(*N*-bromobenzene-1,3-disulfonamide (PBBS) (17), silicotungstic acid (18), and SnCl<sub>2</sub>·2H<sub>2</sub>O (19) and the others done by use of the catalysts such as SBA-15-supported PSFSI (Solvent: DCM) (20), phosphorodiamidic acid (toluene) (21), and Fe(HSO<sub>4</sub>)<sub>3</sub> (DCM) (22), silica-supported cupric fluoroborate [Cu(BF<sub>4</sub>)<sub>2</sub>·SiO<sub>2</sub>] (DCM) (23) and glycerol as a promoting medium (24).

The use of water as a reaction medium is considered to be cheap, safe, and environmentally benign. Hydrophobic effect (25) shown by many organic substrates and internal pressure of water (and its increase by added electrolytes) are two very important factors which enhance the rates of organic reactions involving decrease in the number of molecules. Again, development of chemical processes

\*Corresponding author. Email: mallikak52@yahoo.co.in

without use of any catalyst has currently received considerable importance in synthetic organic chemistry. Recently, Cozzi and Zoli (26) have demonstrated the direct substitution of optically active ferrocenyl alcohols “on-water” with indole, pyrrole, and thiophenols, which gives the product in good yield without the use of Lewis acids, Bronsted acids, or surfactants. In another paper, the same authors (27) have reported that not only ferrocenyl alcohols but also a variety of other alcohols undergo above type of direct nucleophilic substitution “on-water” without the use of Lewis acids, Bronsted acids, or surfactants. Regarding synthesis of BIMs in water, Kamal and Qureshi (28) reported first that these compounds could be obtained by using acetic acid at pH 2.5 at room temperature for over 10 days. They pointed out that no condensation took place in water alone. Subsequently, several other methods for reaction in water have been reported (29, 30). We report herein the direct reaction of indole with aromatic aldehydes “on-water” without the use of any catalyst (five examples) and also using *ca.* 5 mol% benzoic acid, a cheap and very common desk reagent, as catalyst (12 examples).

## Results and discussion

A suspension of a mixture of indole (**1a**) and benzaldehyde (**2a**) (mole ratio 1:2) in water was subjected to heating at 80°C with vigorous stirring until the starting materials disappeared (*ca.* 15 h). Product isolation from the resulting emulsion-like material gave a pure compound (*vide* Experimental), characterization of which from analytical and spectral data showed it to be bis(3-indolyl)phenylmethane (**3a**) (Scheme 1). After getting success in the reaction between benzaldehyde and indole done in the above way, we studied the reactions of indole with 11 other aromatic aldehydes, *viz.*, *p*-methylbenzaldehyde (**2b**), furfural (**2c**), *p*-methoxybenzaldehyde (**2d**), 3,4-dimethoxybenzaldehyde (**2e**), piperonal (**2f**), *p*-chlorobenzaldehyde (**2g**), *p*-bromobenzaldehyde (**2h**), *p*-nitrobenzaldehyde (**2i**), *m*-nitrobenzaldehyde (**2j**), vanillin (**2k**) and 4-*N,N*-dimethylaminobenzaldehyde (**2l**), and chromone-3-aldehyde (**2m**) under similar

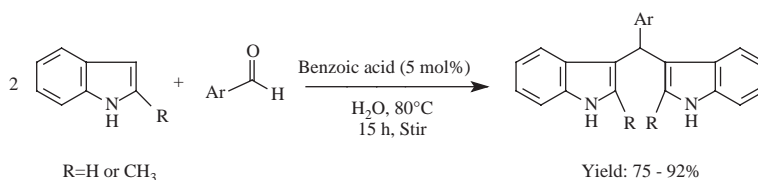
reaction conditions. It was interesting to note that among the above-mentioned aromatic aldehydes only **2b** and **2c** were found to undergo reaction to a very significant extent to give BIMs in very good yield. A careful analysis of this observation led to the suggestion that only those aldehydes that are very susceptible to aerial oxidation gave BIMs in substantial yield. This may be accounted for by considering that during heating of the reaction mixtures in air, these aldehydes are oxidized to yield corresponding carboxylic acids which in low concentration act as catalysts for the BIM formation. This contention was proved to be correct when the extent of BIM formation was found to increase very significantly from any one of the aldehydes **2d–m** under the same reaction condition by use of a small amount of benzoic acid as catalyst. 2-Methylindole was treated in the same way and here also the corresponding BIMs were obtained in very good yield. All the results are presented in Table 1.

## Experimental

All products (Table 1) were characterized from their spectral data and their physical properties were compared with those reported in the literature.

### General procedure for synthesis of bis(3-indolyl) methanes

A mixture of an aromatic aldehyde (1 mmol) and indole (2 mmol) was taken in 50 ml distilled water in a round-bottomed flask. Initially the reactants floated on the water surface owing to their low solubility. The mixture was then subjected to heating at 80°C with vigorous stirring for 15 h. It was then cooled and saturated sodium bicarbonate solution was added dropwise till effervescence ceased. Extraction with chloroform followed by chromatography of the concentrate of the extract over silica gel using petroleum ether-ethyl acetate (9:1) as eluent afforded pure BIM [**3a–c** in very good yield and others in poor yield]. To increase the yield of BIMs from the aldehydes **2d–m**, the same reaction was repeated by addition of a small amount of benzoic acid (5 mol%).



Scheme 1. “On-water” synthesis of bis(3-indolyl)methanes.

Table 1. Synthesis of bis(3-indolyl)methanes in water.



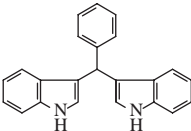

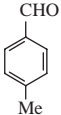
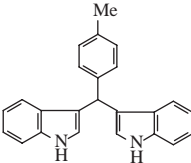

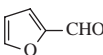
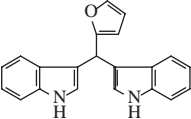

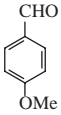
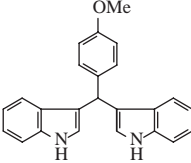

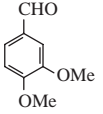
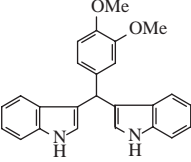

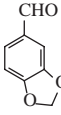
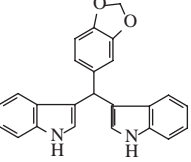
Entry	Indole (1)	Aldehydes (2)	Product (3) <sup>a</sup>	Catalyst	Yield (%) <sup>b</sup> ; melting point (°C) <sup>a</sup>
1			<b>3a</b> 	Without external catalyst	80; 89–91 [Ref. (31), 88–90]
2			<b>3b</b> 	Without external catalyst	78; 93–95 [Ref. (32), 94–96]
3			<b>3c</b> 	Without external catalyst	75; 117–118 [Ref. (33), 117–118]
4			<b>3d</b> 	Benzoic acid (5 mol%)	76; 187 [Ref. (32), 187–189]
5			<b>3e</b> 	Benzoic acid (5 mol%)	75; 196–198 [Ref. (31), 198–200]
6			<b>3f</b> 	Benzoic acid (5 mol%)	83; 94–96 [Ref. (31), 97–99]

Table 1 (Continued)


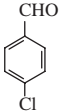
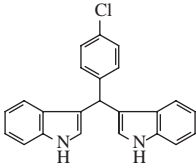

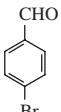
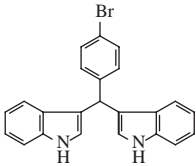

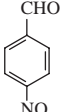
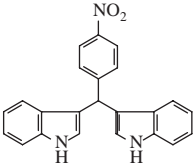

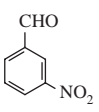
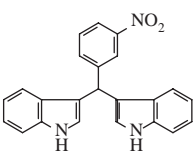

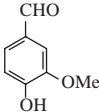
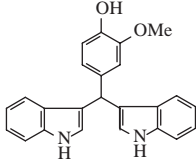

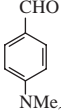
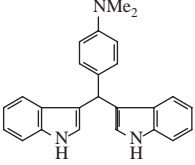
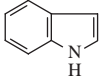
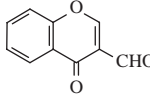
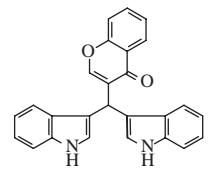
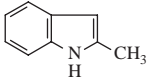

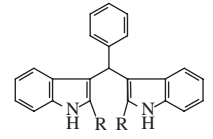
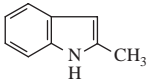
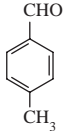
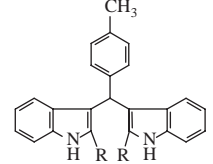
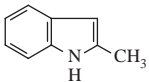
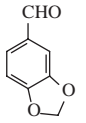
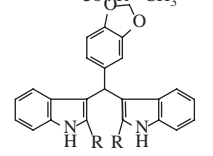
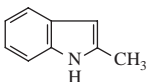
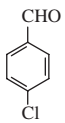
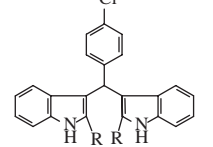
Entry	Indole (1)	Aldehydes (2)	Product (3) <sup>a</sup>	Catalyst	Yield (%) <sup>b</sup> ; melting point (°C) <sup>a</sup>
7			<b>3g</b> 	Benzoic acid (5 mol%)	90; 75 [Ref. (32), 76–77]
8			<b>3h</b> 	Benzoic acid (5 mol%)	92; 108–110 [Ref. (17), 110–112]
9			<b>3i</b> 	Benzoic acid (5 mol%)	91; 215–217 [Ref. (32), 217–219]
10			<b>3j</b> 	Benzoic acid (5 mol%)	92; 220 [Ref. (31), 218–220]
11			<b>3k</b> 	Benzoic acid (5 mol%)	85; 124–125 [Ref. (35), 126–127]
12			<b>3l</b> 	Benzoic acid (5 mol%)	78; 169 [Ref. (24), 168–170]

Table 1 (Continued)

Entry	Indole (1)	Aldehydes (2)	Product (3) <sup>a</sup>	Catalyst	Yield (%) <sup>b</sup> ; melting point (°C) <sup>a</sup>
13			<b>m</b> 	Benzoic acid (5 mol%)	80; 231–233 [Ref. (34), 233–234]
14			 <b>3n</b> : R = CH <sub>3</sub>	Without external catalyst	83; 246–248 [Ref. (35), 247–248]
15			 <b>3o</b> : R = CH <sub>3</sub>	Without external catalyst	78; 173 [Ref. (35), 174–175]
16			 <b>3p</b> : R = CH <sub>3</sub>	Benzoic acid (5 mol%)	88; 226–228
17			 <b>3q</b> : R = CH <sub>3</sub>	Benzoic acid (5 mol%)	90; 238–239

<sup>a</sup>All products were identified by their melting points and spectral data.<sup>b</sup>Isolated yields after column chromatography.

Work up of the reaction mixture in the same way gave pure BIMs (**3d–m**) in good to excellent yield. Reactions with 2-methylindole were also performed in the same way. Most of the BIMs (**3**) were known compounds (referred in Table 1). All the synthesized BIMs were characterized from their physical, analytical, and spectral data. The spectral data of some selected compounds are given in the following section.

### Spectral data for selected compounds

#### *Bis(3-indolyl)-(4-methylphenyl)methane (3b)*

Light pink crystalline solid; IR (KBr,  $\text{cm}^{-1}$ ): 3408 (N–H), 2950, 1606, 1510, 1217, 772;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.37 (s, 3H, Ar–CH<sub>3</sub>), 5.85 (s, 1H, Ar–CH <), 6.67 (s, 2H), 7.00 (t, 2H,  $J=7.2$  Hz), 7.08 (d, 2H,  $J=7.2$  Hz), 7.17 (t, 2H,  $J=7.5$  Hz), 7.23 (d, 2H,  $J=8.1$  Hz), 7.35 (d, 2H,  $J=8.1$  Hz), 7.39 (d, 2H,  $J=7.9$  Hz), 7.91 (br s, 2H, NH); Anal. Calcd. for  $\text{C}_{24}\text{H}_{20}\text{N}_2$  C, 85.68; H, 5.99; N, 8.33%; found: C, 85.49; H, 6.26; N, 8.04%.

#### *Bis(3-indolyl)-(3,4-dimethoxyphenyl)methane (3e)*

Pinkish crystalline solid; IR (KBr,  $\text{cm}^{-1}$ ): 3444 (N–H), 3050, 2990, 1623, 1493, 1217, 1050, 760;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.76 (s, 3H, OCH<sub>3</sub>), 3.85 (s, 3H, OCH<sub>3</sub>), 5.83 (s, 1H, Ar–CH <), 6.67 (s, 2H), 6.76 (d, 1H,  $J=8.4$  Hz), 6.84 (d, 1H,  $J=8.2$  Hz), 6.92 (s, 1H), 7.00 (t, 2H,  $J=7.6$  Hz), 7.17 (t, 2H,  $J=8.0$  Hz), 7.38 (t, 4H,  $J=8.0$  Hz), 7.93 (br s, 2H, NH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.62, 147.23, 136.64, 127.01, 125.99, 124.18, 123.45, 121.85, 120.49, 119.89, 119.15, 112.13, 110.94, 110.81, 55.76 (OCH<sub>3</sub>), 55.73 (OCH<sub>3</sub>), 39.73 (Ar–CH <); Anal. Calcd. for  $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_2$  C, 78.51; H, 5.80; N, 7.32%; found: C, 78.36; H, 5.91; N, 7.20%.

#### *Bis(3-indolyl)-(3,4-methylenedioxyphenyl)methane (3f)*

Pinkish crystalline solid; IR (KBr,  $\text{cm}^{-1}$ ): 3412 (N–H), 2950, 1610, 1510, 1216, 750;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.81 (s, 1H, Ar–CH <), 5.90 (s, 2H, –OCH<sub>2</sub>O–), 6.69 (br. s, 2H), 6.72 (d, 1H,  $J=8.1$  Hz), 6.82 (br. s, 1H), 6.86 (d, 1H,  $J=8.1$  Hz), 7.01 (t, 2H,  $J=7.2$  Hz), 7.17 (t, 2H,  $J=7.8$  Hz), 7.55 (d, 2H,  $J=8.1$  Hz), 7.40 (d, 2H,  $J=7.8$  Hz), 7.93 (br. s, 2H, NH); Anal. Calcd. for  $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2$ : C, 78.67; H, 4.95; N, 7.65%; found C, 78.45; H, 5.21; N, 7.58%.

#### *Bis(3-indolyl)-(4-nitrophenyl)methane (3i)*

Yellow crystalline solid; IR (KBr,  $\text{cm}^{-1}$ ): 3418 (N–H), 3041, 1599, 1350, 1225, 771;  $^1\text{H}$  NMR (300 MHz,

$\text{CDCl}_3$ ):  $\delta$  = 5.99 (s, 1H, Ar–CH <), 6.69 (br. s, 2H), 7.02 (t, 2H,  $J=7.2$  Hz), 7.20 (t, 2H,  $J=7.2$  Hz), 7.33 (d, 2H,  $J=8.1$  Hz), 7.39 (d, 2H,  $J=8.1$  Hz), 7.51 (d, 2H,  $J=8.1$  Hz), 8.02 (br. s, 2H, NH), 8.14 (d, 2H,  $J=8.1$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.83, 146.57, 136.69, 129.52, 126.65, 123.63, 122.36, 119.61, 119.56, 118.14, 111.25, 40.21 (Ar–CH <); Anal. Calcd. for  $\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}_2$ : C, 75.19; H, 4.66; N, 11.44%; found C, 75.02; H, 4.75; N, 11.30%.

#### *Bis(3-indolyl)-(4-N,N-dimethylaminophenyl)methane (3l)*

Pinkish crystalline solid; IR (KBr,  $\text{cm}^{-1}$ ): 3470 (N–H), 3051, 1520, 1462, 1350, 1226, 761;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.91 (s, 6H, NMe<sub>2</sub>), 5.80 (s, 1H, Ar–CH <), 6.66–6.69 (m, 4H), 6.98 (t, 2H,  $J=7.5$  Hz), 7.12–7.21 (m, 4H), 7.34 (d, 2H,  $J=8.1$  Hz), 7.41 (d, 2H,  $J=8.1$  Hz), 7.88 (br. s, 2H, NH); Anal. Calcd. for  $\text{C}_{25}\text{H}_{23}\text{N}_3$ , C, 82.16; H, 6.34; N, 11.50%; found C, 81.98; H, 6.59; N, 11.32%.

#### *Bis(3-indolyl)-(chromone-3-yl)methane (3m)*

Cream-colored crystalline solid; IR (KBr,  $\text{cm}^{-1}$ ): 3336, (N–H), 1628 (C = O), 1616, 1599, 1466, 1216, 850, 736;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.25 (s, 1H, 3-Chr.-CH <), 6.91 (s, 2H), 7.05 (t, 2H,  $J=7.2$  Hz), 7.19 (t, 2H,  $J=7.2$  Hz), 7.35–7.43 (m, 4H), 7.52 (d, 2H,  $J=7.6$  Hz), 7.65 (br. t, 1H,  $J=7.2$  Hz), 7.69 (s, 1H, H-2 of Chr.), 8.01 (br. s, 2H, NH), 8.27 (br. d, 1H, H-5 of Chr.).

#### *Bis(2-methyl-3-indolyl)-(3,4-methylenedioxyphenyl)methane (3p)*

Pinkish crystalline solid; IR (KBr,  $\text{cm}^{-1}$ ): 3384 (N–H), 3049, 1608, 1500, 1485, 1229, 1040, 937, 756;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.06 (s, 6H, 2 × CH<sub>3</sub>), 5.91 (s, 3H, –O–CH<sub>2</sub>–O– and Ar–CH <), 6.67–7.26 (m, 11H, Ar–H), 7.73 (br. s, 2H, NH); Anal. Calcd. for  $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_2$ , C, 79.16; H, 5.62; N, 7.10%; found C, 78.87; H, 5.75; N, 6.86%.

#### *Bis(2-methyl-3-indolyl)-(4-chlorophenyl)methane (3q)*

Pinkish crystalline solid; IR (KBr,  $\text{cm}^{-1}$ ): 3381 (N–H), 3047, 1602, 1487, 1428, 1304, 1243, 1086, 1013, 822, 745;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.08 (s, 6H, 2 × CH<sub>3</sub>), 5.97 (s, 1H, Ar–CH <), 6.88 (t, 2H,  $J=7.2$  Hz), 6.98 (d, 2H,  $J=7.6$  Hz), 7.06 (t, 2H,  $J=7.8$  Hz), 7.21 (s, 4H, 4–Cl–C<sub>6</sub>H<sub>4</sub>–), 7.26 (d, 2H,  $J=7.5$  Hz), 7.77 (br. s, 2H, NH); Anal. Calcd. for  $\text{C}_{25}\text{H}_{21}\text{N}_2\text{Cl}$ , C, 78.01; H, 5.50; N, 7.28%; found C, 77.79; H, 5.39; N, 7.02%.

## Conclusions

We have described an electrophilic substitution reaction of indole “on-water” for generation of BIMs without the use of any Lewis acid catalyst or surfactant, where aerial oxidation of the aldehyde used is very significant. In other cases, addition of a trace amount of benzoic acid (5 mol%) is required. The mild reaction condition, the use of water without the presence of co-solvent, utilization of a small amount of an inexpensive catalyst, and very good yield of the products are all plus points of this methodology. Moreover, it is environmentally benign.

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