RESEARCH LETTER

Synthesis of bis(indolyl)methanes under catalyst-free and solvent-free conditions

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Condensation of indole with aromatic aldehydes has been carried out without using any catalyst and solvent to give bis(indolyl)methanes.

Keywords: bis(indolyl)methanes; solventless; catalyst free; grinding; multicomponent reaction

Introduction

The focus of green chemistry lies on reducing environmental pollution by designing benign reaction processes, avoiding waste generation, and saving energy by reducing number of chemical steps. Multicomponent reactions (1–3) and domino reactions (4–15) are the fascinating offshoots of the search for reducing chemical steps. Solventless or when solvent is a must, water as a preferred medium and use of catalyst or catalyst-free reaction conditions are some of the solutions to avoid waste. Bis(indolyl)methanes (BIMs) have been attractive targets to develop green methodologies because of their wide range of biological, industrial, and synthetic applications (16). (See Supporting information in 16).

The reaction of indole with aldehydes or ketones produces azafulven, which then undergo further addition with another indole molecule to give BIM and water (Scheme 1). Both protic and Lewis acids are known to promote this reaction. However, many Lewis acids are prone to undergo change in the presence of nitrogen containing reactants and this necessitates the use of excess and sometimes stoichiometric amount of Lewis acid catalyst. The various strategies adopted for the synthesis of BIMs and tris(indolyl)methanes (TIMs) have recently been comprehensively reviewed (16). There is continuing interest for the development of a new, practical, economical, and environmental friendly protocol for the synthesis of BIMs. Recent catalysts used for this propose are FeCl₃.6H₂O (17), CuBr (18), CeCl₃.7H₂O (19), silica-bonded S-sulfonic acid (20), N,N,N',N'-tetrabromobenzene-1,3-disulfonamide (TBBDA) and poly(N-bromobenzene-1,3-disulfonamide) (PBBS) (21), cellulose sulfuric acid (22) and ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride (23), polystyrene-supported aluminum chloride (PS–AlCl₃) (24), heteropoly acids (25,26), etc.

A perfectly matching green chemistry protocol would be to carry out the synthesis successfully without the use of any catalyst and solvent. To our knowledge, there are no such reports for the synthesis of BIMs. The only report of catalyst free formation of BIMs is in glycerol (27) at 90 °C. We disclose herein our findings of solventless and catalyst free synthesis of BIMs.

Results and discussion

The propensity with which indole undergoes electrophilic substitution made us to envisage that, for many of the BIMs reported particularly with aryl aldehydes having electron withdrawing groups, there may not be any need of assistance from promoters like protic acids or catalyst. To check this hypothesis, in the first experiment, we mixed o-chlorobenzaldehyde and indole (1:2 mole ratio) and kept at ambient temperature for 45 min Thin Layer Chromatography (TLC). In another experiment a mixture of o-chlorobenzaldehyde and indole (1:2 mole ratio) was ground using mortar and pestle (Method 2)(mechanochemical synthesis)(28,29).

The reaction was found to complete within 15 min TLC, in shorter time than that in the above mixing experiment. Similar procedure was followed for other aryl aldehydes. Aryl aldehyde with an electron donating group at meta position (Entry f) also underwent reaction. Heterocyclic aldehydes (Entry g, h) also reacted successfully. Expectedly, anisaldehyde with electron donating group at para position and

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heptaldehyde failed to react completely. Ketones did not react at all, while 2-methylindole reacted rapidly to give corresponding BIMs (Entry i–p). Even anisaldehyde which failed to give significant product with parent indole gave corresponding BIM product with 2-methylindole (Entry p). To check whether the byproduct water (Scheme 1) was promoting the reaction, deliberately 2–4 drops of water were added to the mixture. However, no enhancement was observed in the rate of reaction, product formation or yield. Another possibility of catalysis by the trace amount of carboxylic acid formed by aerial oxidation of aryl aldehydes cannot be ruled out.

**Experimental**

**Method 1**

Aryl aldehyde (1 equiv.) and indole (2 equiv.) were mixed thoroughly in a test tube and kept at ambient temperature in a test tube for a certain period as stipulated in Table 1. The crude product obtained was recrystallized with chloroform-ethyl acetate mixture.

**Method 2**

Aryl aldehyde (1 equiv.) and indole (2 equiv.) were mixed and ground using mortar and pestle. For

| Entry | \(R^1\)       | R       | Product | Method 1 | Method 2 |
|-------|---------------|---------|---------|----------|----------|
|       |               |         | Reaction time | Yields\(^a\) (%) | Reaction time | Yields\(^a\) (%) |
| A     | 4-NO\(_2\)C\(6\)H\(_4\) | H       | 3a       | 6 days   | 58        | 8 h       | 60 |
| B     | 2-NO\(_2\)C\(6\)H\(_4\) | H       | 3b       | 18 h     | 61        | 6 h       | 61 |
| C     | 4-ClC\(_6\)H\(_4\) | H       | 3c       | 5 days   | 92        | 23 h      | 95 |
| D     | 2-ClC\(_6\)H\(_4\) | H       | 3d       | 45 min   | 96        | 16 min    | 96 |
| E     | C\(_6\)H\(_6\)  | H       | 3e       | 48 h     | 61        | 2 h       | 86 |
| F     | 3-MeOOC\(_6\)H\(_4\) | H       | 3f       | 5 days   | 57        | 13 h      | 86 |
| G     | 2-furyl       | H       | 3g       | 24 h     | 62        | 90 min    | 87 |
| H     | 2-pyridyl     | H       | 3h       | 13 h     | 59        | 10 h      | 94 |
| I     | 4-NO\(_2\)C\(_6\)H\(_4\) | Me      | 3i       | 7 h      | 51        | 105 min   | 60 |
| J     | 4-ClC\(_6\)H\(_4\) | Me      | 3j       | 3 h      | 77        | 100 min   | 97 |
| K     | 2-ClC\(_6\)H\(_4\) | Me      | 3k       | 3 min    | 97        | 2 min     | 98 |
| L     | C\(_6\)H\(_6\)  | Me      | 3l       | 3 days   | 69        | 7 min     | 90 |
| M     | 3-MeOOC\(_6\)H\(_4\) | Me      | 3m       | 3 days   | 63        | 2 h       | 87 |
| N     | 2-furyl       | Me      | 3n       | 10 min   | 77        | 5 min     | 85 |
| O     | 4-MeOOC\(_6\)H\(_4\) | Me      | 3o       | 5 days   | 53        | 2 days    | 83 |
| P     | 2-pyridyl     | Me      | 3p       | 7 h      | 63        | 15 min    | 96 |

\(^a\)Yield of isolated product.
compounds having reaction time of more than 15 min, the initial grinding was done for 15 min and the reaction mixture was kept at ambient temperature. The mixture was ground periodically for a short time after every 30 min till the reaction completed as stipulated in Table 1. The crude product obtained was recrystallized with chloroform-ethyl acetate mixture.

Conclusion

In conclusion, we have accomplished a green protocol for solvent free and catalyst free synthesis of BIMs from indole/2-methylinodole and aryl aldehydes.

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**General methods.** Commercial reagents were used without further purification. $^1$H NMR (300 and 400 MHz) and $^{13}$C NMR (300 and 400 MHz) were recorded using CDCl$_3$ and DMSO-d$_6$ as solvent and TMS as an internal standard. IR spectra's were recorded in KBr. Melting points are uncorrected.

**General procedure; Method-1:** Indole (1) (2 mmol)/2-methyl indole (2) (2 mmol), aryl aldehydes (1a-1p) (1 mmol) were mixed thoroughly in a test tube and kept at ambient temperature. The reaction was monitored using TLC. The crude product was recrystallised using chloroform and ethyla acetate mixture.

**Method-2:** Indole (1) (2 mmol)/2-methyl indole (2) (2 mmol), aryl aldehydes (1a-1p) (1 mmol) was ground using mortar and pestle. The reaction was monitored by TLC. For compounds requiring more than 15 min, the grinding was done intermittently after every 30 min. The crude product was then recrystallised using chloroform and EtOAc.

### Complete Characterization of all the Compounds.

**4a**

Yield 60% (0.221 g); yellow solid; mp 219-220 °C; IR (KBr) 3456, 3387, 1506, 642 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-d$_6$) δ 6.02 (s, 1H, Ar-CH), 10.91 (br, s, 2H, NH), 7.05 (s, 2H), 6.894 (m, 4H), 7.37 (d, 2H), 7.61 (d, 2H), 7.29 (d, 2H), 8.14 (d, 2H); $^{13}$C NMR (400 MHz, DMSO-d$_6$) δ 40.037, 112.064, 117.166, 118.900, 119.389, 121.575, 123.881, 124.340, 126.856, 129.927, 137.086, 146.256, 153.612.

**4b**

Yield 61% (0.223 g); yellow solid; mp 188-190 °C; IR (KBr) 3456, 3423, 3053, 1616, 1550, 1508, 1338 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-d$_6$) δ 6.88 (s, 1H, Ar-CH), 10.91 (br, s, 2H, NH), 5.88 (s, 2H), 7.85 (d, 2H), 7.06 (t, 2H), 7.72 (t, 2H), 7.988 (d, 2H), 7.52-7.46 (m, 4H); $^{13}$C NMR (400 MHz, DMSO-d$_6$) δ 63.631, 111.489, 117.165, 118.607, 119.119, 121.154, 123.314, 123.748, 125.790, 127.913, 128.439, 132.712, 136.373, 139.326, 148.060.
Yield 95% (0.338 g); colorless solid; mp 76-77 °C; IR (KBr) 3412, 3055, 1616, 1591, 808 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.92 (s, 1H, Ar-CH), 7.958 (br, s, 2H, NH), 7.27 (m, 8H), 7.06 (d, 2H), 7.62 (d, 2H); ¹³C NMR (300 MHz, CDCl₃) δ 39.62, 111.12, 119.18, 119.36, 119.81, 122.08, 123.58, 126.88, 128.36, 130.07, 131.79, 136.68, 142.55.

Yield 96% (0.342 g); colorless solid; mp 185-186 °C; IR (KBr) 3421, 3053, 1550, 596 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.374 (s, 1H, Ar-CH), 7.90 (br, s, 2H, NH), 6.64 (s, 2H), 7.23 (m, 8H), 7.37 (d, 2H), 7.26 (d, 1H), 7.44 (m, 2H), 7.46 (d, 1H); ¹³C NMR (300 MHz, CDCl₃) δ 36.63, 111.06, 118.35, 119.31, 119.84, 122.02, 123.77, 126.63, 126.99, 127.50, 129.48, 130.32, 133.96, 136.70, 141.31.

Yield 86% (0.277 g); colorless solid; mp 75-77 °C; IR (KBr) 3412, 3026, 1616, 1598, 850 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.91 (s, 1H, Ar-CH), 7.891 (br, s, 2H, NH), 6.67 (s, 2H), 7.30 (m, 6H), 7.38 (d, 2H), 7.03 (t, 2H), 7.21 (m, 3H); ¹³C NMR (300 MHz, CDCl₃) δ 40.20, 11.10, 119.23, 119.63, 119.93, 121.92, 123.66, 126.16, 127.09, 128.25, 128.75, 136.68, 144.07.

Yield 86% (0.302 g); colorless solid; mp 180 °C; IR (KBr) 3404, 3363, 1608, 1587, 453 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.88 (s, 1H, Ar-CH), 7.91 (br, s, 2H, NH),
6.7 (s, 2H), 7.05 (m, 8H), 7.35 (s, 1H), 7.44 (t, 1H), 7.24 (m, 2H), 3.75 (s, 3H); $^{13}$C NMR (300 MHz, CDCl$_3$) δ 40.21, 110.97, 111.24, 114.73, 119.20, 119.54, 119.88, 121.28, 121.89, 123.54, 127.07, 129.08, 136.66, 145.72, 159.55.

Yield 86 % (0.267 g); colorless solid; mp 101-114 °C; IR (KBr) 3441, 3406, 3107, 1544, 466.77 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 5.90 (s, 1H, Ar-CH), 7.97 (br, s, 2H, NH), 6.32 (s, 2H), 7.165 (m, 11H); $^{13}$C NMR (300 MHz, CDCl$_3$) δ 34.10, 106.63, 110.19, 111.19, 117.07, 119.34, 119.66, 121.94, 123.12, 126.76, 136.51, 141.23, 157.12.

Yield 94 % (0.304 g); white solid; mp 207-208 °C; IR (KBr) 3446, 3138, 1587, 426 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$ + DMSO-d$_6$) δ 6.08 (s, 1H, Ar-CH), 8.00 (br, s, 2H, NH), 6.82 (s, 2H), 7.360 (m, 6H), 7.02 (t, 2H), 7.06 (t, 1H), 7.18 (m, 3H); $^{13}$C NMR (Not clear, need to be re-recorded).

Yield 60 % (0.236 g); yellow solid; mp 239-240 °C; IR (KBr) 3396, 3049, 1593, 1517, 314 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO-d$_6$) δ 6.07 (s, 1H, Ar-CH), 10.86 (br, s, 2H, NH), 2.10 (s, 6H), 7.24 (d, 2H), 6.91 (t, 2H), 6.70 (t, 2H), 6.80 (t, 2H), 7.42 (d, 2H), 8.154 (d, 2H); $^{13}$C NMR (300 MHz, DMSO-d$_6$) δ 12.37, 39.97, 110.95, 11.28, 118.64, 120.20, 123.68, 128.33, 130.26, 133.01, 135.57, 146.14, 153.34.
Yield 97% (0.371 g); white solid; mp 232-234 °C; IR (KBr) 3379, 3061, 1600, 1552, 433 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 5.91 (s, 1H, Ar-CH), 10.75 (br, s, 2H, NH), 2.01 (s, 6H), 7.21 (d, 2H), 6.88 (t, 2H), 6.686 (t, 2H), 6.807 (d, 2H), 7.17 (d, 2H), 7.29 (d, 2H); ¹³C NMR (400 MHz, DMSO-d₆) δ 111.857, 39.500, 110.338, 111.592, 117.975, 118.311, 119.556, 127.813, 128.021, 130.164, 130.437, 132.152, 135.042 143.340.

Yield 98% (0.375 g); colorless solid; mp 218-222 °C; IR (KBr) 3385, 3057, 1618, 501 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 6.07 (s, 1H, Ar-CH), 10.77 (br, s, 2H, NH), 7.423 (m, 12H); ¹³C NMR (300 MHz, DMSO-d₆) δ 12.12, 37.28, 110.866, 110.971, 118.278, 118.568, 120.085, 128.357, 128.77, 129.747, 131.218, 132.667, 135.453, 142.07.

Yield 89% (0.0311 g); colorless solid; mp 246-247 °C; IR (KBr) 3396, 3051, 1425, 497 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 5.94 (s, 1H, Ar-CH), 10.74 (br, s, 2H, NH), 2.08 (s, 6H), 7.235 (d, 2H), 6.89 (t, 2H), 6.68 (t, 2H), 6.82 (d, 2H), 7.24-7.22 (m, 5H); ¹³C NMR (300 MHz, DMSO-d₆) δ 12.36, 39.09, 110.748, 112.642, 118.354, 118.934, 119.958, 126.191, 128.739, 129.155, 129.707, 132.497, 135.525, 144.72.
Yield 87 % (0.331 g); colorless solid; mp 235-236 °C; IR (KBr) 3383, 3099, 1595, 1487, 1242 cm⁻¹;¹H NMR (400 MHz, DMSO-d₆) δ 5.87 (s, 1H, Ar-CH), 10.70 (br, s, 2H, NH), 2.06 (s, 6H), 7.20 (d, 2H), 6.87 (t, 2H), 6.67 (t, 2H), 6.83 (d, 2H), 6.735 (s, 1H), 6.77 (d, 1H), 7.16 (t, 1H), 6.79 (d, 1H), 3.61 (s, 3H);¹³C NMR (400 MHz, DMSO-d₆) δ 11.851, 39.710, 54.775, 110.238, 112.065, 114.985, 117.856, 118.794, 119.463, 119.788, 121.215, 128.215, 128.800, 131.965, 134.996, 145.895, 159.061.

Yield 85 % (0.290 g); colorless solid; mp 208-212 °C; IR (KBr) 3398, 3051, 1618, 1460, 499 cm⁻¹;¹H NMR (400 MHz, DMSO-d₆) δ 5.81 (s, 1H, Ar-CH), 10.72 (br, s, 2H, NH), 2.13 (s, 6H), 7.20 (d, 2H), 6.36 (t, 1H), 7.57 (d, 1H);¹³C NMR (400 MHz, DMSO-d₆) δ 11.495, 32.589, 106.819, 110.254, 110.316, 110.704, 118.004, 118.060, 119.568, 127.754, 131.749, 134.912, 141.184, 157.018.

Yield 83 % (0.323 g); colorless solid; mp 195-196 °C; IR (KBr) 3394, 3047, 1604, 1508, 1236, 493 cm⁻¹;¹H NMR (300 MHz, DMSO-d₆) δ 5.89 (s, 1H, Ar-CH), 10.71 (br, s, 2H, NH), 2.08 (s, 6H), 7.10 (d, 2H), 6.84-6.81 (m, 4H), 6.88 (d, 2H), 7.23 (d, 2H), 6.704 (d, 2H), 3.38 (s, 3H);¹³C NMR (300 MHz, DMSO-d₆) δ 12.36, 38.25, 55.37, 110.72, 112.99, 113.72, 118.33, 118.97, 119.92, 128.74, 130.01, 132.35, 135.52, 136.58, 157.78.
$^1$H NMR spectra of compound 4a
$^{13}$C NMR spectra of compound 4a
$^1$H NMR spectra of compound 4b
$^{13}$C NMR spectra of compound 4b
$^1$H NMR spectra of compound 4C
$^1$C NMR spectra of compound 4C
$^1$H NMR spectra of compound 4d
$^{13}$C NMR spectra of compound 4d
$^1$H NMR spectra of compound 4e
$^{13}$C NMR spectra of compound 4e
\(^1\text{H NMR spectra of compound 4f}\)
$^{13}$C NMR spectra of compound 4f
$^{13}$C NMR spectra of compound 4g
$^1$H NMR spectra of compound 4h
$^{13}$C NMR spectra of compound 4h
$^1$H NMR spectra of compound 4i
$^{13}$C NMR spectra of compound 41
$^1$H NMR spectra of compound 4j
$^{13}$C NMR spectra of compound 4j
$^{13}$C NMR spectra of compound 4j
$^1$C NMR spectra of compound 4k
$^1$H NMR spectra of compound 41
$^{13}$C NMR spectra of compound 4I
$^1$H NMR spectra of compound 4m
$^{13}$C NMR spectra of compound 4m
$^1$H NMR spectra of compound 4n
\(^{13}\)C NMR spectra of compound 4n
$^1$H NMR spectra of compound 4o
$^{13}\text{C}$ NMR spectra of compound 40
\(^{13}\text{C} \text{NMR spectra of compound 4p}\)
HRMS of 4n
LC-MS of 4f
**User Chromatograms**

![Chromatogram Image]

**Integration Peak List**

| Peak | Start | End   | Height | Area   | Area % |
|------|-------|-------|--------|--------|--------|
| 1    | 0.18  | 0.28  | 0.53   | 217.56 | 16970.87 | 70.31 |
| 2    | 2.12  | 2.39  | 2.47   | 2779.34 | 71662.24 | 29.69 |

**Fragmentor Voltage** 390  **Collision Energy** 0  **Ionization Mode** ESI

**User Spectra**

![Spectrum Image]

**Integration Peak List**

| Peak | Start | End   | Height | Area   | Area % |
|------|-------|-------|--------|--------|--------|
| 1    | 2.34  | 2.79  | 2.54   | 148849 | 100    |

**Fragmentor Voltage** 390  **Collision Energy** 0  **Ionization Mode** ESI

**LC-MS of 4j**
User Chromatograms

Integration Peak List

| Peak | Start | RT  | End   | Height | Area    | Area % |
|------|-------|-----|-------|--------|---------|--------|
| 1    | 0.17  | 0.25| 0.33  | 2661.12| 16023.899| 71.94  |
| 2    | 1.08  | 1.14| 1.21  | 97.3   | 303.661 | 1.36   |
| 3    | 2.17  | 2.23| 2.31  | 1941.81| 5947.055| 26.7   |

Fragmentor Voltage: 100
Collision Energy: 0
Ionization Mode: ESI

LC-MS of 4m

*116
*0.24
*0.65
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--- End Of Report ---

LC-MS of 40
Integration Peak List

| Peak | Start | RT | End | Height | Area  | Area % |
|------|-------|----|-----|--------|-------|--------|
| 1    | 0.15  | 0.25 | 0.43 | 331582 | 1874696 | 100    |

User Spectra

Fragmentation Voltage: 100
Collision Energy: 0
Ionization Mode: ESI

ESI Scan 1 (1.42-1.49 min, 8 scans) Frag=100.0V GJP-RP-1399-10-C.d

Counts (%): 221.1

Counts (%): 352.2

ESI Scan 2 (0.20-0.32 min, 13 scans) Frag=100.0V GJP-RP-1399-10-C.d

Counts (%): 111.0

Counts (%): 195.0

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LC-MS of 4p