# Ionic liquid tributyl (carboxymethyl) phosphonium bromide as an efficient catalyst for the synthesis of bis(indolyl)methanes under solvent-free conditions

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A simple green synthesis of bis (indolyl)methanes involved the reaction of indole with aldehydes in the presence of a phosphonium salt ionic liquid as the catalyst. The simple experimental procedures, short reaction times, high yields of product, non-toxic catalyst and the absence of solvent are the advantages of this method.

**Keywords:** ionic liquid, bis (indolyl)methane, phosphonium salt, solvent free conditions

Room-temperature ionic liquids (RTILs) defined as organic salts that are liquid over a wide range of temperatures at or below 100 °C: they often have low vapour pressure, high thermal stability, strong solvent power and low flammability.[1,2] The application of Brønsted acidic ionic liquids as catalysts combine the useful characteristics of solid acids and mineral acids, and they have been used to replace traditional mineral liquid acids, such as hydrochloric acid and sulfuric acid in chemical reactions.[3–7]

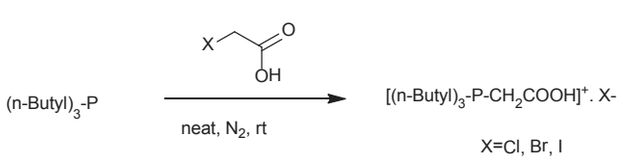
Indole and its derivatives are an important class of nitrogen heterocycles in pharmaceutical as well as synthetic chemistry.[8,9] Bis(indolyl) methane derivatives (BIMs) have been widely isolated from various terrestrial and marine natural sources. These natural products have important biological activities.[10–12] Recently, we reviewed the chemistry of bis- and trisindolyl methanes.[13]

Synthesis of bis(indolyl)methanes *via* the reaction of indole with aldehydes or ketones catalysed by using a various of catalysts such as protic acids, Lewis acids or solid acids, has been reported.[14–24] In spite of their potential utility, some of the reported methods suffer from drawbacks such as longer reaction time, lower yields or the use of organic solvents, and expensive reagents. Therefore, introduction of new methods, catalysts, green solvents and procedures for the preparation of BIMs is still in demand and we have tried to introduce a green phosphonium ionic liquids (PILs) as alternatives to toxic solvents.

## Results and discussion

In continuation of our studies on the synthesis of bis(indolyl) methanes[13] we have prepared Brønsted acidic ILs and applied them as catalysts in organic synthesis.[25–27] In this paper, we report the use of ionic liquid tributyl(carboxymethyl) phosphonium bromide as a highly efficient, homogeneous, and green catalyst for the synthesis of bis(indolyl)methanes at room temperature under solvent-free conditions.

Three COOH-functionalised phosphonium salts (CFPS), tributyl (carboxymethyl)phosphonium bromide, tributyl (carboxymethyl)phosphonium chloride and tributyl (carboxymethyl)phosphonium iodide were prepared according to the literature method[28,29] by the reaction of tributyl phosphine




**Scheme 1** Preparation of phosphonium ionic liquids.

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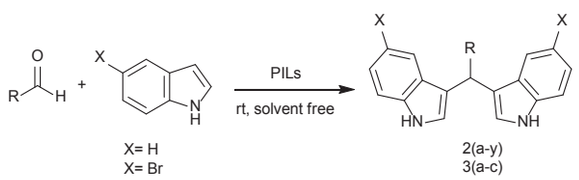



**Scheme 2** Synthesis of bis(indolyl)methanes.

(1 equiv.) with bromo, chloro and iodoacetic acids (1 equiv) (Scheme 1) The structures of the ionic liquids were identified by $^{1}H$ and $^{31}P$ NMR. The corresponding spectroscopic data are reported in the experimental section. Although may ILs do not dissolve in organic solvents, $[n\text{-}Bu_3P\text{–}CH_2COOH]^+Br^-$ ($Cl^-$, $I^-$) dissolves in most organic solvents. This is an important factor for the successful catalysis of reactions in organic media.

We investigated the preparation of bis(indolyl)methanes from indole and aldehydes in the presence of phosphonium ionic liquids (PILs) as catalyst under solvent-free conditions at room temperature. (Scheme 2).

To optimise the reaction conditions, the condensation of indole (2 mmol) with 4-chlorobenzaldehyde (1 mmol) was examined using PILs. The activity of phosphonium halides were affected by the behaviour of anions. With different halide ions, the activity varied in the order: $I^- \geq Br^- > Cl^-$. A possible reason was that $I^-$ ion separates away from the cation more easily than $Br^-$ and $Cl^-$. Because of iodoacetic acid was more toxic, we choose the phosphonium bromide as the catalyst for the synthesis of bis(indolyl)methanes.

Increasing the amount of phosphonium bromide to more than 20 mol% showed no substantial improvement in the reaction results (Table 1), whereas the yield decreased and the reaction times increased by reducing the amount of the catalyst.

In order to show that the phosphonium bromide was responsible for the catalytic results, the model reaction was examined in the presence of 20 mol% of the starting materials used for the preparation of the catalyst ($PBu_3$ and $BrCH_2COOH$) and also in the presence of $CH_3COOH$ and HBr. The results are presented in Table 2. As Table 2 indicates, the phosphonium bromide efficiently catalysed the reaction; $PBu_3$ did not catalyse the reaction; and $BrCH_2COOH$ as well as $CH_3COOH$ and HBr gave low yields of the product over longer reaction times.

**Table 1** Effect of various amounts of the catalyst in the reaction of 4-chlorobenzaldehyde with indole at room temperature under solvent-free conditions

| Entry | Ionic liquid/mol% | Time/min | Yield/% |
|---|---|---|---|
| 1 | 5 | 120 | 40 |
| 2 | 10 | 120 | 50 |
| 3 | 15 | 45 | 89 |
| 4 | 20 | 20 | 90 |
| 5 | 25 | 20 | 90 |

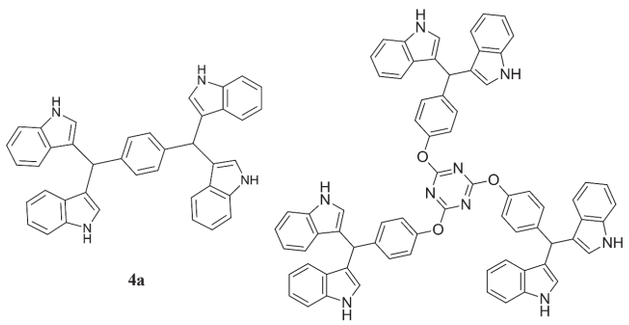
**Table 2** Reaction of 4-chlorobenzaldehyde with indole at room temperature under solvent-free conditions using $CH_3COOH$, HBr, $BrCH_2COOH$, $PBu_3$ and $[Bu_3P\text{-}CH_2COOH]^+.Br^-$

| Entry | Catalyst/20 mol% | Time/min | Yield/% |
|---|---|---|---|
| 1 | Acetic acid | 240 | 35 |
| 2 | HBr | 240 | 55 |
| 3 | Bromo acetic acid | 240 | 45 |
| 4 | Tri-buthyl phosphine | 240 | No reaction |
| 5 | Tributyl(carboxymethyl) phosphonium bromide | 20 | 90 |

To assess the efficiency and the scope of phosphonium bromide in the preparation of bis(indolyl)methanes, different aryl aldehydes, were reacted with indole or 5-bromoindole under the optimal reaction conditions; the results are given in Table 3. As can be seen from Table 3, the catalyst was general and efficient; aryl aldehydes bearing electron-withdrawing substituents, electron-releasing substituents and halogens on the aromatic ring gave the desired bis (indolyl) methanes in high to excellent yields (75–96%) and in relatively short reaction times (15–120 min) (Table 3).

The condensation of indole with terephthaldehyde and tris benzine-2,4,6-aldehyde to give **4a** and **4b** was also successfully completed under the optimum reaction conditions (Scheme 3).

In conclusion, we have introduced phosphonium ionic liquids as new ILs and developed a highly efficient, simple method for the preparation of a wide range of bis(indolyl) methane derivatives. This involved the condensation of aldehydes with indole in the presence of a catalytic amount of tributyl(carboxymethyl)phosphonium bromide as an efficient Brønsted ionic liquid catalyst. This can be prepared from inexpensive starting materials. This method has many advantages, such as generality, simple work-up procedure, mild reaction conditions and clean formulation of the products in high yields.




**Scheme 3** Di (bis-indolyl methane) (**4a**) and tri(bis-indolylmethane) (**4b**).

## Experimental

All commercially available chemicals were obtained from Merck and Alfa Aesar companies, and used without further purifications. All known compounds were identified by comparison of their melting points and spectroscopic data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. Melting points were measured on a Büchi B-545 apparatus in open capillary tubes. The $^1$H NMR (400/500 MHz) and $^{13}$C NMR (100/125 MHz) were run on a Bruker Avance, FT-NMR spectrometer (δ in ppm). Microanalysis was performed on a Perkin-Elmer *240-B* microanalyser.

*Synthesis of ionic liquid phosphonium bromide; general procedure*

Bromoacetic acid (5 mmol) was added to tributyl phosphine (5 mmol)

**Table 3** Synthesis of bis(indolyl)methanes from indole and aldehyde compounds using phosphonium bromide at room temperature

| Entry | $R^1$ | X | Product | Time/min | Yield/%[a] | M.p./°C[lit.] |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | H | **2a** | 20 | 87 | 128–130 (124–125)[19] |
| 2 | 4-Me-$C_6H_4$ | H | **2b** | 15 | 80 | 98–100 (97–98)[19] |
| 3 | 4-MeO-$C_6H_4$ | H | **2c** | 40 | 78 | 188–190 (190–192)[19] |
| 4 | 2-MeO-$C_6H_4$ | H | **2d** | 45 | 75 | 130–132 (134–136)[19] |
| 5 | 2-$NO_2$-$C_6H_4$ | H | **2e** | 35 | 93 | 211–213 (215–217)[16] |
| 6 | 3-$NO_2$-$C_6H_4$ | H | **2f** | 30 | 85 | 220–222 (221–223)[16] |
| 7 | 4-$NO_2$-$C_6H_4$ | H | **2g** | 30 | 83 | 211–213 (215–218)[16] |
| 8 | 2-OH-$C_6H_4$ | H | **2h** | 20 | 78 | 102–104 (123–125)[20] |
| 9 | 3-OH-$C_6H_4$ | H | **2i** | 15 | 88 | 98–100 (98)[14] |
| 10 | 4-OH-$C_6H_4$ | H | **2j** | 20 | 80 | 118–120 (120–121)[19] |
| 11 | 2-OH-3-MeO-$C_6H_3$ | H | **2k** | 35 | 89 | 108–110 |
| 12 | 4-OH-3-MeO-$C_6H_3$ | H | **2l** | 20 | 93 | 110–112 (110–112)[22] |
| 13 | 4-OH-3-EtO-$C_6H_3$ | H | **2m** | 20 | 76 | 102–104 |
| 14 | 2-Cl-$C_6H_4$ | H | **2n** | 15 | 85 | 72–74 (72–74)[19] |
| 15 | 3-Cl-$C_6H_4$ | H | **2o** | 15 | 88 | 77–79 (83–85)[20] |
| 16 | 4-Cl-$C_6H_4$ | H | **2p** | 20 | 89 | 80–82 (76–78)[17] |
| 17 | 2,4-di-Cl-$C_6H_3$ | H | **2q** | 30 | 87 | 108–110 (103–106)[19] |
| 18 | 3-Br-$C_6H_4$ | H | **2r** | 15 | 81 | 180–182 (189–191)[23] |
| 19 | 4-Br-$C_6H_4$ | H | **2s** | 15 | 85 | 110–112 (110–112)[19] |
| 20 | 4-CN-$C_6H_4$ | H | **2t** | 30 | 81 | 193–195 (198–200)[24] |
| 21 | 4-ph-$C_6H_4$ | H | **2u** | 35 | 80 | 241–243 |
| 22 | 3-phO-$C_6H_4$ | H | **2v** | 20 | 75 | 83–85 (84–86)[21] |
| 23 | 2-Naphtyl- | H | **2w** | 35 | 96 | 189–191 (190–192)[24] |
| 24 | 4-BuO-$C_6H_4$ | H | **2x** | 30 | 88 | 256(dec.) |
| 25 | 3-indole | H | **2y** | 120 | 76 | 163(dec.) (160, dec)[17] |
| 26 | 4-ph-$C_6H_4$ | Br | **3a** | 45 | 82 | 241–243 |
| 27 | 2-Naphtyl | Br | **3b** | 40 | 91 | 206–208 |
| 28 | 4-OH-3EtO-$C_6H_3$ | Br | **3c** | 55 | 85 | 101–103 |
| 29 | 4-CHO-$C_6H_4$ | H | **4a** | 60 | 85[b] | 192(dec.) (194, dec)[17] |
| 30 | Tris-aldehyde | H | **4b** | 120 | 77[c] | 230(dec.)[18] |

[a]Isolated yields.

[b]Reaction conditions: indole (4 equiv.), and terephthaldehyde (1 equiv.)

[c]Reaction conditions: indole (6 equiv.), and tris aldehyde (1 equiv.).

under nitrogen over 15 min at room temperature. Upon completion of the addition, the reaction was continued for 24 h. The product was obtained as yellowish, viscous oil. $^1$H NMR($CDCl_3$, 500 MHz): δ 0.97 (t, 9H, $J$ = 7.17 Hz, $CH_3$), 1.59 (m, 12H, $CH_2$), 2.45 (m, 6H, $CH_2$), 4.05 (d, 2H, $J$ = 10 Hz, $CH_2$), 7.79 (s, 1H, OH); $^{31}$P NMR ($CDCl_3$): δ 74.85. Anal. Calcd for $C_{14}H_{30}BrO_2P$ (341.26): C, 49.27; H, 8.86. Found: C, 48.96; H, 8.23%.

*Synthesis of bis(indolyl)methanes; general procedure*

Indole (2 mmol) was added to a mixture of the aldehyde (1 mmol) and phosphonium bromide (0.07 g, 0.2 mmol, 20 mol%) in a mortar, and the resulting mixture was ground at room temperature for the appropriate time (Table 3). After completion of the reaction, as monitored by TLC, $H_2O$ (3 mL) was added, stirred for 3 min and filtered. The solid residue was recrystallised from EtOAc/petroleum ether (1:2) to give the pure product.

*2-(di(1H-Indol-3-yl)methyl)-6-methoxyphenol* (**2k**): Pink solid, FT-IR (KBr) ν/cm$^{-1}$: 3412, 3254, 2957, 1615, 1477, 1272, 743. $^1$H NMR (DMSO, 400 MHz): δ 3.85 (t, 3H, $CH_3$,), 5.83 (b, 1H, OH), 6.30 (s, 1H, CH), 6.74 (s, 2H, HAr), 7.40 (m, 11H, HAr), 7.87 (s, 2H, NH). $^{13}$C NMR (DMSO, 100 MHz): δ 55.2, 56.3, 109.8, 111.0, 119.2, 120.6, 121.9, 124.5, 125.9, 127.1, 130.1, 132.7, 136.7, 143.2, 145.6. Anal. Calcd for $C_{24}H_{20}N_2O_2$ (368.43): C, 78.24; H, 5.47; N, 7.60. Found: C, 78.35; H, 5.39; N, 7.51%.

*4-(di(1H-Indol-3-yl)methyl)-2-ethoxyphenol* (**2m**): Pink solid, FT-IR (KBr) ν/cm$^{-1}$: 3411, 3312, 2930, 1603, 1510, 1456, 1215, 744. $^1$H NMR (DMSO, 400 MHz): δ 1.35 (t, 3H, $CH_3$), 4.08 (q, 2H, $CH_2$), 5.34 (b, 1H, OH), 5.48 (s, 1H, CH), 6.62 (s, 2H, HAr), 6.93 (m, 11H, HAr), 8.39 (s, 2H, NH). $^{13}$C NMR (DMSO, 100 MHz): δ 14.8, 55.3, 65.1, 111.2, 112.3, 115.8, 119.2, 119.9, 120.2, 120.6, 121.9, 124.5, 127.0, 136.7, 137.2, 147.1, 147.6. Anal. Calcd for $C_{25}H_{22}N_2O_2$ (382.45): C, 78.51; H, 5.80; N, 7.32%. Found: C, 78.77; H, 5.61; N, 7.47%.

*3,3'-([1,1'-Biphenyl]-4-yl-methylene)bis(1H-indole)* (**2u**): Pink solid, FT-IR (KBr) ν/cm$^{-1}$: 3420, 2960, 1618, 1487, 1455, 1337, 745. $^1$H NMR (DMSO, 400 MHz): δ 5.93 (s, 1H, CH), 6.72 (s, 2H, HAr), 7.25 (m, 17H, HAr), 8.03 (s, 2H, NH). $^{13}$C NMR (DMSO, 100 MHz): δ 55.3, 111.2, 119.1, 120.5, 121.8, 124.6, 125.7, 127.2, 127.5, 128.6, 136.7, 140.4, 143.2. Anal. Calcd for $C_{29}H_{22}N_2$ (398.50): C, 87.41; H, 5.56; N, 7.03. Found: C, 87.23; H, 5.29; N, 7.21%.

*3,3'-((4-Butoxyphenyl)methylene)bis(1H-indole)* (**2x**). Pink solid, FT-IR (KBr) ν/cm$^{-1}$: 3416, 2955, 1617, 1467, 1275, 749. $^1$H NMR ($CDCl_3$, 500 MHz): δ 0.99 (t, 3H, $CH_3$), 1.55 (m, 4H, $CH_2$), 3.96 (t, 2H, $CH_2$), 5.70 (s, 1H, CH), 6.63 (s, 2H, HAr), 6.68 (d, 2H, HAr), 7.25 (m, 10H, HAr), 8.12 (s, 2H, NH). $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 13.9, 19.3, 31.4, 39.0, 67.7, 112.6, 112.7, 114.4, 119.4, 122.3, 124.7, 124.8, 128.7, 129.4, 135.1, 135.4, 157.7. Anal. Calcd for $C_{27}H_{26}N_2O$ (394.51): C, 82.20; H, 6.64; N, 7.10. Found: C, 82.34; H, 6.37; N, 7.15%.

*3,3'-([1,1'-Biphenyl]-4-yl-methylene)bis(5-bromo-1H-indole)* (**3a**): Pink solid, FT-IR (KBr) ν/cm$^{-1}$: 3446, 2960, 1613, 1458, 1095, 796. $^1$H NMR (DMSO, 400 MHz): δ 5.79 (s, 1H, CH), 6.70 (s, 2H, HAr), 7.25 (m, 15H, HAr), 8.19 (s, 2H, NH); $^{13}$C NMR (DMSO, 100 MHz): δ 54.7, 111.7, 113.1, 119.8, 120.9, 123.5, 124.6, 125.7, 127.1, 127.4, 128.6, 136.3, 136.9, 141.4, 143.4. Anal. Calcd for $C_{29}H_{20}Br_2N_2$ (556.29): C, 62.61; H, 3.62; N, 5.04. Found: C, 62.49; H, 3.67; N, 5.09%.

*3,3'-(Naphthalen-2-ylmethylene)bis(5-bromo-1H-indole)* (**3b**). Pink solid, FT-IR (KBr) ν/cm$^{-1}$: 3425, 2934, 1616, 1484, 1211, 765. $^1$H NMR (DMSO, 400 MHz): δ 5.92 (s, 1H, CH), 6.65 (s, 2H, HAr), 7.26 (m, 6H, HAr), 7.50 (m, 4H, HAr), 7.74 (m, 3H, HAr), 8.09 (s, 2H, NH). $^{13}$C NMR (DMSO, 100 MHz): δ 55.1, 111.5, 113.1, 119.7, 120.7, 121.6, 123.4, 124.5, 125.3, 125.6, 126.3, 127.1, 127.4, 127.8, 132.5, 133.9, 136.4, 142.7. Anal. Calcd for $C_{27}H_{18}Br_2N_2$ (530.25): C, 61.16; H, 3.42; N, 5.28. Found: C, 60.92; H, 3.54; N, 5.11%.

*4-(Bis(5-bromo-1H-indol-3-yl)methyl)-2-ethoxyphenol* (**3c**): Pink solid, FT-IR (KBr) ν/cm$^{-1}$: 3431, 3259, 2941, 1605, 1512, 1121, 749. $^1$H NMR (DMSO, 400 MHz): δ 1.30 (t, 3H, $CH_3$), 3.70 (q, 2H, $CH_2$), 5.65 (s, 1H, CH), 6.63 (s, 2H, HAr), 6.80 (m, 3H, HAr), 7.22 (m, 5H, HAr), 7.47 (s, 2H, HAr), 8.26 (s, 2H, NH). $^{13}$C NMR (DMSO, 100 MHz): δ 14.9, 54.8, 66.5, 111.6, 112.4, 114.3, 118.4, 121.7, 124.6, 125.0, 127.8, 128.4, 135.1, 135.4, 157.7. Anal. Calcd for $C_{25}H_{20}Br_2N_2O_2$ (540.25): C, 55.58; H, 3.73; N, 5.19. Found: C, 55.73; H, 3.81; N, 5.17%.

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