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A distinct novel approach for the synthesis of 3-indolyl-methanamines starting from indoles, aldehydes and nitrobenzenes in water†‡

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3-Indolyl-methanamines have efficiently been synthesized by the treatment of indoles with aldehydes and nitrobenzenes using indium in aqueous HCl at room temperature. The products are formed in excellent yields (91–98%) within a short period of time (30–45 min). Bisindolyl methanes have not been obtained under the present reaction conditions.

Introduction

Indole derivatives have attracted much attention due to their interesting biological properties.[1] They are known to inhibit colon cancer cell and tumour growths.[2] They also act as non-steroidal aromatase inhibitors against breast cancer[3] and HIV-1 integrase inhibitors.[4] Various indole derivatives possess antibacterial, antioxidant and insecticidal properties.[1,5] Some of them are utilized as antibiotics.[1] The indole moiety is also found in several bioactive metabolites of terrestrial and marine organisms.[6] Among various indole derivatives, 3-substituted indoles are most important and many different syntheses of these compounds have been reported.[1a,7] Here we would like to report a distinct approach for the synthesis of 3-indolyl-methanamines in water.

Organic reactions in water are of great current interest, because water is an easily available, economical, safe, and environmentally benign solvent.[8] The development of efficient and convenient synthetic methodologies in water is of paramount significance in recent organic chemistry. Metallic indium in water has now been utilized to carry out various organic transformations.[9] Indium is unreactive towards air and water as well as non-toxic compared to other metals. Its first ionisation potential (5.8 eV) is lower than that of other reducing metals such as zinc (9.4 eV) and tin (7.3 eV) and is close to that of an alkali metal such as sodium (5.1 eV). As a result it can readily participate in single electron transfer processes. The important application of the metal is to reduce the nitro compounds in acidic media.[10] Different indium salts have also been utilized as catalysts to accomplish different organic reactions.[11]

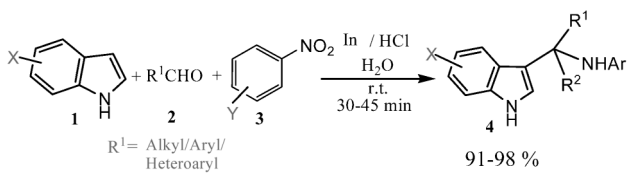
In continuation of our work[12] on the development of useful synthetic methodologies in water we have observed that the treatment of indoles (**1**) with aldehydes (**2**) and nitrobenzenes (**3**) using indium in aqueous HCl afforded the corresponding 3-indolyl-methanamines (**4**) at room temperature (Scheme 1).

Results and discussion

Initially the reaction of indole, benzaldehyde and nitrobenzene was carried out using different metals such as Zn, In, Fe and Sn in aqueous HCl at room temperature (Table 1).

Considering the reaction time and yield indium was found to be the most effective. Subsequently this metal was applied to prepare various 3-indolyl-methanamines from different indoles, aldehydes and nitrobenzenes following the above multicomponent reaction (Scheme 1, Table 2).

The products were derived from aromatic, heteroaromatic as well as aliphatic aldehydes. The aromatic aldehydes contained both electron-donating and electron-withdrawing groups. An acid sensitive aldehyde such as furfuraldehyde (Table 2, entry B) furnished the desired product conveniently. 3-Indolyl-methanamines (**4**) were formed in excellent yields (91–98%) within 30–45 min. However, with aliphatic nitro



Scheme 1 Synthesis of 3-indolyl-methanamines.

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† Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR spectrum of products. See DOI: 10.1039/c3ra41131a

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Table 1 Synthesis of 3-indolyl-methanamine using different metals[a]

Entry	Metal	Time (h)	Yield (%)[b]
1	Zn	5	52
2	Sn	6	61
3	Fe	4	45
4	In	1	96

[a] Reaction Conditions: Nitrobenzene (1.0 mmol), 1 *N* aqueous HCl (1 mL), benzaldehyde (1.0 mmol), indole (1.0 mmol) and water (5 mL) at room temperature. [b] Yields of isolated pure compound after column chromatography.

compounds a mixtures of products were obtained. The structures of **4** were established from their spectral (^{1}H, ^{13}C NMR, ESIMS, HRESIMS) data. The compounds **4Aa**[13] (Table 2, entry a) and **4Af**[13] (Table 2, entry f) are known.

Organic reactions in water have been highly attractive in recent years due to economic benefits. The present conversion has efficiently been carried out in water. The conversion consists of three steps in one pot. Initially the nitrobenzenes upon treatment with In/HCl are reduced to amines which upon reaction with aldehydes form the corresponding imines. Finally, indoles undergoes an electrophilic substitution reaction with these imines to produce 3-indolyl-methanamines.

When amines (instead of nitro compounds) or imines were used earlier for the preparation of 3-indolyl-methanamines, bisindolyl methanes were also formed in several cases.[7b,d,e,f] However, under the present reaction conditions bisindolyl methanes were not obtained here. Possibly, under the present reaction conditions, the aldehydes react more quickly with the amines to form the imines than with the indoles to produce bisindolyl methanes.

Conclusions

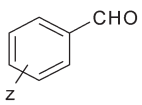
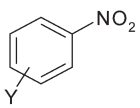
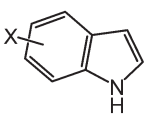
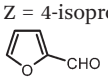
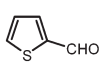
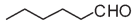
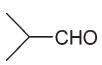
In conclusion, we have developed a novel efficient one-pot synthesis of 3-indolyl-methanamines through a distinct approach involving the multicomponent reaction of indoles, aldehydes and nitrobenzenes using indium in dilute aqueous HCl at room temperature. The application of water as a reaction medium, direct utilization of nitro compounds, mild reaction conditions, formation of only the desired products, rapid conversion and excellent yields are the advantages of the present method.

Experimental section

General experimental procedure

To a mixture of a nitro compound (1.0 mmol), indium powder (325 mesh, 2.0 mmol), 1 *N* aqueous HCl (1 mL) and an aldehyde (1.0 mmol) were added indole (1.0 mmol) and water (5 mL). The mixture was stirred at room temperature and the reaction was monitored by TLC. After completion, the reaction mixture was washed with saturated $NaHCO_3$ solution (3 × 5

Table 2 Synthesis of 3-indolyl-methanamine using indium in dilute aqueous HCl at room temperature[a]

Entry	Aldehyde	Nitrobenzene ($ArNO_2$)	Indole	Time (min)	Yield[b] (%)
A.					
a	Z = H	Y = H	X = H	40	96
b	Z = 4-CH_3	Y = H	X = H	40	96
c	Z = 4-isopropyl	Y = H	X = H	45	94
d	Z = 3,4-di-OMe	Y = H	X = H	45	94
e	Z = 3,4,5-tri-OMe	Y = H	X = H	45	93
f	Z = 4-Cl	Y = H	X = H	40	96
g	Z = 4-F	Y = H	X = H	40	97
h	Z = 4-CN	Y = H	X = H	30	98
i	Z = 4-isopropyl	Y = 3-OMe	X = 5-OMe	40	92
B.		Y = H	X = H	35	97
C.		Y = H	X = H	40	97
D.		Y = H	X = H	45	93
E.		Y = H	X = H	35	92

[a] The structures of the products were settled from their spectral (IR, ^{1}H, ^{13}C NMR and MS) data. [b] Yields of isolated pure compounds after column chromatography.

mL) and water (3 × 5 mL) and was extracted with EtOAc (3 × 5 mL). The extract was concentrated and the residue was subjected to column chromatography (silica gel, hexane–EtOAc) to obtained the pure 3-indolyl-methanamine.

N-((1H-indole-3-yl)(*p*-tolyl)methyl)benzenamine (4Ab)

Violet solid; m.p. 132–134 °C; IR ν_{max} (neat)/cm^{-1} 3407, 1663, 1613, 1457, 1335 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36 (1H, brs), 7.24 (2H, d, J = 8.0 Hz), 7.11–7.01 (7H, m), 6.99 (2H, t, J = 8.0 Hz), 6.85 (2H, t, J = 8.0 Hz), 6.32 (2H, brs), 5.71 (1H, brs), 2.26 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.1, 136.1, 135.2, 129.0, 128.8, 127.0, 123.2, 121.5, 119.8, 119.6, 118.5, 110.5, 39.2, 21.1; ESIMS: m/z 335 $[M + Na]^+$; HRESIMS: m/z 335.1526, Anal. Cald. for $C_{22}H_{20}N_2Na$: m/z 335.1524.

N-((1H-indol-3-yl)(4-isopropylphenyl)methyl)aniline (4Ac)

Violet solid; m.p. 130–133 °C; IR ν_{max} (neat)/cm^{-1} 3412, 1662, 1599, 1458, 1363 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41 (1H, brs), 7.25 (2H, d, J = 8.0 Hz), 7.21–7.01 (9H, m), 6.88 (2H, t, J = 8.0 Hz), 6.32 (2H, brs), 5.73 (1H, brs), 2.82 (1H, m), 1.15 (6H, d, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 146.5, 141.1, 136.2, 128.9, 127.3, 126.0, 123.1, 121.5, 120.1, 119.0, 110.4, 39.2, 32.8, 23.0; ESIMS: m/z 363 $[M + Na]^+$; HRESIMS: m/z 363.1844, Anal. Cald. for $C_{24}H_{24}N_2Na$: m/z 363.1837.

N-((3,4-dimethoxyphenyl)(1H-indole-3-yl)methyl)benzenamine (4Ad)

Light red solid; m.p. 129–131 °C; IR ν_{max} (neat)/cm^{-1} 3373, 1666, 1615, 1511, 1459, 1419, 1266 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.62 (1H, brs), 7.29 (2H, d, J = 8.0 Hz), 7.14–7.00 (5H, m), 6.90 (2H, t, J = 8.0 Hz), 6.80 (1H, d, J = 1.5 Hz), 6.70 (1H, dd, J = 8.0, 1.5 Hz), 6.57 (1H, d, J = 8.0 Hz), 6.32 (2H, brs), 5.70 (1H, brs), 3.71 (3H, s), 3.59 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 148.9, 147.8, 138.0, 127.2, 123.7, 121.5, 120.4 119.7, 119.1, 112.1, 110.5, 110.3, 56.0, 39.9; ESIMS: m/z 381 $[M + Na]^+$; HRESIMS: m/z 381.1575, Anal. Cald. for $C_{23}H_{22}N_2O_2Na$: m/z 381.1578.

N-((1H-indole-3-yl)(3,4,5trimethoxyphenyl)methyl)benzenamine (4Ae)

Light red solid; m.p. 126–129 °C; IR ν_{max} (neat)/cm^{-1} 3382, 1670, 1604, 1528, 1432, 1262 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.86 (1H, brs), 7.36 (2H, d, J = 8.0 Hz), 7.31 (2H, d, J = 8.0 Hz), 7.13 (2H, t, J = 8.0 Hz), 6.99 (3H, t, J = 8.0 Hz), 6.62 (2H, brs), 6.51 (2H, s), 5.76 (1H, brs), 3.80 (3H, s), 3.71 (6H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 152.0, 140.2, 136.2, 134.9, 127.1, 123.3, 120.5 118.8, 117.9, 117.8, 110.2, 106.1, 60.0, 55.0, 39.2; ESIMS: m/z 411 $[M + Na]^+$; HRESIMS: m/z 411.1695, Anal. Cald. for $C_{23}H_{22}N_2O_2Na$: m/z 411.1684.

N-((4-fluorophenyl)methyl)(1H-indole-3-yl)benzenamine (4Ag)

Violet solid; m.p. 121–123 °C; IR ν_{max} (neat)/cm^{-1} 3412, 1605, 1504, 1456, 1417, 1339, 1217 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.81 (1H, brs), 7.31–7.22 (7H, m), 7.11 (2H, t, J = 8.0 Hz), 7.00–6.90 (4H, m), 6.57 (2H, brs), 5.80 (1H, brs); ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.9, 160.0, 139.2, 136.5, 130.0, 127.1, 123.2, 121.3 119.8, 119.1, 119.0, 114.6 (d, J = 10.0), 110.4, 39.2; ESIMS: m/z 339, $[M + Na]^+$; HRESIMS: m/z 339.1285 Anal. Cald. for $C_{21}H_{17}N_2FNa$: m/z 339.1273.

N-((1H-indole-3-yl)(phenylamino)methyl)benzonitrile (4Ah)

Violet solid; m.p. 133–135 °C; IR ν_{max} (neat)/cm^{-1} 3414, 2216, 1620, 1513, 1424, 1342, 1215 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.38 (1H, brs), 7.72–7.58 (4H, m), 7.56–7.42 (2H, m), 7.37–7.20 (4H, m), 7.11–7.02 (2H, m), 6.89 (1H, m), 6.78–6.62 (2H, m), 5.91 (1H, brs); ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.2, 136.5, 131.5, 129.1, 127.9, 126.1, 123.5, 120.8 118.6, 118.5, 118.1, 116.5, 111.2, 108.9, 39.8; ESIMS: m/z 346 $[M + Na]^+$; HRESIMS: m/z 346.1321 Anal. Cald. for $C_{21}H_{17}N_2FNa$: m/z 346.1315.

N-((4-isopropylphenyl)(5-methoxy-1H-indole-3-yl) methyl)-3-methoxybenzenamine (4Ai)

Violet solid; m.p. 139–140 °C; IR ν_{max} (neat)/cm^{-1} 3413, 1622, 1587, 1482, 1451, 1211 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.68 (1H, brs), 7.25–7.03 (7H, m), 6.73 (2H, dd, J = 8.0, 2.0 Hz), 6.71 (2H, d, J = 2.0 Hz), 6.58 (2H, brs), 5.66 (1H, brs), 3.62 (6H, s), 2.83 (1H, m), 1.2 (6H, d, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.0, 146.2, 141.1, 131.3, 128.9, 127.8, 126.4, 124.2, 119.2, 111.3, 111.2, 55.8, 39.9, 33.7, 24.1; ESIMS: m/z 423, $[M + Na]^+$; HRESIMS: m/z 423.2047 Anal. Cald. for $C_{21}H_{17}N_2FNa$: m/z 423.2043.

N-(furan-2-yl(1H-indole-3-yl)methyl)benzenamine (4B)

Violet solid; m.p. 141–142 °C; IR ν_{max} (neat)/cm^{-1} 3403, 1599, 1497, 1456, 1340 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.78 (1H, brs), 7.40 (2H, d, J = 8.0 Hz), 7.30 (1H, m), 7.21 (2H, dd, J = 8.0, 2.0 Hz), 7.10 (3H, t, J = 8.0 Hz), 6.99 (2H, t, J = 8.0 Hz), 6.73–6.69 (2H, m), 6.22 (1H, m), 6.17 (1H, m), 5.82 (1H, brs); ^{13}C NMR (50 MHz, $CDCl_3$): δ 157.0, 141.1, 136.2, 129.2, 126.7, 123.0, 122.2 119.4, 119.1, 117.1, 111.2, 110.3, 106.7, 33.2; ESIMS: m/z 311 $[M + Na]^+$; HRESIMS: m/z 311.1174 Anal. Cald. for $C_{19}H_{16}N_2ONa$: m/z 311.1160.

N-((1H-indole-3-yl)(thiophen-2-yl)methyl) benzenamine (4C)

Violet solid; m.p. 145–147 °C; IR ν_{max} (neat)/cm^{-1} 3408, 1602, 1592, 1487, 1356 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.66 (1H, brs), 7.38 (3H, d, J = 8.0 Hz), 7.21 (1H, m), 7.20 (1H, d, J = 8.0), 7.08 (3H, t, J = 8.0 Hz), 6.95 (2H, t, J = 8.0 Hz), 6.88–6.80 (2H, m), 6.61 (2H, brs), 6.02 (1H, brs); ^{13}C NMR (50 MHz, $CDCl_3$): δ 149.1, 136.9, 129.2, 127.2, 126.5, 125.1, 123.7, 123.2, 121.9, 120.0, 119.3, 111.3, 35.7; ESIMS: m/z 327 $[M + Na]^+$; HRESIMS: m/z 327.0922 Anal. Cald. for $C_{19}H_{16}N_2SNa$: m/z 327.0931.

N-(1-(1H-indol-3-yl)hexyl)aniline (4D)

Violet solid; m.p. 102–104 °C; IR ν_{max} (neat)/cm^{-1} 3410, 1585, 1478, 1373, 1219 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.55 (2H, d, J = 8.0 Hz), 7.38–7.30 (2H, m), 7.09–6.98 (6H, m), 6.70–6.62 (2H, m), 4.35 (H, t, J = 7.0 Hz), 2.15–2.05 (2H, m), 1.41–1.15 (6H, m), 0.83 (3H, t, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 135.6, 128.0, 121.7, 121.5, 120.0, 119.5, 119.0, 110.1, 40.5, 32.5, 29.0, 24.7, 21.6, 14.1; ESIMS: m/z 315 $[M + Na]^+$; HRESIMS: m/z 315.1415 Anal. Cald. for $C_{20}H_{24}N_2Na$: m/z 315.1419.

N-(1-(1H-indole-3-yl)-2-methylpropyl)benzenamine (4E)

Violet solid; m.p. 108–110 °C; IR ν_{max} (neat)/cm^{-1} 3402, 1598, 1468, 1373, 1227 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.55 (2H, d, J = 8.0 Hz), 7.38–7.30 (2H, m), 7.09–6.98 (6H, m), 6.70–6.62 (2H, m), 4.09 (1H, m), 2.51 (1H, m), 0.92 (6H, d, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 135.8, 127.9, 121.9, 121.4, 119.8,

119.7, 118.9, 111.2, 41.0, 32.8, 21.7; ESIMS: *m*/*z* 287 $[M + Na]^+$; HRESIMS: *m*/*z* 287.1514 Anal. Cald. for $C_{18}H_{20}N_2Na$: *m*/*z* 287.1519.

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