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$InCl_3$ and $In(OTf)_3$ catalyzed reactions: synthesis of 3-acetyl indoles, bis-indolylmethane and indolylquinoline derivatives

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Abstract—Indium trichloride and indium triflate were found to be effective catalysts for the acetylation of indoles to 3-acetyl indoles and is reported for the first time in good yield. Indium triflate is also found to be an efficient catalyst for the synthesis of bis-indolylmethane and indolylquinoline derivatives. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Indoles and its myriad derivatives continue to capture the attention of synthetic organic chemists, and a large number of original indole ring syntheses and application of known methods to problems in indole chemistry have been reported.[1] Acetyl indoles are used as starting material for the synthesis of carbazoles,[2] pyridocarbazoles[3] and carbolines.[4] Several catalysts like $Si(O_2CCH_2CH_2COOCH_3)_4/SnCl_2$,[5] $HClO_4$,[6] $SiCl_4$[7] and $ZnCl_2$[8] have been used for the acetylation of indoles, but the yields are very low.

Okauchi et al.[9] reported that the indoles were converted into metal derivatives with Et_2AlCl or Me_2AlCl followed by treatment with acid chloride to give acetyl indoles. We wish to report our observation on acetylation of indoles catalyzed by $InCl_3$ under mild conditions.

In the literature, $InCl_3$ has been used as a catalyst for the aldol condensation,[10] imino Diels–Alder reactions,[11] rearrangement of epoxides,[12] Prins-type cyclization,[13] Bignelli reaction,[14] α-phenyl thioketones.[15] Recently, the synthetic potential of $InCl_3$ in organic synthesis has been reviewed.[16] Similarly, indium triflate is also used for the Friedel–Crafts alkylation,[17] Diels–Alder reaction,[18] acetylation of alcohols and amines[19] and also in the synthesis of tetrahydrofurans.[20]

2. General procedure

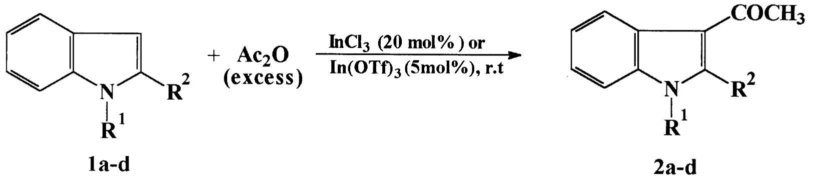
To a stirred solution of indole (**1a**) in excess acetic anhydride, 20 mol% $InCl_3$ or 5 mol% $In(OTf)_3$ is added and stirred for appropriate time. After usual workup, 3-acetyl indoles obtained are given in Table 1 (Scheme 1).

Table 1. Synthesis of 3-acetyl indoles catalyzed by 20 mol% $InCl_3$ and 5 mol% of $In(OTf)_3$

	Substrates		Time (min)		Yield (%)[a,b]	
	R^1	R^2	$InCl_3$	$In(OTf)_3$	$InCl_3$	$In(OTf)_3$
1	H	H	25	30	65	52
2	H	CH_3	30	35	54	68
3	SO_2Ph	H	35	20	81	92
4	Tosyl	H	30	25	78	86

[a] Yield obtained with 20 mol% $InCl_3$ and 5 mol% $In(OTf)_3$.

[b] The yield is based on isolation by column chromatography and the products were characterized by IR, NMR and mass spectrum.



Scheme 1.

Keywords: indium trichloride; indium triflate; acetylation; 3-acetyl indoles; bis-indolylmethane.

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The acid catalyzed reaction of electron-rich heterocyclic compounds with *p*-dimethylaminobenzaldehyde is known as Ehrlich Test[21] for π-electron excessive heterocycles such as pyrrole and indoles. The analogous reaction of indoles with other aromatic or aliphatic aldehydes and ketone produces azafulvenium salts. The azafulvenium salts undergo further addition with another indole molecule to afford bis-indolylmethanes. Protic acids[22] and Lewis acids[23] were found to catalyze this reaction; however, more than stoichiometric amounts of the Lewis acids are required because the acids are trapped by nitrogen.[24] Recently, Yadav et al. reported that the use of 10 mol% of $LiClO_4$ is found to effect the substitution of indoles with carbonyl compounds.[25] Here, we report the indium triflate catalyzed reaction of indoles with substituted benzaldehydes. The catalyst offers several advantages including mild reaction conditions, cleaner reactions, shorter reaction times, high yield of the products, lower catalytic loading as well as simple experimental and isolation procedures which make it useful for the synthesis of bis-indolylmethanes.

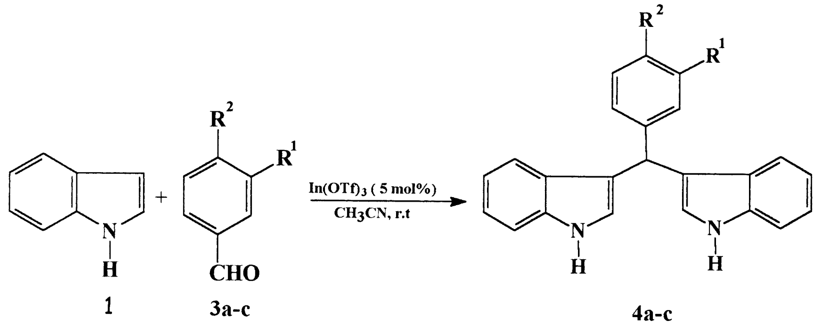
To a stirred solution of indole (**1a**) with benzaldehyde (**3a**), 5 mol% $In(OTf)_3$ is added and stirred for 25 min. After workup, bis-indolylmethane **4a** is obtained in 71% yield (Scheme 2). The results obtained with substituted benzaldehydes are given in Table 2.

Electron withdrawing group, NO_2 decreases the yield of the reaction and electron donating methoxy group increases the rate of the reaction.

Compounds containing either the indole or the quinoline moiety possess a wide range of biological activity. A few reports are available regarding compounds bearing both the indole and quinoline moiety[26–29] which possess a wide range of biological activity. Imino Diels–Alder reaction of imines with electron-rich dienophiles to give simple quinoline derivatives and this reaction is found to be catalyzed by TFA,[30] BF_3–Et_2O[31] and $GdCl_3$.[32] The indolylquinolines have been synthesized by the reaction of indolylimine with cyclopentadiene catalyzed by $In(OTf)_3$.

To a stirred solution of indolylimine (**5a**) with cyclopentadiene in acetonitrile, 5 mol% of $In(OTf)_3$ was added and stirred for 25 min. After workup, the product **6a** was obtained in 82% yield (Scheme 3).

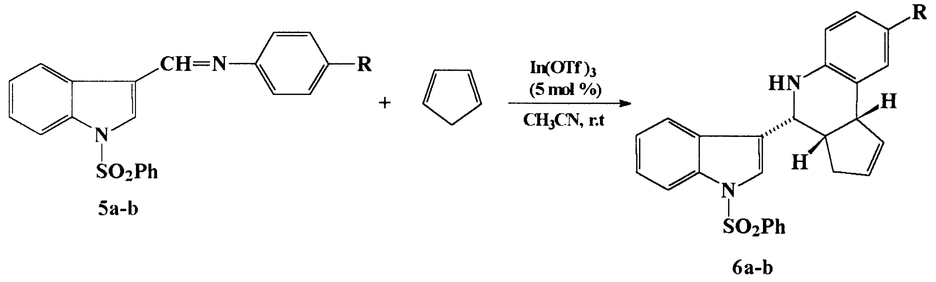
In conclusion, we have shown that $InCl_3$ and $In(OTf)_3$ are found to be efficient catalysts for acetylation of indoles giving better yields in shorter reaction times. Indium triflate, effectively catalyses the reaction of indole with benzaldehydes to give bis-indolylmethane and also in the synthesis of indolyl quinoline derivatives. The catalyst offers several advantages including mild reaction conditions, cleaner reactions, shorter reaction times, high yield of the products, lower catalytic loading as well as simple experimental and isolation procedures, which make it useful for the synthesis of bis-indolylmethanes.



Scheme 2.

Table 2. Reaction of indoles with substituted benzaldehydes employing 5 mol% of $In(OTf)_3$

No.	Substituents		Product	Time (min)	Yield (%)
	R^1	R^2			
1	H	H	**4a**	25(300)[25]	71
2	NO_2	H	**4b**	30(600)[25]	76
3	OMe	OH	**4c**	35	86



Scheme 3. (a) R=H, 82%; (b) R=Cl, 79%.

3. Experimental

Mass spectra were recorded on Varian VG70-70H mass spectrometer. Melting points were measured in capillary tubes and are uncorrected. Analytical TLC was performed on precoated sheets of silica gel G of 0.25 mm thickness containing PF 254 indicator (Merck, Darmstadt). Column chromatography was performed with silica gel (60–120 mesh, S.d Fine, Boisar). IR spectra were recorded as solids in KBr pellets on a Perkin–Elmer FTIR spectrometer. NMR spectra were obtained on a Bruker spectrometer. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ and the chemical shifts are given in δ relative to the solvent (77.0). MeCN was distilled from CaH_2 and dried over 4 Å molecular sieves.

3.1. General procedure for acetylation of indoles to 3-acetyl indoles

To a stirred mixture of the indole (2.5 mmol) in acetic anhydride (5 mL) protected by guard tube, indium triflate (0.07 g, 5 mol%) was added and stirred for appropriate time. After the reaction was complete, water (50 mL) was added and stirred for 15–20 min. To this solid $NaHCO_3$ was added in portions to aid faster precipitation of acetyl indole and extracted with CH_2Cl_2 (3×20 mL) The organic layer was washed with saturated $NaHCO_3$ (10 mL), brine (10 mL) and dried over anhydrous Na_2SO_4, then concentrated under reduced pressure. The residue was purified by column chromatography, eluted with ethylacetate–petroleum ether 3:7 to yield the corresponding 3-acetyl indoles.

3.1.1. 3-Acetyl indole (2a). 0.207 g (52%) of colorless solid; mp 191–192°C (lit.[34] 190–191°C); IR (KBr) 3310, 1675, 1368, 851 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.27 (brs, 1H), 8.45 (s, 1H), 7.76–6.79 (m, 4H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 132.4, 131.6, 122.5, 121.3, 118.9, 111.6, 110.9, 27.8; MS *m/z* 159 (M^{+}); Anal. Calcd for $C_{10}H_9NO$: C, 75.44; H, 5.70; N, 8.81; Found: C, 76.10; H, 5.79; N, 8.75.

3.1.2. 2-Methyl-3-acetyl indole (2b). 0.294 g (68%) of colorless solid; mp 195–196°C (lit.[33] 195–196°C); IR (KBr) 3302, 1658, 1362, 840 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.18 (brs, 1H), 7.80–6.94 (m, 4H), 2.87 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.5, 135.1, 132.3, 128.2, 121.4, 115.3, 110.3, 26.9, 12.6; MS *m/z* 173 (M^{+}); Anal. Calcd for $C_{11}H_{11}NO$: C, 76.26; H, 6.41; N, 8.09; Found: C, 75.78; H, 6.32; N, 7.99.

3.1.3. *N*-Benzenesulfonyl-3-acetyl indole (2c). 0.688 g (92%) of colorless solid; mp 160–161°C (lit.[34] 159–160°C); IR (KBr) 1667, 1383, 842 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.94–7.24 (m, 9H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 137.6, 134.9, 132.7, 131.5, 130.3, 129.2, 127.8, 126.6, 125.4, 123.7, 121.8, 113.5, 27.9; MS *m/z* 299 (M^{+}); Anal. Calcd for $C_{16}H_{13}NO_3S$: C, 64.18; H, 4.38; N, 4.68; Found: C, 64.56; H, 4.31; N, 4.55.

3.1.4. *N-p*-Toluenesulfonyl-3-acetyl indole (2d). 0.673 g (86%) of colorless solid; mp 137–138°C; IR (KBr) 1657, 1378, 857 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, 1H, J=7.2 Hz), 8.22 (s, 1H), 7.94 (d, 2H, J=7.2 Hz), 7.84 (d, 1H, J=6.9 Hz), 7.34 (s, 2H), 7.28 (d, 2H, J=7.2 Hz), 2.57 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 145.9,134.5, 132.2, 130.2, 127.5, 127.1, 125.7, 124.8, 123.1, 121.6, 113.0, 27.8, 21.6; MS *m/z* 313 (M^{+}); Anal. Calcd for $C_{17}H_{15}NO_3S$: C, 65.14; H, 4.83; N, 4.47; Found: C, 65.32; H, 4.76; N, 4.37.

3.2. Typical procedure for the synthesis of bis-indolylmethanes

To a mixture of indole **4a** (2.5 mmol) substituted benzaldehydes **3a–3c** (1.25 mmol) in acetonitrile (7 mL), indium triflate (0.035 g, 5 mol%) was added and stirred at room temperature for the appropriate time. When the reaction was complete, water (10 mL) was added to quench the reaction and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried using anhydrous Na_2SO_4, filtered and the solvent evaporated. The crude products were purified by column chromatography and eluted with ethyl acetate–petroleum ether mixture to afford the products

3.2.1. 3,3′-Bis-indolyl phenylmethane (4a). 0.572 g (71%) of pink colored solid; mp 125–126°C (lit.[35] 124–125°C); IR (KBr) 3416, 1634, 1378, 737 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (brs, 2H), 7.45–7.18 (m, 13H), 6.51 (s, 2H), 5.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 134.3, 133.7, 130.2, 130.1, 130.0, 127.1, 125.1, 123.0, 119.4, 118.9, 114.3, 21.5; MS *m/z* 322 (M^{+}); Anal. Calcd for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69; Found: C, 85.59; H, 5.68; N, 8.54.

3.2.2. 3,3′-Bis-indolyl-(3-nitrophenyl)methane (4b). 0.697 g (76%) of pink colored solid; mp 261–262°C(d) (lit.[35] 260°C) IR (KBr) 3468, 3060, 1649, 1569, 1240, 769 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (brs, 2H), 8.06 (d, 1H, J=7.2 Hz), 7.94 (s, 2H), 7.67 (d, 1H, J=7.5 Hz), 7.41 (m, 4H), 7.17 (t, 2H), 7.03 (d, 2H, J=7.2 Hz), 6.59 (s, 2H), 5.96 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 134.8, 129.1, 126.5, 123.7, 123.5, 122.2, 121.4, 119.5, 118.1, 111.3, 39.9; MS *m/z* 368 (M^{+}); Anal. Calcd for $C_{23}H_{17}N_3O_2$; C, 75.19; H, 4.66; N, 11.44; Found: C, 75.41; H, 4.69; N, 11.54.

3.2.3. 3,3′-Bis-indolyl(4-hydroxy-5-methoxyphenyl)-methane (4c). 0.791 g (86%) of pink colored solid; mp 99–101°C; IR (KBr) 3500, 3412, 1634, 1383, 741 cm^{1}; ^{1}H NMR (300 MHz, $CDCL_3$) δ 9.81 (brs, 2H), 7.91 (s, 1H), 7.39–6.80 (m, 11H), 6.63 (s, 2H), 5.80 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 136.7, 136.1, 127.0, 123.5, 121.9, 121.3, 119.9, 119.2, 114.0, 111.4, 55.8, 39.8; MS *m/z* 368 (M^{+}); Anal. Calcd for $C_{24}H_{20}N_2O_2$; C, 78.23; H,5.47; N, 7.61; Found: C, 78.54; H, 5.39; N, 7.70.

3.3. General procedure for cycloaddition

A mixture of imine **5a** or **5b** (2.5 mmol), $In(OTf)_3$ (0.035 g, 5 mol%) cyclopentadiene (5 mmol) in acetonitrile (7 mL) was stirred at room temperature for the appropriate time. To the reaction mixture was added aqueous saturated $NaHCO_3$ solution (5 mL) and the solution was extracted with $CHCl_3$ (3×10 mL). The combined organic layer was washed with water, brine, dried over Na_2SO_4, filtered and the solvent evaporated. The residue was purified by column chromatography eluting with 90:10 ethyl acetate–petroleum ether to afford the cycloadducts.

3.3.1. 4-[(1-Phenylsulfonyl)-indole-3-yl]-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*] quinoline (6a). 0.873 g (82%) of colorless solid; mp 165–166°C; IR (KBr) 3409, 2949, 1480, 1401, 1385, 720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07–6.80 (m, 12H), 6.72 (m, 1H), 6.68 (d, 1H, J=7.8 Hz), 5.83 (m, 1H), 5.61 (m, 1H), 4.86 (d, 1H, J=2.6 Hz), 4.14 (d, 1H, J=8.1 Hz), 3.77 (brs, 1H, NH), 3.22 (m, 1H), 2.60 (m, 1H), 1.69 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.3, 137.9, 135.3, 135.2,134.1, 133.7, 132.6, 129.6, 127.2, 126.6, 126.5, 126.3, 125.1, 125.0, 123.2, 119.4, 119.1, 116.0, 113.9, 113.7, 50.7, 45.7, 43.2, 32.4; MS m/z 426 (M$^+$); Anal. Calcd for $C_{26}H_{22}N_2O_2S$; C, 73.21; H, 5.20; N, 6.57; Found: C, 72.99; H, 5.21; N, 6.59.

3.3.2. 8-Chloro-4-[(1-phenylsulfonyl)-indole-3-yl]-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*] quinoline (6b). 0.910 g (79%) of colorless solid; mp 182–183°C; IR (KBr) 3425, 3100, 2900, 1450, 1380, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03–7.85 (m, 5H), 7.60–7.21 (m, 5H), 7.02 (s, 1H), 6.92 (d, 1H, J=6.3 Hz), 6.56 (d, 1H, J=8.5 Hz), 5.75 (s, 1H), 5.61 (m, 1H), 4.80 (d, 1H, J=2.6 Hz), 4.06 (d, 1H, J=8.5 Hz), 3.77 (s, 1H), 3.09 (m, 1H), 2.48 (m, 1H), 1.61 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 137.9, 135.5, 134.5, 133.9, 132.6, 130.4, 129.8, 127.9, 127.6, 126.4, 125.6, 124.8, 123.9, 123.7, 122.1, 120.6, 120.1, 117.9, 114.9, 112.9, 51.4, 49.9, 43.6, 32.2; MS m/z 460 (M$^+$), 462 (M+2); Anal. Calcd for $C_{26}H_{21}ClN_2O_2S$; C, 67.74; H, 4.59; N, 6.09; Found: C, 67.94; H, 4.57; N, 6.11.

Acknowledgements

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