



## Iodine in aqueous micellar environment: a mild effective ecofriendly catalytic system for expedient synthesis of bis(indolyl)methanes and 3-substituted indolyl ketones

Nemai C. Ganguly , Pallab Mondal & Sujoy Kumar Barik

To cite this article: Nemai C. Ganguly , Pallab Mondal & Sujoy Kumar Barik (2012) Iodine in aqueous micellar environment: a mild effective ecofriendly catalytic system for expedient synthesis of bis(indolyl)methanes and 3-substituted indolyl ketones, Green Chemistry Letters and Reviews, 5:1, 73-81, DOI: [10.1080/17518253.2011.581700](https://doi.org/10.1080/17518253.2011.581700)

To link to this article: <https://doi.org/10.1080/17518253.2011.581700>



Copyright Taylor and Francis Group, LLC



Published online: 27 Jun 2011.



Submit your article to this journal [↗](#)



Article views: 1393



View related articles [↗](#)



Citing articles: 8 View citing articles [↗](#)

## RESEARCH LETTER

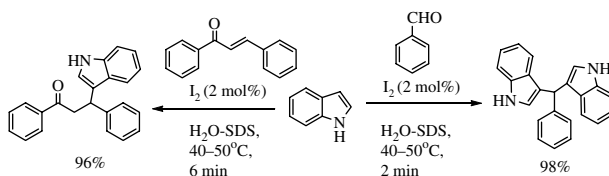
### Iodine in aqueous micellar environment: a mild effective ecofriendly catalytic system for expedient synthesis of bis(indolyl)methanes and 3-substituted indolyl ketones

Nemai C. Ganguly\*, Pallab Mondal and Sujoy Kumar Barik

Department of Chemistry, University of Kalyani, Kalyani 741235, India

(Received 17 September 2010; final version received 13 April 2011)

The three-component condensation reaction of indoles with carbonyl compounds to yield bis(indolyl)methanes has been accomplished with a catalytic amount of iodine (2 mol%) in the presence of sodium dodecylsulfate (SDS) in aqueous solution above its critical micellar concentration (cmc). The surfactant-aided water-compatible Lewis acid catalyst has been found to be efficient for a wide range of carbonyl compounds including aromatic aldehydes bearing electron-releasing and electron-withdrawing groups,  $\alpha,\beta$ -unsaturated aldehydes, heterocyclic aldehydes, cyclic and aromatic ketones with respect to yield, and reaction time. The protocol has been extended to Michael addition of indoles with  $\alpha,\beta$ -unsaturated ketones exclusively yielding 3-substituted indolyl ketones in excellent yields.



**Keywords:** iodine; SDS-H<sub>2</sub>O; bis(indolyl)methanes; 3-substituted indolyl ketones

#### Introduction

Replacement of volatile organic solvents with non-polluting alternative reaction media is one of the major aims of green chemistry (1). Water is the cheapest, noninflammable and environmentally benign solvent that is involved in life-sustaining biochemical processes in living organisms. It has unique physical and chemical properties, which may be utilized for attaining reactivity and selectivity that cannot be realized in common organic solvents. In addition, it is redundant to dry solvents and reagents in reactions in aqueous medium, thereby vastly reducing consumption of drying agents, and energy. Therefore, there is contemporary paradigm shift to explore organic reactions in aqueous medium (2, 3) and evaluate various features, most importantly, kinetic and catalytic ones, of organic reactions in aqueous medium. The major hurdle in these efforts is to solubilize organic substrates, particularly nonpolar ones, in water. Utilization of phase-transfer catalysts, water in combination with antihydrophobic additives, reactions on water surface when one of the organic

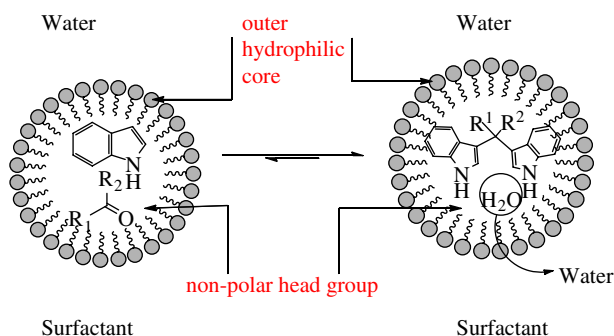
substrates in polar conferring it substantial solubility, and solubilizing organic compounds in aqueous medium in the presence of surfactants are some of the attractive approaches to this end. The micellar solubilization route utilizes inexpensive surfactants as additives that provide heterogeneous microenvironments and, upon self-assembly into micelles, encapsulate otherwise insoluble substrates and catalysts within the lipophilic cores. The concept of surfactant-aided Lewis and Brønsted acid catalysts to mediate carbon–carbon bond formation reactions in water has been developed by Kobayashi et al. (4–7) and applied with remarkable success to a host of organic transformations (8–14). Development of newer protocols for the synthesis of bis(indolyl)methanes is a topic of broad interest over the years. Diheteroaryl-methane motifs in general and bis(indolyl)methanes in particular are important bioactive metabolites of terrestrial and marine origin (15–20). Bis(3'-indolyl)methane itself is a chemopreventive agent from cruciferous plants, and these compounds can act as highly selective fluorescent molecular sensors for

\*Corresponding author. Email: nemai\_g@yahoo.co.in

$\text{Cu}^{+2}$  ions (21) and colon cancer cell inhibitors (22–24). The synthesis of these molecules is traditionally based upon a multicomponent condensation of two molecules of indoles as nucleophilic partners with one molecule of a carbonyl compound in the presence of Brønsted and Lewis acids. A good number of methods are documented in the literature that employ various protic and Lewis acid catalysts such as HCl (25),  $\text{HClO}_4\text{-SiO}_2$  (26),  $\text{KHSO}_4$  (27, 28),  $\text{LiClO}_4$  (29), Zr(IV) salts (30–32),  $\text{InCl}_3$  (33, 34),  $\text{SbCl}_3$  (35),  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  (36, 37),  $\text{SmI}_3$  (38), lanthanide triflates (39–42),  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (43), and ionic liquids (44). However, most of these methods suffer from one or more limitations such as use of expensive catalysts, lack of procedural simplicity such as rigorous exclusion of moisture, toxicity of catalyst. Even when the desired reaction proceeds, trapping of Lewis acids by indole nitrogen necessitates their use in more than stoichiometric amounts (45). In continuation of our interest in organic reactions in aqueous micellar medium mediated by water-tolerant Lewis acids (46–48), we became interested to evaluate the efficacy of iodine catalyst in water in the presence of anionic surfactant sodium dodecylsulfate (SDS) for the synthesis of bis(indolyl)methanes. Recently, this catalytic combination has been effectively used for the deoxygenation (49), iodohydrin formation (50) and, in fact, utilization of iodine as a mild Lewis acid to promote carbon–carbon and carbon–oxygen bond formation reactions has been amply demonstrated in recent times (52–56). Dehydration reactions in water are based upon the concept that Lewis acid catalyst and organic substrates with polar heads would form emulsion droplets with a hydrophobic interior, and surfactant molecules would help to concentrate iodonium cation or metal cation on the surface of these droplets. It was surmised that water formed during the condensation of indoles with carbonyl compounds would be excluded out of hydrophobic core of the micelles, thereby favoring the thermodynamic equilibrium toward formation of the desired target molecules (Scheme 1). Previously, 20 mol% of iodine has been employed in acetonitrile (57) as also solvent-free conditions (58) for the synthesis of bis(indolyl)methanes. We set out to explore iodine as a catalyst in aqueous micellar environment and reveal herein iodine-catalyzed synthesis of bis(indolyl)methanes in water.

## Results and discussion

We examined the base-level reactivity of benzaldehyde toward indole at electron-rich C-3 position to afford **1** in the presence of SDS without iodine catalyst (entries 1–2, Table 1).

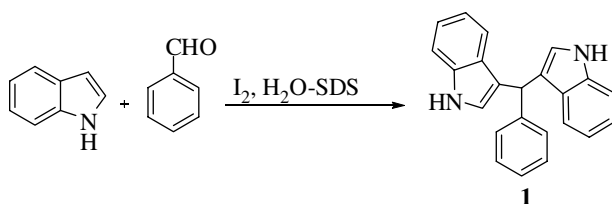


Scheme 1. Iodine-catalyzed formation of bis(indolyl) methane from indole and aldehyde under aqueous micellar conditions.

These initial exploratory experiments resulted in the isolation of **1** in moderate yields without iodine in a sluggish reaction at room temperature. To our delight, there was dramatic acceleration in reaction rate upon addition of 2 mol% of iodine in a thoroughly stirred aqueous solution containing 5 cmc of SDS at room temperature (5 min, 78%). The cationic and neutral surfactants, namely, CTAB (cetyltrimethylammonium bromide) and Triton X-100, were less effective with identical catalyst load under comparable conditions. Encouraged by the report that surfactant-aided catalysts could sustain high temperature (5) the temperature of the reaction was increased to 40–50°C with further enhancement of reaction rate and yield (Figure 1).

The optimized reaction conditions [2 mol% iodine, SDS (5 cmc), 10 mL water  $\text{mmol}^{-1}$  of carbonyl compound, 40–50°C] worked remarkably well for a wide range of carbonyl compounds, as shown in Table 2.

However, steric congestion around carbonyl carbon impedes the reaction rate substantially as reflected in the longer reaction time required for sterically encumbered aromatic aldehydes and ketones (entries 13–15). Gratifyingly, the current method is superior to existing iodine-based methods in bringing down the catalyst load from 20 to 2 mol% without compromising efficiency and operational simplicity. The major reason for this success is presumably due to activation of iodine catalyst by SDS (50), in addition to its facilitating role in solubilizing substrates and iodine. This protocol was further extended to the chemical space of Michael addition of indoles to  $\alpha,\beta$ -enones, leading to 3-substituted indolyl ketones. These compounds form building blocks of several biologically important indolyl alkaloids such as hepalindole D (59). This area has been revisited in recent times (35) from green chemistry perspectives and application of  $\text{I}_2\text{-SDS-H}_2\text{O}$  catalytic system is still unprecedented.

Table 1. Optimization experiments for the synthesis of bis(indolyl)methane **1**.

Entry	Water (mL)	I <sub>2</sub> (mol%)	Surfactant (cmc)	Reaction conditions <sup>a</sup>	Time (min/h)	Yield <sup>b</sup> of <b>1</b> (%)
1	10	–	SDS (5)	Rt	2.5 h	50
2	10	–	SDS (10)	Rt	2 h	58
3	10	2	SDS (10)	Rt	5 min	80
4	10	2	SDS (5)	Rt	10 min	78
5	10	1	SDS (10)	Rt	15 min	70
6	10	2	SDS (5)	40–50°C	2 min	98
7	10	2	CTAB (10)	40–50°C	10 min	85
8	10	2	Triton X 100 (10)	40–50°C	12 min	89

<sup>a</sup>Reactions were performed in 1 millimolar scale of benzaldehyde.

<sup>b</sup>Refers to chromatographically pure isolated yield of **1** with spectral characteristics (IR, NMR, TOF-MS) in good agreement with those reported in literature.

The results of Michael addition of indoles with several  $\alpha,\beta$ -unsaturated ketones are exhibited in Table 3.

Notably, other electron-poor C=C systems such as methyl acrylate, acrylonitrile,  $\beta$ -nitrostyrene, and *p*-benzoquinone were resistant to addition under the conditions of the reaction. It is also remarkable that no N-alkylated byproduct was formed in this reaction. Solid-state iodine-catalyzed (5 mol% of iodine) addition of enones to indoles (60) is reported to afford Michael adducts in varying yields (45–85%) in

20–30 minutes; however, the process suffers from the limitation of using fairly large amount of volatile halogenated solvent (25 mL of dichloromethane per mmol scale) to bring the product into solution. The current protocol is superior to this method in terms of better yields (76–98%) and avoids the use of any environmentally unacceptable solvent. InCl<sub>3</sub> (61, 62) in 10 mol% catalytic amount is reported to afford Michael addition products in 10–24 h in organic solvents. This is, therefore, a method of choice with the right balance of cost compatibility, short reaction times, and good-to-excellent yields.

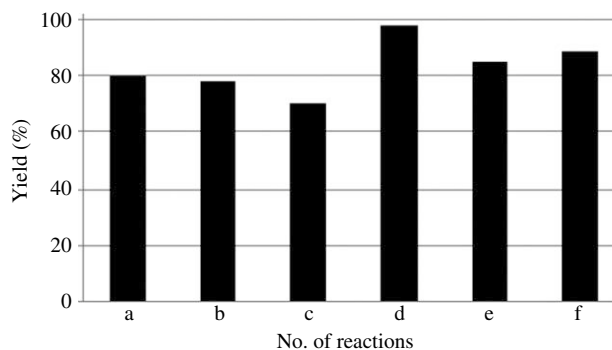


Figure 1. Variation of yield (iodine used in all cases: 2 mol%, except in “c” where 1 mol% iodine was used) of **1** in I<sub>2</sub>-catalyzed synthesis under aqueous micellar conditions. **a** SDS (10 cmc, 5 min, rt); **b** SDS (5 cmc, 10 min, rt); **c** SDS (10 cmc, 15 min, rt); **d** SDS (5 cmc, 40–50°C, 2 min); **e** CTAB (10 cmc, 40–50°C, 10 min); **f** Triton X 100 (10 cmc, 40–50°C, 12 min).

## Experimental

Typical experimental procedure for synthesis of bis(indolyl)methane **1** from indole and benzaldehyde with iodine catalyst in water containing SDS: Finely pulverized solid iodine (5 mg, 2 mol%) was added to a white emulsion SDS (116 mg, 0.4 mmol, 5 cmc) in water (10 mL) and thoroughly stirred until iodine was dissolved imparting brown color to the resulting mixture. It was warmed to 40–50°C and benzaldehyde (106 mg, 1 mmol) followed by indole (234 mg, 2 mmol) were added when instant reaction occurred. TLC monitoring showed complete disappearance of starting materials within 2 minutes. The reaction was quenched by addition of a 5% solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (3 mL) and then brine. Extraction with ethyl acetate (3 × 5 mL), washing the combined organic extract with water (2 × 2 mL), drying (Na<sub>2</sub>SO<sub>4</sub>) and removal

Table 2. I<sub>2</sub>-catalyzed synthesis<sup>a</sup> of bis(indolyl)methanes in aqueous micellar solution.

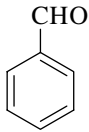
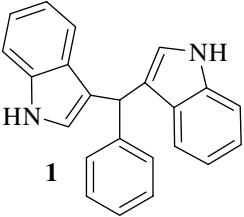
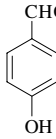
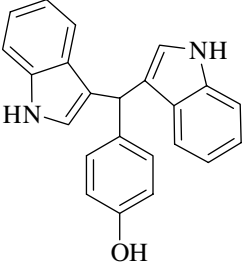
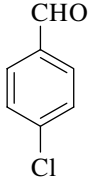
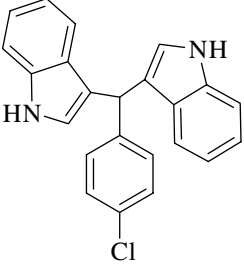
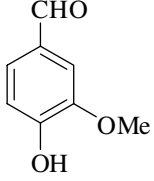
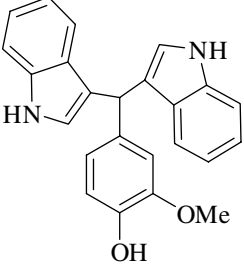
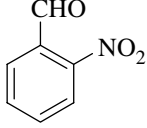
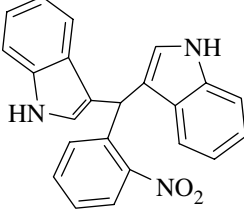
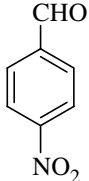
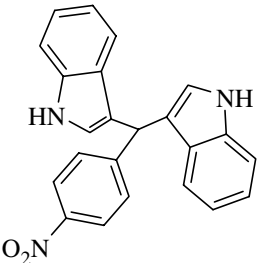
Entry	Indole <sup>b</sup> (A/B)	Aldehyde/ ketone	Product	Time (min/h)	Yield <sup>c</sup> in (%)	Obs. M.P. (°C)	Lit. M.P. (°C)
1	A		 <b>1</b>	2 min	98	124–126	125–126 (39)
2	A			5 min	96	124–126	122–124 (63)
3	A			4 min	98	76–78	76–77 (30)
4	A			5 min	95	100–102	99–101 (39)
5	A			4 min	92	142–144	144 (64)
6	A			4 min	94	216–218	217–220 (65)

Table 2 (Continued)

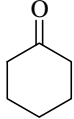
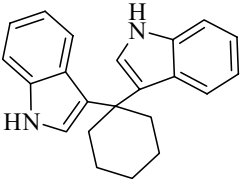
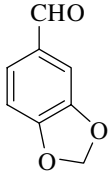
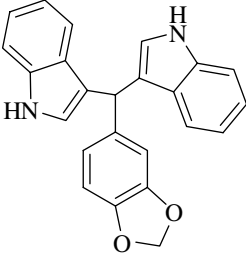
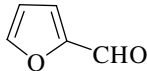
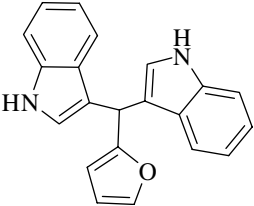
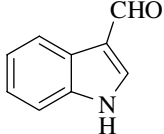
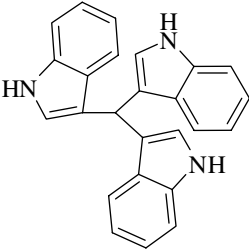
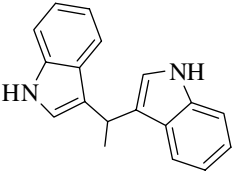
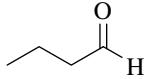
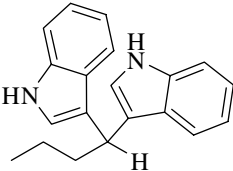
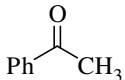
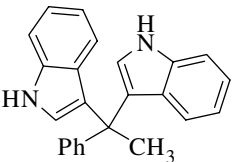
Entry	Indole <sup>b</sup> (A/B)	Aldehyde/ ketone	Product	Time (min/h)	Yield <sup>c</sup> in (%)	Obs. M.P. (°C)	Lit. M.P. (°C)
7	A			3 min	95	118–120	120 (66)
8	A			5 min	95	100–102	98–100 (66)
9	A			2 min	98	112–114	113–115 (67)
10	A			2 min	96	230–232	234–236 (69)
11	A	CH <sub>3</sub> CHO		1 min	99	158–160	158–159 (71)
12	A			3 min	94	150–152	152–154 (71)
13	A			3 h	76	186–188	188–190 (72)

Table 2 (Continued)

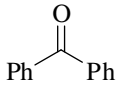
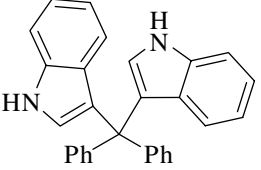
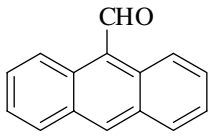
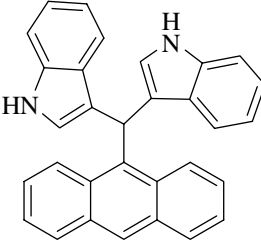
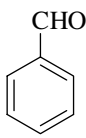
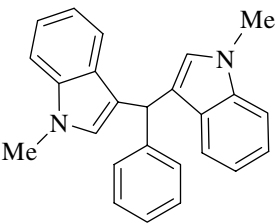
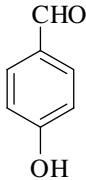
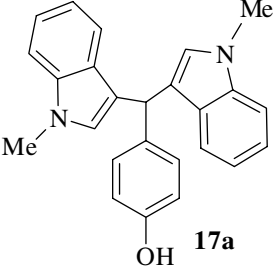
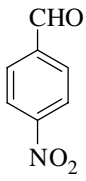
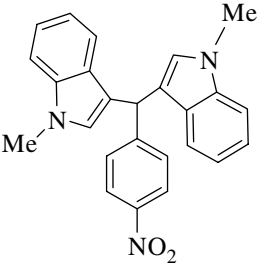
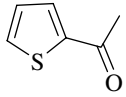
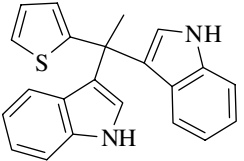
Entry	Indole <sup>b</sup> (A/B)	Aldehyde/ ketone	Product	Time (min/h)	Yield <sup>c</sup> in (%)	Obs. M.P. (°C)	Lit. M.P. (°C)
14	A			4.5 h	78	184–186	– (73)
15	A			3.5 h	92	234–236	236–239 (68)
16	B			3 min	96	202–204	203–205 (69)
17	B			4 min	90	212–214	
18	B			5 min	99	214–216	215–217 (74)
19	A			4 h	80	104–106 (dec.)	–

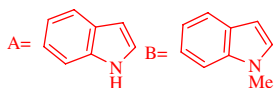
Table 2 (Continued)

Entry	Indole <sup>b</sup> (A/B)	Aldehyde/ ketone	Product	Time (min/h)	Yield <sup>c</sup> in (%)	Obs. M.P. (°C)	Lit. M.P. (°C)
-------	------------------------------	---------------------	---------	-----------------	------------------------------	-------------------	-------------------

<sup>a</sup>Reaction conditions: indole and the carbonyl compound (in 2:1 molar ratio), I<sub>2</sub> (2 mol%), 10 mL H<sub>2</sub>O mmol<sup>-1</sup> of carbonyl compound, SDS (5 cmc), 40–50°C.

<sup>b</sup>A and B represent indole and *N*-methylindole, respectively.

<sup>c</sup>Refers to isolated yields after column chromatographic purification; all the products are known compounds and were characterized from their spectral features (FTIR, <sup>1</sup>HNMR, <sup>13</sup>CNMR and TOF/LCMS) and physical constants which are in good agreement with those reported in literature.

Table 3. I<sub>2</sub>-catalyzed Michael addition<sup>a</sup> of indole with  $\alpha,\beta$ -unsaturated ketones.

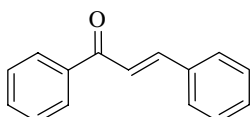
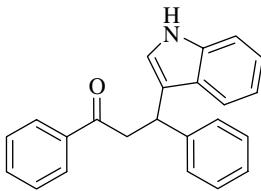
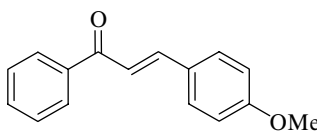
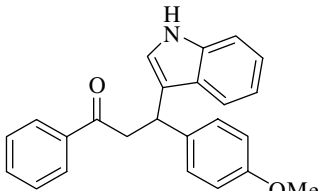
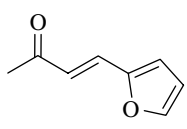
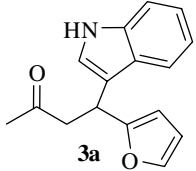
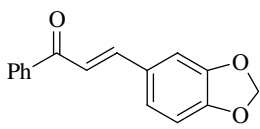
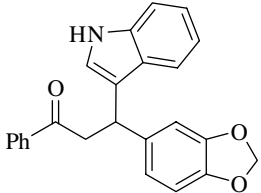
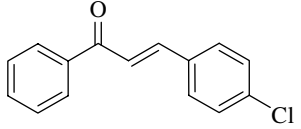
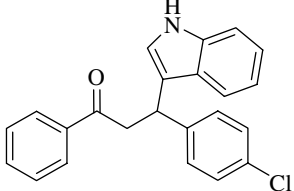
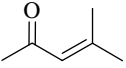
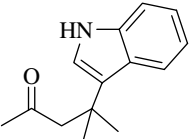
Entry	Indole <sup>b</sup> (A)	Michael acceptor	Product <sup>c</sup>	Time (min/h)	Yield <sup>d</sup> (%)	Obs. M.P. (°C)	Lit. M.P. (°C)
1	A			6 min	96	130–132	128–130 (75)
2	A			6 min	85	128–130	128–130 (76)
3	A			10 min	88	Wine red viscous liquid	
4	A			1 h	76	144–146	145 (35)
5	A			15 min	80	116–118	118–120 (77)



Table 3 (Continued)

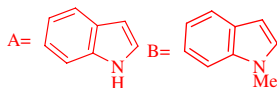
Entry	Indole <sup>b</sup> (A)	Michael acceptor	Product <sup>c</sup>	Time (min/h)	Yield <sup>d</sup> (%)	Obs. M.P. (°C)	Lit. M.P. (°C)
6	A			10 min	95	70–72	71–72 (78)

<sup>a</sup>The reactions were performed at 1 mmol scale using I<sub>2</sub> (2 mol%) of carbonyl compound in aqueous micellar medium under warming condition (40–50°C).

<sup>b</sup>A represents indole.

<sup>c</sup>All products are known compounds except **3a**. These were characterized by FTIR, NMR, and mass spectroscopy.

<sup>d</sup>Isolated yields after column chromatography.



of solvent under reduced pressure yielded almost pure **1**. It was further purified by filtration through a short pad of silica gel (60–120 mesh) using ethyl acetate-hexane (1:4) as eluent to afford **1** (315 mg, 98%), mp 124–126°C [lit. (26) 125–127°C].

### Conclusion

A protocol of synthesis of bis(indolyl)methanes and 3-substituted indolyl ketones has been developed employing 2 mol% of iodine catalyst in aqueous solution in the presence of SDS under warming condition. The surfactant-aided catalytic method in aqueous micellar environment has several key advantageous features such as utilization of inexpensive nontoxic water-tolerant iodine in lower catalyst load compared to that in acetonitrile and under solvent-free conditions, excellent yield and short reaction time.

### Acknowledgements

PM is thankful to CSIR, New Delhi, India, for the award of JRF; and SKB thanks University of Kalyani for financial assistance by way of a research fellowship. Facilities provided by DST-FIST and UGC-SAP Grants, Government of India are also acknowledged.

### References

- Anastas, P.T.; Warner, J.C. *Green Chem. Theory and Practice*; Oxford University Press: Oxford, 2000.
- Grieco, P.A. Ed. *Organic synthesis in water*; Blackie Academic and Professional: London, 1998.
- Li, C.-J.; Chang, T.-H. *Organic Reactions in Aqueous Media*; John Wiley & Sons: New York, 1997.
- Kobayashi, S.; Wakabayashi, T.; Nagayama, S.; Oyamada, H. *Tetrahedron Lett.* **1997**, *38*, 4559–4562.
- Manabe, K.; Mori, Y.; Wakabayashi, T.; Nagayama, S.; Kobayashi, S. *J. Am. Chem. Soc.* **2000**, *122*, 7202–7207.
- Manabe, K.; Kobayashi, S. *Chem. Commun.* **2000**, 669–670.
- Manabe, K.; Limura, S.; Sun, X.-M.; Kobayashi, S. *J. Am. Chem. Soc.* **2002**, *124*, 11971–11978.
- Iranpoor, N.; Firouzabadi, H.; Safavi, A.; Shekarriz, M. *Synth. Commun.* **2002**, *32*, 2287–2293.
- Iranpoor, N.; Firouzabadi, H.; Shekarriz, M. *Org. Biomol. Chem.* **2003**, *1*, 724–727.
- Firouzabadi, H.; Iranpoor, N.; Nowrouzi, F. *Chem. Commun.* **2005**, 789–791.
- Firouzabadi, H.; Iranpoor, N.; Jafari, A. A. *Adv. Synth. Cat.* **2005**, *347*, 655–661.
- Firouzabadi, H.; Iranpoor, N.; Garzan, A. *Adv. Synth. Cat.* **2005**, *347*, 1925–1928.
- Firouzabadi, H.; Iranpoor, N.; Abbasi, M. *Adv. Synth. Cat.* **2009**, *351*, 755–766.
- Firouzabadi, H.; Iranpoor, N.; Alinezhad, H. *J. Iran. Chem. Soc.* **2009**, *6*, 177–186.
- Sundberg, R.J. *The Chemistry of Indoles*; Academic Press: New York, 1970.
- Kam, T.S. In *Alkaloids, Chemical and Biological Perspectives*; Pelletier, S.W., Ed.; Pergamon: Amsterdam, 1999, *4*, 429 pp.
- Irie, T.; Kubushira, K.; Suzuki, K.; Tsukazaki, K.; Umezawa, K.; Nozawa, S. *Anticancer Res.* **1999**, *31*, 3061–3066.
- Amino, N.; Ohse, T.; Koyano, T.; Umezawa, K. *Anticancer Res.* **1996**, *16*, 55–59.
- Bifulco, G.; Bruno, I.; Riccio, R.; Lavayre, J.; Bourdy, G.; *J. Nat. Prod.* **1995**, *58*, 1254–1260.
- Morris, S.A.; Anderson, R.J. *Tetrahedron* **1990**, *46*, 715–720.
- Martinez, R.; Espinosa, A.; Tarraga, A.; Molina, P.; *Tetrahedron* **2008**, *64*, 2184–2191.
- Appendino, G.; Cicione, L.; Minassi, A. *Tetrahedron Lett.* **2009**, *50*, 5559–5561.

- (23) Safe, S.; Papineni, S.; Chintharlapalli, S. *Cancer Lett.* **2008**, *269*, 326–338.
- (24) Lei, P.; Abdelrahim, M.; Cho, S.D.; Liu, S.; Chintharlapalli, S.; Safe, S. *Carcinogenesis* **2008**, *29*, 1139–1147.
- (25) Auria, M. *Tetrahedron* **1991**, *47*, 9225–9230.
- (26) Kamble, V.T.; Kadam, K.R.; Joshi, N.S.; Muley, D.B. *Catal. Commun.* **2007**, *8*, 498–502.
- (27) Nagrajan, R.; Perumal, P.T. *Chem. Lett.* **2004**, *33*, 288–289.
- (28) Niknam, K.; Zolfigol, M.A.; Sadabadi, T.; Nejati, A. *J. Iran. Chem. Soc.* **2006**, *3*, 318–322.
- (29) Yadav, J.S.; Reddy, B.V.S.; Murthy, C.V.S.R.; Kumar, G.M.; Madan, C. *Synthesis* **2001**, 783–787.
- (30) Nagawade, R.R.; Shinde, D.B. *Acta. Chim. Slov.* **2006**, *53*, 210–213.
- (31) Firouzabadi, H.; Iranpoor, N.; Jafarpour, M.; Ghaderi, A. *J. Mol. Catal. A: Chem.* **2006**, *253*, 249–251.
- (32) Zolfigol, M.A.; Salehi, P.; Shiri, M.; Tanbakouchian, Z. *Catal. Commun.* **2007**, *8*, 173–178.
- (33) Babu, G.; Sridhar, N.; Perumal, P.T. *Synth. Commun.* **2000**, *30*, 1609–1614.
- (34) Pradhan, P.K.; Dey, S.; Giri, V.S.; Jaisankar, P. *Synthesis* **2005**, 1779–1782.
- (35) Maiti, G.; Kundu, P.; *Synth. Commun.* **2007**, *37*, 2309–2316.
- (36) Bartoli, G.; Bosco, M.; Foglia, G.; Giuliani, A.; Marcantoni, E. Sambri, L. *Synthesis* **2004**, 895–900.
- (37) Silveira, C.C.; Mendes, S.R.; Libero, F.M.; Lenardão, E.J.; Perinb, G. *Tetrahedron Lett.* **2009**, *50*, 6060–6063.
- (38) Zou, X.; Wang, X.; Cheng, C.; Kong, L.; Mao, H. *Tetrahedron Lett.* **2006**, *47*, 3767–3771.
- (39) Nagarajan, R.; Perumal, P.T. *Tetrahedron* **2002**, *58*, 1229–1232.
- (40) Mi, X.L.; Luo, S.Z.; He, J.Q.; Cheng, J.P. *Tetrahedron Lett.* **2004**, *45*, 4567–4570.
- (41) Ma, S.; Yu, S.; Peng, Z. *Org. Biomol. Chem.* **2005**, *3*, 1933–1936.
- (42) Alam, M.M.; Varala, R.; Adapa, S.R. *Tetrahedron Lett.* **2003**, *44*, 5115–5119.
- (43) Selvam, J.J.P.; Srinivasulu, M.; Suryakiran, N.; Suresh, V.; Reddy, S.M.; Venkateswarlu, Y. *Synth. Commun.* **2008**, *38*, 1760–1767.
- (44) Chakraborty, A.K.; Roy, S.R.; Kumar, D.; Chopra, P. *Green Chem.* **2000**, *10*, 1111–1118.
- (45) Kobayashi, S.; Araki, M.; Yasuda, M.; *Tetrahedron Lett.* **1995**, *36*, 5773–5776.
- (46) Ganguly, N.C.; Barik, S.K. *Synthesis* **2008**, 425–428.
- (47) Ganguly, N.C.; Barik, S.K.; *Synthesis* **2009**, 1393–1399.
- (48) Ganguly, N.C.; Nayek, S.; Barik, S. K. *Synth. Commun.* **2009**, *39*, 4053–4061.
- (49) Gogoi, P.; Hazarika, P.; Konwar, D. *J. Org. Chem.* **2005**, *70*, 1934–1936.
- (50) Cerritelli, S.; Chiarini, M.; Cerichelli, G.; Capone, M.; Marsili, M. *Eur. J. Org. Chem.* **2004**, 623–630.
- (51) Fousteris, M.; Chevrin, C.; Bras, J.L.; Muzart, J. *Green Chem.* **2006**, *8*, 522–523.
- (52) Chu, C.; Gao, S.; Sastry, M.N.V.; Yao, C. *Tetrahedron Lett.* **2005**, *46*, 4971–4974.
- (53) Gao, S.; Tzeng, T.; Sastry, M.N.V.; Chu, C.; Liu, J.; Lin, C.; Yao, C. *Tetrahedron Lett.* **2006**, *47*, 1889–1893.
- (54) Lin, C.; Hsu, J.; Sastry, M.N.V.; Fang, H.; Tu, Z.; Liu, J.; Yao, C. *Tetrahedron* **2005**, *61*, 11751–11757.
- (55) Yadav, J.S.; Reddy, B.V.S.; Reddy, M.S. *Synlett* **2003**, 1722–1724.
- (56) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. *J. Org. Chem.* **2001**, *66*, 7527–7529.
- (57) Bandgar, B.P.; Shaikh, K.A. *Tetrahedron Lett.* **2003**, *44*, 1959–1961.
- (58) Ji, S.-J.; Wang, S.-Y.; Zhang, Y.; Loh, T.-P. *Tetrahedron* **2004**, *60*, 2051–2055.
- (59) Harrington, P.E.; Kerr, M.A. *Synlett.* **1996**, 1047–1048.
- (60) Banik, B.K.; Fernandez, M.; Alvarez, C. *Tetrahedron Lett.* **2005**, *46*, 2479–2482.
- (61) Cozzi, M.P.G.; Giacomooni, M.; Melchiorre, P.; Selva, S.; Ronchi, A.U. *J. Org. Chem.* **2002**, *67*, 3700–3704.
- (62) Yadav, J.S.; Abraham, S.; Reddy, B.V.S.; Sabitha, G. *Synthesis* **2001**, 2165–2169.
- (63) Ramesh, C.; Ravindranath, N.; Das, B. *J. Chem. Res. Synop.* **2003**, 72–74.
- (64) Kundu, P.; Maiti, G. *Indian J. Chem. B:* **2008**, *47B*, 1402–1406.
- (65) Deb, M.L.; Bhuyan, P.J. *Tetrahedron Lett.* **2006**, *47*, 1441–1443.
- (66) Singh, P.R.; Singh, D.U.; Samant, S.D. *Synth. Commun.* **2005**, *35*, 2133–2138.
- (67) Reddy, A.V.; Ravinder, K.; Reddy, V.L.N.; Gound, T.V.; Ravikanth, V.; Venkateswarlu, Y. *Synth. Commun.* **2003**, *33*, 3687–3694.
- (68) Zhang, Z.-H.; Yin, L.; Wang, Y.-M. *Synthesis* **2005**, 1949–1954.
- (69) Nair, V.; Abhilash, K.G.; Vidya, N. *Org. Lett.* **2005**, *7*, 5857–5859.
- (70) Wenkert, E.; Moeller, P.D.R.; Piettre, S.R.; McPhail, A.T. *J. Org. Chem.* **1988**, *53*, 3170–3178.
- (71) Lin, X.-F.; Cui, S.-L.; Wang, Y.-G. *Synth. Commun.* **2006**, *36*, 3153–3160.
- (72) Teimouri, M.B.; Mivehchi, H. *Synth. Commun.* **2005**, *35*, 1835–1843.
- (73) Tabatabaieian, K.; Mamaghani, M.; Mahmoodi, N.; Khorshidi, A. *Can. J. Chem.* **2006**, *84*, 1541–1545.
- (74) Liao, B.-S.; Chen, J.-T.; Liu, S.-T. *Synthesis* **2007**, 3125–3128.
- (75) Nayak, S.K. *Synth. Commun.* **2006**, *36*, 1307–1315.
- (76) Murugan, R.; Karthikeyan, M.; Perumal, P.T.; Reddy, B.S.R. *Tetrahedron* **2005**, *61*, 12275–1228.
- (77) Li, J.-T.; Dai, H.-G.; Xu, W.-Z.; Li, T.-S. *J. Chem. Res. Synop.* **2006**, 41–42.
- (78) Portela-Cubillo, F.; Surgenor, B.A.; Aitken, R.A.; Walton, J.C. *J. Org. Chem.* **2008**, *73*, 8124–8127.