

Research Article

I₂-SDS-H₂O System: A highly Efficient Dual Catalytic Green System for Deprotection of Imines and *in Situ* Preparation of Bis(indolyl)alkanes from Indoles in Water

Parasa Hazarika,^{1,2} Pallab Pahari,² Manash Jyoti Borah,² and Dilip Konwar²

¹ Department of Chemistry, Jorhat Institute of Science and Technology, Assam Jorhat 785010, India

² Synthetic Organic Chemistry Division, North East Institute of Science and Technology, Assam Jorhat 785006, India

Correspondence should be addressed to Dilip Konwar, dkonwar@yahoo.co.uk

Received 27 April 2012; Accepted 7 June 2012

Academic Editors: D. Morales-Morales, G. Palumbo, and J.-P. Praly

Copyright © 2012 Parasa Hazarika et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A novel catalytic system consisting of I₂-SDS-H₂O has been developed which cleaves 2,3-diaza-1,3-butadiene, 1-aza-1,3-butadienes, oximes and in presence of indoles in the medium uses the corresponding aldehyde products to produce bis(indolyl)alkanes *in situ*. This one pot simple and mild dual catalytic system works in water at room temperature under neutral conditions.

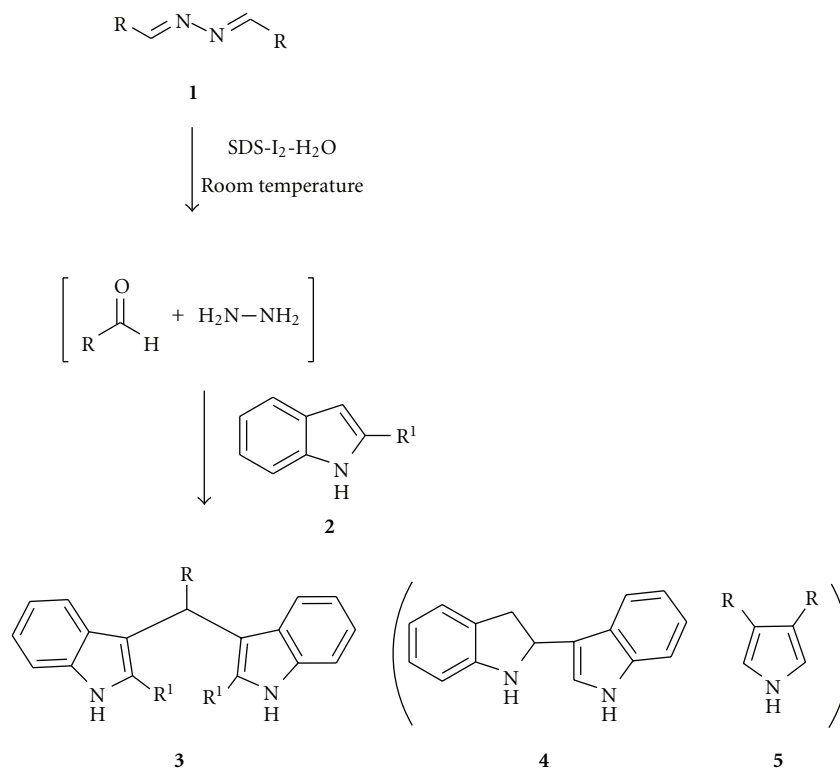
1. Introduction

Using water as solvent in the organic reactions is one of the most important targets to organic chemists because of the easy availability, nontoxicity, and ecofriendly nature of the water [1–7]. In this endeavour, a number of chemical reactions such as Diels Alder, hetero Diels-Alder, 1,3-dipolar cycloaddition, oxidations, reductions, and others are performed successfully in water [1–3]. Also, it is reported that in few cases addition of the water increases the rate and the yield of a reaction and also enhances the enantioselectivity in a chiral synthesis [8]. But the main problems associated with water as a solvent is its poor ability to solubilise organic reactants and incapability to create anhydrous condition for moisture sensitive organic compounds and catalysts. To overcome the solubility problem, generally a surfactant is introduced to the reaction mixture. The surfactant, due to its hydrophobic and hydrophilic nature, forms micelles with water insoluble organic compounds and promote the desired reactions to occur inside the hydrophobic ambience of the micelle core [9, 10].

Cleavage of the C=N bonds is a very important transformation in organic synthesis as the C=N functionality is widely used to protect both the carbonyl and amines.

There are a number of methods used for the cleavage of C=N bonds which include acidic reagents [11–13], oxidizing agents [14], metallic salts [15, 16], (PhSeO)₂O [17], NaHSO₃ [18], and others. Most of these methodologies suffer from serious drawbacks like involvement of strong Lewis and Bronsted acids, use of toxic and costly transition metals (i.e., Cr, Pd, Co), low temperature, longer reaction time, low yield, and difficulties in isolating the products. Therefore, development of efficient, mild and environment friendly reagents are always necessary. On the other hand, bisindoles are recently emerging as extremely important class of compounds because of their novel antibacterial and anticancer activities [19–21]. That is why a number of methodologies have also been postulated for the synthesis of bisindoles [22–29].

In our previous communications, we reported that surfactant- (SDS-) mediated cleavage of C=N bonds could be achieved with acetic anhydride [30] and surfactant-I₂-water can be used for the deprotection of imines to carbonyls [31]. We have also shown that bis- and tris (indolyl)alkanes can be synthesized in presence of Bronsted acid in water [32]. In continuation of our research in hydrated media, herein, we wish to disclose the dual catalytic activity of the system I₂-SDS-H₂O which behaves as a Lewis acid



SCHEME 1: One pot synthesis of bisindoles from protected imine and indole.

TABLE 1: Optimization of the reaction conditions^a.

Entry	Reagent system	Time (h)	Yields ^b (%)
1	I ₂ -SDS-H ₂ O	3.5	93
2	I ₂ -Triton X-H ₂ O	7.0	74
3	I ₂ -Aliquat 336-H ₂ O	8.0	72
4	I ₂ -CTAB-H ₂ O	6.3	69
5	No catalyst	24.0	—

^aThe reactions were carried out using 1 mmol of 1,4-diphenyl-2,3-diaza-1,3-butadiene (**1a**) with 4 mmol of indole (**2a**) in presence of 15 mol% of I₂ and 0.02 g of surfactant.

^bIsolated yield.

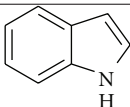
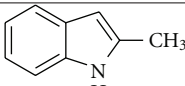
[33] for the cleavage of 2,3-diaza-1,3-butadiene, 1-aza-1,3-butadienes, and oximes to produce carbonyls and amines, and the resulting reaction mixture reacts with indoles to produce bis (indolyl)alkanes *in situ* at room temperature under neutral conditions.

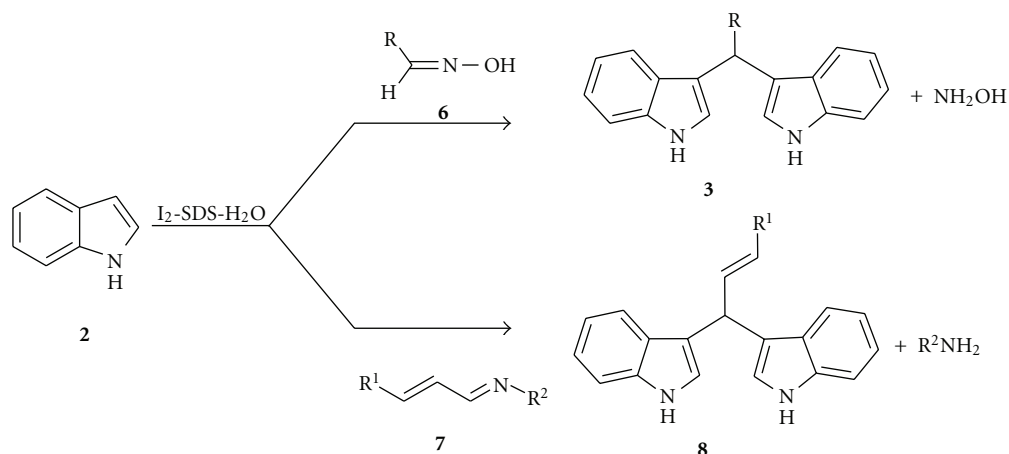
2. Results and Discussion

For an initial study, molecular iodine was added to a mixture of 1,4-diphenyl-2,3-diaza-1,3-butadiene (**1a**) (1 mmol) and indole (**2a**) (2 mmol) in water. It was presumed that the activated imine should produce carbonyl compound in the reaction mixture which might be trapped with indole. But only a trace amount of 3,3'-bis(indolyl)phenylmethane (**3a**) was found to be formed in the reaction. We envisioned that the poor yield of the product may be due to the insolubility of organic substrates in water. Accordingly, we

added a surfactant (SDS) to the reaction flask. To our delight, the reaction produced isolable amount of **3a** as a brown solid but half of the 1,4-diphenyl-2,3-diaza-1,3-butadiene (**1a**) left unreacted in the reaction mixture. So amount of indole (**2a**) was doubled (4 mmol) and the same reaction condition successfully produced quantitative amount of **3a**. The product was filtered out and the filtrate was treated with freshly distilled benzaldehyde (0.05 mmol) in ethanol which furnished **1a** (m.p. 91°C; lit [34] m.p. 92-93°C). This infers the simultaneous involvement of two C=N bonds of bis-anils, leaving behind hydrazine in the reaction mixture. Also, no self-reaction of individual starting materials leading to indole dimer [35] (**4**) or pyrrole formation [36] (**5**) were observed under the same reaction conditions (Scheme 1). Optimization of the reaction conditions was undertaken by employing different catalyst loadings under various surfactant conditions. The results are summarized in Table 1. It was

TABLE 2: Reaction of indoles with 2,3-diaza-1,3-butadienes.

Entry	2,3-diaza-1,3-butadienes 1 (a–i)	Indoles	Products 3 (a–i)	Time (h)	Yield (%) ^a
					
a	$\text{C}_6\text{H}_5\text{CH=CH=N-N=CH-C}_6\text{H}_5$	2	3a	3.5	93
b	$p\text{-H}_3\text{COC}_6\text{H}_4\text{CH=CH=N-N=CH-C}_6\text{H}_4\text{OCH}_3\text{-p}$	2	3b	4.0	90
c	$p\text{-H}_3\text{CC}_6\text{H}_4\text{CH=CH=N-N=CH-C}_6\text{H}_4\text{CH}_3\text{-p}$	2	3c	3.8	91
d	$p\text{-ClC}_6\text{H}_4\text{CH=CH=N-N=CH-C}_6\text{H}_4\text{Cl-p}$	2	3d	4.3	90
e	$p\text{-O}_2\text{NC}_6\text{H}_4\text{CH=CH=N-N=CH-C}_6\text{H}_4\text{NO}_2\text{-p}$	2	3e	3.2	96
f	$p\text{-HOC}_6\text{H}_4\text{CH=CH=N-N=CH-C}_6\text{H}_4\text{OH-p}$	2	3f	4.1	90
g	$p, m\text{-H}_3\text{COC}_6\text{H}_4\text{CH=CH=N-N=CH-C}_6\text{H}_4\text{OCH}_3\text{-m, p}$	2	3g	4.5	90
					
h	$p\text{-H}_3\text{COC}_6\text{H}_4\text{CH=CH=N-N=CH-C}_6\text{H}_4\text{OCH}_3\text{-p}$	2a	3h	4.3	88
i	$p\text{-O}_2\text{NC}_6\text{H}_4\text{CH=CH=N-N=CH-C}_6\text{H}_4\text{NO}_2\text{-p}$	2a	3i	3.5	92

^a Isolated yield.

SCHEME 2: Reaction of azabutadienes and aldioximes with indoles.

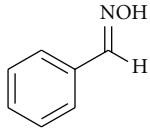
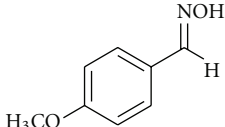
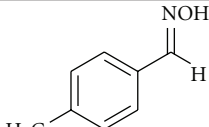
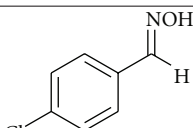
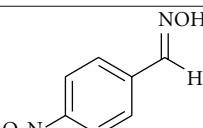
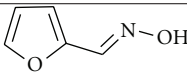
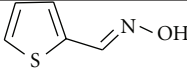
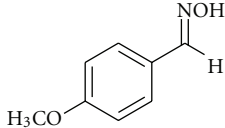
found that the best result was obtained by the application of 15 mol% of I_2 containing sodium dodecyl sulphate (SDS) and water at room temperature (entry 1, Table 1). In absence of the catalyst no formation of **3a** was observed even after stirring for 24 hours (entry 5, Table 1).

To study the scope and limitations of the reaction, $\text{I}_2\text{-SDS-H}_2\text{O}$ system was applied to the reaction of indole (**2**) and 2,3-diaza-1,3-butadiene derivatives (Table 2, entries a–f). The bisindoles were formed in excellent yields under the reaction condition. It was observed that the reaction was relatively faster when an electron withdrawing substituent, for example, NO_2 , was present in the phenyl ring of the 2,3-diaza-1,3-butadienes (Table 2, entry e) in comparison to the electron donating groups, for example, OMe and OH (Table 2, entries b and f). Identical results were obtained


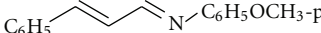
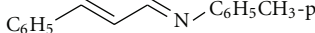
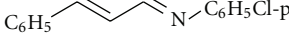
when 2-methylindole (**2a**) was used in place of indole (**2**) (Table 2, entries g and h). All the products were characterized by their IR, ^1H NMR, ^{13}C NMR, and mass spectral data and also by comparison with the literature report (Scheme 2) [24, 25].

In order to further explore the efficiency of the $\text{I}_2\text{-SDS-H}_2\text{O}$ system the reaction of the oximes **6** and indoles **2** was studied. When oximes (1 mmol) and indole (2 mmol) were allowed to react under the same reaction condition described earlier, *bis*-indolylalkanes formed (Table 3). The product was filtered off and the filtrate was treated with benzaldehyde in ethanol. The resulted product was Benzaldoxime, which proved the liberation of hydroxylamine during the reaction. It was found that no Michael addition product [37] was formed and only a trace amount of indole dimer **5** [35] could

TABLE 3: Reaction of indoles with aldoximes.

Entry	Indoles	Aldoximes 6 (a–g)	Products	Time (h)	Yield (%) ^a
a	2		3a	3.0	91
b	2		3b	3.3	89
c	2		3c	3.3	90
d	2		3d	3.1	91
e	2		3e	3.0	93
f	2		3j	3.4	88
g	2		3k	4.0	85
h	2a		3g	3.1	90

^a Isolated yield.TABLE 4: Reaction of 1-azabutadienes with indole (**2**).

Entry	1-azabutadienes 7 (a–d)	Bis(indolyl)alkane	Time (h)	Yield (%) ^a
a		8	2.5	85
b		8	3.0	83
c		8	3.0	85
d		8	2.4	87

^a Isolated yield.

be identified. The system was also applied to the reaction of 1-aza-1,3-butadienes **7** with indole (**2**) which produced bis(indolyl)alkanes **8** in very good yield eliminating aryl amine in the reaction mixture (Table 4). All the products were well characterized by comparison of their spectral and mass data with that of the reported value [24, 25].

3. Conclusions

In conclusion, we have shown the dual catalytic activity of I₂-SDS-H₂O system which deprotects the azadienes, oximes, and azabutadienes and produces bis (alkyl)indoles *in situ* when indole is present in the reaction medium. The two-step

reaction can be carried out without using acid, transition metals, and organic solvents. Besides, the reaction condition is mild and can be done in water under neutral condition which contributes to the criteria of green chemistry.

4. Experimental

Melting points were measured using Buchi B-540 apparatus and are uncorrected. ^1H NMR spectra were recorded on Avance DPX 300 MHz FT-NMR spectrometer. Chemical shifts are expressed in δ units relative to tetramethylsilane (TMS) signal as internal reference. IR spectra were recorded on FT-IR-system-2000 Perkin Elmer spectrometer on KBr pellets or in CHCl_3 . Mass spectra were recorded on ESQUIRE 3000 Mass Spectrometer. All reagents were obtained from commercial sources and used without further purification. The solvents for chromatography were distilled before use.

4.1. General Procedure for the Synthesis of 3,3'-Bis(indolyl)alkanes. In a 50 mL round bottom flask, 15 mol% of I_2 was first dissolved in water (10 mL). 2,3-Diaza-1,3-butadiene (1 mmol) and indole (4 mmol) were added and stirred in the presence of sodium dodecyl sulphate (SDS) (0.02 g) for the stipulated time. The progress of the reaction was monitored by TLC. The product formed was filtered off and washed with water, dried, and recrystallized from ethanol.

Identical reaction condition was followed when 1-aza-1,3-butadienes and oximes were used as reactants. In this case, 2 mmol of indoles were used to react with 1 mmol of imines.

4.2. 3,3'-Bis(indolyl)phenylmethane (3a) [24]. Colorless solid; mp: 150–152°C; FTIR (KBr): ν 3418, 3058, 1623, 1611, 1445, 1093 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.95 (s, 1H, Ar-CH), 6.73 (s, 2H), 7.06 (t, 2H, $J = 6.8$ Hz), 7.18–7.27 (m, 3H), 7.31–7.36 (m, 2H), 7.36–7.42 (m, 6H), 7.98 (br, s, 2H, NH); ^{13}C NMR (75 MHz, CDCl_3): 40.7, 111.2, 119.1, 119.5, 120.4, 122.1, 123.8, 126.9, 126.9, 128.2, 129.1, 136.8, 144.8; HRMS calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2$ (M^+): 322.2851, found 322.2832; Anal.calcd.: C, 85.70; H, 5.59; N, 8.69; found C, 85.75; H, 5.56; N, 8.56.

4.3. 3,3'-Bis(indolyl)-4-chlorophenylmethane (3d) [24]. Pink solid; mp: 76–77°C; FTIR (KBr): ν 3415, 3060, 1491, 1465, 1095 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.91 (s, 1H, Ar-CH), 6.76 (s, 2H), 7.08 (t, 2H, $J = 8.3$ Hz), 7.22 (t, 2H, $J = 7.9$ Hz), 7.28–7.42 (m, 8H), 8.01 (br, s, 2H, NH); ^{13}C NMR (75 MHz, CDCl_3): 39.8, 111.5, 122.6, 123.8, 127.1, 128.4, 129.8, 130.1, 130.9, 131.0, 131.6, 137.2, 143.5; HRMS calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2\text{Cl}$ (M^+): 356.7371; found 356.7324; Anal.calcd.: C, 77.52; H, 4.77; N, 7.86; found C, 77.48; H, 4.72; N, 7.80.

4.4. 3,3-Bis(indolyl)furylmethane (3j) [24]. Brown solid; mp: 323–325°C; FTIR (KBr): ν 3420, 1720, 1455, 1258 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 5.98 (s, 1H, Ar-CH), 6.85 (s, 2H), 7.10–7.55 (m, 11H), 8.05 (br, s, 2H, NH), ^{13}C NMR

(75 MHz, CDCl_3): 34.8, 107.0, 110.0, 111.5, 117.8, 119.9, 120.0, 122.5, 124.8, 127.1, 136.8, 142.2; HRMS calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2$ (M^+): 312.2621; found 312.2611; Anal.calcd. C, 80.84; H, 5.12; N, 8.97; found C, 84.05; H, 5.15; N, 8.94.

All the products were fully characterized by ^1H and ^{13}C NMR and MS analyses. The spectral data of the compounds are available in the Supplementary Material available online at doi: 105402/2012/635835.

Acknowledgments

The authors thank the Director, NEIST, Jorhat, Assam, India, and the Principal, JIST, Jorhat, Assam, India, for their keen interest in carrying out the work.

References

- [1] P. A. Grieco, *Organic Synthesis in Water*, Blackie Academic and Professional, London, UK, 1998.
- [2] C. J. Li and T. H. Chan, *Organic Reactions in Aqueous Media*, John Wiley & Sons, New York, NY, USA, 1997.
- [3] U. M. Lindström, "Stereoselective organic reactions in water," *Chemical Reviews*, vol. 102, no. 8, pp. 2751–2772, 2002.
- [4] S. Kobayashi and K. Manabe, "Development of novel Lewis acid catalysts for selective organic reactions in aqueous media," *Accounts of Chemical Research*, vol. 35, no. 4, pp. 209–217, 2002.
- [5] P. Tundo and P. T. Anastas, *Green Chemistry: Challenging Perspectives*, Oxford University Press, Oxford, UK, 2000.
- [6] P. T. Anastas and T. C. Williamson, *Green Chemistry, Frontiers in Benign Chemical Syntheses and Processes*, Oxford University Press, New York, NY, USA, 1998.
- [7] R. A. Sheldon, "Green solvents for sustainable organic synthesis: state of the art," *Green Chemistry*, vol. 7, no. 5, pp. 267–278, 2005.
- [8] S. Ribe and P. Wipf, "Water-accelerated organic transformations," *Chemical Communications*, no. 4, pp. 299–307, 2001.
- [9] Y. Mori, *Micelles: Theoretical and Applied Aspects*, Springer, 1992.
- [10] S. Taşcıoğlu, "Micellar solutions as reaction media," *Tetrahedron*, vol. 52, no. 34, pp. 11113–11152, 1996.
- [11] M. P. Doyle, M. A. Zaleta, J. E. Deboer, and W. Wierenga, "Reactions of the nitrosonium ion. V. Nitrosative cleavage of the carbon-nitrogen double bond. The attempted exchange of oxygen for nitrogen," *Journal of Organic Chemistry*, vol. 38, no. 9, pp. 1663–1667, 1973.
- [12] E. J. Corey, P. B. Hopkins, S. Kim, S.-E. Yoo, K. P. Nambiar, and J. R. Falck, "Total synthesis of erythromycins. 5. Total synthesis of erythronolide A," *Journal of the American Chemical Society*, vol. 101, no. 23, pp. 7131–7134, 1979.
- [13] A. S. Culf, J. A. Melanson, R. J. Ouellette, and G. G. Briand, "Bis-imine primary amine protection of the dialkyltriamine, norspermidine," *Tetrahedron Letters*, vol. 53, no. 26, pp. 3301–3304, 2012.
- [14] G. H. Imanzadeh, A. R. Hajipour, and S. E. Mallakpour, "Solid state cleavage of oximes with potassium permanganate supported on alumina," *Synthetic Communications*, vol. 33, no. 5, pp. 735–740, 2003.
- [15] P. M. Bendale and B. M. Khadilkar, "Microwave promoted regeneration of carbonyl compounds from oximes using silica

- supported chromium trioxide," *Tetrahedron Letters*, vol. 39, no. 32, pp. 5867–5868, 1998.
- [16] T. Respondek, E. Cueny, and J. J. Kodanko, "Cumyl ester as the C-terminal protecting group in the enantioselective alkylation of glycine benzophenone imine," *Organic Letters*, vol. 14, no. 1, pp. 150–153, 2012.
 - [17] D. H. R. Barton, D. J. Lester, and S. V. Ley, "Regeneration of ketones from hydrazones, oximes, and semicarbazones by benzeneseleninic anhydride," *Journal of the Chemical Society, Chemical Communications*, no. 13, pp. 445–446, 1977.
 - [18] S. H. Pines, J. M. Chemerda, and M. A. Kozlowski, "Cleavage of oximes with bisulfite. A general procedure," *Journal of Organic Chemistry*, vol. 31, no. 10, pp. 3446–3447, 1966.
 - [19] C. G. Yang, H. Huang, and B. Jiang, "Progress in studies of novel marine *bis*(indole) alkaloids," *Current Organic Chemistry*, vol. 8, no. 17, pp. 1691–1720, 2004.
 - [20] R. G. Panchal, R. L. Ulrich, D. Lane et al., "Novel broad-spectrum *bis*-(imidazolinyndole) derivatives with potent antibacterial activities against antibiotic-resistant strains," *Antimicrobial Agents and Chemotherapy*, vol. 53, no. 10, pp. 4283–4291, 2009.
 - [21] A. Andreani, S. Burnelli, M. Granaiola et al., "Antitumor activity of *bis*-indole derivatives," *Journal of Medicinal Chemistry*, vol. 51, no. 15, pp. 4563–4570, 2008.
 - [22] M. Chakrabarty, N. Ghosh, R. Basak, and Y. Harigaya, "Dry reaction of indoles with carbonyl compounds on montmorillonite K10 clay: a mild, expedient synthesis of diindolylalkanes and vibrindole A," *Tetrahedron Letters*, vol. 43, no. 22, pp. 4075–4078, 2002.
 - [23] R. Nagarajan and P. T. Perumal, "InCl₃ and In(OTf)₃ catalyzed reactions: synthesis of 3-acetyl indoles, *bis*-indolylmethane and indolylquinoline derivatives," *Tetrahedron*, vol. 58, no. 6, pp. 1229–1232, 2002.
 - [24] S. J. Ji, S. Y. Wang, Y. Zhang, and T. P. Loh, "Facile synthesis of *bis*-(indolyl)methanes using catalytic amount of iodine at room temperature under solvent-free conditions," *Tetrahedron*, vol. 60, no. 9, pp. 2051–2055, 2004.
 - [25] B. P. Bandgar and K. A. Shaikh, "Molecular iodine-catalyzed efficient and highly rapid synthesis of *bis*(indolyl)methanes under mild conditions," *Tetrahedron Letters*, vol. 44, no. 9, pp. 1959–1961, 2003.
 - [26] L. Wang, J. Han, H. Tian, J. Sheng, Z. Fan, and X. Tang, "Rare earth perfluorooctanoate [RE(PFO)₃]-catalyzed condensations of indole with carbonyl compounds," *Synlett*, no. 2, pp. 337–339, 2005.
 - [27] T. J. K. Gibbs and N. C. O. Tomkinson, "Aminocatalytic preparation of bisindolylalkanes," *Organic & Biomolecular Chemistry*, vol. 3, no. 22, pp. 4043–4045, 2005.
 - [28] S. Ko, C. Lin, Z. Tu, Y. F. Wang, C. C. Wang, and C. F. Yao, "CAN and iodine-catalyzed reaction of indole or 1-methylindole with α,β -unsaturated ketone or aldehyde," *Tetrahedron Letters*, vol. 47, no. 4, pp. 487–492, 2006.
 - [29] M. L. Deb and P. J. Bhuyan, "An efficient and clean synthesis of *bis*(indolyl)methanes in a protic solvent at room temperature," *Tetrahedron Letters*, vol. 47, no. 9, pp. 1441–1443, 2006.
 - [30] S. D. Sharma, P. Gogoi, M. Boruah, and D. Konwar, "SDS/Ac₂O/H₂O: surfactant-mediated cleavage of imines with acetic anhydride to carbonyls and acetanilides in water," *Synthetic Communications*, vol. 37, no. 15, pp. 2473–2481, 2007.
 - [31] P. Gogoi, P. Hazarika, and D. Konwar, "Surfactant/I₂/water: an efficient system for deprotection of oximes and imines to carbonyls under neutral conditions in water," *Journal of Organic Chemistry*, vol. 70, no. 5, pp. 1934–1936, 2005.
 - [32] P. Hazarika, S. Das Sharma, and D. Konwar, "Efficient synthesis of *bis*- and *tris*-indolylalkanes catalyzed by a Brønsted acid-surfactant catalyst in water," *Synthetic Communications*, vol. 38, no. 17, pp. 2870–2880, 2008.
 - [33] A. Hazra, P. Paira, K. B. Sahu, S. Banerjee, and N. B. Mondal, "Molecular iodine: an efficient catalyst of the synthesis of both symmetrical and unsymmetrical triindolylmethanes," *Catalysis Communications*, vol. 9, pp. 1681–1684, 2008.
 - [34] A. I. Vogel and B. S. Furniss, *Vogel's Textbook of Practical Organic Chemistry*, Longman Sci. Tech., Harlow, UK, 5th edition, 1989.
 - [35] H. Chalaye-Mauger, J. N. Denis, M. T. Averbuch-Pouchot, and Y. Vallée, "The reactions of nitrones with indoles," *Tetrahedron*, vol. 56, no. 5, pp. 791–804, 2000.
 - [36] P. A. S. Smith, *Open Chain Nitrogen Compounds*, vol. 2, chapter 9, Benjamin, New York, NY, USA, 1966.
 - [37] D. Prajapati, J. S. Sandhu, T. Kametani, H. Nagase, K. Kawai, and T. Honda, "Dipolar cycloadditions of nitrile imines with aldazines," *Heterocycles*, vol. 23, no. 5, pp. 1123–1126, 1985.

