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NICKEL ACETATE AS EFFICIENT ORGANOMETALLIC CATALYST FOR SYNTHESIS OF BIS (INDOLYL) METHANES

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ABSTRACT

Bis(indolyl) methanes derivatives have been synthesized using a catalytic amount of organometallic anhydrous nickel acetate at room temperature with excellent yields. The remarkable selectivity under mild, neutral and, inexpensive catalyst are attractive features.

Key words: Bis(indolyl) methanes, Nickel acetate, Aldehydes, Ketones.

INTRODUCTION

The development of simple, efficient and economically viable chemical process or methodologies for widely used organic compounds are in great demand[1]. Various methods have been developed for their synthesis using Lewis acid catalysts[2-8], ionic liquids[9], trichloro-1,3,5-triazine[10], and potassium hydrogen sulphate[11]. However, many of these reported methods suffer from one or more disadvantages such as harsh experimental procedure and reagents that are expensive, moisture sensitive. A mild and efficient catalyst for the synthesis of bis(indolyl) methanes is highly desirable.

EXPERIMENTAL

In this communication, we report a synthesis of Bis(indolyl) methanes by using organometallic anhydrous nickel acetate as catalyst. A wide variety of compounds that were

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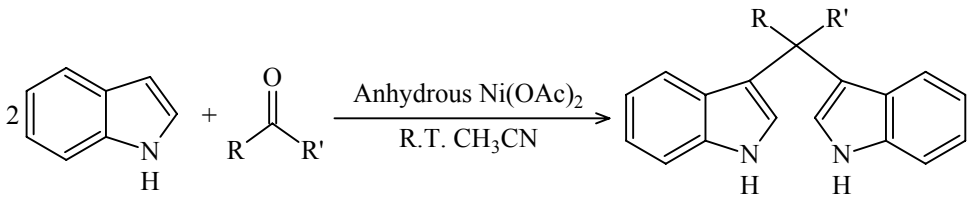
applied to the optimal reaction conditions to prepare a wide range of bis(indolyl) methanes (**Scheme 1**).



R, R'= H , Phenyl, Alkyl

Scheme 1

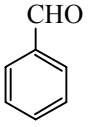
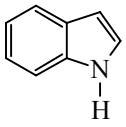
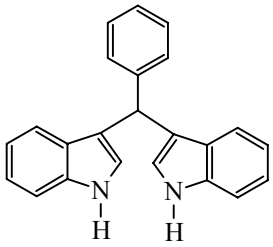
General experimental procedure for Bis(indolyl) methanes

A mixture of benzaldehyde (2 mmol), Indole (4 mmol) and anhydrous $Ni(OAc)_2$ (0.1 mmol, 30 mg) was stirred magnetically at room temperature, acetonitrile (1 mL) and the progress of the reaction was monitored by thin-layer chromatography. The product was dried over anhydrous Na_2SO_4 and further purification by column chromatography.

RESULTS AND DISCUSSION

The reaction proceeded efficiently and smoothly at room temperature in presence of anhydrous $Ni(OAc)_2$ as a catalyst, and the products were obtained in excellent yields. Various aromatic aldehydes, aliphatic aldehyde and ketones gives the corresponding products with excellent yield (Table 1, entries 1-9).

Table 1: Synthesis of bis(indolyl) methanes

Entry	Aldehyde (a)	Indoles	Product (b)	Time (min)	Yield[c] (%)
1				**25**	**94**

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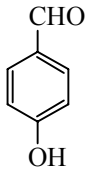
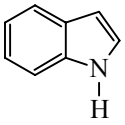
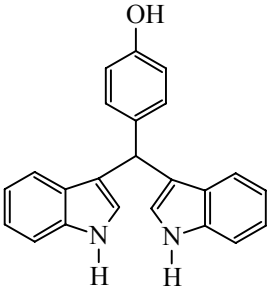
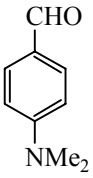
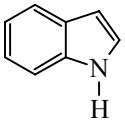
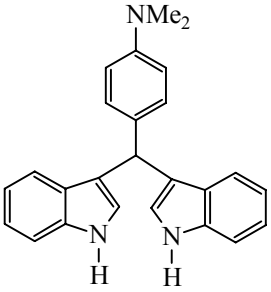
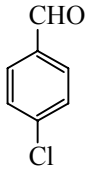
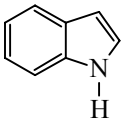
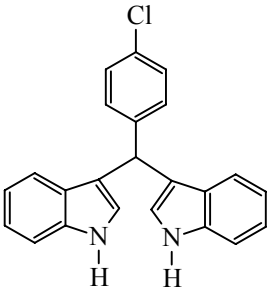
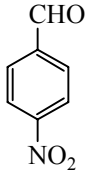
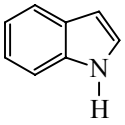
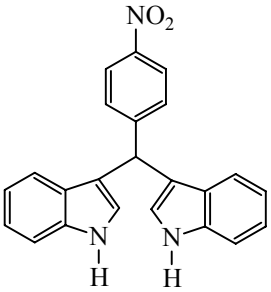
Entry	Aldehyde (a)	Indoles	Product (b)	Time (min)	Yield[c] (%)
2				**25**	**92**
3				**55**	**90**
4				**55**	**87**
5				**75**	**88**

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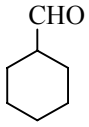
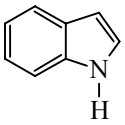
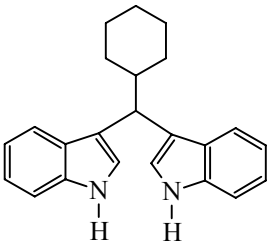
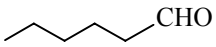
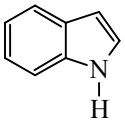
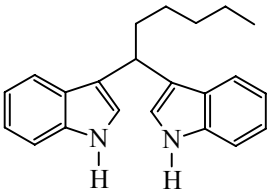
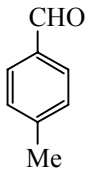
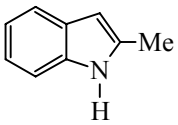
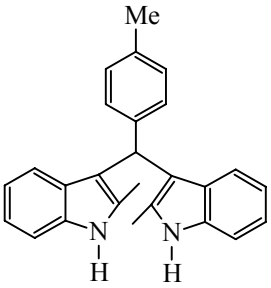
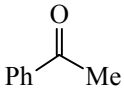
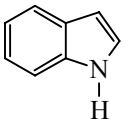
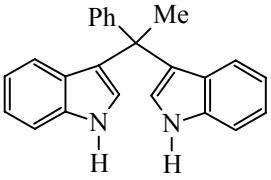
Entry	Aldehyde (a)	Indoles	Product (b)	Time (min)	Yield[c] (%)
6				**75**	**87**
7				**85**	**86**
8				**35**	**89**
9				**110**	**87**

[a]The substrate was treated with indole (4 mmol) by stirring at room temperature with anhydrous $Ni(OAc)_2$ in presence of acetonitrile as solvent;

[b]All products were identified by their IR and ^1H NMR spectra;

[c]Isolated yields after column chromatography

Spectral data

3,3'-Bisindolyl phenyl methane (1b): Pale-red solid, yield 94%, m.p. 122-124°C

IR (KBr): 736, 1012, 1173, 1336, 1415, 1599, 2848, 3024, 3054, 3409 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.8 (s, 2H); 7.1-7.4 (br m, 8H); 6.3-6.8 (m, 5H); 4.1-4.4 (s, 2NH);

2.2 (s, H): ^{13}C NMR ($CDCl_3$): 144.1, 136.7, 128.7, 128.6, 127.2, 126.9, 123.7, 121.9, 119.9, 111.1, 40.2. EIMS; m/z 322

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REFERENCES

1. V. D. Patil, P. V. Gidh, P. C. Patil, N. Sutar and K. P. Patil, Efficient Synthesis of Bis(indolyl) Methanes by using Silica Supported TCAA, Int. J. Chem. Sci., **12(1)**, 248 (2014).

2. J. S. Yaday, V. B. S. Reddy, V. C. R. S. Murthy, M. G. Kumar and C. Madan, Lithium Perchlorate Catalyzed Reaction of Indoles, An Expeditious Synthesis of Bis(indolyl) Methanes, Synthesis, **5**, 783 (2001**)**.

3. R. Nagarajan and P. T. Perumal, $InCl_3$ and In(OTf)x Catalyzed Reaction of 3-Acetylindolylmethanes and Indolylquinoline Derivatives, Tetrahedron, **58**, 1229 (2002).

4. X. L. Mi, S. Z. Luo, J. Q. He and J. P. Cheng, $InCl_3$ Catalysed Conjugate Addition of Indoles with Electron Deficient Olefins, Tetrahedron Lett., **45**, 4567 (2004).

5. S. Ma, S. Yu and Z. Peng, $Sc(OTf)_3$-catalyzed Efficient Synthesis of Beta, Beta-Bis(indolyl) Ketones by the Double Indolylation of Acetic Acid 2-methylene-3-Oxobutyl Ester, Org. Biomol. Chem., **3**, 1933 (2005).

6. P. B. Bandagar and A. K. Shaikh, Molecular Iodine-catalyzed Efficient and Highly Rapid Synthesis of Bis-indolyl-methane Under Mild Conditions, Tetrahedron Lett., **44**, 1959 (2003).

7. L. M. Deb and J. P. Bhuyan, An Efficient and Clean Synthesis of Bis(indolyl) Methanes in a Protic Solvent at Room Temperature, Tetrahedron Lett., **47**, 1441 (2006).

8. R. R. Nagawade and B. D. Shinde, Zirconyl(IV) Chloride-Catalysed Reaction of Indoles: An Expeditious Synthesis of Bis(indolyl) Methanes, Acta. Chim. Slov., **53**, 210 (2006).

9. G. Babu, N. Sridhar and T. P. Perumal, A Convenient Method of Synthesis of Bis-Indolyl-Methane, Indium Trichloride Catalysed Reactions of Indole with Aldehydes and Schiff's Bases, Synth. Commun., **30**, 1609 (2000).

10. H. Firouzabadi, N. Iranpoor and A. Ali Jafari, Preparation of Indolyl Methanes Catalyzed by Metal Hydrogen Sulfates, J. Mol. Cat. A: Chem., **244**, 168 (2006).

11. M. V. G. Sharma, J. J. Reddy and S. P. Lakshmi, A Versatile and Practical Synthesis of Bis-indolyl-methane/bis-indolyl Glycoconjugates Catalysed by Trichloro 1,3,5-Triazine, Tetrahedron Lett., **45**, 7729 (2004).

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