

RESEARCH ARTICLE

An efficient solvent free synthesis of *meso*-substituted dipyrromethanes from lowest pyrrole/aldehyde ratio on grinding

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ABSTRACT:

An efficient and simple methodology has been developed under solvent free condition for the quantitative synthesis of *meso*-substituted dipyrromethanes from lowest pyrrole/aldehyde ratio. The method was carried out by using I₂ as a catalyst. The method is environmentally friendly, easy to workup, and gives excellent yield of the products.

KEYWORDS: Pyrrole, Aldehyde, Dipyrromethanes, Iodine, Solvent free.

INTRODUCTION:

Dipyrromethanes are compounds known for more than a century and are widely being used as important building blocks for the synthesis of porphyrins,¹ Calixpyrrols² and Corroles.³ which have recent applications as chiral catalysts, chiral sensors, synthetic receptors for small molecular devices, potential sensitizers for photodynamic cancer therapy.⁴⁻⁶ In the past decades, a variety of conditions have been established for the synthesis of dipyrromethanes in the presence of various catalysts such as *p*-toluenesulfonic acid,⁷ TiCl₄,⁸ CF₃COOH,⁹ pyrrolidinium tetrafluoroborate.¹⁰ In the synthesis of dipyrromethanes most of the conditions are based on the acid catalyzed condensation of pyrrole with aldehyde. Recently, several methods have been developed, for the synthesis of dipyrromethanes in various catalyst such as ionic liquid [Hmim] BF₄,¹¹ HCl/water,¹² cation exchange resin,¹³ metal triflate catalysis,¹⁴ HCl,¹⁵ iodine/CH₂Cl₂,¹⁶ InCl₃.¹⁷ However, all of the synthetic protocols reported so far suffer from disadvantages such as, use of metal¹⁴ and expensive reagent,¹³ prolonged reaction time,¹⁵ use of organic solvent,¹⁶ harsh reaction condition,¹⁵ use of excess pyrrole¹⁴ and low yield.¹¹ Because of that the researcher still continuous to have a better methodology for the synthesis of dipyrromethanes in terms of simplicity, eco-friendly, economic viability, high yielding at lowest pyrrole/aldehyde ratio which is achieved by using iodine under solvent free condition. In recent years I₂ in solvent free conditions was found to be an efficient catalyst in terms of handling, temperature, reaction time and yield for various organic transformations.¹⁸

MATERIAL AND METHODS:

Purity of the compounds were checked by thin layer chromatography (TLC) on Merck silica gel 60 F254 pre-coated sheets Melting points of the synthesized compounds were determined in open-glass capillaries on a Stuart-SMP10 melting point apparatus. IR absorption spectra were recorded on a Perkin Elmer 1650 FTIR using KBr pellets in the range of 4,000-450 cm⁻¹. ¹H-NMRs were recorded on a Bruker spectrometer operating at 400 MHz. The ¹H-NMR chemical shifts are reported as parts per million (ppm) downfield from TMS (Me₄Si) used as an internal standard. Elemental analyses for C, H, and N were performed using a EuroVector CHNS-O elemental analyzer. All compounds were known, and obtained physical and spectroscopic data were compared with literatures data.^{9c,13,14}

General Procedure for the synthesis of *meso*-substituted dipyrromethanes

A mixture of pyrrole (2 mmol), aldehyde (1 mmol) and I₂ (0.1 mmol) was crushed in a mortar with a pestle at room temperature. Progress of reaction was monitored by TLC. After completion of reaction (< 1 min) the crude product was washed with water, dried and purified by column chromatography using silica gel with petroleum ether/chloroform as the eluent. Pure products were obtained as solids.

Data

5-(4-nitrophenyl)dipyrromethane: Yellow powder; mp: 159–160 °C, IR (KBr) 3395, 3362, 3100, 1597, 1517, 1348, 1120, 1024, 805, 737, 661, 565 cm⁻¹; ¹H NMR(400 MHz, CDCl₃): δ 5.57 (s, 1H, mesoH), 5.85 (br s, 2H, 2C3–H), 6.14 (dd, 2H, J = 2.8, 5.7, 2C4–H), 6.74 (dd, 2H, J = 2.8, 4.2, 2C5–H), 7.37 (d, 2H, J = 8.6, H-Ar), 8.0 (br s, 2H, N–H), 8.13 (d, 2H, J = 8.8, Ar-H).; Anal. Calcd. For