INTERNATIONAL JOURNAL OF APPLIED BIOLOGY AND PHARMACEUTICAL TECHNOLOGY

Volume: 2: Issue-1: Jan-Mar -2011 IJABPT *ISSN 0976-4550*

A NOVEL METHOD FOR THE SYNTHESIS OF MESO SUBSTITUTED DIPYYROMETHANES

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ABSTRACT: Meso-substituted dipyrromethanes have been synthesized in the presence of $SnCl_2.2H_2O$ as a catalyst. The reaction is carried out in water, a very green solvent, under stirring at room temperature. The reaction work-up is simple and the catalyst is easily separated from the products by filtration
Keywords: Meso-substituted dipyrromethane, pyrrole, Aromatic aldehyde, $SnCl_2.2H_2O$.

INTRODUCTION

The development of pyrrole chemistry has largely been associated with the synthesis of natural products. Polypyrrolic compounds are of wide interest in several areas, namely in porphyrins and related macrocycles[1], Science materials[2], optics[3] and medicine[4]. Meso substituted dipyrromethane are important building blocks for the organic synthesis and pharmaceuticals [5, 6]. They were also widely used as ligands in organometallic synthesis and catalysis [7, 8]. Generally, the synthesis of meso substituted dipyrromethane was carried out by the condensation of aldehyde with excess of pyrrole in the presence of strong acid such as trifluoroacetic acid, methyl sulfuric acid [8,9]. The reaction usually needs high temperature, refluxing in ethanol or toluene and using amount of harmful organic solvents in chemical process ionic liquid have been used as catalytic species [Hmim] BF_4 is a brønsted acid in the synthesis of ester and protection of corbonyls[10,11]. The stability of meso substituted dipyrromethane to oxidation is always a cause for concern during the synthetic procedure, isolation and storage of such compounds, a diversity of conditions have been established allowing good to excellent yield of meso substituted dipyrromethane to be obtained in the case where adequate substituents are present on the pyrrole rings. Those substituents provide for the stability of both the pyrrole precursors and the product meso substituted dipyrromethane [12, 13]. Synthesis of meso substituted dipyrromethane has thus far been indirect, requiring either the elimination of a protecting ester group from the pyrrole segment [14, 15] or through the formation of a Grignard reagent[16]. The reaction of pyrrole derivatives with a variety of aromatic aldehydes has been described [17-19] but the major products appear to be azafulvenes. The formation of meso substituted dipyrromethane in acetic acid has been reported when the starting 1H – pyrroles are strongly basic or the aldehyde components carries an electron donating substituent [19] but the earlier work by Treibs et al [18]. Demonstrate that the formation of meso substituted dipyrromethane is unfavorable in the presence of acids. The direct condensation of aromatic aldehydes with unsubstituted pyrrole under a variety of conditions (refluxing in acetic acid [20, 21] in the presence of a Lewis acid [22] or with microwave irradiation [23]) has resulted in tetraphenylporphyrins. In recently, $SnCl_2.2H_2O$ has received considerable attention as an inexpensive, readily available catalyst for various organic transformations, affording the corresponding products in excellent yields with high selectivity. The mild Lewis acidity associated with it enhanced its usage in organic synthesis to realize several organic transformations using stiochiometric levels to catalytic amounts. Owing to numerous advantages associated with this eco-friendly element, $SnCl_2.2H_2O$ has been explored as a powerful catalyst for various organic transformations[24, 25].

We now report here the synthesis of meso substituted dipyrromethane by condensation of pyrrole with various aldehydic carbonyl compounds using $SnCl_2.2H_2O$ in water as an efficient catalyst under stirring at room temperature reaction condition in a very short time <10 min (scheme 1). However, the reported catalysts require longer reaction time giving moderate yields of products for this conversion. The present procedure is superior in comparison with F_3CCOOH, $InCl_3$, BF_3 O $(et)_2$ catalyzed reactions of CH_2 Cl_2 with pyrrole which generated several unexpected products [29]. Where as expensive $InCl_3$, F_3CCOOH, BF_3 O $(et)_2$ catalyzed reactions took a very long reaction time (5 h) [26,29].

MATERIALS AND METHODS

Synthesis of meso substituted dipyrromethane (3)

A solution of pyrrole (2 mmol), aldehyde (1 mmol) and $SnCl_2.2H_2O$ (3 mmol %) dissolved in water (10 mL) were taken in single neck round bottom flask and stirrer the reaction mixture at room temperature for the prescribed time, and then washed with water and finally dried in room temperature. A dark pink colored solid is obtained (80-98 %) yield. A purity check of this material by TLC in methanol : n-Hexane (25:75) show spots of meso substituted dipyrromethane purification of the crude products was affected by column chromatography using silica gel with either pure methanol : n-Hexane (25: 75) as the eluent. As the meso substituted dipyrromethanes undergo slow polymerization upon standing at room temperature.

5-Phenyldipyrromethane (3a). mp 100-101 ^{0}C, lit.:100-101 ^{0}C; yield 98%; IR (KBr) 3449, 2951, 1630, 1510, 1410, 1293, 1225, 1048, 760, 703, 607 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$); δ 5.49(s, 1H, *mesoH*), 5.92 (br s 2H, 2C3-H), 6.14 (dd, *J* 2.8, 5.9, 2H, 2C4-H), 6.68 (dd, *J* 2.6, 4.2, 2H, 2C5-H), 7.22-7.35 (m, 5H, Ar-H), 7.88 (br s,2H, 2N-H); ^{13}C NMR (100MHz, $CDCl_3$): δ 44.10, 107.45, 108.75, 117.12, 127.03, 127.03, 128.51, 128.68, 132.36, 142.23; MS (70 eV) m/z (%): 222 (M^+, 100).

5-(4-Methylphenyl)dipyrromethane (3b). mp 110-111 ^{0}C, lit.:110-111 ^{0}C; yield 90%; IR (KBr) 3417, 2356, 1635, 1508, 1420, 1254, 1089, 1025, 964, 909, 790 ,742, 509cm-1; ^{1}H NMR (400MHz, $CDCl_3$): δ 2.37 (s, 3H, CH_3), 5.44 (s, 1H, *mesoH*), 5.91 (br s, 2H, 2C3-H), 6.13 (dd, *J* 2.8, 5.9, 2H, 2C4-H) 6.66(dd, *J*2.6, 4.2, 2H, 2C5-H), 7.10-7.15 (m, 4H, Ar-H), 7.85 (br s, 2H, 2N-H); ^{13}C NMR (100MHz, $CDCl_3$): δ 21.18, 43.72, 107.32, 108.74, 116.99, 128.42, 129.38, 132.57, 136.42, 139.25; MS (70 eV) m/z (%): 236 (M^+, 100).

5-(4-Methoxyphenyl)dipyrromethane (3c). mp 98-99 ^{0}C, lit.:99 ^{0}C; yield 92 %; IR (KBr) 3405, 2964, 2936, 1616, 1507, 1457, 1299, 1245, 1175, 1103, 1027, 965, 838, 774, 720, 554 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$); δ 3.82 (s, 3H, OCH_3), 5.42 (s, 1H, *mesoH*), 5.90-5.92 (m, 2H, 2C3-H), 6.14 (dd, *J* 2.8, 6.0, 2H, 2C4-H), 6.65-6.67 (m, 2H, 2C5-H), 6.85 (d, *J* 8.6, 2H, Ar-H),7.14 (d, *J* 8.6, 2H, Ar-H), 7.82 (br s, 2H, 2N-H); ^{13}C NMR (100MHz): δ 43.21, 55.15, 107.27, 108.67, 114.03, 117.02, 129.44, 132.76, 134.29, 158.61; MS (70 eV) m/z (%): 252 (M^+ 100)

5-(2-Methoxyphenyl)dipyrromethane (3d). mp 114-115 ^{0}C, lit.: 115 ^{0}C; yield 90% ; IR (KBr) 3425, 1636, 1485, 1242, 1090, 1023, 966, 715, 555 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$); δ 3.83 (s, 3H, OCH_3), 5.82 (s, 1H, *mesoH*), 5.91 (br s, 2H, 2C3-H), 6.15 (d, *J* 2.5, 2H, 2C4-H), 6.63 (d, *J* 1.4, Ar-H), 7.28 (t, *J* 7.8, 1H, Ar-H), 7.97 (br s, 2H, 2N-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.68, 55.74, 107.10, 108.70 ,111.24, 116.67, 121.04, 128.07, 129.60, 131.14, 132.47, 156.73; MS (70 eV) m/z (%): 252 (M^+ 100).

5-(2-Hydroxyphenyl)dipyrromethane (3e). mp 90 ^{0}C; yield 93 % ; IR (KBr) 3418, 2072, 1635, 1493, 1451, 1330, 1255, 1085, 1023, 909, 790, 741, 529 cm-1; ^{1}H NMR (400MHz $CDCl_3$): δ 5.17 (br s, 1H, OH), 5.53 (s, 1H, *mesoH*), 6.01 (br s, 2H, 2C3-H), 6.16 (dd, *J*2.8, 5.9, 2H, 2C4-H), 6.70 (br s, 2H, 2C3-H), 6.16 (dd, *J* 2.8, 5.9, 2H, 2C3-H), 6.70 (dd, *J* 2.6, 4.1, 2H, 2C5-H), 6.87-6.95 (m, 2H, Ar-H), 7.08-7.10 (m, 1H, Ar-H), 7.18-7.22 (m, 1H, Ar-H), 8.14 (br s, 2H, 2N-H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 40.59, 107.22, 108.85, 117.89, 118.00, 121.63,128.52, 128.81, 130.19, 130.78, 153.87; MS (70 eV) m/z (%): 238 (M^+ 100); Anal.Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.48; H, 6.03; N, 11.58.

5-(4-Nitrophenyl)dipyrromethane (3f). mp 159-160 ^{0}C; lit.: 159-160 ^{0}C;yield 97 %; IR (KBr) 3394, 3359, 3101, 1595, 1512, 1348, 1114,1027, 808, 735, 660, 568 cm-1; ^{1}H NMR (400 MHz $CDCl_3$): δ 5.59 (s, 1H, *mesoH*), 5.88 (br s, 2H, 2C3-H), 6.18 (dd, *J* 2.8, 6.0, 2H, 2C4-H), 6.75 (dd, *J* 2.6, 4.2, 2H, 2C5-H), 7.39 (d, *J* 8.6, 2H, Ar-H), 7.98 (br s, 2H, 2N-H), 8.18 (d, *J* 8.8, 2H Ar-H); ^{13}C NMR (100 MHz $CDCl_3$); δ 43.87, 107.92, 108.95, 117.94, 123.80, 129.25, 130.76, 147.02, 149.66; MS (70 eV) m/z (%): 267 (M+100).

5-(2-Nitrophenyl)dipyrromethane(3g) mp 160 ^{0}C; yield 97%; IR (KBr) 3415, 3101, 1580, 1512, 1347,1117, 1093, 1030 cm^{-1}; ^{13}C NMR (100 MHz $CDCl_3$): δ 38.89, 130.77, 107.38, 108.56, 117.65, 148.78, 124.49, 130.95, 137.24, 132.94, 127.73; MS (70 eV) m/z (%):267 (M^+ 100).

5-(4-N,N-Dimethylphenyl)dipyrromethane (3h). mp 124 ^{0}C, lit.: 124 ^{0}C yield 97 %; IR (KBr) 3420, 2960, 2936, 1600, 1507, 1450, 1299, 1245, 1175, 1027, 765, 720, 554 cm^{-1}; ^{13}C NMR (100MHz, $CDCl_3$): δ 42.94, 132.71, 106.67, 108.00, 116.69 133.40 112.63, 128.91, 149.40, 40.60; MS (70 eV) m/z (%): 265 (M^+100).

5-(4-Cynophenyl)dipyrromethane (3i). mp 160-161 ^{0}C, lit.: 161 ^{0}C; yield 93%; IR (KBr) 3505, 2954, 2220, 1590, 1505, 1348, 1114, 808' 762, 660, 586 cm^{-1}; ^{13}C NMR (400 MHz, $CDCl_3$): δ 43.88, 130.76, 107.81, 108.43, 117.86, 147.71, 129.08, 132.12, 107.54, 118.72 MS (70 eV) m/z (%): 247 (M^+ 100).

5-(4-Chlorophenyl)dipyrromethane (3j). mp 112-113 ^{0}C, lit.: 112 ^{0}C; yield 96%; IR (KBr) 3382, 2958, 2923, 2861, 1641, 1485, 1405, 1255, 1087, 1022, 767, 720, 550, 508 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42, (s, 1H, *mesoH*), 5.90 (br s, 2H, 2C3-H), 6.17 (dd, *J* 2.8, 5.8, 2H, 2C4-H), 6.66 (dd, *J* 2.6,4.2 2H, 2C5-H), 7.15 (d, *J* 8.4, 2H, Ar-H), 7.31 (d, *J* 8.4, 2H, Ar-H), 7.80 (br s, 2H, 2N-H); ^{13}C NMR (100 MHz $CDCl_3$): δ 43.35, 107.61, 108.75, 117.42, 128.70, 129.74, 131.88, 132.81, 140.69; MS (70 EV) m/z (%): 256 (M^+ 100).

5-(4-Trifluoromethylphenyl)dipyrromethane (3k). yield 40%; IR (KBr) 3448, 3401, 2980, 1618, 1416, 1326, 1164, 1124, 1067, 1019, 775, 722 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (s, 1H, *meso*H), 5.91 (br s, 2H, 2C3-H), 7.35 (d, *J* 8.3, 2H, Ar-H),7.63 (d, *J* 8.1, 2H, Ar-H), 7.82 (br s, 2H, 2N-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.78, 107.84, 108.82, 117.66, 124.16 (q, $^1J_{C\text{-}F}$ 270.3), 125.54 (q, $^3J_{C\text{-}F}$ 3.7),128.75,129.29 (q, $^2J_{C\text{-}F}$ 32.2), 131.50, 146.28. Anal.Calcd for $C_{16}H_{13}F_3N_2$: C,66.20; H,4.51; N,9.65. Found: C,66.07; H, 4.70; N, 9.59.

5-(4-Fluorophenyl)dipyrromethane (3l). mp 80-81 ^{0}C, lit.: 81 ^{0}C; yield 92%; IR (KBr) 3410, 2928, 1610, 1498, 1451, 1285, 1175, 1103, 960, 764, 554cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.45 (s, 1H, *meso*H), 5.89 (br s, 2H, 2C5-H), 7.00-7.05 (m, 2H, Ar-H),7.16-7.20 (m, 2H, Ar-H), 7.81 (br s, 2H, 2N-H); ^{13}C NMR (100 MHz $CDCl_3$): δ 43.28, 107.55, 108.79, 115.42 (d, $^2J_{C\text{-}F}$ 21.3),117.34, 129.92 (d, $^3J_{C\text{-}F}$ 7.9), 132.24, 137.96 (d, $^4J_{C\text{-}F}$ 3.2), 161.85 (d, $^1J_{C\text{-}F}$ 244.5).

5-(4-Bromophenyl)dipyrromethane (3m). mp 122-123 ^{0}C, lit.: 125-125.5 ^{0}C; yield 95%; IR (KBr) 3374, 3098, 2957, 2920, 2861, 1707, 1481, 1400, 1083, 1021, 765, 720, 643, 544, 503cm^{-1}; ^{1}H NMR (400 MHz $CDCl_3$): δ 5.41 (s, 1H, *meso*H), 5.90 (br s, 2H, 2C3-H), 6.16 (dd, *J* 2.8, 5.9, 2H, 2C4-H), 6.66 (dd, *J* 2.6, 4.2, 2C5-H), 7.10 (d, *J* 8.4, 2H, Ar-H), 7.46 (d, *J* 8.4, 2H, Ar-H), 7.80 (br s, 2H, 2N-H); ^{13}H NMR (100MHz, $CDCl_3$): δ 43.50, 107.65, 108.83, 117.44, 120.95, 130.17, 131.71, 131.77, 141.27. MS (70eV) m/z (%): 301 (M^+ 100).

RESULTS AND DISCUSSION

Meso substituted dipyrromethane were carried out simply by mixing pyrrole with an aldehyde and water in the presence of a catalytic amount (5 %) of $SnCl_2.2H_2O$ under stirring at room temperature reaction conditions. The mixture was ground together in a round bottom flask and stirring at room temperature for several minutes, and then purified by column chromatography, Meso substituted dipyrromethane derivatives were obtained in excellent yield. A rate enhancement with high yield was observed when higher molar ratios of $SnCl_2.2H_2O$ were used. However, no product formation was observed in absence of $SnCl_2.2H_2O$

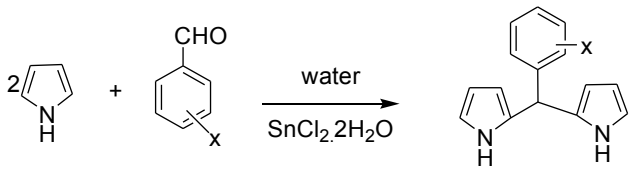
Table 1. catalytic evolution for synthesis of **3a** under stirring at room temperature reaction conditions

Entry	$SnCl_2.2H_2O$ (mol %)	Time (min.)	Yield[a] %)
1	00	60	00
2	01	40	20
3	03	20	85
4	05	10	98
5	10	10	98

Isolated yield after column chromatography.

Meso substituted dipyrromethane are formed in almost quantitative yields when pyrrole was treated with various aldehydes in the presence of a catalytic amount (5 %) of $SnCl_2.2H_2O$ in water. The electrophilic substitution reaction of pyrrole with aldehyde proceeded smoothly at room temperature. The results summarized in (table 2), clearly indicate the scope and generality of the reaction as the reactions of aromatic aldehydes (entries **3a-3n**). A variety of substituted aromatic aldehydes with pyrrole in the presence of $SnCl_2.2H_2O$ (5%) in water gave the corresponding meso substituted dipyrromethanes in excellent yields. It is reported that aromatic aldehydes with strong electron withdrawing substituent on the ring and aromatic aldehyde require longer reaction time giving low to moderate yields of the corresponding meso substituted dipyrromethane.

In this context the present protocol is note worthy because even nitro substituted aromatic aldehydes underwent smooth reactions with pyrrole giving excellent yield of products under stirring and neutral conditions in a very short time (< 10 min). Furthermore, the reaction of pyrrole with α - β unsaturated aldehyde in the presence of $SnCl_2.2H_2O$ (5 %) furnished excellent yield of the corresponding meso substituted dipyrromethane in < 10 min.



1 **2** **3a-n**

X= (a) H; (b) 4-Me; (c) 4-OMe;
(d) 2-OMe; (e) 2-OH; (f) 4-NO_2; (g) 2-NO_2;
(h) 4-NMe_2; (i) 4-CN; (j) 4-Cl;
(k) 4-CF_3; (l) 4-F; (m) 4-Br;
(n) Cinnamaldehyde,

Scheme 1

We now, characterized freshly prepared samples by low/high resolution mass spectrometry and NMR, IR. Confirmed that the desired products were obtained and indicated no discernable impurities. For all the products except **3g**, the base peak in the mass spectra arises from the molecular ion (electron impact source used) with 3g. There is still a significant molecular ion peak (33%) but due to the ortho-nitro substituent, the base peak originates from the ion after loss of water and NO

CONCLUSION

In recent years, $SnCl_2.2H_2O$ has received considerable attention as an inexpensive and easily available catalyst for effecting various organic transformations. Attractive synthetic method has been developed for the preparation of meso substituted dipyrromethane by the reaction of aromatic aldehyde and pyrrole in the presence of $SnCl_2.2H_2O$ and water. The reaction procedure is simple and short reaction time, cleaner reaction, and easy workup makes this protocol practical and economically attractive.

Table 2. $SnCl_2.2H_2O$ catalyzed synthesis of meso substituted dipyrromethane

Compound	Substitution	Yield[a,b] (%)	Melting Point ^0C
3a	H	98 %	100 ^0C
3b	4-Me	90 %	110 ^0C
3c	4-OMe	92 %	98 ^0C
3d	2- OMe	90 %	114 ^0C
3e	2-OH	93 %	90 ^0C
3f	4-NO_2	97 %	160 ^0C
3g	2-NO_2	97 %	160 ^0C
3h	4-NMe_2	97 %	124 ^0C
3i	4-CN	93 %	161 ^0C
3j	4-Cl	96%	112 ^0C
3k	4-CF_3	40 %	Liquid
3l	4-F	92 %	80 ^0C
3m	4-Br	95 %	122 ^0C
3n	Cinnamaldehyde	94 %	120^0C

[a]Yield of isolated pure products. [b]Products were characterized by IR, ^1H NMR, ^{13}C NMR, Mass elemental analysis and comparison with authentic sample[27,28]

ACKNOWLEDGEMENTS

The authors thanks to Maulana Azad college, Aurangabad

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