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Efficient Synthesis of Polysubstituted Pyridine under Solvent-free Conditions without Using Any Catalysts

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Efficient Synthesis of Polysubstituted Pyridine under Solvent-free Conditions without Using Any Catalysts

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Abstract: A convenient and environmentally friendly solvent-free procedure has been developed for the synthesis of polysubsituted pyridine derivatives. Compared with the classical reaction condition, this new synthetic method has the advantage of excellent yields, easy setup, and mild reaction conditions.

Keywords: 2,3-Dihydroinden-1-one, cyclopentanone, pyridine, solvent-free condition

In recent years, solvent-free organic reactions[1] have generated great interest, because of their many advantages such as high efficiency and selectivity, easy separation and purification, mild reaction conditions, reduction in waste produced, and benefit to industry as well as environment. Many articles about solvent-free reactions have been reported, such as Grignard reaction,[2] Reformatsky reaction,[3] aldol condensations,[4] Dieckmann condensations,[5] phenol coupling reaction,[6] reduction reaction,[7] and another reactions.[8]

The pyridine ring system is found in a large number of naturally occurring alkaloids and synthetic products of biological interest.[9] Therefore, new and improved synthetic studies are important in the field of drug design. Many

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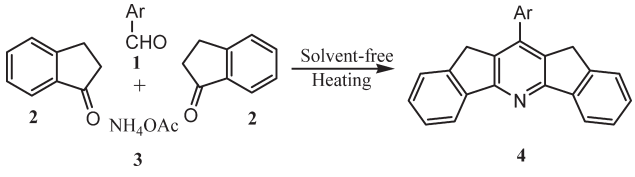
articles[10] have been reported on design of new pyridine derivatives for use in medicine. In continuation of our ongoing endeavor for solvent-free conditions for the synthesis of organic compounds,[11] herein we report a practical and simple method to prepare polysubsitutedpyridine derivatives by heating starting material under dry conditions (Scheme 1).

The mixture of aromatic aldehyde, 2,3-dihydroinden-1-one, and NH_4OAc blended uniformly was put into a reaction flask at 70 °C for about 10 min, and the reaction was completed with high yields. The results of reaction are listed in Table 1. As shown in Table 1, the reaction time was quite short, and the yields of products were very high (>90%). Furthermore, were catalysts not needed and a series of aldehydes bearing either electron-withdrawing or electron-donating groups could perform well in this reaction. Recently, Tu et al.[12a] have reported the use of microwave irradiation for synthesis of similar compounds, but it has limitations in that it can be only carried out in the laboratory and is difficult to apply in industrial processes until now.

To examine the efficiency and the applicability of this method, we chose cyclopentanone, cyclohexanone, and 3,4-dihydronaphthalen-1(2*H*)-one to react with different aldehydes and NH_4OAc (Scheme 2). However, we found the reaction did not carry out as successfully as 2,3-dihydroinden-1-one did. The cyclohexanone and 3,4-dihydronaphthalen-1(2*H*)-one did not react with aldehydes and NH_4OAc at all under the same reaction conditions, and the cyclopentanone could react with aromatic aldehyde and NH_4OAc to give compound **6**, but the yields were very low (<60%) and the reaction needed a longer time. Only four compounds were gained (Table 2). At the same time, to further investigate this reaction, the aliphatic aldehydes, such as formaldehyde and acetaldehyde, were chosen to react with cyclopentanone and NH_4OAc, but no products were obtained. Cyclohexanone, 3,4-dihydronaphthalen-1(2*H*)-one, and aliphatic aldehydes did not fit this reaction.

In conclusion, we have developed a new process for the synthesis of 1-aryldiindeno[1,2-*b*:2′,1′-*e*]pyridine derivatives **4** via the reaction of different aromatic aldehydes, 2,3-dihydroinden-1-one, and NH_4OAc under solvent-free conditions. At the same time, the 3,4-diarylidene-1,2,3,4,5,6-hexahydro-7-aryldicyclopenta[*b,e*]pyridine **6** was gained when cyclopentanone was chosen to react with aromatic aldehydes and NH_4OAc under same conditions. On the basis of results of the reaction, we could conclude that 2,3-dihydroinden-1-one was the best fit for this reaction. Furthermore,



Scheme 1.

Table 1. Reaction time, yields, and melting point of product **4**

Entry	Ar	Time (min)	Yield (%)	Mp (°C)
4a	4-FC_6H_4	10	92	>300 (>300)[12c]
4b	4-ClC_6H_4	10	90	>300 (>300)[12b]
4c	4-BrC_6H_4	10	93	>300 (>300)[12b]
4d	4-$CH_3C_6H_5$	10	95	>300 (>300)[12c]
4e	4-$CH_3OC_6H_4$	10	92	256–258 (251.8–252.2)[12a]
4f	2,4-$Cl_2C_6H_3$	10	94	276–278 (>300)[12c]
4g	3,4-$OCH_2OC_6H_3$	10	93	>300 (>300)[12b]
4h	3,4-$(CH_3O)_2C_6H_3$	10	90	252–254

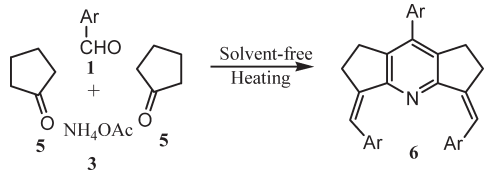
because it avoided use of a toxic organic solvent, this new protocol has the advantages of good yield, lower cost, reduced environmental impact, and convenient procedure.

EXPERIMENTAL

Melting points were determined on an XT-5 microscopic melting-point apparatus and were uncorrected. IR spectra were recorded on a FT IR-8101 spectrometer. ^{1}H NMR spectra were obtained from solution in DMSO-d_6 with Me_4Si as internal standard using a Bruker-400 spectrometer. Microanalyses were carried out using a Perkin-Elmer 2400 II analyzer.

General Procedure for the Synthesis of Polysubsitutedpyridine (4 and 6)

Aromatic aldehyde **1** (1 mmol or 3 mmol), 2,3-dihydroinden-1-one **2** (or cyclopentanone **5**) (2 mmol), and NH_4OAc **3** (4 mmol) were blended uniformly and put into a reaction flask at 70 °C. The reaction could be completed within 10 min (or 80 min). Then the reaction mixture was poured into water. The product was filtered, dried, and recrystallized from 95% ethanol.



Scheme 2.

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Table 2. Reaction time, yields, and melting point of product **6**

Entry	Ar	Time (min)	Yields (%)	Mp (°C)
6a	4-$CH_3C_6H_4$	80	53	237–238
6b	4-$CH_3OC_6H_4$	80	59	184–186
6c	4-ClC_6H_4	80	56	192–194
6d	3-ClC_6H_4	80	50	230–232

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Spectral Data

Compound 4a. IR (KBr) 3043, 2898, 1608, 1594, 1564, 1514, 1466, 1439, 1399, 1366, 1314, 1286, 1227, 1203, 1182, 1163, 1094, 1017, 948, 862, 852, 835, 792, 741, 704, 688, 652, 614, 576 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) 8.12 (d, $J = 8.0$ Hz, 2H, 5,6-H), 7.85 (d, $J = 8.0$ Hz, 2H, ArH), 7.67 (d, $J = 7.2$ Hz, 2H, 2,9-H), 7.63 (t, $J = 7.2$ Hz, 2H, 3,8-H), 7.53 (t, $J = 7.2$ Hz, 2H, 4,7-H), 7.47 (d, $J = 8.0$ Hz, 2H, ArH), 3.97 (s, 4H, 1,10-H). Anal. calcd. for $C_{25}H_{16}FN$: C, 85.94; H, 4.62; N, 4.01. Found: C, 85.89; H, 4.56; N, 4.10.

Compound 4b. IR (KBr) 3047, 2896, 1601, 1572, 1557, 1491, 1466, 1440, 1396, 1364, 1314, 1284, 1202, 1182, 1149, 1085, 1017, 852, 832, 704, 647, 613 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) 8.13 (d, $J = 7.6$ Hz, 2H, 5,6-H), 7.86 (d, $J = 8.0$ Hz, 2H, ArH), 7.66 (d, $J = 7.2$ Hz, 2H, 2,9-H), 7.64 (t, $J = 7.2$ Hz, 2H, 3,8-H), 7.52 (t, $J = 7.2$ Hz, 2H, 4,7-H), 7.46 (d, $J = 8.0$ Hz, 2H, ArH), 3.97 (s, 4H, 1,10-H). Anal. calcd. for $C_{25}H_{16}ClN$: C, 82.07; H, 4.41; N, 3.83. Found: C, 82.10; H, 4.38; N, 3.79.

Compound 4c. IR (KBr) 3045, 2894, 1595, 1570, 1556, 1502, 1489, 1466, 1440, 1397, 1364, 1314, 1202, 1282, 1181, 1149, 1094, 1067, 1011, 975, 960, 946, 850, 830, 742 703, 690, 645, 613, 574 cm^{-1};^1H NMR (400 MHz, DMSO-d_6) 8.12 (d, $J = 7.2$ Hz, 2H, 5,6-H), 7.82 (d, $J = 8.0$ Hz, 2H, ArH), 7.78 (d, $J = 7.2$ Hz, 2H, 2,9-H), 7.73 (t, $J = 7.2$ Hz, 2H, 3,8-H), 7.64 (t, $J = 7.2$ Hz, 2H, 4,7-H), 7.50 (d, $J = 8.0$ Hz, 2H, ArH), 3.96 (s, 4H, 1,10-H). Anal. calcd. for $C_{25}H_{16}BrN$: C, 73.18; H, 3.93; N, 3.41. Found: C, 73.25; H, 3.89; N, 3.35.

Compound 4d. IR (KBr) 3050, 2892, 1600, 1562, 1519, 1504, 1489, 1463, 1440, 1390, 1314, 1290, 1202, 1180, 1090, 850, 770 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) 8.17 (d, $J = 8.0$ Hz, 2H, 5,6-H), 8.12 (d, $J = 8.0$ Hz, 2H, ArH), 7.85 (d, $J = 7.2$ Hz, 2H, 2,9-H), 7.66 (t, $J = 7.2$ Hz, 2H, 3,8-H), 7.64 (t, $J = 7.2$ Hz, 2H, 4,7-H), 7.50 (d, $J = 8.0$ Hz, 2H, ArH), 3.97 (s, 4H, 1,10-H), 2.35 (s, 3H, CH_3). Anal. calcd. for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.46; H, 5.48; N, 4.10.

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Compound 4e. IR (KBr) 3051, 2893, 1612, 1561, 1517, 1464, 1440, 1288, 1025, 859, 831, 776 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) 8.11 (d, $J = 7.2$ Hz, 2H, 5,6-H), 7.76 (d, $J = 8.0$ Hz, 2H, ArH), 7.63 (d, $J = 7.2$ Hz, 2H, 2,9-H), 7.51 (t, $J = 7.2$ Hz, 2H, 3,8-H), 7.45 (t, $J = 7.2$ Hz, 2H, 4,7-H), 7.14 (d, $J = 8.0$ Hz, 2H, ArH), 3.95 (s, 4H, 1,10-H), 3.87 (s, 3H, OCH_3). Anal. calcd. for $C_{26}H_{19}NO$: C, 86.40; H, 5.30; N, 3.88. Found: C, 86.57; H, 5.26; N, 3.94.

Compound 4f. IR (KBr) 3050, 2891, 1592, 1566, 1504, 1476, 1439, 1367, 1314, 1282, 1202, 1181, 1149, 1097, 1061, 1027, 948, 862, 825, 776, 745, 704, 673, 651, 612 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) 8.13 (d, $J = 8.0$ Hz, 2H, 5,6-H), 7.97 (d, $J = 8.0$ Hz, 2H, ArH), 7.82 (d, $J = 7.2$ Hz, 2H, 2,9-H), 7.73 (d, $J = 7.2$ Hz, 2H, 3,8-H), 7.67 (d, $J = 8.0$ Hz, 2H, 4,7-H), 7.60 (d, $J = 8.0$ Hz, 1H, ArH), 4.12 (s, 4H, 1,10-H). Anal. calcd. for $C_{25}H_{15}Cl_2N$: C, 75.01; H, 3.78; N, 3.50. Found: C, 75.10; H, 3.86; N, 3.60.

Compound 4g. IR (KBr) 3053, 2896, 1601, 1563, 1488, 1443, 1397, 1367, 1332, 1314, 1285, 1237, 1202, 1181, 1150, 1124, 1092, 1037, 938, 921, 908, 860, 824, 800, 746, 719, 706, 615, 575 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) 8.11 (d, $J = 7.6$ Hz, 2H, 5,6-H), 7.78 (d, $J = 7.6$ Hz, 2H, ArH), 7.71 (d, $J = 8.0$ Hz, 2H, 2,9-H), 7.65 (d, $J = 7.2$ Hz, 2H, 3,8-H), 7.50 (t, $J = 7.2$ Hz, 2H, 4,7-H), 7.12 (s, 1H, ArH), 6.15 (d, $J = 6.4$ Hz, 2H, CH_2), 3.98 (s, 4H, 1,10-H). Anal. calcd. for $C_{26}H_{17}NO_2$: C, 83.18; H, 4.56; N, 3.73. Found: C, 83.25; H, 4.45; N, 3.68.

Compound 4h. IR (KBr) 3050, 2892, 1609, 1588, 1559, 1520, 1466, 1444, 1416, 1397, 1364, 1315, 1299, 1283, 1224, 1180, 1147, 1101, 1050, 1023, 948, 887, 823, 750, 712 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) 8.12 (d, $J = 7.6$ Hz, 2H, 5,6-H), 7.80 (d, $J = 7.6$ Hz, 2H, ArH), 7.71 (d, $J = 8.0$ Hz, 2H, 2,9-H), 7.65 (d, $J = 7.2$ Hz, 2H, 3,8-H), 7.50 (t, $J = 7.2$ Hz, 2H, 4,7-H), 7.32 (s, 1H, ArH), 6.15 (d, $J = 6.4$ Hz, 2H, CH_2), 3.97 (s, 4H, 1,10-H), 3.82 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3). Anal. calcd. for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 82.79; H, 5.49; N, 3.64.

Compound 6a. IR (KBr) 3016, 2918, 2871, 1569, 1558, 1541, 1510, 1457, 1426, 1363, 1297, 1270, 1240, 1183, 896, 807 cm^{-1}; ^1H NMR (DMSO-d_6) 7.51 (dd, $J = 4.0$ Hz, $J = 4.0$ Hz, 6H, ArH, 2 × ArCH═), 7.40 (d, $J = 8.0$ Hz, 2H, ArH), 7.33 (d, $J = 8.0$ Hz, 2H, ArH), 7.25 (d, $J = 8.0$ Hz, 4H, ArH)), 3.10-3.11 (br, 4H, 1,6-H), 2.96-2.98 (br, 4H, 2,5-H), 2.39 (s, 3H, CH_3), 2.34 (s, 6H, 2 × CH_3), Anal. calcd. for $C_{34}H_{31}N$: C, 90.02; H, 6.89; N, 3.09. Found: C, 90.16; H, 7.00; N 2.98.

Compound 6b. IR (KBr) 3035, 2914, 2835, 1605, 1561, 1532, 1510, 1455, 1440, 1417, 1359, 1291, 1251, 1203, 1175, 1229, 1034, 950, 930, 893, 872,

857, 821, 806, 757, 682, 645, 589 cm^{-1}; ^1H NMR (DMSO-d_6) 7.55 (d, $J = 8.8$ Hz, 4H, ArH), 7.46 (t, $J = 8.4$ Hz, 4H, ArH), 7.06 (d, $J = 8.4$ Hz, 2H, 2 × ArCH═), 7.01 (d, $J = 8.4$ Hz, 4H, ArH)), 3.82 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 3.07–3.08 (br, 4H, 1,6-H), 2.96–2.98 (br, 4H, 2,5-H), Anal. calcd. for $C_{34}H_{31}NO_3$: C, 81.41; H, 6.23; N, 2.79. Found: C, 81.62; H, 6.18; N, 2.86.

Compound 6c. IR (KBr) 3028, 2933, 2843, 1595, 1490, 1460, 1405, 1361, 1296, 1262, 1223, 1134, 1091, 1013, 825, 734 cm^{-1}; ^1H NMR (DMSO-d_6) 7.66 (dd, $J = 6.4$ Hz, $J = 6.4$ Hz, 4H, ArH), 7.59 (t, $J = 5.6$ Hz, 4H, ArH), 7.37 (dd, $J = 2.0$ Hz, $J = 2.0$ Hz, 2H, 2 × ArCH═), 7.27 (t, $J = 4.2$ Hz, 4H, ArH)) 3.07–3.08 (br, 4H, 1,6-H), 2.96–2.98 (br, 4H, 2,5-H), Anal. calcd. for $C_{31}H_{22}C_{l3}N$: C, 72.32; H, 4.31; N, 2.72. Found: C, 72.59; H, 4.27; N, 2.80.

Compound 6d. IR (KBr) 3045, 2921, 2851, 1589, 1561, 1542, 1479, 1458, 1419, 1360, 1299, 1284, 1264, 1238, 1200, 1137, 1098, 1080, 996, 911, 860, 787, 773, 751, 677 cm^{-1}; ^1H NMR (DMSO-d_6) 7.63 (dd, $J = 4.8$ Hz, $J = 4.8$ Hz, 4H, ArH), 7.59 (d $J = 8.4$ Hz, 3H, ArH), 7.55 (m, 2H, 2 × ArCH═), 7.46–7.51 (m, 5H, ArH,)), 3.15–3.18 (br, 4H, 1,6-H), 3.00–3.02 (br, 4H, 2,5-H), Anal. calcd. for $C_{31}H_{22}C_{l3}N$: C, 72.32; H, 4.31; N, 2.72. Found: C, 72.61; H, 4.23; N, 2.84.

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