Synthesis of 2,2′-bis(1-(2-aryl)-1H-pyrazol-4-yl)-3,3,3′,3′-tetramethyl-3H,3′H-5,5′-biindoles and 2,7-bis(1-(3-aryl)-1H-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-g]indoles

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Abstract
2,2′-(Biphenyl-4,4′-diyl)bis(hydrazinium) chloride and 2,2′-(naphthalene-1,5-diyl)bis(hydrazinium) chloride were converted via Fischer syntheses with 3-methylbutan-2-one into bisindolenines, 2,2′,3,3,3′,3′-hexamethyl-3H,3′H-5,5′-biindole 10 and 2,3,3,7,8,8-hexamethyl-3H,8H-indolo[7,6-g]indole 14, respectively. Exposure of the bisindolenines to the Vilsmeier reagent produced tetraformyl compounds 11 and 15, which reacted with hydrazine and arylhydrazines to give the corresponding pyrazoles 12 and 16 in excellent yields.

Keywords: Arylhydrazines, bisindolenine, Fischer reaction, hydrazine, pyrazole, Vilsmeier reagent

Introduction

We recently described the reaction of 2,3,3-trimethylindolenines (3H-indoles) 1 with the Vilsmeier reagent formed from dimethylformamide and phosphorus oxychloride to produce aminomethylene malondialdehydes 2 (Scheme 1).1,2 Additionally we showed that the pyridoindolenines 2,3,3-trimethyl-3H-pyrrolo[2,3-f]quinoline and 2,3,3-trimethyl-3H-pyrrolo[3,2-h]quinoline 4 behave similarly (Scheme 2).3

Scheme 1
The malondialdehydes 2,5 reacted with hydrazine or arylhydrazines to produce substituted pyrazoles 3,6,1,3,4 We have now been able to show that the principles embodied in these transformations can be incorporated into bisindolenine systems, and thus have prepared several more complex pyrazoles.

Scheme 2

For the mechanism of formation of the aminomethylene malondialdehydes, we suggested that a small equilibrium concentration of an enamine tautomer 7 is successively C-substituted and thus, before hydrolysis during work-up, species 8 is present (Scheme 3). We propose that a comparable mechanism operates in the work described herein.

Scheme 3

Results and Discussion

Diazotisation of benzidine and naphthalene-1,5-diamine, then reduction of the diazonium salts with tin(II) chloride, produced the corresponding bis hydrazinium chlorides 9 and 13.5 Reaction of 2,2′-(biphenyl-4,4′-diyl)bis(hydrazinium)chloride 9 with isopropyl methyl ketone in a Fischer reaction6 produced the bisindolenine 2,2′,3,3′,3′-hexamethyl-3H,3′H-5,5′-biindole 10 in good yield (Scheme 4).
Similarly, 2,2′-(naphthalene-1,5-diyl)bis(hydrazinium) chloride 13 reacted with isopropyl methyl ketone in hot acetic acid to give 2,3,3,7,8,8-hexamethyl-3H,8H-indolo[7,6-g]indole 14 (Scheme 5), which was used previously in the synthesis of photochromic compounds.8

The structure of the bisindolenine 10 was evident from its molecular formula, the twelve-hydrogen singlet for the geminal methyl groups, at δ 1.33 ppm, and a singlet signal for the imine methyl groups resonating at δ 2.30 ppm.

Each of the bisindolenines 10, 14 was now reacted with the Vilsmeier reagent in yields of 90% and 85%, respectively, and tetraformyl compounds 11, 15 were obtained (Schemes 4 and 5). The structures of the aminomethylene malodialdehydes rests on the observation of two two-hydrogen singlets at δ 9.79 and δ 9.83 for 11 and δ 9.83 and δ 9.87 for 15 corresponding to aldehyde protons. Absorptions at 3136 cm⁻¹ and 3130 cm⁻¹ for 11 and 15, respectively, were evidence for the presence of N-H bonds, further confirmed by ¹H NMR two-hydrogen signals for the N-hydrogens appearing at δ 13.64 (11) and δ 14.35 (15), respectively. As in our previous work,1,3 the aminomethylene malodialdehydes reacted with hydrazine and various arylhydrazines to give pyrazoles, with migration of the double bond to reform the imine unit (Schemes 4 and 5). For pyrazoles 12a-f, the newly formed five-membered heterocyclic ring protons resonated in the range δ 8.35-9.37 and for the pyrazoles 16a-e in the range δ 8.50-9.38.
Scheme 5

Conclusions

We have been able to show that the principles embodied in transformations of simple indolenines via Vilsmeier formylations can be incorporated into more complex bisindolenine systems and thus have prepared several pyrazoles in excellent yields.

Experimental Section

General. Melting points were recorded on a Philip Harris C4954718 apparatus. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance AQS 300 MHz spectrometer, at 300 MHz and 75 MHz respectively. Chemical shifts $\delta$ are in parts per million (ppm) measured in CDCl$_3$ and DMSO-$d_6$ as solvents and relative to TMS as the internal standard. Infrared spectra were recorded on a Themnicqet-Nexus 670 FT-IR instrument. High resolution mass spectra were recorded on an Agilent Technology (HP), MS Model: 5973 Network Mass, selective Detector Ion source: Electron Impact (EI) 70 eV, ion source temperature: 230 °C Analyzer: quadrupole, and relative abundances of fragments are quoted in parentheses after the $m/z$ values.
2,2',3,3,3',3'-Hexamethyl-3H,3'H-5,5'-biindole (10). A mixture of 2,2'-(biphenyl-4,4'-diyl)bis(hydrazinium)chloride (8.29 g, 28.9 mmol) and isopropyl methyl ketone (6.52 mL, 60.60 mmol) was heated at reflux in acetic acid (50 mL) for 12 h and then cooled, diluted with water (50 mL), and neutralized with NaOH 2M, then extracted with ethyl acetate (4 × 100 mL). The organic layer was dried over Na₂SO₄. The solvent was evaporated and the resulting viscous oil crystallized from EtOH to give the 2,2',3,3,3',3'-hexamethyl-3H,3'H-5,5'-biindole (10). (6.38 g, Yield 70%); mp 104-106 °C; FT-IR (KBr) ν max/cm–1: 2962, 2927, 1685, 1574, 1458, 1409; 1H NMR (CDCl₃): δ 1.33 (s, 12H), 2.30 (s, 6H), 7.49 (s, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H); 13C NMR (CDCl₃): δ 15.45, 23.18, 53.75, 119.95, 120.30, 126.81, 138.70, 146.32, 152.99, 188.21; MS (EI, 70 ev): m/z (%) 316 (M +, 100), 301 (32), 285 (10), 84 (82), 47 (20). Found: [M]+ 316.1939, C₂₂H₂₄N₂ requires [M]+ 316.1939.

2,2'-((3,3,3',3',3',3')-Tetramethyl-5,5'-biindoline-2,2'-diylidene)dimalonaldehyde (11). To N,N-dimethylformamide (2 mL) cooled in an ice bath was added dropwise phosphorus oxychloride (1.6 mL, 17.4 mmol) with stirring at below 5 °C. After this addition, a solution of 10 (2.9 mmol, 0.918 g) in DMF (2 mL) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 75 °C for 12 h. The resulting solution was added to ice-cooled water and made alkaline with NaOH (aq.) solution. The resulting precipitate was collected by filtration after 24 h, dried in air, recrystallized from ethanol, to give (1.12 g, Yield 90%); mp 213-215 °C; FT-IR (KBr) ν max/cm–1: 3136, 2967, 2926, 2765, 1677, 1601, 1520, 1473, 1202; 1H NMR (CDCl₃): δ 1.82 (s, 12H), 7.50 (s, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 9.79 (s, 2H), 9.83 (s, 2H), 13.64 (bs, 2H); 13C NMR (CDCl₃): δ 23.46, 51.49, 109.65, 112.96, 120.96, 127.40, 138.50, 138.95, 141.65, 179.37, 187.81, 192.59; MS (EI, 70 ev): m/z (%) 428 (M+, 15), 400 (13), 361 (52), 291 (38), 248 (36), 191 (30), 149 (38), 57 (100), 41 (51). Found: [M]+ 428.1737, C₂₆H₂₄N₂O₄ requires [M]+ 428.1736.

General procedure for synthesis of (12a-f)
A mixture of the tetraformyl compound 11 (0.117 mmol) and the hydrazine or aryl hydrazine (0.23 mmol) in absolute ethanol (5 mL) was heated with stirring at reflux for 6-8 h. After cooling and concentrating the solution, the resulting crystals were collected by filtration and recrystallized from EtOH to give the corresponding pyrazoles.

3,3',3',3'-Tetramethyl-2,2'-di(1H-pyrazol-4-yl)-3H,3'H-5,5'-biindole (12a). (0.044 g, Yield 90%); mp 218-220 °C; FT-IR (KBr) ν max/cm–1: 3168, 2964, 1612, 1567, 1535, 1458; 1H NMR (DMSO-d₆): δ 1.50 (s, 12H), 7.53 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.81 (s, 2H), 8.35 (s, 2H), 12.75 (bs, 2H); 13C NMR (DMSO-d₆): δ 24.71, 53.24, 115.28, 119.81, 120.41, 126.68, 127.70, 137.73, 147.78, 153.39, 179.45; MS (EI, 70 ev): m/z (%) 420 (M+, 63), 405 (24), 370 (17), 354 (13), 302 (100), 287 (47), 44 (18). Found: [M]+ 420.2062, C₂₆H₂₄N₆ requires [M]+ 420.2062.

2,2'-Bis[1-(2-chlorophenyl)-1H-pyrazol-4-yl]-3,3',3'-tetramethyl-3H,3'H-5,5'-biindole (12b). (0.067 g, Yield 89%); mp 155-157 °C; FT-IR (KBr) ν max/cm–1: 2967, 2927, 1612, 1576, 1527, 1492, 1459; 1H NMR (DMSO-d₆): δ 1.59 (s, 12H), 7.56-7.76 (m, 12H), 7.91 (s, 2H), 8.51 (s,
2H), 9.04 (s, 2H); 13C NMR (DMSO-d6): δ 24.58, 53.44, 116.48, 119.84, 120.75, 126.99, 128.25, 128.77, 128.83, 128.87, 131.01, 133.82, 137.71, 138.26, 141.32, 147.60, 151.97, 178.78; MS (EI, 70 ev): m/z (%) 644 (1), 642 (6), 640 (M+,10), 480 (28), 467 (29), 440 (26), 412 (100), 397 (32), 111 (10). Found: [M]+ 640.1909, C38H30Cl2N6 requires [M]+ 640.1909.

2,2′-Bis[1-(3-chlorophenyl)-1H-pyrazol-4-yl]-3,3′,3′-tetramethyl-3H,3′H-5,5′-biindole (12c). (0.064 g, Yield 85%); mp 153-155 °C; FT-IR (KBr) νmax/cm–1: 2967, 2928, 1620, 1593, 1529, 1487, 1461, 1408; 1H NMR (DMSO-d6): δ 1.61 (s, 12H), 7.43 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.8 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.91 (s, 2H), 8.03 (d, J = 7.8 Hz, 2H), 8.2 (s, 2H), 8.48 (s, 2H), 9.33 (s, 2H); 13C NMR (DMSO-d6): δ 24.36, 53.46, 117.95, 118.31, 119.02, 120.23, 120.59, 126.88, 127.14, 128.76, 131.74, 134.56, 138.18, 140.75, 142, 148.05, 153.02, 178.52; MS (EI, 70 ev): m/z (%) 644 (1), 642 (6), 640 (M+,10), 480 (35), 467 (30), 440 (25), 412 (100), 397 (30), 111 (18). Found: [M]+ 640.1908, C38H30Cl2N6 requires [M]+ 640.1909.

2,2′-Bis[1-(4-chlorophenyl)-1H-pyrazol-4-yl]-3,3′,3′-tetramethyl-3H,3′H-5,5′-biindole (12d). (0.071 g, Yield 95%); mp 222-225 °C; FT-IR (KBr) νmax/cm–1: 2968, 2927, 1610, 1577, 1529, 1499, 1463; 1H NMR (DMSO-d6): δ 1.14 (s, 12H), 7.54-7.61 (m, 8H), 7.84 (s, 2H), 8.01 (d, J = 8.7 Hz, 4H), 8.40 (s, 2H), 9.21 (s, 2H); 13C NMR (DMSO-d6): δ 24.38, 53.44, 118.27, 120.21, 120.57, 121.05, 126.85, 128.57, 129.94, 131.57, 138.13, 138.47, 141.79, 148.04, 153.13, 178.56; MS (EI, 70 ev): m/z (%) 644 (1), 642 (6), 640 (M+,10), 480 (28), 467 (43), 440 (27), 412 (100), 397 (44), 111 (13). Found: [M]+ 640.1909, C38H30Cl2N6 requires [M]+ 640.1909.

2,2′-Bis[1-(4-methoxyphenyl)-1H-pyrazol-4-yl]-3,3′,3′-tetramethyl-3H,3′H-5,5′-biindole (12e). (0.067 g, Yield 90%); mp 182-186 °C; FT-IR (KBr) νmax/cm–1: 2963, 2928, 1610, 1560, 1514, 1459, 1250, 1172, 1034; 1H NMR (DMSO-d6): δ 1.64 (s, 12H), 3.82 (s, 6H), 7.11 (d, J = 8.4 Hz, 4H), 7.63 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 7.8 Hz, 2H), 7.88 (s, 2H), 8.01 (d, J = 8.4 Hz, 4H), 8.39 (s, 2H), 9.12 (s, 2H); 13C NMR (DMSO-d6): δ 24.63, 53.41, 55.98, 115.11, 116.54, 119.39, 120.86, 121.21, 127.09, 129.17, 133.05, 138.31, 141.51, 147.35, 150.85, 158.84, 178.99; MS (EI, 70 ev): m/z (%) 632 (M+, 2), 476 (50), 463 (58), 436 (31), 408 (100), 393 (87), 204 (33), 77 (22), 57 (23), 43 (23). Found: [M]+ 632.2898, C40H36N6O2 requires [M]+ 632.2899.

2,2′-Bis[1-(4-bromophenyl)-1H-pyrazol-4-yl]-3,3′,3′-tetramethyl-3H,3′H-5,5′-biindole (12f). (0.074 g, Yield 87%); mp 230-233 °C; FT-IR (KBr) νmax/cm–1: 2969, 2927, 1611, 1577, 1529, 1495, 1463; 1H NMR (DMSO-d6): δ 1.63 (s, 12H), 7.64 (d, J = 7.8 Hz, 2H), 7.72 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 8.1 Hz, 4H), 7.96 (s, 2H), 8.02 (d, J = 8.1 Hz, 4H), 8.57 (s, 2H), 9.37 (s, 2H); 13C NMR (DMSO-d6): δ 24.47, 53.46, 117.48, 119.73, 120.09, 120.81, 121.48, 127.06, 129.27, 132.90, 138.35, 138.72, 142.135, 147.60, 151.44, 178.71; MS (EI, 70 ev): m/z (%) 732 (2), 730 (4), 728 (M+, 2), 485 (54), 417 (54), 327 (23), 171 (100), 92 (43), 65 (57), 43 (35). Found: [M]+ 728.0897, [M+2]+ 730.0878, C38H30Br2N6 requires [M]+ 728.0899, [M+2]+ 730.0878.

2-(1,1,6,6-Tetramethylindolo[7,6-g]indole-2,7(1H,3H,6H,8H)-diylidenedimalonaldehyde (15). To N,N-dimethylformamide (3 mL) cooled in an ice bath was added dropwise phosphorus oxychloride (2.2 mL, 24 mmol) with stirring at below 5 °C. After this addition, a solution of 14 (1.16 g, 4 mmol) in DMF (2.5 mL) was added dropwise. The cooling bath was removed and the
reaction mixture was stirred at 75 °C for 12 h. The resulting solution was added to ice-cooled water and made alkaline with NaOH (aq.) solution. The resulting precipitate was collected by filtration after 24 h, dried in air, recrystallized from ethanol, to give 15. (1.37 g, Yield 85%); mp 215-218 °C; FT-IR (KBr) νmax/cm⁻¹: 3130, 2924, 2854, 2766, 1679, 1614, 1592, 1516, 1308; ¹H NMR (CDCl₃): δ 1.86 (s, 12H), 7.63 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 9.83 (s, 2H), 9.87 (s, 2H), 14.35 (bs, 2H); ¹³C NMR (CDCl₃): δ 22.87, 52.66, 110.20, 118.83, 120.50, 120.75, 135.48, 137.45, 179.94, 187.65, 192.73; MS (EI, 70 ev): m/z (%) 402 (M⁺, 68), 374 (43), 359 (80), 335 (32), 265 (57), 237 (46), 222 (100), 194 (39), 165 (30), 69 (36), 44 (98). Found: [M⁺] 402.1580, C₂₄H₂₂N₂O₄ requires [M⁺] 402.1579.

General procedure for synthesis of (16a-e)
A mixture of the tetraformyl compound 15 (0.2 mmol) and the hydrazine or aryl hydrazines (0.4 mmol) in absolute ethanol (10 mL) was heated with stirring at reflux for 10-12 h. After cooling and concentrating the solution, the resulting crystals were collected by filtration and recrystallized from EtOH to give the corresponding pyrazoles.

1,1,6,6-Tetramethyl-2,7-di(1H-pyrazol-4-yl)-1,6-dihydroindolo[7,6-g]indole (16a). (0.063 g, Yield 80%); mp 220-221 °C; FT-IR (KBr) νmax/cm⁻¹: 3191, 2961, 2925, 2861, 1627, 1572, 1517; ¹H NMR (DMSO-d₆): δ 1.52 (s, 12H), 7.74 (d, J = 8.1 Hz, 2H), 8.38 (d, J = 8.1 Hz, 2H), 8.50 (s, 4H), 13.38 (bs, 2H); ¹³C NMR (DMSO-d₆): δ 24.36, 54.37, 115.56, 120.02, 120.32, 127.01, 130.95, 142.56, 149.62, 179.68; MS (EI, 70 ev): m/z (%) 394 (M⁺, 100), 379 (46), 261 (32), 83 (23), 57 (42), 43 (66). Found: [M⁺] 394.1906, C₂₄H₂₂N₆ requires [M⁺] 394.1906.

2,7-Bis(1-(3-chlorophenyl)-1H-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-g]indole (16b). (0.11 g, Yield 89%); mp 234-237 °C; FT-IR (KBr) νmax/cm⁻¹: 2960, 2926, 2863, 1610, 1595, 1571, 1488, 1457; ¹H NMR (DMSO-d₆): δ 1.60 (s, 12H), 7.42 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 8.1 Hz, 2H), 7.79 (d, J = 8.1 Hz, 2H), 8.03 (d, J = 7.8 Hz, 2H), 8.20 (s, 2H), 8.44 (d, J = 8.1 Hz, 2H), 8.54 (s, 2H), 9.33 (s, 2H); ¹³C NMR (DMSO-d₆): δ 23.97, 54.58, 117.90, 118.60, 118.98, 120.23, 120.87, 127.01, 130.95, 142.56, 149.62, 179.68; MS (EI, 70 ev): m/z (%) 618 (1), 616 (4), 614 (M⁺, 7), 482 (18), 441 (22), 394 (24), 371 (100), 356 (31), 152 (35), 127 (40), 57 (47), 43 (67). Found: [M⁺] 614.1754, C₃₆H₂₈Cl₂N₆ requires [M⁺] 614.1753.

2,7-Bis(1-(4-chlorophenyl)-1H-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-g]indole (16c). (0.108 g, Yield 88%); mp 213-215 °C; FT-IR (KBr) νmax/cm⁻¹: 2971, 2930, 1612, 1567, 1495, 949; ¹H NMR (DMSO-d₆): δ 1.63 (s, 12H), 7.64 (d, J = 8.4 Hz, 4H), 7.86 (d, J = 8.1 Hz, 2H), 8.10 (d, J = 8.4 Hz, 4H), 8.54 (d, J = 8.1 Hz, 2H), 8.64 (s, 2H), 9.38 (s, 2H); ¹³C NMR (DMSO-d₆): δ 24.15, 54.57, 117.37, 120.63, 121.50, 126.06, 129.54, 129.72, 130, 131.88, 138.31, 142.27, 143.08, 179.30; MS (EI, 70 ev): m/z (%) 618 (1), 616 (4), 614 (M⁺, 7), 482 (18), 441 (22), 394 (24), 371 (100), 356 (31), 152 (35), 127 (40), 57 (47), 43 (67). Found: [M⁺] 614.1751, C₃₆H₂₈Cl₂N₆ requires [M⁺] 614.1753.

2,7-Bis(1-(4-methoxyphenyl)-1H-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-g]indole (16d). (0.115 g, Yield 95%); mp 223-225 °C; FT-IR (KBr) νmax/cm⁻¹: 2971, 2930, 1612,
1578, 1515, 1255, 1175; $^1$H NMR (DMSO-$d_6$): $\delta$ 1.64 (s, 12H), 3.82 (s, 6H), 7.12 (d, $J$ = 8.4 Hz, 4H), 7.88 (d, $J$ = 8.7 Hz, 2H), 7.95 (d, $J$ = 8.4 Hz, 4H), 8.60 (d, $J$ = 8.7 Hz, 2H), 8.65 (s, 2H), 9.33 (s, 2H); $^{13}$C NMR (DMSO-$d_6$): $\delta$ 24.26, 54.51, 55.98, 115.11, 116.16, 116.82, 120.55, 121.21, 122.24, 126.24, 129.04, 133.09, 141.52, 142.91, 158.81, 179.45; MS (EI, 70 ev): $m/z$ (%): 606 (M+, 100), 591 (30), 434 (9), 367 (16), 303 (20), 108 (16), 77 (14), 44 (16). Found: [M]$^+$ 606.2744, C$_{38}$H$_{34}$N$_6$O$_2$ requires [M]$^+$ 606.2743.

2,7-Bis(1-(4-bromophenyl)-1H-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-g]indole (16e). (0.122 g, Yield 87%); mp 229-230 °C; FT-IR (KBr) $\nu_{max}$/cm$^{-1}$: 2969, 2927, 1619, 1573, 1524, 1494; $^1$H NMR (DMSO-$d_6$): $\delta$ 1.62 (s, 12H), 7.77 (d, $J$ = 8.4 Hz, 4H), 7.85 (d, $J$ = 8.1 Hz, 2H), 8.05 (d, $J$ = 8.4 Hz, 4H), 8.51 (d, $J$ = 8.1 Hz, 2H), 8.61 (s, 2H), 9.36 (s, 2H); $^{13}$C NMR (DMSO-$d_6$): $\delta$ 24.10, 54.58, 120.06, 120.54, 121.48, 124.48, 129.16, 132.21, 132.44, 132.63, 132.90, 138.77, 142.14, 143.12, 179.12; MS (EI, 70 ev): $m/z$ (%): 706 (4), 704 (8), 702 (M+, 4), 614 (20), 524 (34), 484 (32), 458 (100), 441 (40), 229 (18), 171 (25), 65 (23), 43 (41). Found: [M]$^+$ 702.0744, [M+2]$^+$ 704.0721, C$_{36}$H$_{28}$Br$_2$N$_6$ requires [M]$^+$ 702.0742, [M+2]$^+$ 704.0722.

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References