**Thermolysis of Benzannulated Enyne–Carbodiimides. Application in the Synthesis of
Pyrido[1',2':1,2]pyrimido[4,5-*b*]indoles and Related Heteroaromatic Compounds**

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12-Phenylpyrido[1',2':1,2]pyrimido[4,5-*b*]indole (4a). The following procedure for the synthesis of **4a** is representative. To a solution of 0.187 g (0.528 mmol) of the iminophosphorane **9** in 10 mL of anhydrous *p*-xylene was introduced via cannula a solution of 0.116 g (0.529 mmol) of the isocyanate **8a** in 10 mL of anhydrous *p*-xylene under a nitrogen atmosphere at rt. After 5 h, the reaction mixture was heated under reflux for 12 h before it was allowed to cool to rt. The mixture was then concentrated to yield a solid residue. After three cycles of washing the residue with 40 mL of diethyl ether followed by centrifugation and decanting the supernatant liquid, the remaining solid was pumped to dryness in vacuo to afford **4a** (0.090 g, 0.305 mmol, 58%) as an orange solid: compound turns black without melting at 317 °C; IR (KBr) 1553, 760, 732 cm⁻¹; ¹H δ 8.03 (1 H, dm, *J* = 7.7, 0.5 Hz), 7.90 (2 H, dm, *J* = 7.7, 0.8 Hz), 7.82–7.76 (3 H, m), 7.64–7.52 (4 H, m), 6.99 (1 H, td, *J* = 7.9, 0.8 Hz), 6.89–6.82 (2 H, m); ¹³C δ 159.9, 158.7, 146.2, 139.1, 131.5, 131.1, 130.4, 130.0, 129.8, 129.4, 129.0, 127.0, 122.5, 122.0, 119.8, 119.1, 118.6, 113.0.

12-Octylpyrido[1',2':1,2]pyrimido[4,5-*b*]indole (4c). The same procedure was repeated as described for **4a** except that 0.125 g (0.353 mmol) of the iminophosphorane **9**, 0.090 g (0.353 mmol) of the isocyanate **8c** were used to afford **4c** (0.080 g, 0.242 mmol, 69%) as a bright golden yellow solid. Recrystallization from chloroform afforded yellow flakes: compound turns black and melts at 188–190 °C; IR (KBr) 1636, 741 cm⁻¹; ¹H δ 8.19 (1 H, d, *J* = 7.1 Hz), 7.95 (1 H, d, *J* = 7.6 Hz), 7.90 (1 H, d, *J* = 8.2 Hz), 7.74 (1 H, d, *J* = 9.0 Hz), 7.59 (1 H, t, *J* = 7.4 Hz), 7.47 (1 H, t, *J* = 6.6 Hz), 7.22 (1 H, t, *J* = 7.4 Hz), 6.95 (1 H, t, *J* = 6.6 Hz), 3.52 (2 H, t, *J* = 7.9 Hz), 1.81 (2 H, quintet, *J* = 7.8 Hz), 1.58 (2 H, quintet, *J* = 7.2 Hz), 1.42–1.2 (8 H, m), 0.86 (3 H, t, *J* = 6.6 Hz); ¹³C δ 159.3, 158.1, 145.9, 141.7, 131.0, 129.1, 127.3, 126.9, 122.6, 121.7, 119.8, 119.1,

117.1, 113.4, 31.7, 29.7, 29.2, 29.0, 28.9, 26.4, 22.5, 14.0. The structure of **4c** was established by the X-ray structure analysis, although the tail end of the octyl group showed significant disorder.

Iminophosphorane 13. The same procedure was repeated as described for **9** except that 0.285 g (3.00 mmol) of aminopyrazine, 1.393 g (3.30 mmol) of Ph_3PBr_2 , 1.04 mL (7.50 mmol) of anhydrous triethylamine in 30 mL of anhydrous benzene were used to afford 0.847 g (2.39 mmol, 80%) of **13** as a white solid: mp 173–175 °C; IR (KBr) 1567, 1482, 723 cm^{-1} ; ^1H δ 8.31 (1 H, s), 7.9–7.74 (7 H, m), 7.72–7.64 (2 H, m), 7.58–7.4 (8 H, m); ^{13}C δ 160.1 (d, $J = 6.7$ Hz), 141.8 (d, $J = 25.8$ Hz), 141.0, 133.0 (d, $J = 9.8$ Hz), 131.84, 131.80, 129.2 (d, $J = 99.7$ Hz), 128.4 (d, $J = 11.9$ Hz).

6-Phenylpyrazino[1',2':1,2]pyrimido[4,5-*b*]indole (14a). To a solution of 0.163 g (0.459 mmol) of the iminophosphorane **13** in 5 mL of anhydrous *p*-xylene was introduced via cannula a solution of 0.100 g (0.457 mmol) of the isocyanate **8a** in 5 mL of anhydrous *p*-xylene under a nitrogen atmosphere at rt. The reaction mixture was kept at 45 °C for 12 h and then was heated under reflux at 138 °C for an additional 12 h before it was allowed to cool to rt. The mixture was concentrated to yield a solid residue. After three cycles of washing the residue with 40 mL of diethyl ether followed by centrifugation and decanting the supernatant liquid, the remaining solid was pumped to dryness in vacuo to afford **14a** (0.064 g, 0.216 mmol, 47%) as a pale orange red solid. Recrystallization from chloroform afforded orange flakes: compound turns black without melting at 299 °C; IR (KBr) 1654, 763, 744 cm^{-1} ; ^1H δ 9.26 (1 H, d, $J = 1.1$ Hz), 7.95 (1 H, d, $J = 8.2$ Hz), 7.85–7.78 (5 H, m), 7.70–7.66 (2 H, m), 7.62 (1 H, ddd, $J = 8.4, 6.9, 1.6$ Hz), 7.10 (1 H, td, $J = 7.9, 1.1$ Hz), 7.03 (1 H, dm, $J = 7.9, 0.8$ Hz); ^{13}C δ 158.8, 158.6, 154.0, 138.6, 138.3, 131.6, 130.6, 130.5, 129.5, 128.9, 128.5, 122.9, 121.6, 121.0, 119.7, 119.5, 119.2.

11-Methyl-6-phenyl-11*H*-pyrazino[1',2':1,2]pyrimido[4,5-*b*]indol-5-ium Iodide

(15a). To a solution of 0.010 g (0.034 mmol) of **14a** in 7 mL of chloroform was added 13.5 mL of a 0.05 M solution of methyl iodide (0.675 mmol) in chloroform. The reaction mixture was stirred at rt for 96 h. The organic solvent was removed, and the remaining solid was washed with one mL of chloroform (chilled at 0 °C) to afford **15a** (0.0148 g, 0.033 mmol, 99%) as a yellow solid. Recrystallization from chloroform containing 1% of absolute ethanol afforded yellow needles: mp 316–317 °C; ¹H δ 9.79 (1 H, s), 8.54 (1 H, d, *J* = 4.8 Hz), 8.33 (1 H, d, *J* = 4.8 Hz), 8.08 (2 H, dd, *J* = 7.9, 2.6 Hz), 7.88–7.81 (4 H, m), 7.70 (1 H, d, *J* = 8.4 Hz), 7.34 (1 H, t, *J* = 7.9 Hz), 7.10 (1 H, d, *J* = 7.9 Hz), 4.23 (3 H, s). The structure of **15a** was established by the X-ray structure analysis.

Iminophosphorane 17. The same procedure was repeated as described for **9** except that 0.261 g (2.74 mmol) of 4-aminopyrimidine, 1.237 g (2.93 mmol) of Ph₃PBr₂, 0.97 mL (7.0 mmol) of anhydrous triethylamine in 30 mL of anhydrous benzene were used to afford 0.938 g (2.64 mmol, 96%) of **17** as a white solid: mp 118–120 °C; IR (KBr) 1574, 1462, 720, 695 cm⁻¹; ¹H δ 8.28 (1 H, s), 8.09 (1 H, dd, *J* = 5.8, 2.6 Hz), 7.83–7.75 (6 H, m), 7.57–7.42 (9 H, m), 6.80 (1 H, dd, *J* = 5.8, 1.0 Hz); ¹³C δ 168.3 (d, *J* = 6.7 Hz), 157.5, 154.5 (d, *J* = 4.1 Hz), 133.1 (d, *J* = 10.2 Hz), 131.9 (d, *J* = 2.6 Hz), 128.9 (d, *J* = 99.8 Hz), 128.5 (d, *J* = 12.4 Hz), 114.7 (d, *J* = 24.3 Hz).

6-Propylpyrimido[6',1':2,3]pyrimido[4,5-*b*]indole (21b). The same procedure was repeated as described for **21a** except that 0.251 g (0.707 mmol) of the iminophosphorane **17** in 5 mL of anhydrous *p*-xylene and 0.131 g (0.708 mmol) of the isocyanate **8b** in 10 mL of anhydrous *p*-xylene were used. To the crude solid residue was added 2 mL of absolute ethanol, and the

mixture was kept at $-20\text{ }^{\circ}\text{C}$ for 3 h followed by filtration to afford 0.050 g of **21b** as a reddish brown solid. The ethanol filtrate was concentrated to yield a solid residue. The solid residue was washed three times with 2 mL of diethyl ether and one time with 0.5 mL of absolute ethanol (chilled at $0\text{ }^{\circ}\text{C}$) to give an additional 0.010 g of **21b**. The combined yield of **21b** was 0.060 g (0.229 mmol, 32%): mp $217\text{--}219\text{ }^{\circ}\text{C}$; IR (KBr) $1635, 1587, 749\text{ cm}^{-1}$; ^1H δ 10.33 (1 H, d, $J = 1.0\text{ Hz}$), 8.44 (1 H, d, $J = 6.4\text{ Hz}$), 8.15 (1 H, d, $J = 7.7\text{ Hz}$), 7.96 (1 H, d, $J = 7.9\text{ Hz}$), 7.73 (1 H, dd, $J = 6.4, 1.2\text{ Hz}$), 7.63 (1 H, td, $J = 7.2, 1.0\text{ Hz}$), 7.44 (1 H, td, $J = 7.9, 1.0\text{ Hz}$), 3.39 (2 H, t, $J = 7.7\text{ Hz}$), 2.03 (2 H, sextet, $J = 7.5\text{ Hz}$), 1.15 (3 H, t, $J = 7.4\text{ Hz}$); ^{13}C δ 162.8, 151.8, 147.2, 143.5, 141.4, 127.5, 123.1, 122.0, 121.8, 119.3, 116.3, 38.6, 21.7, 14.3.

Urea 24b. The same procedure was repeated as described for **24a** except that 0.102 g (0.708 mmol) of 1-aminoisoquinoline (**23**) and 0.131 g (0.708 mmol) of the isocyanate **8b** were used to give 0.217 g (0.660 mmol, 93%) of **24b** as a white solid: mp $172.5\text{--}173.0\text{ }^{\circ}\text{C}$; IR (KBr) $1682, 1513, 750\text{ cm}^{-1}$; ^1H δ 12.84 (1 H, s), 8.74 (1 H, s), 8.41 (1 H, d, $J = 8.2\text{ Hz}$), 8.31 (1 H, d, $J = 8.4\text{ Hz}$), 8.11 (1 H, d, $J = 5.8\text{ Hz}$), 7.82 (1 H, d, $J = 8.2\text{ Hz}$), 7.73 (1 H, t, $J = 6.6\text{ Hz}$), 7.62 (1 H, t, $J = 8.4\text{ Hz}$), 7.47 (1 H, d, $J = 7.7\text{ Hz}$), 7.37–7.30 (2 H, m), 7.06 (1 H, t, $J = 7.4\text{ Hz}$), 2.55 (2 H, t, $J = 7.1\text{ Hz}$), 1.67 (2 H, sextet, $J = 7.1\text{ Hz}$), 1.03 (3 H, t, $J = 7.2\text{ Hz}$); ^{13}C δ 153.8, 150.6, 140.3, 138.1, 137.3, 132.5, 130.7, 128.2, 127.4, 127.1, 122.9, 122.8, 120.8, 118.7, 115.5, 114.6, 96.0, 22.4, 21.9, 13.6.

8-Propylisoquinolino[2',1':1,2]pyrimido[4,5-*b*]indole (26b). To a solution of 0.135 g (0.319 mmol) of Ph_3PBr_2 and 0.40 mL (2.90 mmol) of anhydrous triethylamine in 10 mL of anhydrous dichloromethane was added dropwise, using a pressure equalizing addition funnel over 3 h, a solution of 0.048 g (0.146 mmol) of the urea **24b** in 25 mL of anhydrous

dichloromethane. After 12 h of stirring at rt, 50 mL of anhydrous *p*-xylene was introduced, and dichloromethane was removed by distillation under reduced pressure. The triethylammonium bromide precipitate was removed by filtration under a nitrogen atmosphere and was washed twice with 5 mL of anhydrous *p*-xylene. The combined filtrate was heated under reflux at 138 °C for 15 h. The reaction mixture was then allowed to cool to rt and concentrated to yield a solid residue. After three cycles of washing the residue with 40 mL of ethyl acetate followed by centrifugation and decanting the supernatant liquid, the remaining solid was pumped to dryness in vacuo. The solid was again washed three times with 1 mL of dichloromethane to yield **26b** (0.022 g, 0.071 mmol, 48%) as an off-white solid: mp >360 °C; IR (KBr) 1652, 1613, 794, 750 cm⁻¹; ¹H (6% CD₃OD in CDCl₃) δ 9.02 (1 H, d, *J* = 7.7 Hz), 8.83 (1 H, d, *J* = 7.7 Hz), 7.92–7.84 (3 H, m), 7.79–7.65 (3 H, m), 7.55 (1 H, td, *J* = 7.7, 1.1 Hz), 7.30 (1 H, t, *J* = 7.9 Hz), 3.90 (2 H, t, *J* = 7.9 Hz), 1.95 (2 H, sextet, *J* = 7.7 Hz), 1.21 (3 H, t, *J* = 7.4 Hz); ¹³C δ 151.6, 150.5, 146.7, 141.6, 134.0, 131.8, 130.8, 130.0, 127.4, 126.7, 125.3, 124.1, 123.7, 122.8, 119.6, 117.9, 114.2, 113.0, 31.7, 20.5, 13.8.

13-Methyl-8-phenylisoquinolino[2',1':1,2]pyrimido[4,5-*b*]indol-7-ium Triiodide

(27a). A mixture of 8 mg (0.023 mmol) of **26a** and 3 mL of methyl iodide in 1 mL of ethanol and 10 mL of dichloromethane was kept at rt for 40 days. The reaction mixture was then concentrated, and the resulting **27a** was obtained as a brown powder, which was essentially pure without the need for further purification: mp 222–223 °C; IR (KBr) 1654, 1578, 785 cm⁻¹; ¹H δ 9.53 (1 H, d, *J* = 7.9 Hz), 8.25 (1 H, d, *J* = 7.7 Hz), 8.08–8.00 (3 H, m), 7.90 (5H, s), 7.82–7.71 (3 H, m), 7.32 (1 H, t, *J* = 8.2 Hz), 6.98 (1 H, d, *J* = 7.9 Hz), 4.34 (3 H, s). The structure of **27a** was established by the X-ray structure analysis.

8-Propyl-13*H*-isoquinolino[2',1':1,2]pyrimido[4,5-*b*]indol-7-ium Triiodide (28b). To a tube were loaded 15.0 mg (0.048 mmol) of **26b**, 2 mL of acetonitrile, 1.0 mL of chloroform, 1.0 mL of absolute ethanol, and 0.4 mL of methyl iodide. The tube was flushed with nitrogen for one minute and then sealed. It was heated to 70 °C for 96 h before it was allowed to cool to rt. The solution was concentrated to yield a solid residue. The solid residue was washed twice with 1 mL of ethyl acetate and then twice with 1 mL of chloroform to afford 24.1 mg (0.035 mmol, 72%) of **28b** as a brown powder. Recrystallization from dichloromethane afforded reddish brown crystals: mp 204–205 °C; ¹H (CD₂Cl₂) δ 10.31 (1 H, br), 9.43 (1 H, d, *J* = 7.7 Hz), 8.61 (1 H, d, *J* = 7.7 Hz), 8.31 (1 H, d, *J* = 8.4 Hz), 8.14–7.92 (5 H, m), 7.86 (1 H, t, *J* = 7.4 Hz), 7.67 (1 H, t, *J* = 7.4 Hz), 3.96 (2 H, t, *J* = 7.7 Hz), 2.19–2.10 (2 H, m), 1.34 (3 H, t, *J* = 7.1 Hz). The structure of **28b** was established by the X-ray structure analysis.