The dilemma between acid and base catalysis in the synthesis of benzimidazole from o-phenylenediamine and carbon dioxide.

Martin Hulla, Simon Nussbaum, Alexy R. Bonnin and Paul J. Dyson

Supporting Information

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**General procedures**

All reagents and solvents were purchased from commercial suppliers (Sigma-Aldrich, Acros or TCI) and used without further purification. Unless otherwise indicated, extra dry solvents (Acros) were used in all the experiments. NMR spectra were recorded on a Bruker DMX 400 spectrometer in DMSO-d6 with TMS as the proton internal standard. GC/MS analysis was recorded on an Agilent 7000C GC/MS fitted with a HP-5MS column.

**Standard N-formylation catalyst testing procedure**

O-phenylenediamine (0.25 mmol, 27 mg) and the appropriate catalyst (0.025 mmol) were added to a three-neck round bottom flask. The flask was connected to a Schlenk line, CO₂ balloon and sealed with a septum. After three CO₂ – vacuum cycles the solvent (0.5 mL) was injected into the flask followed by phenylsilane (0.25 mmol, 0.03 mL). The reaction was stirred for 5 hours at 23 °C. The reaction yield was determined by ^1^H NMR spectroscopy in DMSO-d₆ with CH₂Br₂ as an internal standard.

**Standard cyclization catalyst testing procedure**

N-(2-aminophenyl)formamide (0.25 mmol, 34 mg) and the appropriate catalyst (0.025 mmol) were added to a two-neck round bottom flask. The flask was connected to a Schlenk line and sealed with a septum. After three N₂ – vacuum cycles dry DMSO (0.5 mL) was injected into the flask and the reaction mixture heated to the appropriate temperature (23 or 70 °C) and left to stir for 5 hours. The reaction was stirred for 5 hours at 23 °C. The reaction yield was determined by ^1^H NMR spectroscopy in DMSO-d₆ with CH₂Br₂ as an internal standard.

**General procedure for the synthesis of benzimidazole**

O-phenylenediamine (0.25 mmol, 27 mg) was added to a three-neck round bottom flask. The flask was connected to a Schlenk line, CO₂ balloon and sealed with a septum. After three CO₂ – vacuum cycles the DMSO (0.5 mL) was injected into the flask followed by phenylsilane (0.25 mmol, 0.03 mL). The flask was then gradually heated to 70°C over a period of 0.5 hour and then stirred at the temperature for 5.5 hours. BBr₃ (0.025mmol) in 1M hexane solution was injected into the flask and the resulting solution was stirred for another 2 hours at 70°C. The reaction yield was determined by ^1^H NMR spectroscopy in DMSO-d₆ with CH₂Br₂ as an internal standard.
$^1$H NMR spectroscopic (kinetic) studies

O-phenylenediamine (0.25 mmol, 27 mg), the appropriate catalyst (0.025 mmol) and DMSO-$d_6$ (1.5 mL) were added to a 10 mm high pressure NMR tube. The tube was pressurized with CO$_2$ (5 bar) and transferred into the NMR spectrometer and the reaction was monitored for up to 13 hours.

Figure S 1: In-situ $^1$H NMR spectroscopic monitoring of the N-formylation and cyclization of o-phenylenediamine to N-[(2-aminophenyl)]formamide and benzimidazole, respectively. Reaction conditions: o-phenylenediamine (0.25 mmol), phenylsilane (0.25 mmol), CO$_2$ (5 bar), DMSO-$d_6$ (2 mL), 25 °C, 13 h.

Figure S 2: In-situ $^1$H NMR spectroscopic monitoring of the N-formylation and cyclization of o-phenylenediamine to N-[(2-aminophenyl)]formamide and benzimidazole, respectively. Reaction conditions: o-phenylenediamine (0.25 mmol), phenylsilane (0.25 mmol), [TBA][OAc] catalyst (0.025 mmol), CO$_2$ (5 bar), DMSO-$d_6$ (2 mL), 25 °C, 13 h.
Synthesis and characterization of N-(2-aminophenyl)formamide

A solution of acetic formic anhydride (0.1 mol, 8.81 g) in THF (20 mL) at -15 °C was added to a solution of o-phenylenediamine (0.1 mol, 10.8 g) in THF (40 mL). The reaction mixture was stirred for 15 minutes and then the solvent was evaporated on the Schlenk line. The product N-(2-aminophenyl)formamide was purified by crystallization in DCM (40 mL) from 23 °C to -15 °C and washed with cold Et₂O (3 x 5 mL), white crystals 42% yield.

Mixture of cis and trans rotamers (33 : 66); ¹H NMR (400 MHz, DMSO-d₆): δ 9.36 (s, 1H), 9.30 (d, J = 11.0 Hz, 0.5H), 8.29 (d, J = 10.8 Hz, 0.5H), 8.21 (d, J = 0.4 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.95 – 6.85 (m, 1.5H), 6.71 (t, J = 7.5 Hz, 1.5H), 6.54 (t, J = 7.4 Hz, 1.5H), 5.00 (s, 1H), 4.87 (s, 2H); ¹³C NMR (101 MHz, DMSO-d₆): δ 164.1, 160.0, 141.9, 141.5, 126.8, 126.6, 124.7, 123.3, 123.1, 123.0, 117.0, 116.7, 116.3, 115.9; ESI-MS for C₇H₉N₂O+ (m/z): calc.137.1, found 137.0

Figure S3: ¹H NMR spectrum of N-(2-aminophenyl)formamide in DMSO-d₆ at 25 °C.
Figure S 4: $^{13}$C NMR spectrum of N-(2-aminophenyl)formamide in DMSO-$d_6$ at 25 °C.