Electronic Supplementary Material (ESI) for Chemical Communications

Oxidative Carbonylation of Amines to Formamides Using $NaIO_4$

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Supplementary Information

Experimental Section

General: Starting materials and reagents were purchased from Sigma-Aldrich or Acros Organics and used without further purification unless specified. 4-Methoxybenzylamine (**1**) was purified by distillation under reduced pressure. Carbon monoxide was purchased from Airgas. ^{1}H and ^{13}C NMR spectra were obtained on Varian Gemini 300, VXR 300, and Mercury 300 MHz spectrometers. ^{2}H NMR spectra were obtained on an Inova 500 MHz spectrometer. Infrared spectra were measured on a Perkin-Elmer 1600 FTIR either as pure solid or as neat oil. Elemental analysis was performed at the University of Florida. High-resolution mass spectrometry (HRMS) was performed by the University of Florida analytical service.

General Procedure A. ***N*-(4-Methoxybenzyl)formamide (2)**. To a 300 mL glass liner for a Parr high-pressure vessel were added methanol (60 mL), NaI (0.5996 g, 4.000 mmol), $NaIO_4$ (1.369 g, 6.400 mmol), potassium carbonate (2.211 g, 16.00 mmol) and 4-methoxybenzylamine (**1**) (0.631 g, 4.06 mmol). The liner was placed in the vessel and methanol was added to the space between the liner and vessel. The vessel was then closed, charged to 45 atm with carbon monoxide gas, heated to 90 ^{o}C and stirred for 24 h. At the completion of the reaction the solution was placed in a separatory funnel. Saturated sodium sulfite was added to the solution and mixed thoroughly. Water was added to dissolve the solid salt present and the mixture was extracted with methylene chloride (3 x 25 mL). The organic layers were combined and the solvent was removed via rotary evaporation leaving an off white solid residue. The solid

was purified via column chromatography using silica gel and ethyl acetate/hexanes as the eluent (50:50 ethyl acetate: hexanes shifted to pure ethyl acetate) to provide **2** as a white solid (0.6043 g, 80% yield). The compound was identified by comparison with literature data.[1] ^{1}H NMR (DMSO-d_6): δ 8.43 (br s, 1 H), 8.10 (s, 1 H), 7.19 (d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 4.23 (d, *J* = 6.0 Hz, 2 H), 3.73 (s, 3 H); IR(solid) ν_{CO} 1641 cm^{-1}; HRMS (ESI): Calcd for $C_9H_{11}NO_2$ $[M+Na]^+$ 188.0682, found 188.0690.

***N*-(Benzyl)formamide (3)**. Procedure A was used with benzylamine (0.429 g, 4.00 mmol) and afforded the product in 61% yield. The product was identified by comparison with literature data.[2] ^{1}H NMR (DMSO-d_6): δ 8.51 (br s, 1 H), 8.14 (s, 1 H), 7.42 - 7.13 (m, 5 H), 4.30 (d, *J* = 6.1 Hz, 2 H); IR (solid) ν_{CO} 1638 cm^{-1}.

***N*-(4-Iodobenzyl)formamide (4)**. Procedure A was altered to use methanol (20 mL), NaI (0.225 g, 1.49 mmol), $NaIO_4$ (0.513 g, 2.40 mmol), potassium carbonate (0.828 g, 5.99 mmol) and 4-iodobenzylamine·HCl (0.404 g, 1.49 mmol) to afford the product in a 36% yield. ^{1}H NMR (DMSO-d_6): δ 8.52 (br s, 1 H), 8.12 (s, 1 H), 7.68 (d, *J* = 8.3 Hz, 2 H), 7.07 (d, *J* = 8.2 Hz, 2 H), 4.24 (d, *J* = 6.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$): δ 160.9, 137.8, 137.2, 129.6, 93.1, 41.6; IR (solid) ν_{CO} 1648 cm^{-1}; HRMS (APCIMS): Calcd for C_8H_9INO $[M+H]^+$ 261.9723, found 261.9723; Anal. Calcd for C_8H_8INO: C, 36.81; H, 3.09; N, 5.37; found: C, 37.06; H, 3.03; N, 5.13.

***N*-(4-Bromobenzyl)formamide (5).** Procedure A was used with 4-bromobenzylamine (0.8351 g, 4.488 mmol) and afforded the product in 86% yield. ^{1}H NMR (DMSO-d_6): δ 8.54 (br s, 1 H), 8.15 (s, 1 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, J = 8.0 Hz, 2 H), 4.27 (d, *J* = 6.0 Hz, 2 H); ^{13}C NMR (DMSO-d_6): δ 161.1, 138.5, 131.2, 129.5, 119.9, 40.1; IR (solid) ν_{CO} 1647 cm^{-1}; HRMS (APCIMS): Calcd for C_8H_9BrNO $[M+H]^+$ 213.9862, found 213.9867; Anal. Calcd for C_8H_8BrNO: C, 44.89, H, 3.77; N, 6.54; found: C, 44.87; H, 3.77; N, 6.54.

***N*-(4-Chlorobenzyl)formamide (6)**. Procedure A was used with 4-chlorobenzyl amine (0.526 g, 3.72 mmol) and afforded the product in a 92% yield. The solid was identified by comparison with literature data.[3] ^{1}H NMR (DMSO-d_6): δ 8.53 (br s, 1 H), 8.16 (s, 1 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 4.30 (d, *J* = 6.2 Hz, 2 H); IR (solid) ν_{CO} 1647 cm^{-1}.

***N*-(4-Fluorobenzyl)formamide (7)**. Procedure A was used with 4-fluorobenzylamine (0.5006 g, 4.000 mmol) and afforded the product in trace amounts. The product was tentatively identified by the formamide carbonyl IR stretch. IR (solid) ν_{CO} 1651 cm^{-1}.

***N*-(4-Nitrobenzyl)formamide (8)**. Procedure A was used with 4-nitrobenzylamine·HCl (0.7554 g, 4.005 mmol) and afforded the product in trace amounts. The product was tentatively identified by the formamide carbonyl IR stretch. IR (solid) ν_{CO} 1659 cm^{-1}.

***N*-(methoxybenzyl)formamide-d, *p*-$CH_3OC_6H_4CH_2NHCDO$ (2-*d*)**. Procedure A was used at 25 ºC with 4-methoxybenzylamine (**1**) (0.2849 g, 2.077 mmol), $NaIO_4$ (0.6845 g, 3.200 mmol), potassium carbonate (1.106 g, 8.003 mmol) and 20 mL CH_3OD. The product was identified by comparison with literature data.[1] ^{1}H NMR (DMSO-d_6): δ 8.10 (s, 0.1 H), 7.19 (d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 4.23 (d, *J* = 6.0 Hz, 2 H), 3.73 (s, 3 H); ^{2}H NMR (DMSO) 8.10 (s); IR (solid) ν_{CO} 2186, 2171, 1623 cm^{-1}; HRMS (DART): Calcd for $C_9H_{10}DNO_2$ $[M+H]^+$ 167.0925, found 167.0928.

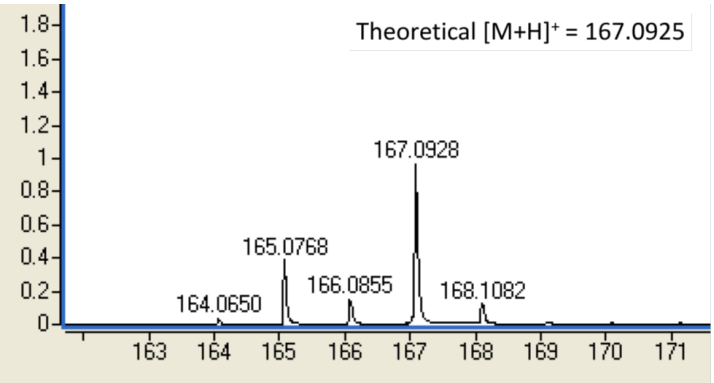

Figure S1 Mass spectrum of **1-*d***.

General Procedure B. *N*-formylpiperidine (9). To a 300 mL glass liner for a Parr high-pressure vessel were added methanol (60 mL), $NaIO_4$ (1.369 g, 6.400 mmol), potassium carbonate (2.211 g, 16.00 mmol) and piperidine (0.3569 g, 4.191 mmol). The liner was placed in the vessel and methanol was added to the space between the liner and vessel. The vessel was then closed, charged to 45 atm with carbon monoxide gas, heated to 90 ^{o}C and stirred for 24 h. At the completion of the reaction the solution was placed in a separatory funnel. Saturated sodium sulfite was added to the solution and mixed thoroughly. Water was added to dissolve the solid salt present and the mixture was extracted with chloroform (3 x 25 mL). The organic layers were combined and the solvent was removed via rotary evaporation leaving a yellow oil residue. The oil was purified via column chromatography using silica gel and $CHCl_3/CH_3OH/NH_4OH$ as the eluent (100:5 $CHCl_3/CH_3OH$ shifted to 100:5:0.1 $CHCl_3/CH_3OH/NH_4OH$) to provide *N*-formylpiperidine as a colorless oil (0.2762 g, 58% yield). The compound was identified by comparison with literature data.[4]

***N*-formylpyrrolidine (10)**. Procedure B was used with pyrrolidine (0.2988 g, 4.202 mmol) and afforded the product in a 51% yield. The oil was identified by comparison with literature data.[4]

References

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