

NaIO₄-oxidized carbonylation of amines to ureas

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Supplementary Information

Experimental Section

General: ¹H and ¹³C NMR spectra were obtained on Varian Gemini 300 and VXR 300 and Mercury 300 spectrometers. Infrared spectra were measured on a Perkin-Elmer 1600 FTIR. Mass spectrometry and elemental analyses were performed by the University of Florida analytical service. All chemicals were purchased in reagent grade and used with no further purification unless stated otherwise.

General Procedure for Carbonylation of Amines: Procedure A. To a 300 mL glass liner in a 300 mL Parr high pressure vessel were added 4-methoxybenzylamine (0.260 mL, 2.00 mmol), K₂CO₃ (0.414 g, 3.00 mmol), NaI (0.150 g, 1.00 mmol), NaIO₄ (0.342 g, 1.60 mmol) and 15.0 mL of CH₂Cl₂/15.0 mL of H₂O. The vessel was then charged with 45 atm of CO and left to stir at room temperature for 16 h. The pressure was released and the aqueous layer was separated from the CH₂Cl₂ solution, and extracted twice with a 3:1 mixture of chloroform to ethanol. The combined organic layers were removed under reduced pressure. The solid was redissolved in CH₂Cl₂ and washed with 20 mL of 1 M HCl. Removal of the organic solvent afforded an off-white solid which was recrystallized from CH₂Cl₂ to provide 1,3-bis(4-methoxybenzyl)urea in 81% yield.

General Procedure for Carbonylation of Amines: Procedure B. Identical to procedure A except 4-dimethylaminopyridine (0.367 g, 3.00 mmol) was used as base and the reaction time was 8 h.

1,3-Dibutylurea. Procedure A afforded the product in 86% yield while the yield from procedure B was in 94%. The solid was identified by comparison with literature data.¹

1,3-Diisobutylurea. Procedure A afforded the product in 84% yield while the yield from procedure B was 96%. The solid was identified by comparison with literature data.¹

1,3-Diisopropylurea. Procedure A afforded the product in 38% yield while the yield from procedure B was 91% . The solid was identified by comparison with literature data.²

1,3-Di-tert-butylurea. Procedure A afforded the product in 33% yield while the yield from procedure B was 20%. The solid was identified by comparison with literature data.³

1,3-Bis(4-methoxybenzyl)urea. Procedure A and B both afforded the product in 81% yield. The solid was identified by comparison with literature data.⁴

1,3-Bis(4-methylbenzyl)urea. Procedure A afforded the product in 61% yield while the yield from procedure B was 78%. The solid was identified by comparison with literature data.¹

1,3-Dibenzylurea. Procedure A afforded the product in 46% yield while the yield from procedure B was 34%. The solid was identified by comparison with literature data.¹

1,3-Bis(4-carbomethoxybenzyl)urea Procedure A afforded the product in 10% yield while the yield from procedure B was 85% yield. ^1H NMR ($\text{DMSO}-d_6$) δ 7.86 (d, 4H), 7.33 (d, 4H), 6.60 (br t, 2H), 4.26 (d, 4H), 3.79 (s, 6H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 166.77, 158.68, 147.39, 129.80, 128.56, 127.71, 52.69, 43.45; IR (solid) 3313, 1718, 1611, 1568. Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_5$: C, 64.04; H, 5.66; N, 7.86. Found: C, 64.27; H, 5.56; N, 7.85.

1,3-Bis(4-nitrobenzyl)urea. Procedure A afforded the product in 1% yield while the yield from procedure B was 79% . The solid was identified by comparison with literature data.⁵

1,3-Bis(4-fluorobenzyl)urea. Procedure A afforded the product in 0% yield while the yield from procedure B was 72%. ^1H NMR (DMSO) δ 7.28 (dd, 4H, $^3J_{\text{FH}} = 9.1$ Hz), 7.20 (dd, 4H, $^4J_{\text{FH}} = 5.6$ Hz), 6.44 (br t, 2H), 4.18 (d, 4H); IR (solid) 3321, 1611. Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{F}_2\text{N}_2\text{O}$: C, 65.21; H, 5.11; N, 10.14. Found: C, 65.09; H, 5.12; N, 10.03.

1,3-Bis(4-chlorobenzyl)urea. Procedure A afforded the product in 7% yield and in 72% yield by procedure B. The solid was identified by comparison with literature data.⁵

1,3-Bis(4-bromobenzyl)urea. Procedure A afforded the product in 21% yield while the yield from procedure B was 78%. The solid was identified by comparison with literature data.⁵

1,3-Bis(4-iodobenzyl)urea. Procedure A afforded the product in 27% yield while the yield from procedure B was 87%. ^1H NMR ($\text{CD}_3\text{CO}_2\text{D}$) δ 7.74 (d, 4H), 6.95 (d, 4H), 4.48 (s, 4H); IR (solid) 3317, 1609. Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{I}_2\text{N}_2\text{O}$: C, 36.61; H, 2.87; N, 5.69. Found: C, 36.31; H, 2.73; N, 5.48.

N-(4-methoxybenzyl)formamide. Identical to procedure A except I₂ (0.2538 g, 1.00 mmol) replaced NaI. This procedure afforded the formamide in 68% NMR yield. The product was identified by comparison with literature data.⁶

References

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