Efficient Transesterification/Acylation Reactions Mediated by *N*-Heterocyclic Carbenes

Gabriela A. Grasa, Tatyana Güveli, Rohit Singh and Steven P. Nolan

*Department of Chemistry
University of New Orleans
New Orleans, Louisiana 70148*

snolan@uno.edu

Supporting Information

General Information

- All esters and alcohols (Aldrich) were degassed or used as recieved. THF (anhydrous, Aldrich) was distilled under argon from sodium benzophenone ketyl. Potassium *tert* butoxide and sodium hydride (Aldrich) were stored under argon in a MBraun glovebox. Ionic liquids IMeBu.HBF₄, IMeHex.HBF₄, IMeOct.HBF₄ were purchased from Strem Chemicals. Flash chromatography was performed on silica gel 60 (230-400 mesh) (Natland International Corporation) using hexanes or 10% ethyl acetate/hexanes.
- *N*-heterocyclic carbenes were synthesized according to literature procedures: Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, A.; Hugh, A.; Goerlich, J. R.; William, J.. M.; Unverzagt, M. *Tetrahedron*, **1999**, 55, 14523-14534; Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, 113, 361-363; Arnold, P. L.; Cloke, F. G. N.; Geldbach, T.; Hitchcock, P. B. *Organometallics* **1999**, 18, 3228-3233; Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. J. *J. Am. Chem. Soc.* **1994**, 116, 4391-4393; Arduengo, A. J., III; Davidson, F.; Kraftczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, 17, 3375-3382.
- ¹H and ¹³C NMR and spectra were recorded on a Varian-300 or Varian-400 MHz spectrometer at ambient temperature in CDCl₃ (Cambridge Isotope Laboratories, Inc.).

- All reactions were carried out under an atmosphere of argon in screw cap vials with magnetic stirring, unless otherwise indicated.
- The identity of every product was confirmed by comparison with literature spectroscopic data: **3**,¹ **4a**,² , **5a**,³ **6a**,⁴ , **7a**,⁵ **7b**,⁶ **7c**,⁷ **11a**,⁸ **14a**,⁹ **15a**,⁹ **16a**,⁹ **16b**,¹⁰ **17a**,¹¹ **18b**.¹² **20a**,¹³ , **20b**.¹⁴

Transesterification of Esters with Alcohols.

Procedure A. *Esterification of Vinyl acetate with Alcohols.* Under an atmosphere of argon, 1 mL of THF, 1 mmol of alcohol and 1.2 mmol of vinylacetate was added sequentially to a screw cap vial loaded with 0.5 mol% catalyst. The resulting mixture was stirred at room temperature for the indicated time; the solvent and ester excess were evaporated and the residue was purified flash chromatography using 10% ethylacetate/hexanes.

Procedure B. *Esterification of Methyl Acetate/Ethyl Acetate with Alcohols.* Under an atmosphere of argon, 1 mL of methyl acetate (ethyl acetate) and 1 mmol of alcohol was added sequentially to a screw cap vial loaded with 2.5 mol% catalyst and 0.5 g 4 Å (5 Å for ethyl acetate) molecular sieves. The resulting mixture was stirred at room temperature for the indicated time; the acetate was evaporated and the residue was purified flash chromatography using 10% ethyl acetate/hexanes.

Procedure C. *Esterification of Methyl Esters with Benzyl Alcohol.* Under an atmosphere of argon, 1 mL of THF and 2 mmol of benzyl alcohol was added sequentially to a screw cap vial loaded with 2.5 mol% catalyst and 0.5 g molecular sieves. The resulting mixture was stirred at room temperature for the indicated time; the solvent was evaporated and the residue was purified flash chromatography using 10% ethyl acetate/hexanes.

Benzyl dimethoxyacetate (13a) (Table 2, entry 5): ¹H NMR: (400 MHz,CDCl₃) δ 3.41 (s, 6H), 4.84 (s, 1H), 5.24 (s, 2H), 7.34-7.4 (m, 5H). ¹³C NMR: (400 MHz,CDCl₃) δ 167, 135.4, 128.8, 128.6, 99, 77.2, 67.2, 54. Anal.Calcd. for C₁₁H₁₄O₄: C, 64.13; H, 6.71; O, 30.44. Found: C, 63.8; H, 6.62; O, 30.58.

Benzyl acrylate (9a) (Table 1, entry 8): ^1H NMR: (300 MHz, CDCl_3) δ 5.21 (s, 2H), 5.84 (d, 1H, $J_{\text{H-H}} = 9$ Hz), 6.18 (q, 1H, $J_{\text{H-H}} = 9$ Hz), 6.46 (d, 1H, $J_{\text{H-H}} = 18$ Hz), 7.37 (m, 5H). ^{13}C NMR: (300 MHz, CDCl_3) δ 166.1, 136, 131.2, 128.7, 128.4 (br), 128.39, 128.36, 66.44.

¹. Aldrich Library, **1** (2), 1201B.

². Aldrich Library, **1** (1), 998B.

³. Aldrich Library, **1** (2), 1201B.

⁴. D'Sa, B.; Verkade, J. G. *J. Org. Chem.* **1996**, *61*, 2963-2966.

⁵. Aldrich Library, **1** (2), 1244A.

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⁷. Engman, L. *J. Org. Chem.* **1989**, *54*, 884-890.

⁸. NMR spectra compared to the authentic sample: <http://www.sigmaaldrich.com/cgi-bin/hsrun/Distributed/HahtShop/HAHTpage/frmCatalogSearchPost?Brand=ALDRICH&ProdNo=S458538>, Javascript:showLinks('/spectra/fnmr/FNMR004032.PDF').

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¹⁰. Brown, H. C.; Kulkarni, S. V.; Racherla, U. S. *J. Org. Chem.*, **1994**, *59*, 365-369.

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¹². (a) Ames, D. E.; Ribeiro, O. *J. Chem. Soc., Perkin Trans. I* **1975**, *14*, 1390-1395.

(b) Bowles, T.; Jones, R.; Porter, A. E. A.; Rechka, J. A.; Rzepa, H. S.; Williams, D. J. *J. Chem. Soc., Perkin Trans. I* **1988**, *5*, 1023-1027

¹³. NMR spectra compared to the authentic sample: <http://www.sigmaaldrich.com/cgi-bin/hsrun/Distributed/HahtShop/HAHTpage/frmCatalogSearchPost?Brand=FLUKA&ProdNo=72351>, Javascript:showLinks('/spectra/fnmr/FNMR008745.PDF')

¹⁴. Zawisza, T.; Kuczynski, L. *Pol. J. Pharmacol. Pharm.* **1973**, *25*, 447-453.