

SUPPORTING INFORMATION

Title: A Remarkably Efficient Markovnikov Hydrochlorination of Olefins and Transformation of Nitriles into Imidates by Use of AcCl and an Alcohol

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2-(1-chloroethyl)naphthalene (colorless liquid): ^1H NMR δ 7.84-7.79 (m, 4H), 7.57-7.44 (m, 3H), 5.27-5.22 (q, $J = 6.8$ Hz, 1H), 1.92 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR δ 140.0, 133.13, 133.06, 128.6, 128.1, 127.7, 126.4, 125.2, 124.5, 59.0, 26.4. $\text{C}_{12}\text{H}_{11}\text{Cl}$ (190.05): calcd. C 75.59, H 5.81; found C 75.50; H, 5.75.

(1-chloroethyl)benzene (colorless liquid): ^1H NMR δ 7.42-7.09 (m, 5H), 5.12-5.06 (q, $J = 6.8$ Hz, 1H), 1.84 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR δ 142.8, 128.6, 128.2, 126.5, 58.7, 26.5. $\text{C}_8\text{H}_9\text{Cl}$ (140.04): calcd. C 68.33, H 6.45; found C 68.25, H 6.40%.

4-Methoxy-(1-chloroethyl)benzene (colorless liquid): ^1H NMR δ 7.36 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 2H), 5.14-5.09 (q, $J = 6.8$ Hz, 1H), 3.81 (s, 3H), 1.86 (d, $J = 6.8$ Hz, 3H). ^{13}C

NMR δ 159.4, 134.9, 127.7, 113.9, 58.7, 55.2, 26.4. C₉H₁₁ClO (170.05): calcd. C 63.35, H 6.50; found C 63.25, H 6.40%.

1,7-Dichloro-3,7-dimethyl-2-octene (colorless liquid): ¹H NMR δ 5.46 (t, *J* = 7.0 Hz, 1H), 4.10 (d, *J* = 8.0 Hz, 2H), 2.07 (t, *J* = 6.5 Hz, 2H), 1.73 (s, 3H), 1.71-1.59 (m, 4H), 1.57 (s, 6H). ¹³C NMR δ 142.2, 120.6, 70.8, 45.2, 40.9, 39.1, 32.4, 22.8, 15.8. C₁₀H₁₈Cl₂ (208.08): calcd. C 57.42, H 8.67; found C 57.34, H, 8.60%.

5-(2-Chloropropyl)-2-methyl-2-cyclohexen-1-one (colorless liquid): ¹H NMR δ 6.77 (d, *J* = 6.1 Hz, 1H), 2.73-2.70 (m, 1H), 2.60-2.53 (m, 1H), 2.43-2.34 (m, 2H), 2.29-2.21 (m, 1H), 1.79 (s, 3H), 1.60 (s, 3H), 1.59 (s, 3H). ¹³C NMR δ 199.3, 144.4, 135.1, 71.2, 47.1, 39.9, 30.4, 30.2, 27.8, 15.4. C₁₀H₁₅ClO (186.08): calcd. C 64.34, H 8.10; found C 64.24, H 7.97%.

Ethyl α -phenyl acetimidate (colorless liquid): ¹H NMR δ 7.29-7.18 (m, 5H), 4.12-4.07 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). ¹³C NMR δ 171.4, 134.0, 129.1, 128.4, 126.9, 60.7, 41.3, 14.0. C₁₀H₁₃NO (163.10): calcd. C 73.59, H 8.03; found: C 73.49, H 7.95%.

Isopropyl α -phenyl acetimidate (colorless liquid): ¹H NMR δ 7.37-7.19 (m, 5H), 5.11-5.09 (m, 1H), 3.49 (s, 2H), 1.27 (d, *J* = 6.4 Hz, 6H). ¹³C NMR δ 171.3, 135.2, 129.6, 128.8, 127.2, 68.0, 42.1, 21.7. C₁₁H₁₅NO (177.12): calcd. C 74.54, H 8.53; found C 74.42, H, 8.46%.

Isobutyl α -phenyl acetimidate (mixture of isomers in the ratio 4.9:1, liquid): ¹H NMR δ 7.34-7.20 (m), 3.87 (d, *J* = 6.6 Hz), 3.62 (s), 3.55 (s), 2.02-1.87 (m), 0.95 (d, *J* = 6.6 Hz), 0.89 (d, *J* = 6.6 Hz). ¹³C NMR δ 172.3, 171.6, 135.2, 134.2, 129.6, 129.2, 128.8, 128.5, 127.2, 127.0, 72.2,

70.9, 41.8, 41.5, 27.7, 19.2, 19.0, 18.9. C₁₂H₁₇NO (191.13): calcd. C 75.35, H 8.96; found C 75.29, H, 8.90%.

Ethyl butyrimidate (colorless liquid): ¹H NMR δ 4.08-4.03 (q, *J* = 7.1 Hz, 2H), 2.15 (t, *J* = 7.6 Hz, 2H). 1.56-1.51 (sextet, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). ¹³C NMR δ 173.0, 61.0, 37.6, 19.3, 14.1, 13.4. C₆H₁₃NO (115.10): calcd. C 62.57, H 11.38; found C 62.44, H 11.26%.

Ethyl benzimidate (colorless liquid): ¹H NMR δ 7.74 (d, *J* = 7.1 Hz, 2H), 7.46-7.37 (m, 3H), 4.35-4.30 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ¹³C NMR δ 167.7, 132.9, 130.7, 128.3, 126.6, 61.7, 14.1. C₉H₁₁NO (149.08): calcd. C 72.46, H 7.43; found C 72.30, H, 7.35%.

Ethyl 4-chlorobenzimidate (colorless liquid): ¹H NMR δ 7.77-7.69 (m, 2H), 7.43-7.36 (m, 2H), 4.32-4.27 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). C₉H₁₀ClNO (183.05): calcd. C 58.86, H 5.49; found C 58.77, H, 5.40%.

Ethyl 4-methoxybenzimidate (colorless liquid): ¹H NMR δ 7.71 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.33-4.28 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ¹³C NMR δ 167.4, 161.6, 128.4, 125.4, 113.6, 61.6, 55.4, 14.3. C₁₀H₁₃NO₂ (179.09): calcd. C 67.02, H 7.31; found C 66.90, H 7.25%.