Supporting Information

Ionic Liquid as Catalyst and Reaction Medium. The Dramatic Influence of a Task Specific Ionic Liquid [bmIm]OH in Michael Addition of Active Methylene Compounds to Conjugated Ketones, Carboxylic Esters and Nitriles

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Representative Experimental Procedure for Michael Addition of Methyl Vinyl Ketone with Ethyl 2-Oxo-cyclopentane Carboxylate (entry 19, Table 1). Methyl vinyl ketone (420 mg, 6 mmol) was added dropwise to a well stirred mixture of ethyl 2-oxo-cyclopentane carboxylate (755 mg, 5 mmol) in [bmIm]OH (468 mg, 3 mmol) and the reaction mixture was stirred for 0.5 h till completion of the reaction (TLC). The product was then distilled off directly from the reaction mixture to provide pure Michael adduct (1.08 g, 96%) as a colorless oil. If the reaction was carried out in relatively smaller scale (1-2 mmol), the reaction mixture was extracted with ethyl acetate. The extract was washed with brine, dried (Na_2SO_4) and evaporated the leave the crude product which was purified by column chromatography over silica gel to provide the pure product. The compound was identified by comparison of its IR, ^1H and ^{13}C NMR spectroscopic data with those of an authentic sample.

Representative Experimental Procedure for Bis-Michael Addition of Methyl Acrylate with Ethyl Cyanoacetate (entry 16, Table 1). Methyl acrylate (1.032 g, 12 mmol) was added dropwise to a well stirred mixture of ethyl cyanoacetate (565 mg, 5 mmol) in [bmIm]OH (468 mg, 3 mmol) and the reaction mixture was stirred for 2.5 h till completion of the reaction (TLC). The product was isolated in the same way as described in the previous experiment. The product was characterized by its spectroscopic data and elemental analysis, which are reported below in entry 16.

Characterization Data

Spectroscopic data (IR, ¹H NMR and ¹³C NMR) and elemental analysis of products in entries 6,16,17, 20, 22 and 23 in Table 1

Entry 6. Colorless liquid; IR(neat) 1735, 1712, 1438 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) (1.08 (t, J = 7.0 Hz, 3H), 1.90-2.02 (m, 11H), 3.46 (s, 6H), 4.01 (q, J = 7.0 Hz, 2H); ¹³C NMR (75 MHz) (13.7, 26.3 (2C), 26.4, 28.5 (2C), 51.5 (2C), 61.4, 61.5, 171.1, 172.6, 203.8. Anal. Calcd for C₁₄H₂₂O₇ : C, 55.62; H, 7.33. Found : C, 55.54; H, 7.21.

Entry 16 : Colorless liquid; IR(neat) 2250, 1739, 1438, 1200 cm⁻¹; ¹H NMR (1.25 (t, J = 6.9 Hz, 3H), 2.06-2.21 (m, 4H), 2.23-2.53 (m, 4H), 3.60 (s, 6H), 4.18 (q, J = 6.9 Hz, 2H); ¹³C NMR (14.0, 29.9 (2C), 31.9 (2C), 47.8, 51.9 (2C), 63.0, 117.7, 167.5, 171.5 (2C); Anal. Calcd for C₁₃H₁₉NO₆ : C, 54.73; H, 6.71; N, 4.91. Found : C, 54.53; H, 6.60; N, 4.69.

Entry 17. Colorless liquid; IR(neat) 2252, 1739, 1448 cm⁻¹; ¹H NMR (1.37 (t, J = 7.0 Hz, 3H), 2.15-2.33 (m, 2H), 2.33-2.43 (m, 2H), 2.52-2.67 (m, 4H), 4.35 (q, J = 7.0 Hz, 2H); ¹³C NMR (13.6, 13.7 (2C), 32.3 (2C), 47.7, 64.3, 116.1, 117.0 (2C), 166.0. Anal. Calcd for C₁₁H₁₃N₃O₂ : C, 60.26; H, 5.98; N, 19.17. Found : C, 60.05; H, 5.79; N, 19.21.

Entry 20. Colorless liquid; IR(neat) 1739, 1735, 1440 cm⁻¹; ¹H NMR (1.18 (t, J = 7.0 Hz, 3H), 1.80-1.97 (m, 6H), 2.13-2.31 (m, 2H), 2.33-2.45 (m, 2H), 3.59 (s, 3H), 4.09 (q, J = 7.0 Hz, 2H); ¹³C NMR (13.8, 19.3, 28.1, 29.3, 33.4, 37.6, 51.4, 58.9, 61.2, 170.7, 173.1, 214.1. Anal. Calcd for C₁₂H₁₈O₅ : C, 59.49; H, 7.49. Found : C, 59.34; H, 7.37.

Entry 22. Colorless liquid; IR(neat) 1735, 1712, 1456, 1436 cm⁻¹; ¹H NMR (1.03 (d, J = 6.6 Hz, 3H), 1.43-1.52 (m, 1H), 1.78-1.93 (m, 4H), 1.98-2.12 (m, 2H), 2.14 (s, 3H), 2.25-2.33 (m, 2H), 2.50-2.69 (m, 2H), 3.73 (s, 3H); ¹³C NMR (14.9, 20.4, 26.5, 30.0, 34.2, 35.0, 38.9, 42.3, 52.2, 60.6, 172.7, 207.5, 210.7. Anal. Calcd for C₁₃H₂₀O₄: C, 64.98; H, 8.39. Found : C, 64.80; H, 8.21.

Entry 23. Colorless liquid; IR(neat) 1737, 1707, 1456, 1436 cm⁻¹; ¹H NMR (1.11 (d, J = 6.6 Hz, 3H), 1.43-1.49 (m, 1H), 1.77-1.97 (m, 3H), 2.11-2.22 (m, 3H), 2.26-2.32 (m, 2H), 2.45-2.59 (m, 2H), 3.65 (s, 3H), 3.71 (s, 3H); ¹³C NMR (14.9, 20.1, 27.7, 29.3, 33.6, 34.9, 42.2, 51.6, 52.4, 60.9, 172.5, 173.4, 210.4. Anal. Calcd for C₁₃H₂₀O₅ : C, 60.92; H, 7.87. Found : C, 60.73; H, 7.68.