

Supporting Information

The Journal of Organic Chemistry

Investigation into the Allylation Reactions of Aldehydes promoted by $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI System as Lewis Acid.

Giuseppe Bartoli,[‡] Marcella Bosco,[‡] Arianna Giuliani,[†] Enrico Marcantoni,^{†} Alessandro
Palmieri,[†] Marino Petrini,[†] Letizia Sambri[‡]*

[†]Dipartimento di Scienze Chimiche, Università di Camerino, via S. Agostino 1, I-62032 Camerino
(MC), Italy

[‡]Dipartimento di Chimica Organica "A. Mangini", Università di Bologna, viale Risorgimento 4, I-
40136 Bologna, Italy

enrico.marcantoni@unicam.it

Contents:

General Methods S2

Experimental procedure and characterizations for compounds: 1-(3-nitrophenyl)-3-buten-1-ol (**5f**),
(7Z)-1,7-decadien-4-ol (**5k**) S2

General Methods. Most solvents and reagents were used without purification unless mentioned otherwise. Solvents (EtOAc and hexanes) for flash chromatography were distilled. TLC was runned on silica gel 60 F₂₅₄ plates (0.25 mm thick), and visualized by UV light or Iodine or a Ce-Mo staining solution (phosphomolybdate, 25 g; Ce(SO₄)₂·2H₂O, 10 g; H₂SO₄ 60 mL, concentrated; water, 940 mL) with heating. Flash chromatography was performed using a silica gel 60 (mesh size 0.040-0.063 mm) using a silica gel:crude compound weight ratio of *ca.* 30:1. Analytical GC was performed with a capillary fused silica column (0.32 mm x 25 mt), stationary phase OV1 (film thickness 0.40-0.45 µm). FT-IR spectra were obtained using thin films on NaCl plates. Only the characteristic peaks are reported. ¹H NMR (300 MHz) spectra were taken in CDCl₃ with residual signals of CHCl₃ (7.26 ppm) as an internal standard. ¹³C NMR (75.5 MHz) spectra were recorded in CDCl₃ and chemical shifts are reported relative to the center line of the triplet at 77.00 ppm for deuteriochloroform. Mass spectra were determined with a capillary GC operating in split mode with helium as the carrier gas and fitted with mass-selective detector by means of the EI technique (70 eV). A fused silica column (30 mt x 0.25 mm; cross-linked 5% Ph-Me siloxane, 0.10 µm film thickness) was used with a helium carrier flow of 30 mL/min. The temperature of the column was varied, after a delay of 3 min from the injection, from 65°C to 300°C with a slope of 15°C min⁻¹.

General Procedure for the Allylation (5a-m). To a suspension of CeCl₃·7H₂O (1.0 mmol) and NaI (0.1 mmol) in acetonitrile (12 mL) was added successively aldehydes (**3a-m**) (1.0 mmol) and allyltributylstannane **4** (1.1 mmol) at room temperature. After being stirred at that temperature for the time request, the reaction mixture was quenched with 0.5 N HCl solution. The aqueous layer was extracted with diethyl ether and the combined organic leyers were stirred for 1h with 10% KF in H₂O (10 mL). The organic phase was separated and the washed with brine, dried with Na₂SO₄ and concentrated at reduced pressure to furnish the crude product, which was purified by silica gel chromatography (hexanes:EtOAc).

1-(3-Nitrophenyl)-3-buten-1-ol (5f): yellow oil (yield 95%); IR (neat, cm⁻¹) 3400, 3078, 1641, 1529, 1350; ¹H NMR δ 2.50-2.65 (m, 3H), 4.82-4.90 (m, 1H), 5.12-5.26 (m, 2H), 5.70-5.91 (m, 1H), 7.40-7.52 (m, 1H), 7.75 (d, 1H, J = 1.27 Hz), 8.13 (d, 1H, J = 1.10 Hz), 8.23 (s, 1H); ¹³C NMR δ 40.0, 74.5, 113.6, 123.6, 124.0, 130.2, 134.6, 136.2, 139.0, 148.2; EI-MS *m/z* 193[M⁺], 152 (100), 105, 77, 65, 51, 41. Anal. Calcd for C₁₀H₁₀NO₃: C, 62.49; H, 5.24; N, 7.29. Found: C, 62.45; H, 5.27; N, 7.32.

(7Z)-1,7-Decadien-4-ol (5k): oil (yield 93%); IR (neat, cm⁻¹) 3368, 3077, 1640; ¹H NMR δ 0.93 (t, 3H, J = 7.32 Hz), 1.45-1.53 (m, 2H), 1.71 (bs, 1H, OH), 1.98-2.10 (m, 5H), 2.13-2.17 (m, 1H), 3.57-3.69 (m, 1H), 5.06-5.13 (m, 2H), 5.35 (dt, 2H, J = 8.55 and 7.34 Hz), 5.73-5.85 (m, 1H); ¹³C NMR δ 14.0, 15.8, 22.0, 28.6, 39.2, 69.9, 113.2, 126.8, 130.6, 132.6; EI-MS *m/z* 154[M⁺], 136, 113, 95 (100), 69, 55, 41. Anal. Calcd for C₁₀H₁₈O: C, 77.87; H, 11.76. Found: C, 77.85; H, 11.29.