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SHORT SYNTHETIC PATHWAY TO 4-METHYLNONAN-1-OL, A RACEMIC ANALOG OF THE SEX PHEROMONE OF *Tenebrio molitor*

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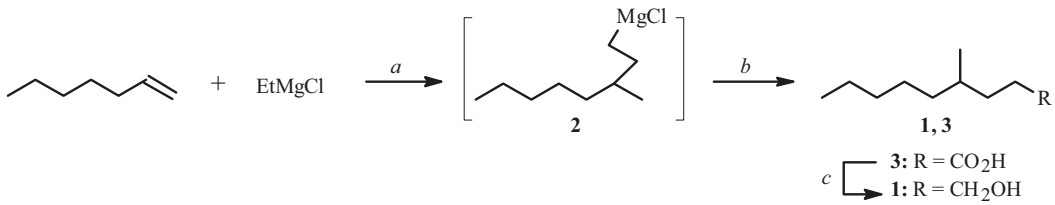
The sex pheromone of *Tenebrio molitor* L. (mealworm) was identified as 4*R*-methylnonan-1-ol [1], which is biologically active, and its racemic analog [2].

Known methods for synthesizing 4-methylnonan-1-ol (**1**) have multiple steps and in most instances use difficultly accessible compounds as starting materials. The yields of the target product are low [1, 3, 4].

We developed an effective synthetic method for the racemic analog of **1** that was based on the recently discovered regioselective reductive β-metalloethylation of alkenes using ethylmagnesium derivatives with tantalum complex catalysts [5, 6].

The reaction of hept-1-ene with EtMgCl in the presence of $TaCl_5$–$(i\text{-}OPr)_3P$ catalyst [EtMgCl–hept-1-ene–$TaCl_5$-$(i\text{-}OPr)_3P$, 24:20:1; $TaCl_5$-$(i\text{-}OPr)_3P$, 1:1; EtMgCl concentration 0.5 mM in THF; 20°C; 3 h] in THF at room temperature formed organomagnesium compound **2**. For this, a solution of EtMgCl (12 mmol) in THF (24 mL) was treated with hept-1-ene (10 mmol, 1.4 mL), $TaCl_5$ (0.2 g, 0.5 mmol), and $(i\text{-}OPr)_3P$ (0.1 g, 0.5 mmol). CO_2 was slowly passed through the resulting mixture at 0°C for 3 h. The mixture was treated with HCl solution (15 mL, 10%) to afford carboxylic acid **3** (1.7 g, 97%, bp 272°C at 750 mm Hg) with IR spectrum (ν, cm^{-1}): 1710; PMR spectrum (δ, ppm): 0.88–0.92 (2H, m), 1.16–1.52 (10H, m), 1.56–1.80 (1H, m), 2.28–2.38 (2H, m), 11.40 (1H, s); ^{13}C NMR spectrum (δ, ppm): 14.03, 19.75, 23.19, 28.30, 31.83, 31.97, 32.27, 33.10, 37.10, 179.37), which was extracted with Et_2O (3 × 50 mL). The extract was dried over anhydrous $MgSO_4$ and evaporated. The residue was dissolved in anhydrous Et_2O (10 mL), treated under Ar with $LiAlH_4$ (0.42 g, 11 mmol), refluxed for 2 h, treated with H_2O (10 mL), and extracted with Et_2O (3 × 50 mL). The extract was dried over Na_2SO_4 and evaporated to afford **1** (1.5 g, 95%) (Scheme 1).

The structure of **1** was elucidated using IR, PMR, and ^{13}C NMR spectral methods and GC-MS and comparisons with an authentic sample [4].



a. $TaCl_5(OP_n^i)_3P$, THF, 3 h; *b*. 1. CO_2, 2. HCl/H_2O; *c*. $LiAlH_4/Et_2O$

Scheme 1

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