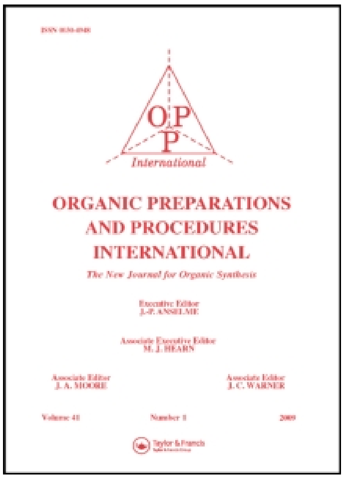

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AN IMPROVED SYNTHESIS OF 2,4-HEXADIEN-l-OL

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AN IMPROVED SYNTHESIS OF 2,4-HEXADIEN-1-OL[†]

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(12/20/91)

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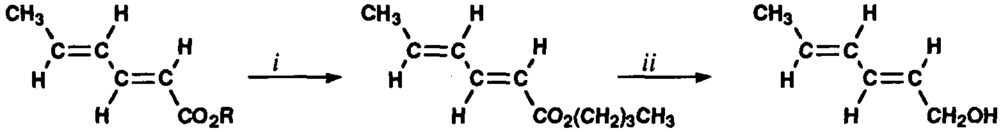
2,4-Hexadien-1-ol (**3**), an useful intermediate for the synthesis of 8 (E), 10 (E)-dodecadien-1-ol[1] which is a sex pheromone component of many insect species,[2] can be prepared from 2,4-hexadienoic acid (**1a**)[3] by reduction with lithium aluminum hydride, however, the yield is very poor (~10-15%). Although esters of **2** can be reduced with LAH in yields of 50%, hexanol is also formed in addition to the target compound (**3**). Red-Al [sodium *bis*(2-methoxyethoxy)aluminum hydride in toluene, 70%] which is a softer reagent,[4] produces a mixture of **3** and 2-methoxyethanol. The yield of **3** is about 90%. The standard procedures for Red-Al reduction of carbonyl compounds use solvents (THF, benzene) having boiling points near that of the product (**3**). For this reason, the separation of product and side-product distillation is rather difficult. We now report a modified procedure in which the same amount of toluene was used which can be found in Red-Al (about 30% of reagent). In this case, after reduction and quenching the reaction mixture with saturated aqueous sodium sulfate the mixture was filtered and the target compound **3** could be separated readily from the filtrate by distillation.



1 2 (95%) 3 (95%)

a) R = H, b) R = K

i) $CH_3(CH_2)_3Br$/Aliquat 336, 6 hrs, heating at reflux
ii) $NaAl(OCH_2CH_2OCH_3)_2H_2$ (in toluene), 0.5 hr, 25°

The starting material for this process was the potassium salt of sorbic acid (**1b**) which is an important material of can and food industry. The butyl ester derivative (**2**) of **1b** was formed using PTC conditions without solvent.[5]

EXPERIMENTAL SECTION

^1H NMR (400 MHz), and ^{13}C NMR (101 MHz) spectra were determined on a VARIAN XL-400 instrument using $CDCl_3$ as solvent. All signals were reported in ppm (δ) downfield from TMS, used as an internal standard. The GC analysis were carried out by HP 5890 Series II instrument with HP-1 capillary column (5 m x 0.53 mm i.d; df = 2.65 μm) and FID detector. Temp. of injector: 100°; temp. of detector: 250°; temp. of column: 50° for 3 min, then 5°/min to 250°. Carrier: N_2; 13 mL/min; split = 1:10.

Butyl 2,4-Hexadienoate (2).- To a mixture of butyl bromide (200 mL; 1.86 mol) and Aliquat 336 (7 mL; Aldrich) potassium salt of sorbic acid (**1b**; 100 g, 0.67 mol) was added with vigorous stirring. The resulting mixture was heated at reflux for 6 hrs and the precipitate formed was filtered off from the cooled mixture. The butyl 2,4-hexadienoate (**2**) was separated from the filtrate by distillation to yield 106 g (95%) colorless liquid, bp. 108-110°/14 mm, lit.[6] bp. 115°/16 mm; GC: t_{ret}: 10.3 min (**2**).
^1H NMR: δ 0.92 (t, J = 7 Hz, 3H, $-CH_3$ (in the ester group)); 1.20-1.80 (m, 4H, $-(CH_2)_2-$); 1.83 (dd, J(1) = 5.0 Hz, J(2) = 0.5 Hz, 3H, $=C-CH_3$); 4.14 (t, J = 6 Hz, 2H, $-OCH_2-$) 5.80 (dd, J(1) = 15.0 Hz, J(2) = 1.0 Hz, 1H, =CHC=O); 6.11 (m, 1H, -C(5)H=); 6.24 (m, 1H, -C(4)H=); 7.28 (dd + l.r., J(1) = 15.0 Hz, J(2) = 10.0 Hz, -C(3)H=).
^{13}C NMR: 167.28 (C-1), 119.25 (C-2), 144.83 (C-3), 129.97 (C-4), 139.00 (C-5), 18.59 (C-6), 64.06

(C-1'), 30.91 (C-2'), 19.27 (C-3'), 13.76 (C-4').

2,4-Hexadien-1-ol (3).- Red-Al^R (3.4 M solution of sodium *bis*(2-methoxyethoxy) aluminum hydride in toluene, 185 mL, 0.655 mol) was added to butyl 2,4-hexadienoate (**2**; 100 g; 0.595 mol) dropwise while stirring; the temperature of mixture was kept at 25°. The resulting mixture was stirred for 0.5 hr at room temperature and then quenched with a saturated solution of aqueous sodium sulfate (270 mL) with cooling and vigorous stirring. The precipitate formed was filtered off and the 2,4-hexadien-1-ol (**3**) was separated from the filtrate by distillation to yield 55 g (95%) of colorless liquid, bp. 81°/21 mm, lit.[7] bp. 76- 77°/12 mm; purity: 95%; GC: t_{ret}: 1.45 min (**1**), 0.46 min. ($HO(CH_2)_2OCH_3$), 0.63 min ($HO(CH_2)_5CH_3$).

^{1}H NMR: δ 1.49 (s, 1H, -OH, exchangeable with D_2O); 1.75 (d, J = 6.5 Hz, 3H, $-CH_3$); 4.15 (d, J = 5.5 Hz, 2H, $-CH_2O$); 5.70 (m, 2H, 2x-CH=); 6.05 (m, 1H, -CH=); 6.21 (m, 1H, -CH=).

^{13}C NMR: 62.7 (C-1), 131.29 (C-2), 129.73 (C-3), 129.23 (C-4), 131.41 (C-5), 18.04 (C-6).

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