

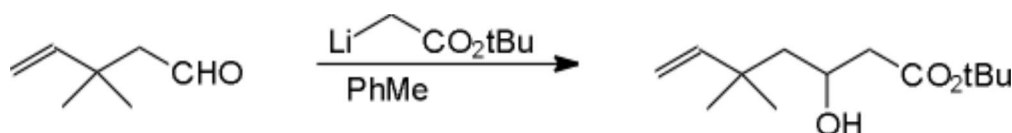
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tert-Butyl-3-hydroxy-5,5-dimethyl-6-heptenoate

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Scheme

As part of our continuing studies of stereocontrol during the intramolecular Diels-Alder (IMDA) reaction leading to medium rings [1-3], we have targeted poitediol [4] as a structure of interest accessible through this technology. Construction of a suitable IMDA trienone for model studies began with the preparation of the title compound from the known aldehyde [5]. Reformatsky reaction of the aldehyde with methyl bromoacetate in benzene or dimethoxymethane with or without mercuric chloride as a catalyst could not be accomplished. However, alkylation with lithio *tert*-butylacetate in toluene at 0 °C [6] provided the β-hydroxy ester in 54% unoptimized yield.

To a solution of lithio *tert*-butyl acetate (55 mg, 0.45 mmol) in dry toluene (1 ml) under Ar at room temperature, the aldehyde (43 mg, 0.38 mmol) in toluene (1 ml) was added. After 30 minutes, the reaction was quenched with sat aq Na₂SO₄ and concentrated to give, after flash chromatography (4 : 1 pet ether : ether), *tert*-butyl-3-hydroxy-5,5-dimethyl-6-heptenoate as a colorless oil, 48 mg, in 54 percent yield.

¹H NMR (CDCl₃): δ 5.48 (dd, J = 17.6, 10.7Hz, 1H), 4.95 (dd, J = 10.7, 1.3Hz, 1H), 4.92 (dd, J = 17.6, 1.3Hz, 1H), 4.03 (m, 1H), 2.29 (d, J = 6.3Hz, 2H), 1.6-1.3 (m, 2H), 1.41 (s, 9H), 1.03 (s, 6H).

IR (CH₂Cl₂): 3560, 2960, 1720, 1375, 1155.

MS (m/e): 213, 172, 154 (100), 128, 102, 94, 84, 70, 50.

HRMS: calc. for C₉H₁₆O₃ (M - C₄H₉): 172.1099; found: 172.1099.

References and Notes

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Sample Availability: No sample available.

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