

## HIGHLY STEREOSELECTIVE AND PRACTICAL SYNTHESIS OF (8E,10Z)-TETRADECADIEN-1-YL ACETATE, COMPONENT SEX PHEROMONE BLEND OF TENTIFORM LEAF-MINER PHYLLONORYCTER INSIGNITELLA

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The interest in biological methods for the control of insect pests has been intensified during the last two decades, and particularly so the interest in the use of the semiochemicals. These compounds have characteristic scent through which animal species, such as insects, communicate and which initiate a behavioural response or a biological activity. Some semiochemicals, mostly sex pheromones, for control of insect pests have also been commercially available for several years now. In contrast to the conventional chemical pesticides the activity of pheromones for this purpose is directed almost entirely to the specific insect pest, and as pheromones are naturally occurring substances they do not give rise to resistance problems. Hovever, for the wider application of the pheromones, the pheromone-based techniques should be made more effective and economical. It can be realised by designing more efficient and stereoselective methods of obtaining the pheromone. Here we want to present the new, very effective and highy stereoselective way of synthesis of (8E,10Z)-tetradecadien-1-yl acetate (1, the component of sex pheromone blend of P. insignitella<sup>1</sup>). The general strategy for the synthesis of acetate 1 is based on retrosynthetic analysis as shown in the scheme below. The key step of our method, a construction of the conjugated diene moiety, is based on Pd(0) catalyzed crosscoupling reaction of the vinyl iodide 2 with 1-pentynylmagnesium bromide (generated in situ from ethylmagnesium bromide).<sup>2</sup> Iodide 2 was prepared in 3 steps from the commercial 3-nonyn-1-ol by isomerisation to 8-nonyn-1-ol,<sup>3</sup> hydroxyl group protection with isobutene<sup>4</sup> and hydroalumination-iodination reaction<sup>4</sup> in 68% overall yield. Enyne 3 was converted to the corresponding acetate (in 90% yield) by treatment with an anhydrous acetic anhydride and FeCl<sub>3</sub>,<sup>4</sup> and finally the acetate was selectively reduced with activated Zn (galvanized with Cu)<sup>5</sup> to diene 1 in 90% yield and ca. 99% isomeric purity. The overall yield for the six-step sequence was above 50%.

$$0 \text{Ac} \Rightarrow \sqrt{\frac{1}{3}} \text{Ot-Bu} \Rightarrow \sqrt{\frac{1}{2}} \text{Ot-Bu} \Rightarrow \text{H}_3\text{C}(\text{CH}_2)_4\text{C} = \text{C}(\text{CH}_2)_2\text{OH}}$$

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