CHEMISTRY LETTERS, pp. 975-976, 1977. Published by the Chemical Society of Japan

# A SIMPLE SYNTHESIS OF 1-OCTEN-3-OL(MATSUTAKE ALCOHOL) BY THE TITANIUM-CATALYZED HIGHLY SELECTIVE REDUCTION OF THE BUTADIENE TELOMER WITH $LiAlH_4$

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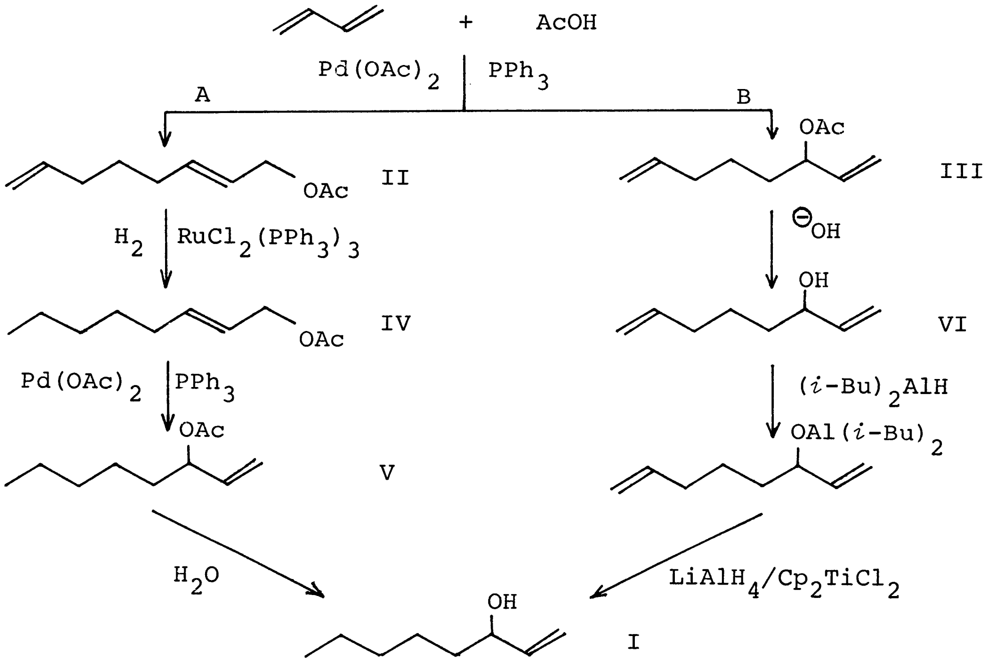
Treatment of 1,7-octadien-3-ol with di-iso-butylaluminum hydride, followed by highly selective reduction of $C_7$-olefin with $LiAlH_4$ catalyzed by dicyclopentadienyltitanium dichloride produced 1-octen-3-ol.

Selective reduction of double bonds under different steric environments is often very difficult, but an important and challenging problem in organic synthesis. We now wish to report a highly selective reduction of one of two terminal double bonds in 1,7-octadien-3-ol(VI), leading to a very simple synthesis of Matsutake alcohol(1-octen-3-ol (I)), contained in Japanese mushroom. Synthesis of this alcohol has been reported by combining two smaller carbon units. Reactions of pentyl Grignard reagent with acrolein[1-3] and vinyl Grignard reagent with hexanal[4] were carried out. Another method is the Friedel-Crafts reaction of hexanoyl chloride with ethylene.[5] We have reported the synthesis of the alcohol from the easily available 2,7-octadienyl acetate (II). Palladium catalyzed telomerization of butadiene with acetic acid produces two unsaturated $C_8$ acetates II and III.[6] Selective hydrogenation of the terminal olefin of II to give IV catalyzed by $RhCl(PPh_3)_3$ or better $RuCl_2(PPh_3)_3$, followed by palladium catalyzed allylic rearrangement of IV, produced acetate of Matsutake alcohol V (Method A).[7]



However, it is apparent that the other telomer III has the more suitable functionality for the synthesis of Matsutake alcohol, if the selective reduction of the terminal $C_7$ olefin without attacking the other teminal $C_1$ olefin could be done cleanly. This type of selective reduction seems to be nearly impossible by common methods of reduction. Attempted homogeneous hydrogenation of III and VI with the Rh and Ru complexes was not selective. Now we have succeeded in this highly selective reduction of $C_7$ olefin of VI with $LiAlH_4$ and achieved the simple, one pot synthesis of Matsutake alcohol (Method B).

Our method utilizes a new method of hydroalumination of olefins with $LiAlH_4$ catalyzed by titanium compounds. Recently Sato and coworkers reported that hydroalumination of olefins with $LiAlH_4$ proceeds easily by the catalysis of titanium compounds.[8,9] The hydroalumination products are converted into reduced products in a high yield by treatment with dilute aqueous acid. The characteristic point of this method is a high selectivity observed when there are two double bonds under different steric environments.

In our synthesis, the two double bonds in III or VI must be differentiated in the hydroalumination reaction. We considered that the hydroxy group at $C_3$ plays a key role and found that the conversion of the hydroxy group to dibutylaluminum alkoxide by the reaction of diisobutylaluminum hydride not only protects the hydroxy group but also masks the neighbouring $C_1$ double bond for the reduction.

A heptane solution of dibutylaluminum hydride (11.0 mmol) was added dropwise to a THF solution of 1,7-octadiene-3-ol (1260 mg, 10 mmol) at 0°C until hydrogen evolution stopped. Then $LiAlH_4$ (126 mg, 3.3 mmol) and dicyclopentadienyltitanium dichloride (124.4 mg, 0.5 mmol) were added and the deep violet solution was stirred for 1 h at 0°C and 12 h at 25°C. The reaction mixture was quenched at 80% conversion with dilute hydrochloric acid and extracted with dichloromethane. The solvent was evaporated and column chromatography of the residue gave Matsutake alcohol (970 mg). Gas chromatographic analysis (PEG 20M on Celite 545) showed the product was 86% pure and contained 3-octanol (11%) and 7-octen-3-ol (3%). The Matsutake alcohol was further purified by preparative gas chromatography and identified by comparison of spectral data with those of an authentic sample.[7]

IR (film): 3350 (OH) and 920 $cm^{-1}$ ($CH_2$=); NMR ($CCl_4$) $\delta$ 0.90 (t, 3H, $\underline{CH_3}CH_2$-), 1.36 (m, 8H, $-(CH_2)_4-$), 1.96 (s, 1H, -OH), 4.07 (m, 1H, $\underline{CH}$OH), 4.90-5.40 (m, 2H, $\underline{CH_2}$=), and 5.55-6.20 (m, 1H, -CH=).

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(Received June 20, 1977)