# Preparation of Matsutake Alcohol (1-Octen-3-ol) from a Butadiene Telomer

Jiro TSUJI, Katsuhiko TSURUOKA, and Keiji YAMAMOTO

*Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152*

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A simple preparation of 1-octen-3-ol so called Matsutake alcohol using a butadiene telomer is described: selective hydrogenation of the terminal double bond of 2,7-octadienyl acetate gave 2-octenyl acetate which was converted *via* palladium-catalyzed allylic rearrangement and hydrolysis into 1-octen-3-ol.

Naturally occurring *l*-1-octen-3-ol is known as Matsutake alcohol.[1] The racemic form of this alcohol has been prepared by a reaction of pentylmagnesium bromide with acrylaldehyde, and resolved.[1,2] Two other procedures have been reported which involve Friedel-Crafts reaction of hexanoyl chloride with ethylene[3] and Grignard reaction of vinyl bromide with hexanal.[4]

As part of studies on the utilization of butadiene telomers[5] for organic synthesis, we wish to describe a simple preparation of *dl*-1-octen-3-ol starting from 2,7-octadienyl acetate(**1**), which is readily obtained, along with 1-vinyl-5-hexenyl acetate(**2**), by the palladium-catalyzed telomerization of butadiene with acetic acid (Eq. 1).[6]

$$2CH_2{=}CH{-}CH{=}CH_2 + AcOH \xrightarrow{(Pd)} \underset{\mathbf{1}}{CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2OAc} + \underset{\mathbf{2}}{CH_2{=}CHCH_2CH_2CH_2CH(OAc)CH{=}CH_2} \quad (1)$$

The compound **2** seemed to be the most suitable precursor of 1-octen-3-ol. However, attempted homogeneous hydrogenation of **2** catalyzed by chlorotris(triphenylphosphine)rhodium(I) in a benzene solution did not proceed selectively, and a mixture of three possible hydrogenation products was formed even at 40% conversion.

It has been found that **1** is readily equilibrated with **2** in a ratio of *ca.* 3 : 1 by way of an allylic rearrangement under the influence of the palladium catalyst. Therefore, **1** may be a suitable starting material for 1-octen-3-ol, if a sequence of partial hydrogenation and the rearrangement of the acetoxyl group shown below is possible.

$$CH_2{=}CH(CH_2)_3CH{=}CHCH_2OAc \longrightarrow \underset{\mathbf{1}}{} \quad CH_3(CH_2)_4CH{=}CHCH_2OAc \xrightarrow{\text{-O-}} \underset{\mathbf{3}}{} \quad CH_3(CH_2)_4CH(OAc)CH{=}CH_2 \quad \mathbf{5}$$

Thus **1** was hydrogenated at room temperature in the presence of chlorotris(triphenylphosphine)rhodium-(I) (0.5—1.0 mol%) in purified benzene under hydrogen pressure (17.5 kg/cm$^2$ initial pressure). Analysis of the reaction mixture by GLC showed the formation of 2-octenyl acetate(**3**) as a main product and octyl acetate(**4**) as a minor product in a ratio of 80 : 20 at about 90% conversion. This result is satisfactory for preparative purpose.

The selectivity for partial hydrogenation of **1** apparently depends on the conversion as shown in Table 1. The results indicate that the rate difference is rather small in the consecutive hydrogenation of the terminal and the internal olefinic bonds of **1**. Attempts to improve the selectivity for partial hydrogenation of **1** by using a cationic rhodium complex, $[(NBD)Rh(PPhMe_2)_2]^+ClO_4^-$ (NBD=norbornadiene),[7] were fruitless.

The distilled product containing both **3** and **4** was then subjected to allylic 1,3-shift of the acetoxyl group. When palladium acetate (3 mol%) combined with three equivalents of triphenylphosphine was used as a catalyst in the presence of potassium acetate in *t*-butyl alcohol, **3** was readily equilibrated with 3-acetoxy-1-octene(**5**) in 3 h at 70 °C in a ratio of 1.9 : 1.0 on the basis of GLC, while **4** remained intact. The lower boiling **5** was isolated by distillation, further purified by preparative GLC and characterized by NMR and IR spectra (see Experimental). The mixture of **3** and **4** undistilled was again subjected to the conversion into **5** under the same conditions as above. In preparative scale synthesis, the lower boiling product **5** can be continuously distilled out by fractionation, while the rearrangement of the higher boiling **3** to **5** proceeds in the vessel containing the active catalyst system to completion.

Finally, **5** was hydrolyzed in aqueous methanolic alkali to give 1-octen-3-ol in a high yield.

TABLE 1. SELECTIVE PARTIAL HYDROGENATION OF 2,7-OCTADIENYL ACETATE (**1**) CATALYZED BY $ClRh(PPh_3)_3$ AT ROOM TEMPERATURE

| Conditions | | Conversion of **1** (%) | Product ratio[a] | |
|---|---|---|---|---|
| Catalyst concentration (mol%) | Initial pressure of $H_2$ (kg/cm$^2$) | | **3** | **4** |
| 1.0 | 6.0 | 39 | 96 | 4 |
| 1.0 | 17.5 | 47 | 92 | 8 |
| 1.0 | —[b] | 52 | 94 | 6 |
| 0.5 | 17.5 | 79 | 85 | 15 |
| 0.5[c] | 17.5 | 89 | 82 | 18 |
| 0.5 | 17.5 | 91 | 79 | 21 |
| 0.5 | 17.5 | 95 | 75 | 25 |

a) Determined by GLC. b) Normal pressure. c) $(1/2[(C_6H_{10})RhCl]_2 + Ph_2PCH_2CH_2PPh_2)$ prepared *in situ*.

## Experimental

*Materials.* Fractionally distilled 2,7-octadienyl acetate(**1**) (bp 106.5 °C/24 mmHg) was still contaminated with a small amount (*ca.* 6%) of unidentified material,

whereas 1-vinyl-5-hexenyl acetate(**2**) (bp 92.0 °C/24 mmHg) was pure by GLC.

*GLC Analysis.* A column (3 mm×3 m) packed with 20% UCON oil (50 HB-2000) on Celite (60—80 mesh) was used at 140 °C with 0.8 kg/cm² (40 ml/min) of hydrogen as a carrier gas. Under these conditions, **1** eluted in 11.3 min while **2** in 5.7 min, and all hydrogenation products were satisfactorily separated from each other.

*Attempted Partial Hydrogenation of 2.* In a 100 ml glass vessel flushed with dry nitrogen was placed a solution of 0.45 g (2.7 mmol) of **2**, 25 mg ($2.7\times10^{-2}$ mmol) of $ClRh(PPh_3)_3$ in 5 ml of purified benzene. The mixture was shaken at room temperature under hydrogen atmosphere for 4 h. GLC analysis showed that the product contains **2**, **5** (and/or 1-ethyl-5-hexenyl acetate, and 1-ethylhexyl acetate in the ratio 62 : 21 : 18. 3-Octyl acetate was obtained independently by thorough hydrogenation of **2** using 5% Pd-C in benzene–ethanol solution.

*Partial Hydrogenation of 1.* The following is typical: In a 100 ml-micro autoclave were placed 9.09 g (54 mmol) of **1**, 250 mg (0.27 mmol, 0.5 mol%) of $ClRh(PPh_3)_3$, and 30 ml of pure benzene. Hydrogen (17.5 kg/cm²) was charged after purging air twice with hydrogen and the mixture was magnetically stirred for 5 h. GLC analysis of the reaction mixture indicated the presence of **3** and **4** in a ratio of 75 : 25 at 95% conversion of **1**. Two other very minor unidentified products were detected by GLC. Another run under 40 kg/cm² of initial hydrogen pressure gave exactly the same results as above. The product ratio of **3** to **4** decreased with the increasing conversion of **1** as shown in Table 1. Benzene was removed by evaporation and the residue was distilled *in vacuo* to give 7.52 g of a mixture of **3** and **4**, bp 96—97 °C/17 mmHg.

*Rearrangement of 3 to 5.* To a mixture of 0.297 g (1.3 mmol) of palladium acetate, 1.04 g (4.0 mmol) of triphenylphospine, 4.32 g (44 mmol) of potassium acetate and 2.65 g (44 mmol) of acetic acid in 50 ml of *t*-butyl alcohol was added 7.52 g of the above distillate in one portion. The mixture was heated at 70 °C with stirring for 3 h, during which time **3** gradually rearranged into **5** to attain an equilibrium. The reaction mixture was poured into 50 ml of water, extracted three times with hexane. GLC showed the extracts to contain **5** and **3**, in the ratio 1 : 1.9, in addition to **4**. The acetates (5.20 g) were obtained by flush-distillation (~60 °C/4 mmHg). The combined distillate (10.38 g) of two runs was fractionally distilled to give 2.50 g of almost pure **3**, bp 82—84 °C/13 mmHg, which was further purified by preparative GLC. NMR($CCl_4$, $\delta$) 0.89 (deformed t, 3H, $\underline{CH_3}CH_2$), 1.34 (br, s, 8H, $(\underline{CH_2})_4$), 1.99 (s, 3H, $\underline{CH_3}CO$), and 4.97—6.04 ppm (m, 4H, $\underline{CH}OAc$ and $\underline{CH}=\underline{CH_2}$). IR (film) 1750($\nu_{CO}$) and 1240 cm$^{-1}$($\delta_{CO}$).

The remainder in the pot-still (7.50 g), containing **3**, **4**, and **5** in a ratio of 53 : 40 : 7, was again treated with palladium acetate (3 mol%) in the same manner as indicated above to give **3** by equilibration. Higher temperature (90 °C) for the catalyzed 1,3-shift was found to cause considerably the elimination of the acetoxyl group from **5** to form 1,3-octadiene.

Hydrolysis of **5** with 1 M potassium hydroxide in aqueous methanol (1/1) gave nearly quantitatively 1-octen-3-ol, which was purified by preparative GLC. NMR and IR spectra of 1-octen-3-ol were in good accord with those reported previously.[4] NMR ($CCl_4$, $\delta$) 0.90 (deformed t, 3H, $\underline{CH_3}$-$CH_2$), 1.36(br.s, 8H, $(\underline{CH_2})_4$), 2.15 (s, 1H, $\underline{OH}$), 4.00 (m, 1H, $\underline{CH}OH$), 4.95—5.25 (m, 2H, $\underline{CH_2}$=), and 5.56—6.10 ppm (m, 1H, -$\underline{CH}$=). IR(film) 3400 ($\nu_{OH}$) and 920 cm$^{-1}$ ($\delta_{CH_2=}$).

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