A New Synthesis of (−)-*β*-Pinene from (−)-*α*-Pinene

Yang-Fu MIN, Bao-Wen ZHANG, Yi CAO*

Institute of Photographic Chemistry, Academia Sinica, Beijing, People's Republic of China

Pyrolysis of *β*-pinene gives myrcene which is an important raw material in perfume industry. Unfortunately, the content of *α*-pinene in natural turpentine oil is high (about 80%), but that of *β*-pinene is very low. This led us to search for a simple method of obtaining *β*-pinene from *α*-pinene. There are many patents on the conversion of *α*-pinene to *β*-pinene. The most popular method, metal-catalyzed isomerization of *α*-pinene, gives a yield of only 3-7%[1]. A method for this conversion through an organoborane intermediate has been reported but no yield data were given[2]. Recently, a four-step synthesis of *β*-pinene from *α*-pinene has been reported[3], with an overall yield of 25%. In this paper, we report a novel method for this conversion.

Photooxygenation ($^1O_2$) of alkyl-substituted olefins gives rise to the allylic hydroperoxides with the double bond shifted[4], which are subsequently transformed to the corresponding allylic alcohols on reduction[4]. It has been reported that hydrogenolysis of allylic alcohol with lithium aluminium hydride/aluminium chloride or lithium aluminium hydride/titanium tetrachloride gives alkenes[5,6,7]. We have applied these two reactions to effect an efficient conversion of *α*-pinene to *β*-pinene with an overall yield higher than any previously reported procedure.

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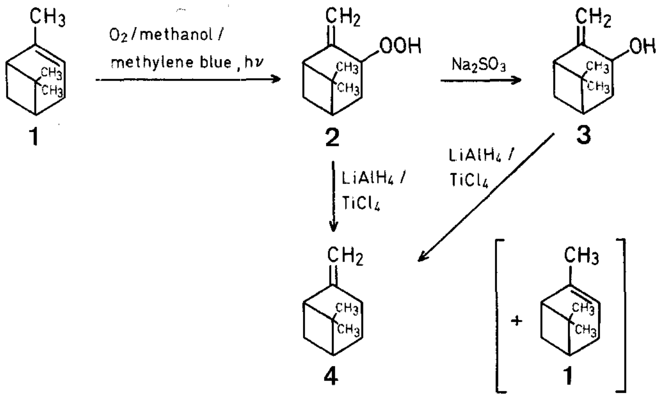

Photooxygenation of (−)-α-pinene (**1**) in methanol in the presence of methylene blue produced the corresponding hydroperoxide (**2**) which was reduced with sodium sulfite to pinocarveol (**3**)[8,9] in 75% yield. Hydrogenolysis of **3** with lithium aluminium hydride/titanium tetrachloride gave (−)-β-pinene (**4**) in 53% yield after separation from (−)-α-pinene by distillation. The overall yield of (−)-β-pinene from (−)-α-pinene is 40% in two steps. This conversion could also be conveniently accomplished by treatment of **2** directly with lithium aluminium hydride/titanium tetrachloride. The yield of (−)-β-pinene after distillative purification is 42% (purity: 93% by G.L.C.).

G.L.C. analysis of the crude product in both cases indicated that α-pinene was present in the reaction mixture, 16% in the hydrogenolysis of the hydroperoxide and 13% in the hydrogenolysis of pinocarveol. G.L.C. analysis of **2** and **3** did not show the presence of α-pinene. Basic as well as acidic work-up after hydrogenolysis gave similar ratios of α-pinene : β-pinene. An authentic sample of β-pinene (94% purity by G.L.C.) did not isomerize to α-pinene on washing with 2 normal hydrochloric acid. All these data seem to imply that α-pinene is a by-product of the lithium aluminium hydride/titanium tetrachloride hydrogenolysis of **2** as well as of **3**. However, α-pinene can be satisfactorily removed if distillation is carried out carefully.

G.L.C. analyses were carried out using a Shanghai Fen Xi Yi Qi Chang Model 100 Gas Chromatograph. A 1 m × 4 mm (internal diameter) column with 10% Carbowax 20M on 60–80 mesh Chromasorb G NAW was used for analysis of pinocarveol. A 2 m × 4 mm (internal diameter) column with 25% di-*n*-decyl phthalate was used for analysis of α-pinene and β-pinene. I.R. spectra were recorded on a Perkin-Elmer Model 577 spectrophotometer. N.M.R. spectra were taken using a Varian XL-200 instrument. Mass spectra were recorded on a Finnigan Model 4021C mass spectrometer.

Pinocarveol (3):

A solution of (−)-α-pinene (**1**; 13.9 g, 0.1 mol) and methylene blue (0.2 g) in methanol (300 ml) is poured into a photochemical reactor (ACE Glass, Incorporated). A slow stream of oxygen is passed through the solution while it is irradiated with a 500W iodine-tungsten lamp. The temperature of the solution is maintained at 28 °C by passing water through the lamp holder. After 30 h the dye becomes slightly bleached and irradiation is stopped. The solution is evaporated in a rotary evaporator to 50 ml, which is then added dropwise to an aqueous solution of sodium sulfite (25 g in 150 ml) while being cooled in an ice-bath. After the addition, the mixture is stirred at room temperature for 12 h. The solution is extracted with ether. The ethereal solution is dried with anhydrous potassium carbonate. Evaporation of the solution under vacuo using a rotary evaporator yields an oil which is distilled under reduced pressure to give **3**; yield: 11.7 g (75%); b.p. 59–60 °C/2 torr.

M.S.: $m/e = 152$ (M^+), 135.

I.R. (neat film): $\nu = 3395, 3068, 1646, 899\ \text{cm}^{-1}$.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 5.01$ (s, 1 H); 4.90 (s, 1 H); 4.42 (d, $J = 7.0$ Hz, 1 H); 2.50–1.73 (m, 6 H); 1.27 (s, 3 H); 0.64 ppm (s, 3 H).

Hydrogenolysis of Pinocarveol (3):

To a stirred solution of titanium tetrachloride (3.4 ml, 30 mmol) in anhydrous tetrahydrofuran (100 ml), is added lithium aluminium hydride (4 g, 105 mmol) in an argon atmosphere while being cooled in an ice-bath. To the resulting black mixture is added a solution of **3** (2 g, 13 mmol) in anhydrous tetrahydrofuran (20 ml). The resulting mixture is refluxed for 4 h. Excess hydride reagents are decomposed by addition of 2 normal hydrochloric acid. The aqueous mixture is extracted with ether. The organic extract is washed with saturated aqueous sodium hydrogen carbonate solution and water, and dried with anhydrous potassium carbonate. Evaporation of the solvent gives a yellow oil; yield: 1.95 g.

The whole procedure is repeated and vacuum distillation (14 cm Vigreux column) is carried out on the crude products of both reactions to give (−)-β-pinene (**4**); yield: 1.9 g (53%); b.p. 63.5–64.5 °C/23 torr (Ref.[3], b.p. 70–71 °C/28 torr); purity: 94% by G.L.C. Other spectral data are identical to an authentic sample of (−)-β-pinene (Carl Roth OHG).

Hydrogenolysis of Hydroperoxide (2):

(−)-α-Pinene (**1**; 1.98 g, 14 mmol) and methylene blue (0.03 g) are dissolved in methanol (50 ml). The resultant solution is placed in a photochemical reactor (ACE Glass, Incorporated). A slow stream of oxygen is passed through the solution while it is irradiated with a 500 W iodine-tungsten lamp. The temperature of the solution is maintained at 28 °C by passing water through the lamp holder. After 30 h the dye becomes slightly bleached and irradiation is stopped. The solution is evaporated using a rotary evaporator to dryness. The resulting viscous blue oil (2.8 g) is reduced according to the procedure for the hydrogenolysis of pinocarveol except that the amount of lithium aluminium hydride is increased to 4.4 g (128 mmol). The yield of (−)-β-pinene is 42%.

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