trans-Pinocarveol from New Zealand Turpentine

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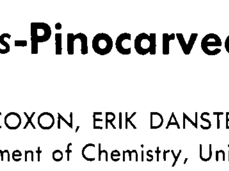
The conversion of β-pinene into *trans*-pinocarveol using only catalytic amounts of selenium dioxide is described.

TWO METHODS for the conversion of β-pinene into *trans*-pinocarveol (1) have been described (*2, 4*). The reaction of β-pinene with lead tetraacetate followed by hydrolysis gives a mixture of myrtenol (2) and *trans*-pinocarveol (1), from which the latter may be separated with difficulty in 32% yield (*2*). Oxidation of β-pinene with molar quantities of selenium dioxide gives *trans*-pinocarveol (1) in yields of 25 to 62% (*4*). The use of this procedure for large-scale reactions is complicated by the formation of large quantities of selenium and organoselenides.


(1)


(2)

trans-Pinocarveol (1) can also be prepared in a yield of 35% from α-pinene by photosensitized oxidation, followed by reduction of the corresponding hydroperoxide (*5*) and from α-pinene oxide—92% yield—by reaction with lithium-diethylamine (*1*).

A procedure is now reported for the preparation of *trans*-pinocarveol (1) from β-pinene or from New Zealand turpentine—(−)β-pinene, 67.6%; α-pinene, 30.2%; dipentene, 1.5%; camphene, 0.5%; myrcene, 0.2%—using only catalytic amounts of selenium dioxide. Regeneration of the selenium dioxide *in situ* is achieved using hydrogen peroxide in a two-phase or a one-phase (*tert*-butanyl alcohol cosolvent) system. This procedure significantly improves the availability of (+) *trans*-pinocarveol (1) from (−)β-pinene containing raw materials.

EXPERIMENTAL

Example 1. New Zealand sulfate turpentine—816 grams, 6 moles; (−)β-pinene, 67.6%; α-pinene, 30.2%; dipentene, 1.5%; camphene, 0.5%; myrcene, 0.2%—was added to a stirred solution of selenium dioxide (4 grams, 36 mmoles) in aqueous hydrogen peroxide (517 ml., 35%), and the reaction mixture stirred at 50° C. for 6 hours. The organic layer was separated, washed 3 times with 100 ml. of water, and dried. Fractional distillation of this product through a 25- × 1.5-cm. glass helix column under reduced pressure gave recovered turpentine—253 grams; β-pinene, 30.3%; α-pinene, 67.5%; dipentene, 1.5%; camphene, 1.0%—and *trans*-pinocarveol (224 grams; 44% based on β-pinene consumed), n_D^{21} 1.4964, $[\alpha]_D^{CHCl_3}$ + 51.8° (*c* 1.05), purity 95% by gas-liquid chromatography on columns with 3% Carbowax 20M on Chromosorb G, 60-80. Purification by preparative gas-liquid chromatography gave material $[\alpha]_D^{CHCl_3}$ + 59.9° (*c* 1.01), n_D^{20} 1.4965. Literature values (*6*), n_D^{20} 1.4963, $[\alpha]_D$ + 59° and (*3*), n_D^{21} 1.4995, $[\alpha]_D$ + 67°.

Example 2. Hydrogen peroxide (70 ml.; 50%) was added over 90 minutes to a solution of β-pinene (136 grams; $[\alpha]_D^{CHCl_3}$ − 17°, *c* 1.00) and selenium dioxide (1.48 gram) in *tert*-butanyl alcohol (150 ml.). The stirred mixture was kept at 40° C. for 3½ hours. Benzene (100 ml.) was added and the organic layer washed three times with 100-ml. portions of saturated ammonium sulfate solution, dried, and a small amount of hydroquinone added. Fractional distillation (as above) under reduced pressure gave *trans*-pinocarveol (74 to 84 grams), n_D^{22} 1.4971, $[\alpha]_D^{CHCl_3}$ + 48° (*c* 1.04), purity 95% by gas-liquid chromatography.

LITERATURE CITED

(1) Crandall, J.K., Chang, Luan-Ho, *J. Org. Chem.* **32**, 435 (1967).
(2) Hartshorn, M.P., Wallis, A.F.A, *J. Chem. Soc.* **1964**, 5254.
(3) Joshel, L.M., Palkin, S., *J. Am. Chem. Soc.* **64**, 1008 (1942).
(4) Quinn, J.M., J. CHEM. ENG. DATA **9**, 389 (1964).
(5) Schenck, G.O., Eggert, H., Denk, W., *Ann. Chem.* **584**, 177 (1953).
(6) Schmidt, Harry, *Chem. Ber.* **62**, 189 (1929).

RECEIVED for review December 12, 1968. Accepted November 21, 1969.