



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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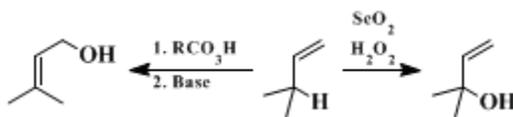
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

3600 medium, 3460 broad, medium, 1645 medium; $^1\text{H NMR}$ (CCl_4), δ (multiplicity, coupling constant J in Hz., number of protons): 0.63 (s, 3H), 1.26 (s, 3H), 1.6–2.5 (m, 6H), 2.88 (s, 1H, OH), 4.33 (approx. d, $J = 7$, 1H), 4.74 (approx. s, 1H), 4.96 (approx. s, 1H).

3. Discussion

trans-Pinocarveol is an important intermediate in the preparation of substituted pinane systems. It has been prepared by oxidation of β -pinene with lead tetraacetate and hydrolysis of the corresponding ester (32%);² by photosensitized oxidation of α -pinene, followed by reduction of the corresponding hydroperoxide (35%);³ by oxidation of β -pinene with molar quantities of selenium dioxide (53–64%);⁴ and by epoxidation of α -pinene followed by isomerization with a variety of bases, of which lithium diethylamide (74–80% yield over the two steps) is best.⁵

The present procedure is a convenient, one-step method of preparing optically active *trans*-pinocarveol. Although lower in yield than the lithium diethylamide procedure, it is more readily adaptable to large-scale work. Moreover, the two methods are complimentary in the conditions required (neutral vs. basic) and in the overall transformation accomplished:



Since only catalytic quantities of selenium dioxide are required, the danger of handling large quantities of this material (Note 1) is avoided. Furthermore, the problems associated with the formation of selenium and organoselenides, which commonly arise in oxidations using molar quantities of selenium dioxide, are not encountered.

References and Notes

1. Department of Chemistry, University of Canterbury, Christchurch 1, New Zealand.
2. M. P. Hartshorn and A. F. A. Wallis, *J. Chem. Soc.*, 5254 (1964).
3. G. O. Schenck, H. Eggert, and W. Denk, *Justus Liebigs Ann. Chem.*, **584**, 177 (1953).
4. J. M. Quinn, *J. Chem. Eng. Data*, **9**, 389 (1964).
5. J. K. Crandall and L. C. Crawley, *Org. Synth.*, **Coll. Vol. 6**, 948 (1988) and references cited therein.

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

trans-Pinocarveol

Benzene (71-43-2)

methanol (67-56-1)

hydroquinone (123-31-9)

sodium sulfate (7757-82-6)

selenium dioxide (7446-08-4)

hydrogen peroxide (7722-84-1)

ammonium sulfate (7783-20-2)

selenium

tert-butyl alcohol (75-65-0)

lithium diethylamide

Bicyclo[3.1.1]heptan-3-ol, 6,6-dimethyl-2-methylene-, (1 α ,3 α ,5 α)-

α -pinene (7785-70-8)

β -pinene (18172-67-3)

lead tetraacetate (546-67-8)