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A STEREOSELECTIVE 1,3-TRANSPOSITION REACTION OF ALLYLIC ALCOHOLS

Arata Yasuda, Hisashi Yamamoto,* and Hitosi Nozaki
Department of Industrial Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

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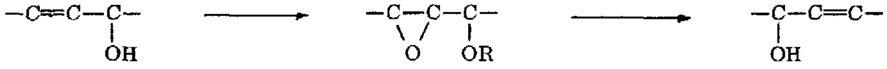
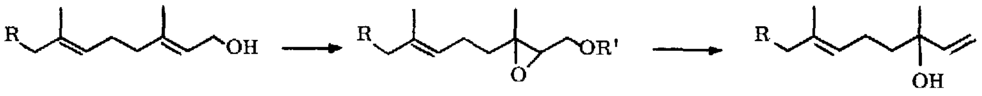
Although many conceptually different approaches for stereoselective preparation of allylic alcohols have been explored with considerable success,[1] the importance of the allylic alcohol moiety in organic synthesis makes the ability to relocate it within a molecule an important and challenging problem.

We have devised a new approach of some generality for the solution of this synthetic problem. The approach is schematized by the conversion **A** → **D**, involving the use of reductive elimination of epoxy mesylate **C**, which is efficiently prepared from allylic alcohol **A** with high stereospecificity by transition metal catalyzed epoxidation[2] followed by mesylation.[3,4]



A **B**: R = H; **C**: R = SO_2Me **D**

The representative procedure is illustrated by the transformation of geraniol (**1a**) to linalool (**4a**).[5] 2,3-Oxidogeraniol (**2a**), readily prepared from epoxidation of geraniol (**1a**) with the $VO(acac)_2$-t-BuOOH reagent,[2a] is treated with triethylamine (1.2 equiv) followed with methanesulfonyl chloride (1.2 equiv) in methylene chloride at -26° for 1 hr to furnish (94%) the epoxy mesylate **3a**.[6] Freshly cut sodium is added in small pieces to a mixture of the epoxy mesylate **3a**, tetrahydrofuran, and liquid ammonia at -35 to -37° (cooling bath temperature), until the blue color persists. After another 10 min, solid ammonium chloride is added and the ammonia is left to evaporate. Work-up in the usual way gives linalool (**4a**), in 88% yield.[7] Treatment of **3a** with sodium-naphthalene in tetrahydrofuran at room temperature for 10 min[8] also gives a respectable yield (83%) of linalool. Similarly, nerolidol (**4b**) is obtained by reaction of the epoxy mesylate **3b** (79% from farnesol (**1b**)) dissolved in liquid ammonia-tetrahydrofuran with sodium in 87% yield.[7]

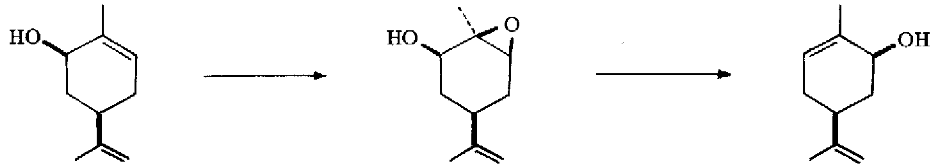


1a: R = H
1b: R = $Me_2C{=}CHCH_2$

2a: R = R' = H
2b: R = $Me_2C{=}CHCH_2$, R' = H
3a: R = H, R' = Ms
3b: R = $Me_2C{=}CHCH_2$, R' = Ms

4a: R = H
4b: R = $Me_2C{=}CHCH_2$

The versatility of this procedure is particularly well demonstrated by the transformation of (-)-cis-carveol (5) to (+)-cis-carveol (8). Thus, (-)-cis-carveol(5)[9] is selectively oxidized to the cis-epoxy alcohol 6[10] by the vanadium reagent. Dissolving sodium metal reaction with the mesylate 7 furnishes 57% yield of (+)-cis-carveol (8).[11] Employed a series of reactions which paralleled described above, (+)-cis-carveol (8)[12] is transformed into (-)-cis-carveol (5).[13]



5

6, R = H

7, R = Ms

8

REFERENCES AND NOTES

1. (a) J. Reucroft and P. G. Sammes, Quart. Rev. (London), 25, 135 (1971); (b) R. S. Lenox and J. A. Katzenellenbogen, J. Amer. Chem. Soc., 95, 957 (1973); (c) K. B. Sharpless and R. F. Lauer, ibid., 95, 2697 (1973); (d) A. Yasuda, S. Tanaka, K. Oshima, H. Yamamoto, and H. Nozaki, ibid., 96, 6513 (1974).
2. (a) K. B. Sharpless and R. C. Michaelson, J. Amer. Chem. Soc., 95, 6136 (1973); (b) S. Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson, and J. D. Cutting, ibid., 96, 5254 (1974).
3. For some interesting reports on the reductive elimination of mesylate groups, see (a) J. C. Carnahan, Jr. and W. D. Closson, Tetrahedron Lett., 3447 (1972); (b) S. Bank and M. Platz, ibid., 2097 (1973), and references therein.
4. Replacing the mesylate group with benzoate or phosphonate group is tested without any success.
5. Several related methods were reported for preparing linalool from derivatives of geraniol; (a) from citral, G. V. Nair and G. D. Pandit, Tetrahedron Lett., 5097 (1966); (b) from geranyl iodide, S. K. Pradhan and V. M. Girijavollabhan, ibid., 3103 (1968).
6. All new compounds give nmr and ir spectral data in agreement with the indicated structure.
7. Identical in all respects with an authentic sample.
8. The best method is to add the epoxy mesylate to an approximately 0.3 M solution of sodium-naphthalene in THF with stirring, dropwise over a period of 10 min, see ref. 3a.
9. Prepared from (-)-carvone by reduction with LiAlH$_4$, $[\alpha]^{25}$D -26.4 (c 5.6,EtOH). From the reported rotation at 25° of +22.8° for (+)-cis-carveol , and +202° for (+)-trans-carveol (R. G. Johnson and J. Read, J. Chem. Soc., 233 (1934)), the product mixture is estimated to contain 98% of (-)-cis-carveol; see also H. G. Kuivila and O. F. Beumel, Jr., J. Amer. Chem. Soc., 83, 1246 (1961).
10. > 94% pure by glpc analysis.
11. $[\alpha]^{25}$D +37.0 (c 4.3, EtOH) ; containing 92% of (+)-cis-carveol.
12. $[\alpha]^{25}$D +35.9 (c 5.6, EtOH) ; containing 92% of (+)-cis-carveol.
13. $[\alpha]^{25}$D -23.0 (c 5.6, EtOH) ; containing 100% of (-)-cis-carveol.