Tetrahedron Letters,Vol.24,No.35,pp 3741-3744,1983
Printed in Great Britain

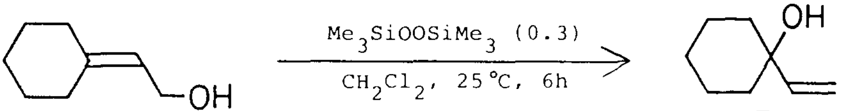
0040-4039/83 $3.00 + .00
©1983 Pergamon Press Ltd.

ISOMERIZATION OF PRIMARY ALLYLIC ALCOHOLS TO TERTIARY ONES BY MEANS OF $Me_3SiOOSiMe_3$-$VO(acac)_2$ CATALYST

Seijiro Matsubara, Kazuhiko Takai,* and Hitosi Nozaki
Department of Industrial Chemistry, Faculty of Engineering
Kyoto University, Yoshida, Kyoto 606, Japan

Abstract: The title rearrangement proceeds in dichloromethane at 25°C in the presence of the catalyst prepared *in situ* to give tertiary isomers in good yields. Other rearrangements of sec. → tert. or sec. → sec. have been examined.

It is of interest to examine the direction of allylic isomerizations.[1] The allylic primary acetates are produced by treating its tertiary esters (or alcohols) with acetic anhydride,[2] or alternatively with a palladium(II) complex.[3,4] Rearrangements in the opposite sense (prim. → tert.) are encountered in solvolysis reactions, which are complicated by accompanying elimination, cyclization, and skeletal rearrangement.[5] Here we wish to report a novel catalysis promoting allylic isomerization of primary alcohols to tertiary ones in aprotic solvent under mild conditions.



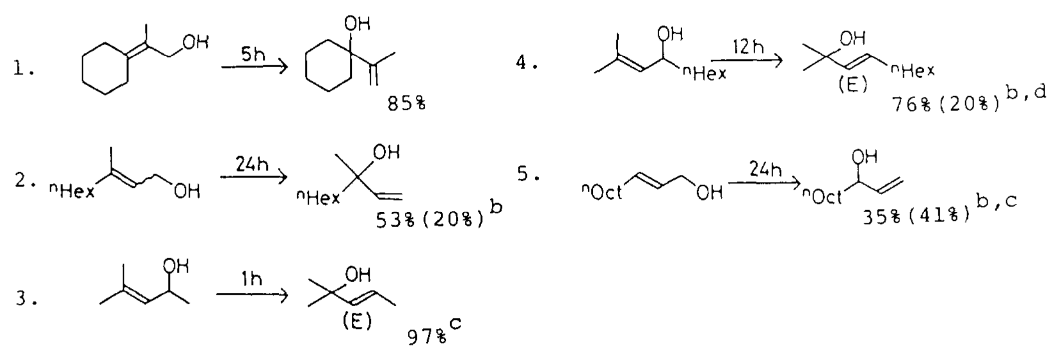
(1)

I II

$VO(acac)_2$	(0.1)	GLPC yield	92%	(recovery 2%)
$MoO_2(acac)_2$	(0.1)		76%	(3%)

To a stirred solution of $VO(acac)_2$ (53 mg, 0.2 mmol) in dichloromethane (8 ml) was added at 25°C a dichloromethane solution (8 ml) of $Me_3SiOOSiMe_3$[6] (0.11 g, 0.6 mmol) under an argon atmosphere. The blue colour of the reaction mixture turned to purple immediately. The mixture was stirred at 25°C for 15 min. To this was added a solution of cyclohexylideneethanol (I, 0.25 g, 2.0 mmol) in dichloromethane (8 ml) at the same temperature and the whole was stirred for an additional 6 h. The mixture was poured into brine (20 ml) and extracted with ether. The separated organic layer was dried (Na_2SO_4) and concentrated. Purification by preparative thin layer chromatography (hexane-ethyl acetate, 2:1) on silica gel gave 1-vinylcyclohexanol (II) in 80% yield (0.20 g) as a colourless liquid.[7]

Table 1. Allylic Isomerization Catalyzed by $Me_3SiOOSiMe_3$-$VO(acac)_2$ System[a]



a) The substrate (2.0 mmol) was treated at 25°C with a catalyst prepared by $Me_3SiOOSiMe_3$ (0.6 mmol) and $VO(acac)_2$ (0.2 mmol) in CH_2Cl_2. b) Recoveries of the unchanged materials are shown in parentheses. c) GLPC yield. d) See ref.9.

The same rearrangement took place with $MoO_2(acac)_2$ instead of $VO(acac)_2$. α,β-Epoxy alcohols were scarcely produced with $Me_3SiOOSiMe_3$-$VO(acac)_2$ system in sharp contrast to the Sharpless' epoxidation reagent[8] of ^tBuOOH-$VO(acac)_2$.

As shown in Table 1, allylic secondary alcohols isomerized to tertiary ones under the same condition. The resulting double bond exhibited *E* configuration in run 3 and 4. Isomerization of a primary into a secondary alcohol, however, gave less satisfactory result (run 5).

Table 2 shows the reactions of geraniol, nerol, and linalool with this system. The isomer distributions of these terpene alcohols were nearly identical irrespective of the starting alcohols in the present reaction. In contrast, the solvolysis[10] of neryl chloride gives α-terpineol as the main

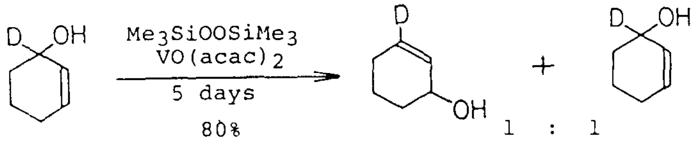
Table 2. Isomerization of Geraniol, Nerol, and Linalool with $Me_3SiOOSiMe_3$-$VO(acac)_2$ System[a]

	Time (h)	Product (%)[b]			
		geraniol	nerol	linalool	α-terpineol
geraniol	7	(10)	8	68	2
nerol	7	11	(11)	70	3
linalool	12	8	5	(60)	2

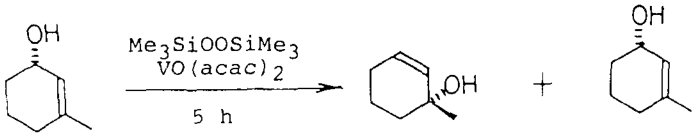
a) Reactions were performed on 2.0 mmol scale at 25°C in CH_2Cl_2. The catalyst was prepared by $Me_3SiOOSiMe_3$ (0.6 mmol) and $VO(acac)_2$ (0.2 mmol) in CH_2Cl_2. b) GLPC yield.

product, while linalool is produced from geranyl chloride under the S_N1 condition.

The equilibrium between the starting allylic alcohol and the rearranged one has been examined with 1-deuterio-2-cyclohexen-1-ol. An equimolar mixture of 3-deuterio and 1-deuterio compounds was resulted (Eq. 2).[11]



(2)



(3)

III 40%ee S-(-)

IV 29%ee R-(+) 35%

38%ee S-(-) 40%

Treatment of (S)-(-)-3-methyl-2-cyclohexen-1-ol (III, 40% e.e.)[12] with this catalyst gave (R)-(+)-1-methyl-2-cyclohexen-1-ol[13] in 35% yield (IV, 29% e.e.) and the unchanged starting material in 40% recovery as shown in Eq. 3. Hydroxyl group of the substrate III, therefore, migrates mainly on the same side of the olefinic double bond. This result suggests that the isomerization does not proceed *via* a free allylic cation. The conclusion is consonant with the observed production of a trace amount of cyclized α-terpineol from nerol.[14]

Although the responsible species are still obscure,[15,16] the allylic isomerization of the reverse direction provides a useful tool for synthesis.

References and Notes

1. For general reviews, see: J. March, "Advanced Organic Chemistry," 2nd ed., McGraw-Hill Kogakusha, Tokyo (1977), pp. 303-307; E. A. Braude, *Q. Rev.*, 4, 404 (1950); R. H. Dewolfe and W. G. Young, "The Chemistry of the Alkenes," E. S. Patai, Ed., Interscience, New York (1964), Chapter 10.
2. J. H. Babler and D. O. Olsen, *Tetrahedron Lett.*, 1974, 351; K. Kogami and J. Kumanotani, *Bull. Chem. Soc. Jpn.*, 47, 226 (1974); W. G. Young and I. D. Webb, *J. Am. Chem. Soc.*, 73, 780 (1951).
3. L. E. Overman and F. M. Knoll, *Tetrahedron Lett.*, 1979, 321; J. Tsuji, K. Tsuruoka, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, 49, 1701 (1976).
4. L. E. Overman, C. B. Campbell, and F. M. Knoll, *J. Am. Chem. Soc.*, 100, 4822 (1978); B. M. Trost, J. M. Timko, and J. L. Stanton, *J. Chem. Soc.*,

Chem. Commun., 1978, 436.

5. P. Valenzuela and O. Cori, *Tetrahedron Lett.*, 1967, 3089; K. L. Stevens, L. Jurd, and G. Manners, *Tetrahedron*, 28, 1939 (1972); D. V. Banthorpe, P. A. Boullier, and W. D. Fordham, *J. Chem. Soc., Perkin Trans. I*, 1974, 1637.
6. P. G. Cookson, A. G. Davies, and N. Fazal, *J. Organomet. Chem.*, 99, C31 (1975).
7. GLPC yield (10% PEG 20M, 3% $AgNO_3$, 1.5 m, 110°C) of II was determined with hexadecane as the internal standard.
8. K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta*, 12, 63 (1979) and references cited therein.
9. Bp 112°C (bath temp, 2 Torr); IR (neat): 3400, 3050, 1150, 970, 910 cm^{-1}; NMR (CCl_4): δ 0.87 (t, $J = 6$ Hz, 3H), 1.22 (s, 6H), 1.00-1.53 (m, 9H), 1.75-2.15 (m, 2H), 5.40-5.55 (m, 2H); MS m/e (%): 170 (M^+, 2), 155 (25), 95 (32), 85 (77), 71 (100), 68 (52). GLPC analysis (20% PEG 6000, 1.2 m, 122°C) of the crude product showed a single peak having a retention time at 18.5 min ((*E*)-isomer). (*Z*)-Isomer ($T_r = 17.2$ min) was not detected.
10. C. A. Bunton, O. Cori, D. Hachey, and J.-P. Leresche, *J. Org. Chem.*, 44, 3238 (1979); C. D. Poulter and C. R. King, *J. Am. Chem. Soc.*, 104, 1422 (1982).
11. The increased amount of the catalyst did not affect the ratio of the two allylic isomers.
12. S. Terashima, N. Tanno, and K. Koga, *J. Chem. Soc., Chem. Commun.*, 1980, 1026; K. Mori, S. Tamada, M. Uchida, N. Mizumachi, Y. Tachibana, and M. Matsui, *Tetrahedron*, 34, 1901 (1978); E. L. Pummer, T. E. Stewart, K. Byrne, G. T. Pearce, and R. M. Silverstein, *J. Chem. Ecol.*, 2, 307 (1976). III: $[\alpha]_D^{20} = -35.1°$ ($c = 1.86$, $CHCl_3$)
13. A. A. Renwick and P. R. Huges, *Insect Biochem.*, 5, 459 (1975). IV: $[\alpha]_D^{20} = +15.5°$ ($c = 1.65$, $CHCl_3$). The authentic sample of (R)-(+)-IV was prepared from (S)-(−)-III according to the literature about 1,3-transposition of allylic alcohols: A. Yasuda, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 52, 1757 (1979).
14. Y. Kitagawa, S. Hashimoto, S. Iemura, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, 98, 5030 (1976).
15. Heating of a tertiary allylic alcohol with $O{=}V(OR)_3$ at 160°C gives a mixture of its primary isomer and the reactant alcohol. See, P. Chabardes, E. Kuntz, and J. Varagnat, *Tetrahedron*, 33, 1775 (1977).
16. IR analysis of a mixture of $Me_3SiOOSiMe_3$ and $VO(acac)_2$ indicated a new absorption at 900 cm^{-1}, while the absorption frequency of $Me_3SiOOSiMe_3$ was 850 cm^{-1}

(Received in Japan 19 May 1983)