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Isomerization of Allylic Alcohols Catalyzed by Vanadium or Molybdenum Complexes[1)]

Seijiro Matsubara, Takashi Okazoe, Koichiro Oshima, Kazuhiko Takai,* and Hitosi Nozaki
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606

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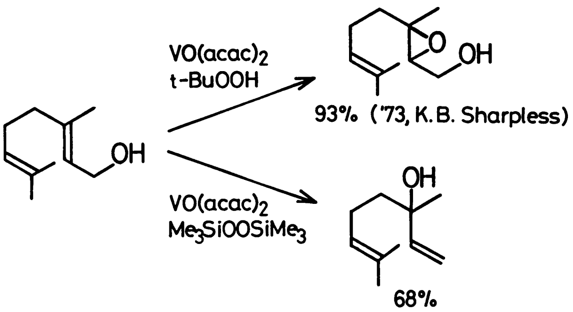
Isomerization of primary allylic alcohols proceeds in dichloromethane at 25 °C in the presence of the catalyst prepared *in situ* from $VO(acac)_2$ or $MoO_2(acac)_2$, and $Me_3SiOOSiMe_3$ to give tertiary isomers in good yields. The catalysts are also effective for the rearrangements of *sec.→tert.* allylic alcohols. The isomerization of an allenyl allylic alcohol, 6-methyl-1,2,5-heptatrien-4-ol, gives either (*E*)-2-methyl-3,5,6-heptatrien-2-ol or (*E*)-6-methyl-3,5-heptadien-2-one selectively depending on the reaction conditions.

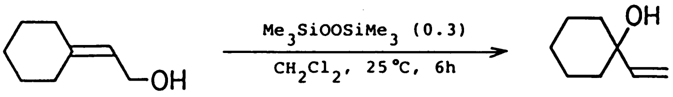
Allylic transposition reactions have been widely studied.[2)] Treatment of allylic tertiary acetates (or alcohols) with acetic anhydride produces their primary isomers.[3)] Palladium(II) complex is an effective catalyst for the isomerization of allylic tertiary acetates to primary ones.[4,5)] Rearrangements in the opposite sense (*primary→tertiary*) are encountered in solvolysis reactions, which are complicated by accompanying elimination, cyclization, and skeletal rearrangement.[6)] Here we wish to report the catalysts which are prepared from $VO(acac)_2$ or $MoO_2(acac)_2$ and $Me_3SiOOSiMe_3$ and are effective in (1) allylic isomerization of primary or secondary alcohols to tertiary ones and (2) regioselective isomerization of 6-methyl-1,2,5-heptatrien-4-ol into either (*E*)-2-methyl-3,5,6-heptatrien-2-ol or (*E*)-6-methyl-3,5-heptadien-2-one. Both reactions proceed in an aprotic solvent under mild conditions.

(1) Isomerization of Primary Allylic Alcohols to Tertiary Ones. Most recently, much attention has been paid on the synthetic utility of bis(trimethylsilyl) peroxide,[7,8)] which is an equivalent of 100% H_2O_2. The peroxide easily prepared from 30% H_2O_2[7)] possesses high solubility in organic solvents and thermal stability. The enhanced nucleophilicity of the oxygen by trimethylsilyl group has effectively been used for the oxidation reaction such as Baeyer-Villiger reaction[8a)] or pyridinium dichromate-catalyzed oxidation of alcohols into carbonyl compounds.[8b)] In further study of this unique reagent in combination with several transition metal catalysts, we have found that the $VO(acac)_2$ or $MoO_2(acac)_2$ catalyst activated with $Me_3SiOOSiMe_3$ effectively induces the title isomerization which is in sharp contrast to the well-known Sharpless' epoxidation of allylic alcohols (Scheme 1).[9)]

No allylic rearrangement occurs in the absence of $Me_3SiOOSiMe_3$ as far as we utilize $VO(acac)_2$ system. Meanwhile, $MoO_2(acac)_2$ catalyst has proved to be effective to bring about the isomerization with or without the peroxide, although several undesired side reactions are accompanied in the latter case. In general, $VO(acac)_2$–$Me_3SiOOSiMe_3$ system gave better yeilds of tertiary alcohol than $MoO_2(acac)_2$ one. For instance, treatment of 2-cyclohexylideneethanol (**1**) with $VO(acac)_2$–$Me_3SiOOSiMe_3$ provided the tertiary alcohol **2** in 92% GLPC yield (2% recovery of **1**), whereas $MoO_2(acac)_2$ system gave **2** in 76% or 35% yield with or without $Me_3SiOOSiMe_3$ respectively (Scheme 2).



Scheme 1.



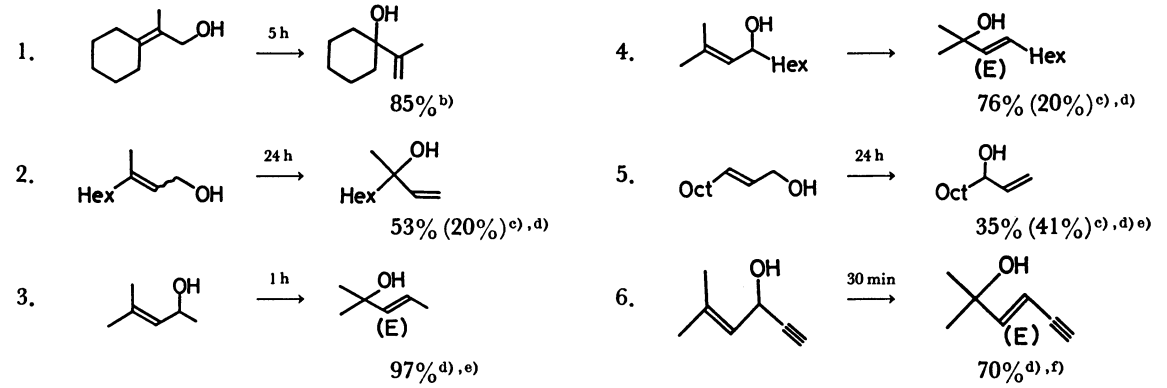
1 **2**

$VO(acac)_2$ (0.1)	GLPC yield	92%	(recovery 2%)
$MoO_2(acac)_2$ (0.1)		76%	(3%)
[$MoO_2(acac)_2$ (0.1) only		35%	(<2%)]

Scheme 2.

The results of allylic isomerization with $VO(acac)_2$-$Me_3SiOOSiMe_3$ are summarized in Table 1. A general procedure is as follows. $Me_3SiOOSiMe_3$ (30 mol%) was added to a solution of $VO(acac)_2$ (10 mol%) in CH_2Cl_2 at 25 °C. The blue color of the solution turned immediately to purple. A solution of a primary alcohol in CH_2Cl_2 was added and the whole was stirred at 25 °C for 6 h. The product was purified by preparative thin-layer chromatography on silica gel. Rearrangement of primary allylic alcohols proceeded very smoothly to give tertiary ones in good yields. In contrast, isomerization of a primary into a secondary alcohol gave less satisfactory results (run 5). The resulting double bond exhibited *E* configuration in runs 3, 4,

Table 1. Allylic isomerization catalyzed by $VO(acac)_2$-$Me_3SiOOSiMe_3$ system[a)]



a) The substrate (2.0 mmol) was treated at 25 °C with a catalyst prepared from $Me_3SiOOSiMe_3$ (0.6 mmol) and $VO(acac)_2$ (0.2 mmol) in CH_2Cl_2. b) See Ref. 10. c) Recoveries of the unchanged materials are shown in parentheses. d) See experimental section. e) GLPC yield. f) The isomerization of this substrate was also performed in 76% yield with the $MoO_2(acac)_2$ (5 mol%) without $Me_3SiOOSiMe_3$. The reaction was complete within 10 min.

Table 2. Isomerization of geraniol, nerol, and linalool with $VO(acac)_2$-$Me_3SiOOSiMe_3$ system[a)]

	Time	Products (%)[b)]			
	h	Geraniol	Nerol	Linalool	α-terpineol
geraniol	7	(10)	8	68	2
(geranyl chloride)[c)]		10	0	81	7
nerol	7	11	(11)	70	3
(neryl chloride)[c)]		0	2	20	72
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 yields (10% PFG 20 M, 3% $AgNO_3$, 1.5 m, 110 °C) of these terpene alcohols were determined with hexadecane as the internal standard. c) The results of the solvolysis reaction (H_2O/acetone=95/5) of geranyl chloride or neryl chloride are cited from the literature of C. A. Bunton *et al.* (Ref. 11).

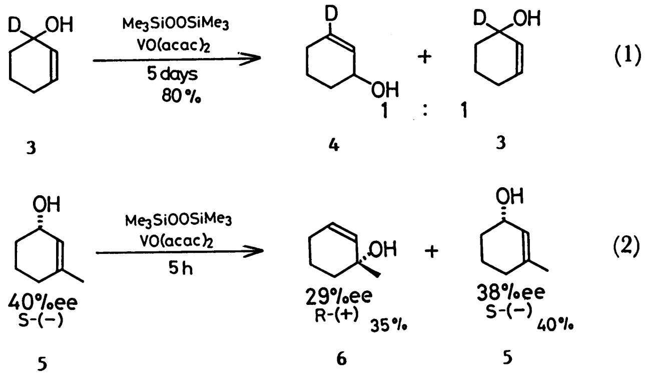
and 6.

Table 2 is concerned with the reaction of geraniol, nerol, and linalool with $VO(acac)_2$–$Me_3SiOOSiMe_3$ system. The isomer distributions of these terpene alcohols were nearly identical irrespective of the starting alcohols in the present reaction. On the other hand, the solvolysis of neryl chloride is recorded to give α-terpineol as the main product, while linalool is produced from geranyl chloride under the S_N1 conditions.[11)]

Following reactions in Scheme 3 gave us some information about the mechanism of this isomerization reaction. The equilibrium between a starting allylic alcohol and the rearranged one has been examined with 1-deuterio-2-cyclohexen-1-ol (**3**). An equimolar mixture of 3-deuterio and 1-deuterio compounds was produced (Eq. 1).[12)]

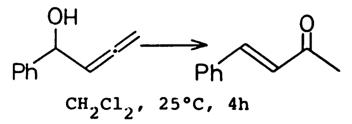
Treatment of (*S*)-(−)-3-methyl-2-cyclohexen-1-ol[13)] (**5**, 40% e.e.) with this $VO(acac)_2$-$Me_3SiOOSiMe_3$ catalyst gave (*R*)-(+)-1-methyl-2-cyclohexen-1-ol[14)] in 35% yield (**6**, 29% e.e.) and the unchanged starting material in 40% recovery as shown in Eq. 2. The hydroxyl group of the substrate **5**, therefore, resides mainly on the same side of the olefinic double bond. This suggests that the isomerization does not proceed *via* a free allylic cation.[15)] The conclusion is consonant with the observed production of a trace amount of cyclized α-terpineol from nerol (Table 2).[16)]

(2) Regioselective Isomerization of 6-Methyl-1,2,5-heptatrien-4-ol. The rearrangement of allenic alcohols proceeds as smoothly as allylic ones. For



Scheme 3.

instance, (*E*)-4-phenyl-3-buten-2-one was produced from 1-phenyl-2,3-butadien-1-ol in good yields (Scheme 4) with Mo or V catalysis. Addition of $Me_3SiOOSiMe_3$ was essential for $VO(acac)_2$ catalysis, but $MoO_2(acac)_2$ turned out to be effective without $Me_3SiOOSiMe_3$. The application of this rearrangement technique to 6-methyl-1,2,5-heptatrien-4-ol (**7**) led to regioselective formation of either (*E*)-2-methyl-3,5,6-heptatrien-2-ol (**8**) and (*E*)-6-methyl-3,5-heptadien-2-one (**9**) depending on conditions (Table 3,4).

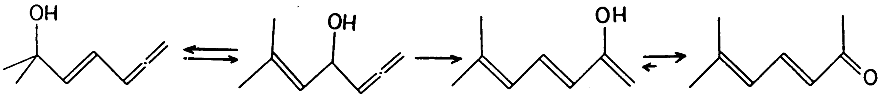


$MoO_2(acac)_2$ (0.1)	75%
$MoO_2(acac)_2$ (0.1)-$Me_3SiOOSiMe_3$ (0.3)	83%
$VO(acac)_2$ (0.1)	0%
$VO(acac)_2$ (0.1)-$Me_3SiOOSiMe_3$ (0.3)	81%

Scheme 4.

Treatment of **7** with 5 mol% of $MoO_2(acac)_2$ in dichloromethane at 25 °C for 10 min provided the enone **9** in 90% yield. The reaction temperature strongly affected the product distributions. The reaction at −78 °C gave tertiary alcohol **8** as a sole product and no trace of **9** was detected in the reaction mixture. The addition of $Me_3SiOOSiMe_3$ to $MoO_2(acac)_2$ did not alter the results dramatically. Following assumptions explain the observations. (1) An equilibrium of Scheme 5 exists between the two alcohols **7** and **8** in the presence of the $MoO_2(acac)_2$ catalyst. (2) At lower temperature, the kinetically favored tertiary alcohol **8** is produced. (3) At 25 °C, the isomerization to the kinetically less favored trienol **10** competes with the rearrangement of **7** to **8** and the thermodynamically more stable enone **9** is produced exclusively from the tautomerization of **10**.

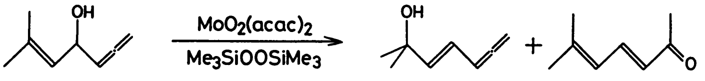
As shown in Table 4, $VO(acac)_2$ was less effective in



8 7 10 9

Scheme 5.

Table 3. Isomerization of 6-methyl-1,2,5-heptatrien-4-ol with $MoO_2(acac)_2$ system[a)]

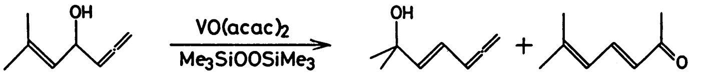


7 **8** **9**

Run	$MoO_2(acac)_2$	$Me_3SiOOSiMe_3$	Time	Temp	Yield[b)]		
					8	**9**	Recov.
1	5 mol%	—	10 min	25 °C	<2%	90%	<2%
2	5 mol%	—	10 min	−78 °C	94%	<2%	<2%
3	5 mol%	5 mol%	10 min	25 °C	<2%	94%	<2%
4	5 mol%	15 mol%	10 min	25 °C	13%	82%	<2%

a) Reactions were performed on 2.0 mmol scale in CH_2Cl_2. b) Products were isolated as a mixture and the ratio was determined by nmr analysis.

Table 4. Isomerization of 6-methyl-1,2,5-heptatrien-4-ol with $VO(acac)_2$ system[a)]



7 **8** **9**

Run	$VO(acac)_2$	$Me_3SiOOSiMe_3$	Time	Temp	Yield[b)]		
					8	**9**	Recov.
1	5 mol%	—	10 min	25 °C	<2%	<2%	75%
2	5 mol%	—	16 h	25 °C	63%	24%	<2%
3	5 mol%	5 mol%	10 min	25 °C	68%	17%	5%
4	5 mol%	15 mol%	10 min	25 °C	80%	7%	<2%

a) Reactions were performed on 2.0 mmol scale in CH_2Cl_2. b) Products were isolated as a mixture and the ratio was determined by NMR analysis.

the isomerization of **7**. The presence of $Me_3SiOOSiMe_3$ was essential to obtain a reasonable reaction rate. The catalyzed rearrangement provided a mixture of **8** and **9** in a 4:1 ratio (run 3). Increasing the amount of $Me_3SiOOSiMe_3$ improved the selectivity of the reaction slightly. The ratio of **8**/**9** was 11/1 with 5 mol% of $VO(acac)_2$ and 15 mol% of $Me_3SiOOSiMe_3$ (run 4).[19)]

Experimental

The IR spectra were determined on a Shimadzu IR-27-G spectrometer, the mass spectra on a Hitachi M-80 machine, and the NMR spectra on a Varian EM-360 spectrometer. The chemical shifts are given in δ, with tetramethylsilane as an internal standard. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Dichloromethane was dried on P_2O_5 and distilled. All the experiments were carried out under an argon atmosphere. Purification of products were performed by preparative thin-layer chromatography (TLC) or column chromatography on silica gel (Wakogel C-100). Analytical GLPC was performed with a Yanagimoto GCG-550-F and a Shimadzu GC-4CPT. Preparative GLPC was performed with a JEOL-JGC-20K apparatus.

Bis(trimethylsilyl) Peroxide: The following procedure is a modification of the method described by P. G. Cookson *et al.* too much briefly.[7)] Hydrogen peroxide (30%, 11.3 g, 100 mmol) was added in less than 1 min to a stirred solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 5.6 g, 50 mmol) in diethyl ether (80 ml) at 0 °C and the resulting mixture was stirred for 15 min. Precipitated white solid was filtered through a glass filter, and dried *in vacuo* at room temperature for 5 h. This is the DABCO–hydrogen peroxide complex and is easily decomposed by a catalytical amount of metals. Danger of explosion should be taken care. This DABCO–hydrogen peroxide complex (5.9 g, 33 mmol), DABCO (3.7 g, 33 mmol), and dichloromethane (50 ml) were placed in a flame-dried flask. Chlorotrimethylsilane (12.0 g, 0.111 mol, neat) was added dropwise at 0 °C within 15 min to the solution. After being stirred for 5 h at room temperature, the resulting mixture was filtered to remove DABCO–HCl salt, and the filtrate was concentrated at room temperature under 100 Torr (1 Torr=133.322 Pa). The residue was diluted with pentane, filtered to remove the salt, and the solution concentrated at room temperature under 100 Torr. Distillation of the crude product under reduced pressure provided $Me_3SiOOSiMe_3$ in 32% yield (5.6 g, 32 mmol) as a colorless liquid, bp 40—41 °C/28 Torr: IR (neat): 2960 (s), 1250 (s), 920 (w), 840 (s), 730 (s).[20)]

1-Ethenylcyclohexanol (2): A dichloromethane solution (5 ml) of $Me_3SiOOSiMe_3$ (0.11 g, 0.60 mmol) was added at 25 °C under an argon atmosphere to a stirred solution of $VO(acac)_2$ (53 mg, 0.20 mmol) in dichloromethane (4 ml). The blue color of the reaction mixture turned to purple immediately and the resulting mixture was stirred at 25 °C for 10 min. A solution of 2-cyclohexylideneethanol (**1**, 0.25 g, 2.0 mmol) in dichloromethane (8 ml) was added 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 (2×20 ml). The separated organic layers were dried (Na_2SO_4) and concentrated. Purification by preparative thin-layer chromatography (hexane–ethyl acetate, 2:1) on silica gel gave 1-ethenylcyclohexanol (**2**) in 80% yield (0.20 g) as a colorless liquid.[21)] GLPC yield 92% of **2** (10% PEG 20 M, 3% $AgNO_3$, 1.5 m, 110 °C) was determined with hexadecane as the internal standard: Bp. 70 °C (bath temp, 10 Torr); IR (neat): 3400, 1642, 1455, 960, 915 cm^{-1}; NMR (CCl_4): δ=1.00—1.80 (m, 11H), 4.88 (dd, J=10.5, 1.5 Hz, 1H), 5.12 (dd, J=17.6, 1.5 Hz, 1H), 5.87 (dd, J=17.6, 10.5 Hz, 1H); MS m/z (%): 126 (M$^+$, 6), 93 (11), 83 (100), 70 (68), 67 (21), 55 (56).

3-Methyl-1-nonen-3-ol:[22)] Bp 45 °C (bath temp, 1 Torr); IR (neat): 3400, 3100, 1645, 1400, 970, 915 cm^{-1}; NMR (CCl_4): δ=0.87 (t, J=6 Hz, 3H), 1.00—1.70 (m, 10H), 1.20 (s, 3H), 1.95—2.20 (m, 1H), 4.92 (dd, J=10.5, 1.5 Hz, 1H), 5.07 (dd, J=17.5, 1.5 Hz, 1H), 5.79 (dd, J=17.5, 10.5 Hz, 1H); MS m/z (%): 156 (M$^+$, 0.3), 141 (11), 129 (8), 96 (6), 81 (10), 71 (100), 58 (16).

(E)-2-Methyl-3-penten-2-ol.[23)] This compound was produced from 4-methyl-3-penten-2-ol as described above. GLPC analysis (10% PEG 20 M, 3% $AgNO_3$, 1.5 m, 45 °C) of the crude product showed a single peak having a retention time at 4.8 min ((*E*)-isomer). (*Z*)-Isomer (T_r=5.2 min), which was prepared from (*Z*)-1-bromo-1-propene and acetone, was not detected in the reaction mixture. GLPC yield 97% of (*E*)-2-methyl-3-penten-2-ol was determined with dodecane as the internal standard: Bp 70 °C (bath temp, 100 Torr); IR (neat): 3400, 3050, 1675, 970 cm^{-1}; NMR (CCl_4): δ=1.21 (s, 6H), 1.50—1.70 (m, 1H), 1.63 (d, J=5.5 Hz, 3H), 5.40—5.60 (m, 2H); MS m/z (%): 100 (M$^+$, 19), 85 (100), 67 (68), 59 (36), 43 (90).

(E)-2-Methyl-3-decen-2-ol: This compound was produced from 2-methyl-2-decen-4-ol as described above. 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. 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), 1.00—1.53 (m, 9H), 1.22 (s, 6H), 1.75—2.15 (m, 2H), 5.40—5.55 (m, 2H); MS m/z (%): 170 (M$^+$, 2), 155 (25), 95 (32), 85 (77), 71 (100), 68 (52); Found: C, 77.52; H, 13.02%. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02%.

1-Undecen-3-ol:[24)] This compound was produced from (*E*)-2-undecen-1-ol as described above. GLPC yield 35% of 1-undecen-3-ol (10% PEG 20M, 3% $AgNO_3$, 1.5 m, 116 °C) was determined with hexadecane as the internal standard.

(E)-2-Methyl-3-hexen-5-yn-2-ol:[25)] Bp 44 °C (bath temp, 9 Torr); IR (neat): 3250, 2070, 1605, 1140, 955 cm^{-1}; NMR (CCl_4): δ=1.30 (s, 6H), 2.00—2.35 (m, 1H), 2.68 (d, J=2.8 Hz, 1H), 5.60 (dd, J=15.6, 2.8 Hz, 1H), 6.24 (d, J=15.6 Hz, 1H); MS m/z (%): 110 (M$^+$, 1.7), 109 (12), 95 (100), 77 (10), 67 (24), 43 (54).

(S)-(−)-3-Methyl-2-cyclohexen-1-ol (5):[13)] This compound was prepared by asymmetric reduction of 3-methyl-2-cyclohexen-1-one according to the reported procedure[26)]: $[\alpha]_D^{25}$=−35.1° (c=1.86, $CHCl_3$). Enantiomeric excess (40% e.e.) of this alcohol was determined by NMR with $Eu(hfc)_3$ shift reagent.[13)]

(R)-(+)-1-Methyl-2-cyclohexen-1-ol (6):[14)] Treatment of (*S*)-(−)-3-methyl-2-cyclohexen-1-ol (**5**, 40% e.e.) with $VO(acac)_2$–$Me_3SiOOSiMe_3$ catalyst as described above gave a mixture of **5** (35% yield) and **6** (40% recovery). Yields were determined by GLPC (10% PEG 20 M, 3% $AgNO_3$, 1.5 m,

110 °C) with hexadecane as the internal standard. Purification by preparative GLPC (20% PEG 6000, 1 m, 110 °C) gave pure **5** (38% e.e.) and **6** [29% e.e., $[\alpha]^{25}_{D}=+15.5°$ (c=1.65, $CHCl_3$)]. Enantiomeric excess of these alcohols were determined by NMR with $Eu(hfc)_3$ shift reagent.[13]

The authentic sample of **6** [$[\alpha]^{25}_{D}=17.3°$ (c=2.0, $CHCl_3$)] was prepared from **5** (40% e.e.) according to the literature about stereoselective 1,3-transposition of allylic alcohols.[27] **6**: Bp 90 °C (bath temp, 50 Torr); IR (neat): 3400, 3050, 1180, 1125, 1020, 855 cm^{-1}; NMR (CCl_4): δ=1.20 (s, 3H), 1.50—2.10 (m, 7H), 5.35—5.75 (m, 2H); MS m/z (%): 112 (M^+, 9.9), 97 (100), 84 (45), 79 (43), 69 (85), 55 (32).

1-Phenyl-2,3-butadien-1-ol:[28] This compound was prepared from benzaldehyde and propargyl alcohol according to the literature.[29] Bp 72 °C (bath temp, 10 Torr); IR (neat): 3250, 1942, 1020, 846 cm^{-1}; NMR (CCl_4): δ=1.78 (bs, 1H), 4.70 (d, J=2 Hz, 1H), 4.77 (d, J=2 Hz, 1H), 5.07 (dt, J=6, 2 Hz, 1H), 5.15—5.40 (m, 1H), 6.87—7.53 (m, 5H); MS m/z (%): 146 (M^+, 2.3), 145 (10), 128 (8), 107 (100), 79 (55), 77 (23).

6-Methyl-1,2,5-heptatrien-4-ol (*7*):[30] The title compound was prepared from 3-methyl-2-butanal and propargyl alcohol according to the reported procedure:[29] Bp 47 °C (bath temp, 9 Torr); IR (neat): 3250, 1940, 1010, 840 cm^{-1}; NMR (CCl_4): δ=1.67 (s, 3H), 1,72 (s, 3H), 2.20—2.50 (m, 1H), 4.50—4.90 (m, 3H), 4.97—5.30 (m, 2H); MS m/z (%): 124 (M^+, 2), 109 (43), 91 (21), 85 (100), 81 (12), 79 (10), 67 (10), 55 (11).

(E)-2-Methyl-3,5,6-heptatrien-2-ol (**8**): A dichloromethane solution (7 ml) of 6-methyl-1,2,5-heptatrien-4-ol (**7**, 0.25 g, 2.0 mmol) was added to a solution of $MoO_2(acac)_2$ (33 mg, 0.10 mmol) in dichloromethane (4 ml) at −78 °C under an argon atmosphere. After being stirred at the same temperature for 10 min, the resulting mixture was poured into brine (20 ml) and extracted with ether (2×20 ml). The separated organic layers were dried and concentrated. Purification by preparative thin-layer chromatography (hexane–ethyl acetate, 5:1) on silica gel gave (*E*)-2-methyl-3,5,6-heptatrien-2-ol (**8**) in 94% yield (0.23 g) as a colorless liquid: Bp 70 °C (bath temp, 7 Torr); IR (neat): 3300, 1925, 1620, 1140, 965, 842; NMR (CCl_4): δ=1.30 (s, 6H), 2.15 (bs, 1H), 4.72—4.90 (m, 2H), 5.15—6.05 (m, 3H); MS m/z (%): 124 (M^+, 9.0), 109 (86), 91 (43), 85 (27), 81 (41), 65 (16), 59 (11), 55 (13), 53 (13), 43 (100); Found: C, 77.09; H, 9.98%. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74%.

(E)-6-Methyl-3,5-heptadien-2-one (*9*):[31] Treatment of 6-methyl-1,2,5-heptatrien-4-ol (**7**, 0.25 g, 2.0 mmol) with $MoO_2(acac)_2$ (33 mg, 0.10 mmol) in dichloromethane at 25 °C for 10 min as described above gave (*E*)-6-methyl-3,5-heptadien-2-one (**9**) in 90% yield (0.22 g): Bp 45 °C (bath temp, 10 Torr); IR (neat): 1654, 1620, 1580, 1260, 984, 960 cm^{-1}; NMR (CCl_4): δ=1.90 (s, 6H), 2.16 (s, 3H), 5.88 (d, J=12 Hz, 1H), 5.90 (d, J=15 Hz, 1H), 7.23 (dd, J=15, 12 Hz, 1H); MS m/z (%): 124 (M^+, 12), 109 (100), 81 (39), 79 (16), 53 (12), 43 (22).

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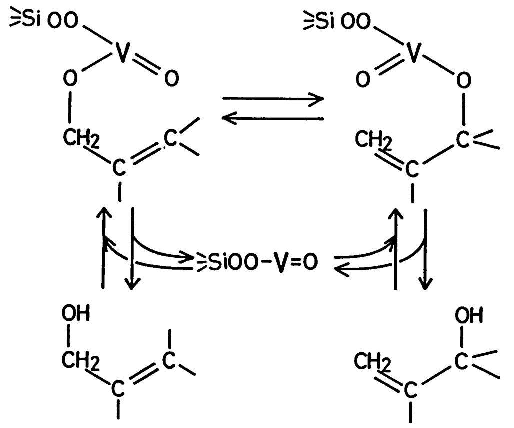
16) A [3,3] sigmatropic rearrangement of inorganic ester such as vanadate or molybdate is considered to be one of the reasonable mechanisms. Actually, it has been reported that heating of a tertiary allylic alcohol with $O=V(OR)_3$[17a] or $O=W(OR)_4\cdot L$[17b] at 160—200 °C gave a mixture of its primary isomer and the starting alcohol via [3,3] sigmatropic rearrangement. In our new method, the rearrangement took place in an opposite direction (primary→tertiary) under much milder conditions. These differences could be ascribed to the presence of Me_3SiOO- group attached on vanadium atom[18] in the [3,3] sigmatropic rearrangement (Scheme 6).



Scheme 6.

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