

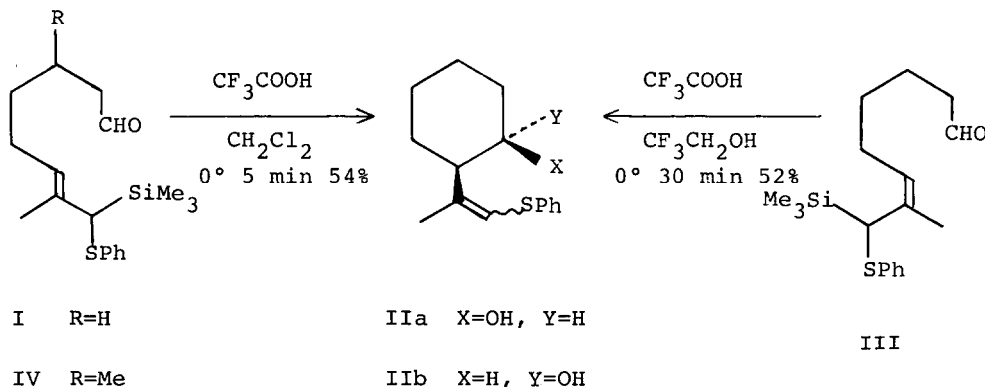
STEREOSPECIFIC 2-VINYLCYCLOHEXANOL FORMATION VIA INTERNAL ATTACK OF
 AN ALLYLSILANE MOIETY ON AN ALDEHYDE GROUP

Akira Itoh, Koichiro Oshima*, and Hitosi Nozaki
 Department of Industrial Chemistry, Faculty of Engineering
 Kyoto University, Yoshida, Kyoto 606, Japan

Summary: Acid catalyzed cyclization of (E)-HCO-(CH₂)₄-CH=C(Me)-CH(SPh)SiMe₃ affords cis-2-substituted cyclohexanol, while (Z) compound affords the trans isomer. Those cyclized products are transformed to the corresponding α -methyl γ -lactones.

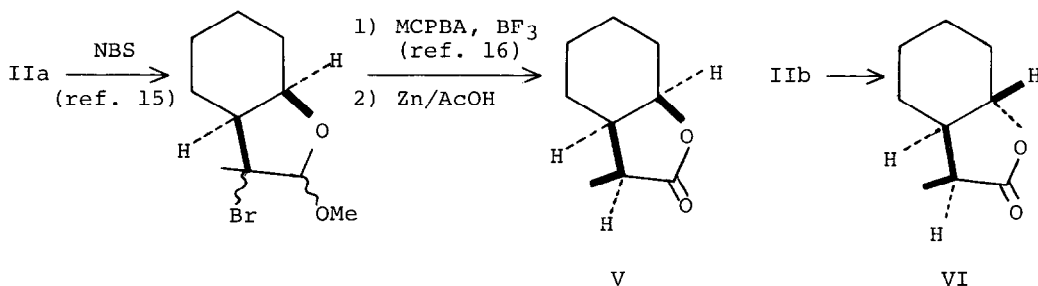
Allylsilanes have similar π -bond nucleophilicity as the enolate ions toward the carbonyl compounds. Little is known, however, about the stereochemical outcome of the allylsilane reactions as compared with enolate ion cases^{1,2} in spite of the well-recognized synthetic importance of allylsilane.³

We have now prepared (*vide infra*) the silylated aldehydes I and III stereoselectively and examined their cyclization with several reagents.⁴ Cyclization of I with a Lewis acid (SnCl₄, TiCl₄, and BF₃·Et₂O) or *n*-Bu₄NF gave a mixture of IIa and IIb.⁵ With CF₃COOH/CH₂Cl₂ or CF₃CH₂OH,⁶ however, I⁷ provided a single product IIa⁸ (contaminated by <2% of the geometrical isomer IIb). It was ascertained that both of the hydroxyl and isopropenyl groups occupied the cis position after desulphurization by means of Raney Ni.⁸ Meanwhile, the stereoisomer III⁹ afforded the almost homogeneous opposite isomer IIb¹⁰ (>93% trans) under the similar conditions.

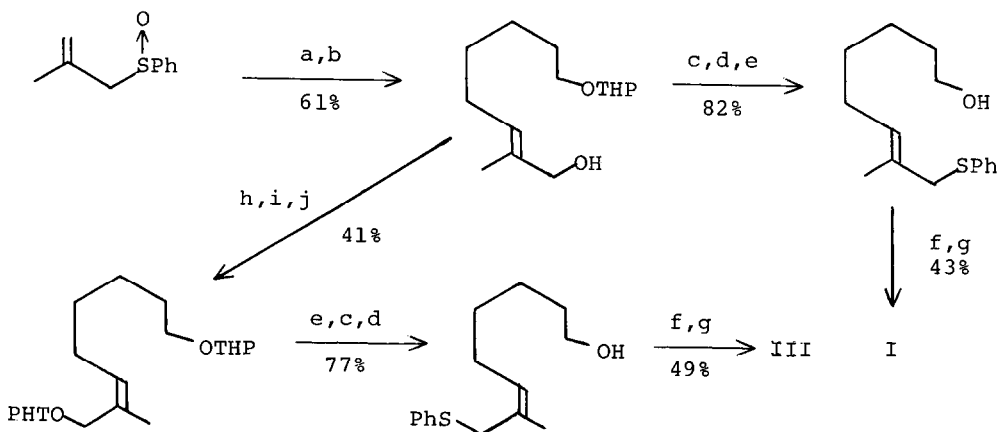


Because of the industrial importance of *l*-menthol, the cyclization of citronellal has been studied in detail.¹¹ Earlier methods result in the mixture of all possible stereoisomers of isopulegol which is an important intermediate for menthol synthesis. Treatment of the compound IV derived from citronellol with 2.0 equivalents of CF_3COOH in CH_2Cl_2 at 0° , followed by Raney Ni desulphurization, provided only *neo*-isopulegol (50% overall) and a trace of *neois*-isopulegol¹², both of which had the *cis* configuration with respect to the hydroxyl and isopropenyl groups.¹³

The cyclized product IIa could be easily converted to the *cis*-fused α -methyl- γ -lactone V (65% overall) and IIb could be transformed to *trans*-fused isomer VI (74% overall), respectively. The stereochemistry of the lactones was clear upon the comparison of the spectral data (NMR, IR) with those of the authentic samples.¹⁴ The indicated configuration suggests the introduction of a proton from the less hindered side of each lactone enolate.



The following scheme shows the preparation of the starting silylated aldehydes I and III.¹⁸

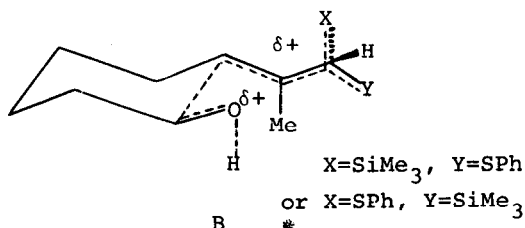
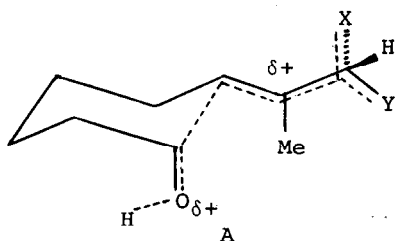


a, n -BuLi, $I(CH_2)_5OTHP$; b, $(MeO)_3P$; c, Me_2S-NCS^{17} , d, PhSNa; e, p -TsOH-MeOH; f, s -BuLi (2 equiv), Me_3SiCl , HCl; g, Me_2S-NCS , Et_3N ; h, DHP-TsOH; i, MCPBA; j, $LiPPh_2$, MeI

References and Notes

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- The effective use of the silylated compounds for the termination of the acid-induced cyclization has been reported. (a) allylsilane for termination: I. Fleming and A. Pearce, *J. C. S. Chem. Comm.*, 182 (1976) T. K. Sarkar and N. H. Anderson, *Tetrahedron Lett.*, 3513 (1978). (b) silyl-acetylene: K. Utimoto, M. Tanaka, M. Kitai, and H. Nozaki, *ibid.*, 2301 (1978); W. S. Johnson, T. M. Yornell, R. F. Myers and D. R. Morton, *ibid.*, 2549 (1978). (c) silyl enol ether: S. Hashimoto, A. Itoh, Y. Kitagawa, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **99**, 4192 (1977).
- Reagent (1.0 equiv), condition, yield, ratio of IIa/IIb: $SnCl_4$, -78° 10 min in hexane, 58%, 65/35; $TiCl_4$, -78° 10 min in CH_2Cl_2 , 60%, 70/30; $BF_3 \cdot Et_2O$, -78° 15 min in hexane, 50%, 85/15; nBu_4NF , 0° 10 min in THF, gave a complex mixture and the ratio was not determined.
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- Spectral characteristics of I were IR(neat) 1726 cm^{-1} (CHO); NMR(CCl_4) δ 0.13 (s, 9H, $Si(CH_3)_3$), 1.63 (s, 3H, $=CCH_3$), 3.16 (s, 1H, $CH(SPh)SiMe_3$), 5.09 (t, $J=7.4$ Hz, 1H, $=CH$), 7.03-7.27 (m, 5H, aromatic protons), 9.61 (t, $J=2.3$ Hz, 1H, CHO); exact mass spectrum m/e 320.164 (calcd for $C_{18}H_{28}OSSi$ 320.163).
- IIa: IR(neat) 3450, 1580, 960, 730 cm^{-1} ; NMR(CCl_4) δ 1.87 (s, 3H, $=CCH_3$) 3.97 (m, 1H, $CHOH$), 5.83(s) and 5.90(s) (1:3 ratio, 1H, $=CHSPh$), 7.2 (m, 5H, aromatic protons); *cis*-2-isopropenylcyclohexanol: IR(neat) 3440, 1645, 890 cm^{-1} ; NMR(CCl_4) δ 1.78 (s, 3H, $=CCH_3$), 3.87 (m, 1H, $CHOH$), 4.72 (m) and 4.87(m) (1H each, $=CH_2$).
- III: IR(neat) 1726 cm^{-1} (CHO); NMR(CCl_4) δ 0.16 (s, 9H, $Si(CH_3)_3$), 1.77 (s, 3H, $=CCH_3$), 3.56 (s, 1H, $CH(SPh)SiMe_3$), 5.10 (t, $J=6.4$ Hz, 1H, $=CH$), 7.10-7.40 (m, 5H, aromatic protons), 9.77 (t, $J=2.3$ Hz, 1H, CHO); exact mass spectrum m/e 320.161 (calcd for $C_{18}H_{28}OSSi$ 320.163).

10. IIb: IR(neat) 3425, 1580, 950, 720 cm^{-1} ; NMR(CCl_4) δ 1.78 (s, 3H, $=\text{CCH}_3$), 3.40 (bm, 1H, CHOH), 5.95(s) and 6.0(s) (1:3 ratio, 1H $=\text{CHSPh}$), 7.2 (m, 5H, aromatic protons); after desulphurization (trans-2-isopropenyl-cyclohexanol): IR(neat) 3390, 1644, 890 cm^{-1} ; NMR(CCl_4) δ 1.70 (s, 3H, $=\text{CCH}_3$), 3.33 (m, 1H, CHOH), 4.79 (m, 2H, $=\text{CH}_2$).
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13. We are tempted to explain the observed stereoselectivity by favouring the transition state A over B.



14. V: IR(neat) 1770, 1170, 960 cm^{-1} ; NMR(CCl_4) δ 1.09 (d, \underline{J} =7 Hz, 3H, CH_3), 2.65 (m, five bands of multiplet visible and separated by 7 Hz, 1H, CH-C=O) 4.32 (m, 1H, CH-O-). VI: IR(neat) 1778, 1173, 1015 cm^{-1} ; NMR(CCl_4) δ 1.16 (d, \underline{J} =7 Hz, 3H, CH_3), 2.17 (m, 1H, signal partially superimposed on ring protons, CH-C=O), 3.60 (m, 1H, CH-O-). J. A. Marshall and N. Cohen, *J. Org. Chem.*, 30, 3475 (1965); W. Herz and L. A. Glick, *ibid.*, 29, 613 (1964).
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