

MAGNESIUM IODIDE INDUCED REARRANGEMENT OF α,β -EPOXYSILANES TO β -KETOSILANES
AS APPLIED TO THE STEREOSELECTIVE SYNTHESIS OF
TETRAHOMOTERPENOID OF CODLING MOTH

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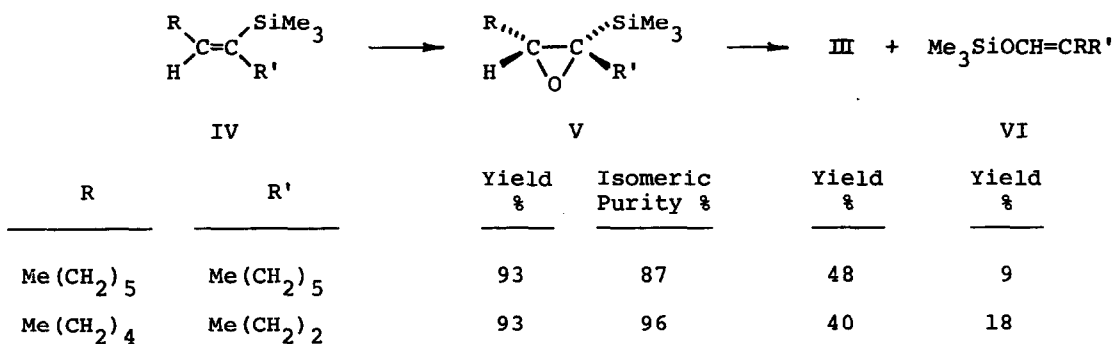
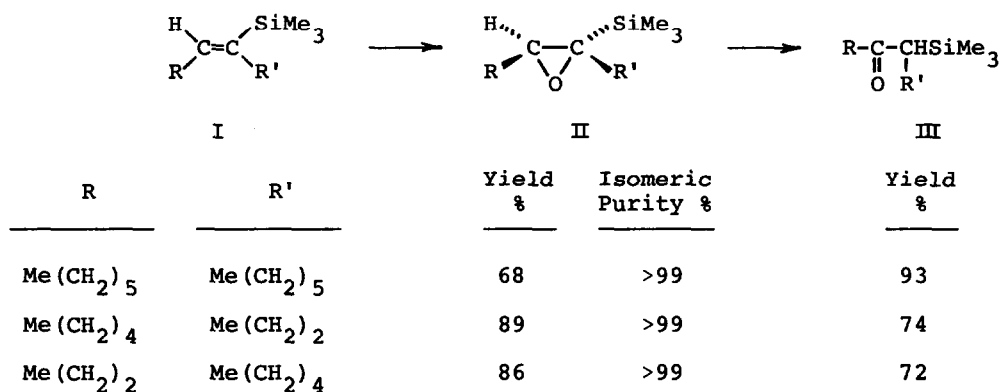
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(Received in Japan 14 March 1977; received in UK for publication 7 April 1977)

Recently β -ketosilanes have attracted considerable attention as useful intermediate for stereoselective olefin synthesis.^{1,2} This paper describes the rearrangement of α,β -epoxysilanes induced by magnesium iodide affording a novel procedure for the synthesis of β -ketosilanes from readily accessible vinylsilanes.³ An application of this procedure to the stereoselective olefin synthesis has provided 7-methyl-3-propyl-2(Z),6(Z)-decadien-1-ol (IX), a tetrahomoterpene alcohol obtained from the codling moth.⁴

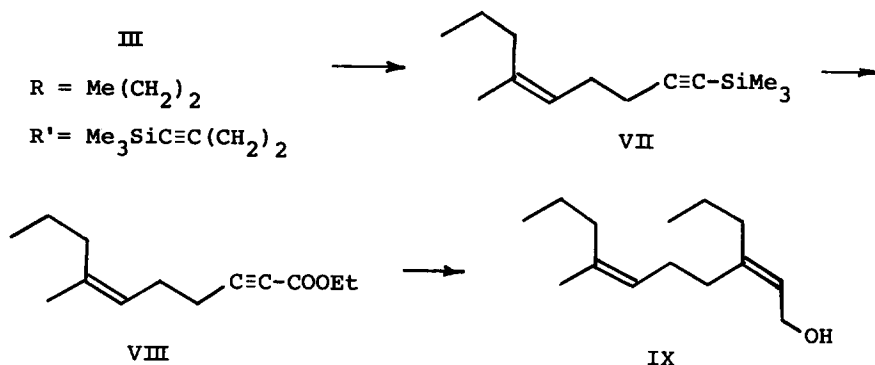
Treatment of 5-trimethylsilyl-4(E)-decene^{3e} (1.04 g, 4.91 mmol) with m-chloroperbenzoic acid (85% purity, 1.2 g, 6 mmol) in CH_2Cl_2 at 0°C overnight gave the epoxysilane II [R = $\text{Me}(\text{CH}_2)_2$, R' = $\text{Me}(\text{CH}_2)_4$]⁵ in 86% yield (E>99%). To a solution of magnesium iodide (10 mmol) in 10 ml of ether was added the above II (0.228 g, 1 mmol dissolved in 5 ml of ether). The resulting mixture was stirred at reflux for 120 min and then treated with 6 ml of 1,4-dioxane at 0°C. The solution was freed from solids by filtration, washed (sat. NaHCO_3 and sat. NaCl) and dried (MgSO_4). Chromatography of the concentrate on silica gel column (benzene) afforded the β -ketosilane III [R = $\text{Me}(\text{CH}_2)_2$, R' = $\text{Me}(\text{CH}_2)_4$]² in 72% yield.

In contrast with II, the corresponding diastereomer V gave a mixture of III and enol silyl ether VI⁶ as shown in the following scheme. Possible account for this specificity will be given in a full paper.⁷



Combined with reported reductive alkylation of $\text{C}\equiv\text{C}-\text{Si}$ moiety³ as well as the olefin synthesis from β -ketosilanes,^{1,2} the above described procedure opens a stereoselective reductive double alkylation of acetylene. The utility of the present method has been illustrated by the synthesis of IX.

Epoxyasilane II [$\text{R} = \text{Me}(\text{CH}_2)_2$, $\text{R}' = \text{Me}_3\text{SiC}\equiv\text{C}(\text{CH}_2)_2$] was prepared from vinylsilane I [$\text{R} = \text{Me}(\text{CH}_2)_2$, $\text{R}' = \text{Me}_3\text{SiC}\equiv\text{C}(\text{CH}_2)_2$]^{3e} in quantitative yield and was converted to β -ketosilane III [$\text{R} = \text{Me}(\text{CH}_2)_2$, $\text{R}' = \text{Me}_3\text{SiC}\equiv\text{C}(\text{CH}_2)_2$]. Further treatment with MeLi , AcONa/AcOH ² gave a trisubstituted ethylene VII ($Z = 95\%$) in 51% yield from II. Direct carbethoxylation of VII to acetylenic ester VIII ($Z = 96\%$) was effected by treatment with MeLi/HMPA , ClCOOEt in 70% yield. The acetylenic ester VIII was transformed into the tetrahomoterpenoid IX by the reported procedure.⁴



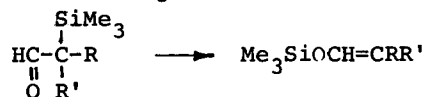
Acknowledgement. The authors wish to thank the Ministry of Education, Japan, for Grant-in-Aid (911506, 011010, 110309).

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- (4) (a) S. B. Bowlus and J. A. Katzenellenbogen, *ibid.*, 1277 (1973); (b) *idem*, J. Org. Chem., 38, 2733 (1973); (c) M. P. Cooke, Tetrahedron Lett., 1281 (1973).
- (5) IR (neat) 1243, 839, 752, 693 cm⁻¹; nmr (CCl₄) δ ppm, 0.00 (9H, s), 0.67-1.10 (6H, m), 1.10-1.70 (12H, m), 2.45-2.70 (1H, m); ms m/e (rel %), 228 (M⁺, 0.5), 213 (2), 199 (13), 185 (3), 171 (5), 143 (4), 130 (11), 113 (4), 75 (29), 73 (100), 59 (15), 43 (9).
- (6) VI [R = R' = Me(CH₂)₅], ir (neat) 1661, 1251, 1190, 1156, 1100, 881, 845, 757 cm⁻¹; nmr (CCl₄) δ ppm, 0.13 (9H, s), 0.60-1.05 (6H, m), 1.05-1.65 (16H, m), 1.65-2.30 (4H, m), 5.90 (1H, broad s); ms m/e (rel. %), 284

(M⁺, 10), 269 (3), 255 (1), 227 (1), 213 (38), 199 (5), 157 (9), 143 (79), 81 (16), 75 (20), 73 (100), 67 (15), 55 (16), 43 (20).

- (7) Formation of β -ketosilanes was explained by α -cleavage of α,β -epoxysilanes (ref. 8, 9) and migration of H or R. Product distribution indicated that H was more labile than R and that atom or group syn to Me₃Si had higher migratory aptitude. Enol silyl ether VI formation was explained by 1,3-migration of Me₃Si group.



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