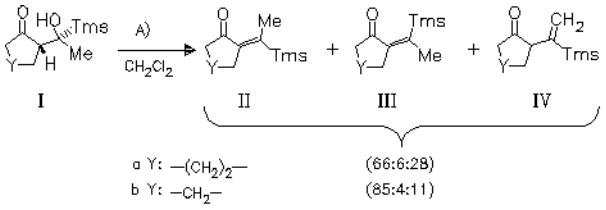
stereochemistry (general, optical resolution)

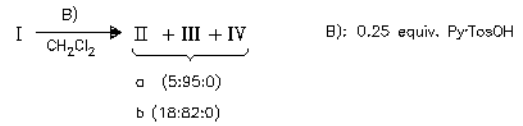
O 0030

18 - 036

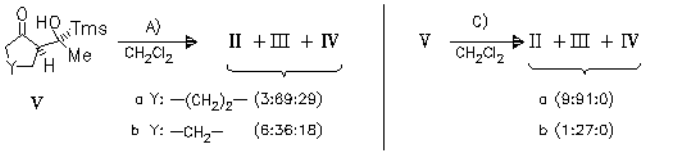
Syntheses and Theoretical Studies of Exocyclic γ-Oxoalkenyltrimethylsilanes. An Approach to the Stereodefined Exocyclic Tetrasubstituted Alkenes. — The dehydration of α-hydroxy-γ-oxoalkyltrimethylsilanes, e. g. (I) or (V), under acidic conditions leads stereoselectively to thermodynamically more stable (Z)-γ-oxoalkenylsilanes such as (III). The preferential formation of the (Z)-isomers is due not only to steric but also electronic effects of Si as is shown by the formation of (VII) by dehydration of compound (VI) containing a -tBu group instead of -Tms. The (Z)-isomers represent a novel type of alkenyl metal compounds in organic synthesis as demonstrated by the formation of the exocyclic tetrasubstituted alkene (X) from (IIIa). — (NAKATANI, K.; IZAWA, T.; ISOE, S.; J. Org. Chem. 59 (1994) 20, 5961-5969; Dep. Synth. Chem. Biol. Chem., Fac. Eng., Kyoto Univ., Kyoto 606-01, Japan; EN)



A): 12.6 equiv. Et_3N/6 equiv. MesCl, 0°C



B): 0.25 equiv. Py·TosOH



C): 0.25 equiv. camphorsulfonic acid