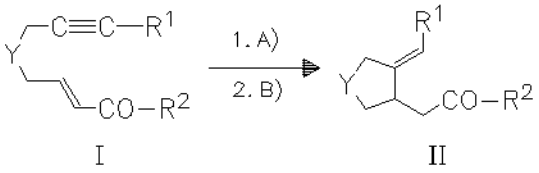
cyclopentane derivatives

Q 0030

09 - 072

Intramolecular Cyclization of 2,7- or 2,8-Bis-unsaturated Esters Mediated by (η^2-Propene)Ti(O-i-Pr)$_2$. Facile Construction of Mono- and Bicyclic Skeletons with Stereoselective Introduction of a Side Chain. A Synthesis of d-Sabinene. — The low-valent titanium-mediated cyclization of bis-unsaturated compounds having a conjugated ester moiety is found to be a versatile method to obtain mono- and bicyclic compounds. The diastereoselective reaction of aldehydes and ketones with the intermediate titanium species allows facile stereoselective extension of side chains from the cyclization products. Alternatively, the stereoselective cyclization controlled by an appropriate substituent in the substrate is also useful for the construction of a ring structure of defined stereochemistry. This transformation circumvents the use of CO in the preparation of bicyclic ketones. The high diastereoselectivity of the intramolecular cyclization is applied to an optically active enynoate (XVIII) which leads to the title monoterpene with complete chirality transfer. — (URABE, H.; SUZUKI, K.; SATO, F.; J. Am. Chem. Soc. 119 (1997) 42, 10014-10027; Dep. Biomol. Eng., Tokyo Inst. Technol., Midori, Yokohama 226, Japan; EN)

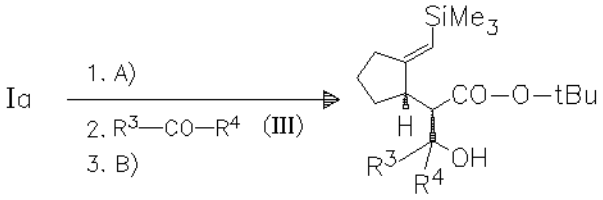


I II

a Y: $-CH_2-$; R^1: $-SiMe_3$; R^2: $-O-tBu$ 83%
b Y: $-(CH_2)_2-$; R^1: $-SiMe_3$; R^2: $-O-tBu$ 52%
c Y: $-CH_2-$; R^1: $-(CH_2)_4-Me$; R^2: $-NEt_2$ 80%

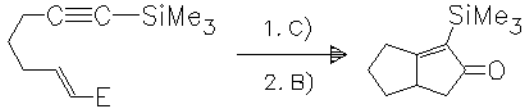
A): $Ti(O-iPr)_4/iPrMgCl$ (1:2), Et_2O, −78 -> −20°C

B): 1N aq. HCl, Et_2O

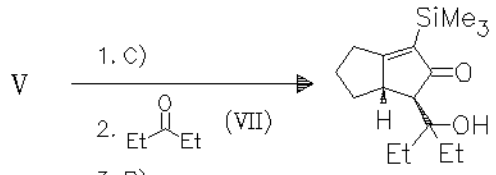


Ia IV

a R^3, R^4: —H 62% (92% d.e.)
b R^3, R^4: —Me 34% (100% d.e.)



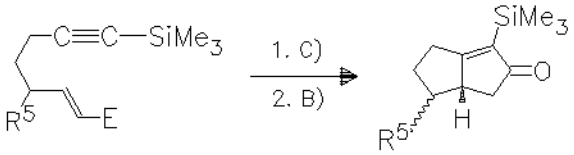
V VI 80%



V VIII 65%

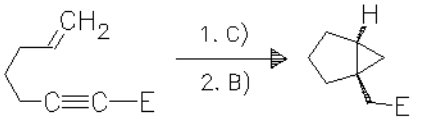
E: —CO—O—Et

C): $TiCl(O-iPr)_3/iPr-MgCl$ (1:2), Et_2O, −78 -> −20°C

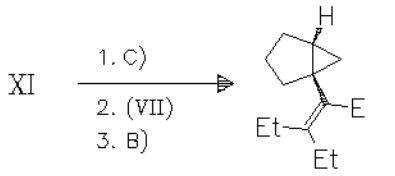


IX X

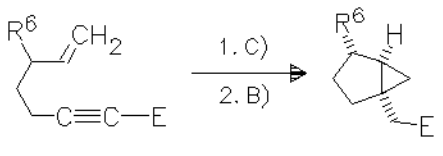
a R^5: —O—Tbs 69% (80% d.e.)
b R^5: —Bu 89% (94% d.e.)



XI XII 74%

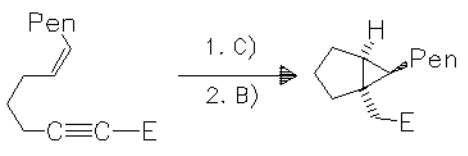


XI XIII 58%



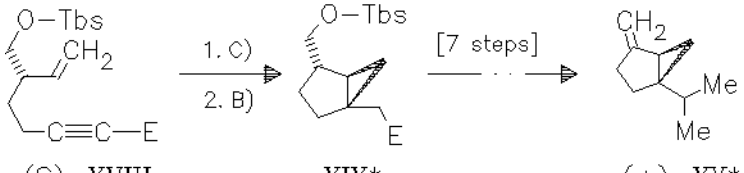
XIV XV

a R^6: —Bu 63%
b R^6: $-CH_2-O-Tbs$ 78%



XVI XVII 51%

Pen: $-(CH_2)_4-Me$



(S)—XVIII XIX* (+)—XX*

78% (80% e.e.)