

## Isomerization of Unsaturated Terpenes *via* Allylstannanes: a New Short Synthesis of (+)- $\beta$ -Pinene from (+)- $\alpha$ -Pinene

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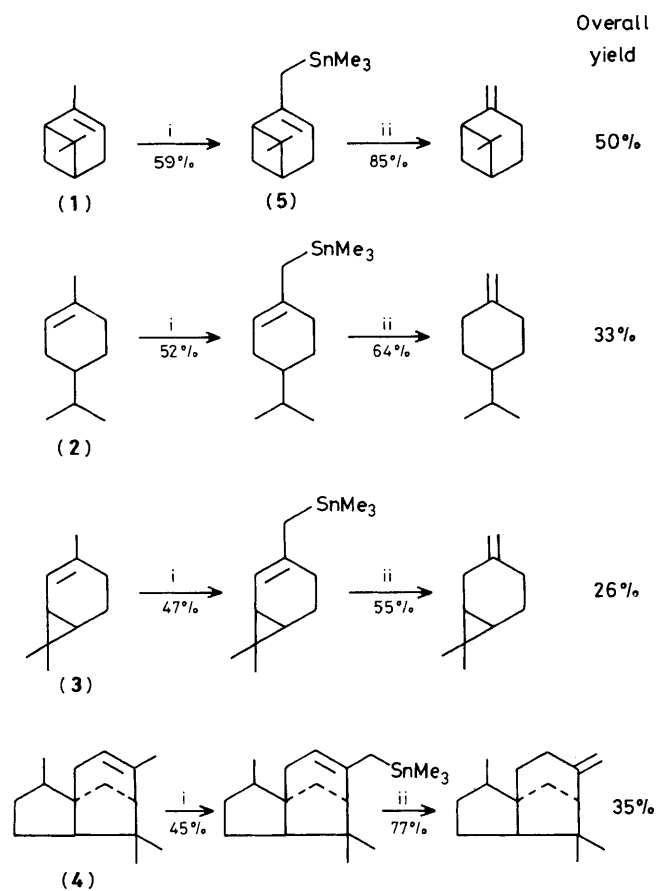
A two-step isomerization of unsaturated terpenes *via* allyltin compounds is reported, by which route (+)- $\alpha$ -pinene has been converted into (+)- $\beta$ -pinene in 50% yield.

We have recently reported<sup>1</sup> the synthesis of terpenoid allylstannanes from hydrocarbons by metallation with *n*-butyllithium–tetramethylethylenediamine (TMEDA) complex followed by quenching with trimethyltin chloride. We have also shown that this reaction leads to the most stable allyltin compounds.

Since the cleavage of allylic derivatives of tin with protic acids is accompanied by a total allylic rearrangement,<sup>2</sup> we describe here the isomerization of the unsaturated terpenes (1)–(4) *via* allylstannanes (Scheme 1). In particular, we describe a new short synthesis of (+)- $\beta$ -pinene.  $\beta$ -Pinene is the

minor constituent of numerous essential oils together with its  $\alpha$ -isomer, and is the starting material for the manufacture of perfumes, chemicals, and polyterpene resins. The conversion of  $\alpha$ -pinene into the less easily available  $\beta$ -pinene has been investigated,<sup>3</sup> but most of reported methods using various catalysts led to ineffective conversion with poor yields.

More recently two new syntheses of  $\beta$ -pinene from  $\alpha$ -pinene have been reported. Julia<sup>4</sup> described a four-step method which involves a reductive fission of alkenephosphonates with lithium aluminium hydride, leading to  $\beta$ -pinene with an overall yield of 25%. The conversion proposed by Cao<sup>5</sup> gave a



**Scheme 1.** Reagents: i, Bu<sup>n</sup>Li-TMEDA, Me<sub>3</sub>SnCl; ii, HCl in MeOH-4% H<sub>2</sub>O.

mixture from which  $\beta$ -pinene could only be obtained by careful distillation.

Our new method converts  $\alpha$ -pinene into  $\beta$ -pinene with an overall yield of 50% in two steps; we have obtained (+)- $\beta$ -pinene with high isomeric and optical purity. This uncommon dextrorotatory form of  $\beta$ -pinene has so far been detected<sup>6,7</sup> in very few plants.

The allyl-stannane derivative (5) was directly obtained in 59% yield from (+)- $\alpha$ -pinene (1) by metallation with BuLi-TMEDA followed by trapping of the lithio-salt with Me<sub>3</sub>SnCl. Treatment of (5) with HCl in MeOH-4% H<sub>2</sub>O gave (+)- $\beta$ -pinene (2) in 85% yield [ $\alpha$ ]<sub>D</sub> +14.90° (c 2.8, CHCl<sub>3</sub>).

A similar procedure was also effective for the isomerization of *p*-menth-1-ene (2), car-2-ene (3), and  $\alpha$ -cedrene (4) into their less stable exocyclic methylene isomers (Scheme 1) and can be considered as a general route for the isomerization of unsaturated terpenes.†

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† The purities of the allyltin compounds and of the terpenes were checked by gas chromatography and their structures were firmly established by spectral data (i.r., <sup>1</sup>H and <sup>13</sup>C n.m.r., and mass).