SHORT-STEP SYNTHESES OF (±)-BAZZANENE AND (±)-TRICHODIENE

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Sesquiterpene hydrocarbons, bazzanene and trichodiene, were synthesized in three steps from a substituted allyl formate $\underline{3}$.

Bazzanene $\underline{1}^{(1)}$ and trichodiene $\underline{2}^{(2)}$ (diastereomers each other) are bicyclic sesquiterpenes and are important biological precursors of sesquiterpenoids. Although stereoselective total syntheses of $(\pm)-\underline{1}^{(3)}$ and $(\pm)-\underline{2}^{(4)}$ have been reported, no synthetic approach to be able to produce both $\underline{1}$ and $\underline{2}$ seems to be described yet in the literature. Attempts⁴⁾ to prepare $\underline{1}$ by the similar procedure to the one for the synthesis of $\underline{2}$ have met with no success thus far. And synthetic method for $\underline{1}^{(3)}$ is not applicable to the synthesis of 2.



This paper describes short-step total syntheses of (\pm) -bazzanene and (\pm) -trichodiene. In the crucial step, we utilized a Wittig reaction of an appropriately functionalized allyl formate to produce an allyl vinyl ether. Reactivity of allyl formates toward Wittig reagents has been recently reported by the present author.⁵⁾

The whole synthetic pathway is shown in Scheme. Thus, a formate 3, which was prepared from the known ethyl 2-methyl-1-cyclopentenecarboxylate $4^{\overline{6}}$ (LAH reduction and subsequent esterification), was treated⁵⁾ in THF with a phosphonium ylid 5, which was generated in situ from the corresponding phosphonium salt $6^{.7}$ Produced allyl vinyl ether $7^{.8}$ was, without purification, heated in xylene for 24hrs. In this case, Claisen rearrangement was unusually slow presumably due to the highly crowded structure of the substrate. Purification of the product by column chromatography afforded the aldehyde $8^{.9}$ in 50% yield (from 6). The NMR spectrum of 8 exhibited two singlets (1:1 ratio) at δ 9.59 and 9.60 for the aldehyde proton, indicating that the product was a 1:1 mixture of the two diastereomers. Finally, Wolff-Kishner reduction (hydrazine hydrate

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in butanol and then t-BuOK in toluene) produced the desired hydrocarbons as a l:l mixture of $(\pm)-\underline{1}$ and $(\pm)-\underline{2}$ in 73% yield. Chromatography on silver nitrate (5%)-impregnated silica gel (eluent hexane containing 0.5% ether) could separate the isomers, bazzanene eluting first. Although ir and mass spectra of $\underline{1}$ and $\underline{2}$ are almost indistinguishable, their NMR spectra are slightly different and an absorption at δ 4.74($\underline{1}$) and δ 4.68($\underline{2}$) can be used for the identification. The hydrocarbons obtained here exhibit identical ir, mass and NMR spectra with the natural products.¹⁰



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- 8) NMR(CDCl₃) δ 4.17(2H,s), 5.30(1H,bs), 6.80 and 6.88(1H,two bs).
- 9) NMR(CDCl₃) & 1.10(3H,s), 1.58(3H,s), 4.77(1H,bs), 5.05(1H,bs), 5.38(1H,m), 9.59 and 9.60(1H,two s). Correst elemental analysis.
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