UTILIZATION OF OPTICALLY ACTIVE 4-TRITYLOXYMETHYL-2-BUTEN-4-OLIDE IN PHOTOINDUCED ASYMMETRIC (2+2) CYCLOADDITION

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Among the naturally occurring terpenoides, β -bourbonene (1) and spatol (2) have unique tricyclo[5,3,0,0^{2,6}]decane skeleton. For the construction of this system by (2+2) cycloaddition, we utilized chiral butenolide (3) as a chiral source in the asymmetric induction and as carbon frameworks of 7 and 10, key intermediates in the syntheses of 1 and 2, respectively.

In the photocycloaddition of $\underbrace{4}$ and $\underbrace{5}^{1}$, the stereochemistry of the adduct was controlled by a chiral center at $\underbrace{4}$, and the stereoselectivity was explained by the least hindered approach of $\underbrace{5}$ to $\underbrace{4}$. On the other hand, in the intramolecular cycloaddition of $\underbrace{8}$, the direction of approach reversed and the adduct $\underbrace{9}$ was obtained exclusively.

These photoadducts (6, 9) were converted to the key intermediates (7, 10) by the removal of original chiral centers and elabolation of butan-4-olide moieties.

1) K. Tomioka, M. Tanaka, and K. Koga, Tetrahedron Lett., 23, 3401 (1982).