ALDOL REACTION

inthetic Applications:

first enantioselective total synthesis of (–)-denticulatin A was accomplished by W. Oppolzer. ⁸³ The key step in first enantioselective total synthesis of (–)-denticulatin A was accomplished by W. Oppolzer. ⁸³ The key step in approach was based on enantiotopic group differentiation in a meso dialdehyde by an aldol reaction. In the reaction they utilized a bornanesultam chiral auxiliary. The enolization of N-propionylbornane-10,2-sultam held the (Z)-borylenolate derivative, which underwent an aldol reaction with the meso dialdehyde to afford the fluct with high yield and enantiopurity. In the final stages of the synthesis they utilized a second, double-tuct with high yield and reaction. Aldol reaction of the (Z)-titanium enolate gave the anti-Felkin syn product. The reochemical outcome of the reaction was determined by the α-chiral center in the aldehyde component.

Ouring the total synthesis of rhizoxin D by J.D. White et al., an asymmetric aldol reaction was utilized to achieve the coupling of two key fragments. The aldol reaction of the aldehyde and the chiral enclate derived from (+)-chlorodiisopinocampheylborane afforded the product with a diastereomeric ratio of 17-20:1 at the C13 stereocenter. During their studies, White and co-workers also showed that the stereochemical induction of the chiral boron substituent and the stereocenters present in the enclate reinforce each other thus representing a "matched" aldol reaction.

A possible way to induce enantioselectivity in the aldol reaction is to employ a chiral catalyst. M. Shibasaki and coworkers developed a bifunctional catalyst, (S)-LLB (L=lanthanum; LB=lithium binaphthoxide), which could be successfully applied in direct catalytic asymmetric aldol reactions. An improved version of this catalyst derived from (S)-LLB by the addition of water and KOH was utilized in the formal total synthesis of fostriecin. Be

in aldehyde or under certain mpound. The acetaldehyde, 3ronsted base condensation. application of s in the aidol es have been olybdenum_is ity regio- and (E)-Enolates r. Lewis acid pure starting stilizing chiral yrrolidinones. pplying chiral d boronates, reactions can etal complex

R³
R⁴
s' ated

R⁶

, **B**, Al, Si,

enol, which attack by fition of the formation of with high the major nan-Traxler controlling a state.

OH O R²
anti

Q Q X R² syn

catalyst