Commentary

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Photochemical Isomerization: Central Transfer of Chirality with a Photoresponsive Catalyst

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Description

Alkylation of a -keto ester is a common reaction for forming carbon–carbon bonds. However, due to the product's ease of racemization in acidic or basic conditions, extension to a stereoselective reaction remains a significant obstacle. A hybrid system that uses Pd and Ru complexes to catalyze the asymmetric dehydrative condensation of cinnamyl-type allylic alcohols with -keto esters is described in this paper. An allylated mono-substituted product with high regio-, diastereo-, and enantioselectivity can be produced from non-substituted keto ester. Due to the nearly neutral conditions, there is no epimerization, which is made possible by a quick proton transfer from the formation of Pd-enolates to Ru-allyl complexes. By altering the stereochemistry of the Pd or Ru complex, four diastereomers can be synthesized at any time. Using diastereoselective reduction of the products' ketone, eight stereoisomers with three adjacent stereogenic centers can be produced. The usefulness of the reaction is demonstrated by the formal synthesis of (+)-pancratistatin. In organic synthesis, -Hydroxy esters (HEs) are common structural motifs. The most promising method for producing -HEs is the asymmetric hydrogenation of -keto ester. The -alkylation of HEs is inefficient, despite the fact that chiral -alkylated HE is frequently required for the construction of other complex structures. For diastereoselective synthesis2, acetalization, deprotonation, alkylation, and deacetalization are typically required. Through dynamic kinetic resolution, diastereoselective and enantioselective hydrogenation of -substituted keto esters is appealing. However, the product is diastereospecific and the substrate's scope is limited. The acetoacetic ester synthesis, also known as the enantioselective alkylation of -keto ester and the diastereoselective reduction of the carbonyl group appear appealing from this vantage point.

Atroposelective Synthesis

Examples of dynamic chirality transfer between various chirality elements, such as from central to either helical or axial chirality and back again, have been shown in recent advances in molecular design. It is intriguing to design chiral molecular switches that can provide selective and dynamic control of axial chirality with an external stimulus to modulate stereochemical functions, even though significant progress has been made in atroposelective synthesis. A photoresponsive bis (2-phenol)-substituted molecular switch 1 was synthesized and characterized in this paper. A dynamic hybrid central-helical-axial transfer of chirality is present in this one-of-a-kind design. The biaryl motif's change in preferential axial chirality is coupled with the fixed stereogenic center's reversible switching of the overcrowded alkene core's helicity. By successfully reversing enantioselectivity for several substrates, the use of (R)-1 as a switchable catalyst to direct the stereochemical outcome of the catalytic enantioselective addition of diethylzinc to aromatic aldehydes demonstrated the potential for dynamic control of axial chirality.By harnessing the pairing of hybrid helical-axial chiralities within chiroptical switchable units, we anticipated that the creation of new bis (2-phenol)-functionalized switchable catalysts would enable unprecedented dual stereoselectivity with noninvasive control and high spatiotemporal resolution.

Asymmetric Addition

A light-responsive BINOL-type catalyst based on a chiral molecular switch that exhibits dual stereocontrol in an asymmetric addition of organozinc reagents to aromatic aldehydes is the subject of the photochemical control of axial biaryl chirality described here. The conformation of the bis (2-phenol) unit is determined by the dynamic stereochemistry of the central photoswitchable scaffold via internal dynamic transfer of chirality. The bis (2-phenol) unit functions as a chiral flexible bifunctional catalytic unit. In addition, the catalyst described here has a switch core unit that is extremely thermally stable and can be photoisomerized only reversibly between two pseudoenantiomeric forms. The stereogenic center of the switch, highlighted in red, is the first component. It can exist in either the R or S configuration. The overcrowded alkene's helicity, highlighted in blue, is the second component. It is controlled by the stereogenic center's configuration but can be reversed by photoisomerization. In conclusion, the following components form the foundation of our design:a) selective and reversible photoisomerization of the crowded alkene scaffold between just two states; (b) the unique change in the chiroptical switch's helicity that is controlled by the stereogenic center's fixed configuration;c) a central-to-helical-to-axial transfer of

chirality that results in a coupled change in the biaryl core's axial chirality;d) the introduction of switchable chiral biphenol functionality, which has the potential to be used in a number of different ways in catalytic enantioselective transformations. The experimental results demonstrated that the most preferred conformation of the lower aryl substituent in the crystal lattice is parallel to the fluorenyl lower half of the switch core (synclinal), confirming the proposed model of coupled helical-to-axial transfer of helicity. The solid-state X-ray structure revealed a dihedral angle of +55.7° (plus 52.7° by calculation, as shown in the infrared spectrum).The latter is the result of aldehyde reduction, which is a known process that takes place during a slow addition process. It is thought that this reaction results from the reduction of the substrate and the -hydride removal of organozinc species in poorly activated zinc complexes. The 1,2-addition of diethylzinc to benzaldehyde successfully reversed stereoselectivity, as anticipated by photoinduced switching of ligand (R)-1.