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Axial Preference of Bulky Group- and Electron-Withdrawing Group-Substituted Oxygen Atom on the Chair-Type Cyclohexanone, Glutaric Anhydride, and Glutarimide.

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It has been established by ^1H NMR and X-ray analysis that cyclohexanones with alkoxy, acyloxy, and siloxy groups at C4 exists predominantly as an axial conformer both in solution and in a solid state. The axial preference of these groups may be interpreted in terms of space-through interaction such as electrostatic attraction and/or an $n-\pi^*$ orbital overlap between the oxygen atom of these substituents and the carbonyl group.

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Generalization, Alteration, and Enhancement of the Stereoselectivity in the Cieplak-Mode Reductions of 4-Alkoxy(or Silyloxy)-cyclohexanones.

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Reduction of 4-benzyloxy- and 4-(*t*-butyldiphenylsilyloxy)cyclohexanones with lithium aluminum hydride, diisobutylaluminum hydride, and lithium tri-*sec*-butylborohydride afforded the corresponding *cis* alcohols with 73-80% selectivities. However, in the presence of ethylaluminum dichloride, diisobutylaluminum hydride reduction of the former ketone gave the *trans* alcohol with 93% selectivity. With the latter ketone, the *cis* alcohol was obtained in 94% selectivity.

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Highly Diastereoselective Alkylation of Chiral Tin(II) Enolates onto Cyclic Acyl Imines, An Efficient Asymmetric Synthesis of Bicyclic Alkaloids Bearing a Nitrogen Atom Ring Junctionure.

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Asymmetric alkylation onto 5-acetoxy-2-pyrrolidinone employing chiral tin(II) enolates, generated from 3-acyl-4(*S*)- or 3-acyl-4(*R*)-isopropyl-1,3-thiazolidine-2-thiones, afforded the C5-alkylated 2-pyrrolidinones in a highly diastereoselective manner. A six-membered transition state involving a divalent tin atom with four ligands is proposed for the highly diastereoselective alkylation. The method was applied to the synthesis of bicyclic alkaloids like (-)-trachelanthamidine, and (-)- and (+)-epilupinine.