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[Lab. of Pharm. Synthetic Chemistry]

On the Mechanism of Stereoisomerization of Methyl Groups of 1,3-Diaxial [*cis*-3-(Benzyloxy)cyclohexyl]chlorodimethylstannane.

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The ^{13}C NMR chemical shifts for (*cis*-3-(benzyloxy) cyclohexyl) chlorodimethylstannane, which adopts a 1,3-diaxial conformation not only in the solid state but also in solution by intramolecular hypervalent Sn-O interaction, are found to be temperature-dependent. The degenerate stereoisomerization of methyl groups of the 1,3-diaxial (*cis*-3-(benzyloxy) cyclohexyl) chlorodimethylstannane is interpreted in terms of a dissociation-inversion mechanism which involves an intervention of the corresponding 1,3-diequatorial conformer, followed by stereoisomerization by pseudorotation.

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[Lab. of Pharm. Synthetic Chemistry]

Nucleophilic Vinylic Substitutions of (*Z*)-(β -(Phenylsulfonyl) alkenyl)-iodonium Tetrafluoroborates with Tetrabutylammonium Halides: Retention of Configuration.

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In contrast to the $\text{S}_{\text{N}}2$ type reaction of (*E*)-(β -alkyl) vinyliodonium salts with $n\text{-Bu}_4\text{NX}$, which proceeds with complete inversion of configuration, nucleophilic vinylic substitutions of (*Z*)-(β (phenylsulfonyl) alkenyl) iodonium salts with $n\text{-Bu}_4\text{NX}$ proceed with exclusive retention of configuration, which is compatible with an addition-elimination mechanism. The β -phenylsulfonyl group makes it possible the perpendicular attack of halide ions to the π^* orbital, which produces an α -sulfonyl-stabilized carbanion. The internal 60°C rotation followed by reductive elimination of the hypernucleofuge would reasonably explain the retention of configuration.

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Stereoselective Synthesis of Highly Labile (*Z*)- β -Alkylvinyl (phenyl) iodonium Perchlorates.

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Labile (*Z*)-vinyl (phenyl) iodonium perchlorates were synthesized from (*Z*)-vinylsilanes by the reaction with (diacetoxyiodo) benzene in the presence of $\text{BF}_3\text{-Et}_2\text{O}$ in dichloromethane, followed by quenching with an aqueous potassium perchlorate solution. These synthetic operations should be carried out quickly at 0°C to avoid extensive decomposition of the product. The (*Z*)-vinyl (phenyl) iodonium perchlorates are highly labile both in the solid state and in solution. The rate of decomposition of (*Z*)-decenyl (phenyl) iodonium perchlorate in CDCl_3 at room temperature, which yields 1-decyne quantitatively through the reductive *anti* β -elimination, is large and the half-life period is about 20 min.